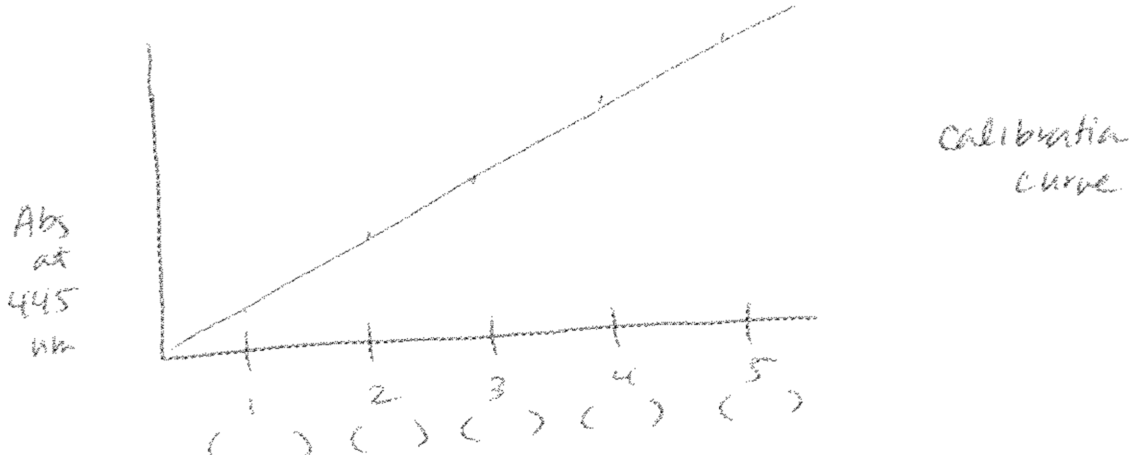
K_{eq} for $FeSCN^{+2}$ (Expt 19) notes:



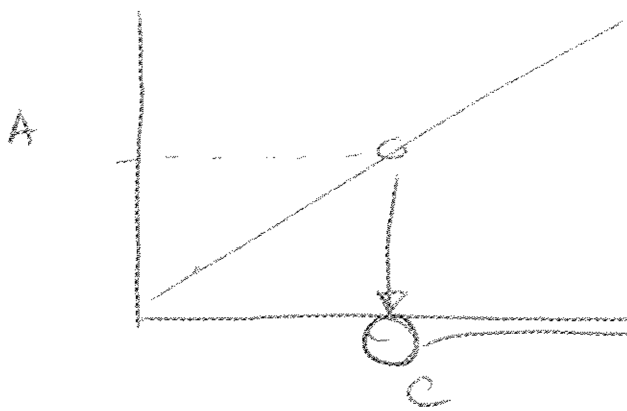
↑ conc for $FeSCN^{+2}$ = SCN^- = HSCN = KSCN

$\boxed{\text{ex}}$

5 x calc
Test soln # 1

$(2.0 \times 10^{-3} M)(2.0 mL) = \boxed{\quad\quad} (100 mL)$

original KSCN



$Fe^{+3} + HSCN \rightleftharpoons FeSCN^{+2} + H^+$

	Fe^{+3}	HSCN	$FeSCN^{+2}$	H^+
I			0 M	0.50 M
C				
E				

$(2 \times 10^{-3} M)(5 mL) = \_\_\_\_ (10 mL)$

$(2 \times 10^{-3} M)(1.0 mL) = \_\_\_\_ (10 mL)$

Determination of the Equilibrium Constant for the Formation of $FeSCN^{2+}$

Preliminary Lab Assignment

Name____________________ Date__________ Class__________

1. Define equilibrium.

2. The reaction for the formation of the diamminesilver ion is as follows:

$$Ag^{+}(aq) + 2\ NH_3(aq) \rightleftarrows Ag(NH_3)_2^{+}$$

(a) Write the equilibrium constant expression for the reaction.

(b) An experiment was carried out to determine the value of the equilibrium constant, K_c for the reaction.

Total moles of Ag^+ present = 3.6×10^{-3} moles
Total moles of NH_3 present = 6.9×10^{-3} moles
Measured concentration of $Ag(NH_3)_2^+$ at equilibrium = 3.4×10^{-2} M
Total solution volume = 100 mL

Calculate the equilibrium concentration of Ag^+ (uncomplexed).

Calculate the equilibrium concentration of NH_3 (uncomplexed).

Calculate the value of the equilibrium constant.

Determination of the Equilibrium Constant for the Formation of $FeSCN^{2+}$

There are many reactions that take place in solution that are equilibrium reactions; that is, they do not go to completion, and both reactants and products are always present. Examples of this type of reaction include weak acids such as acetic acid dissociating in water, weak bases such as ammonia reacting with water, and the formation of "complex ions" in which a metal ion combines with one or more negative ions. We will study a reaction involving the formation of a complex ion which occurs when solutions of iron(III) are combined with the negative thiocyanate ion.

The equation for the reaction is as follows:

$$Fe^{3+}(aq) + HSCN(aq) \rightleftarrows FeSCN^{2+}(aq) + H^{+}(aq)$$

The product, $FeSCN^{2+}$, is a complex ion in which Fe^{3+} ions are combined with SCN^{-} ions to form thiocyanatoiron(III) ions. It is possible to follow this reaction and calculate the equilibrium constant because the complex ion has a deep wine-red color in solution, and therefore its concentration can be determined using a spectrophotometer.

The experiment involves two major parts. First, a series of solutions of $FeSCN^{2+}$ must be prepared in which the concentration of $FeSCN^{2+}$ ions is known. A spectrophotometer is used to measure the absorbance of light of each of these standard solutions, and then a graph of concentration of $FeSCN^{2+}$ vs. absorbance is prepared. This graph serves as a calibration curve which will be used to determine the concentration of the complex ion in solutions of unknown concentration.

Secondly, a series of solutions is prepared in which varying amounts of the Fe^{3+} ion and HSCN are present. The absorbance of each solution is measured in the spectrophotometer, and the concentration of each substance present is determined. These values are used to determine the equilibrium concentrations and equilibrium constant for the reaction. We will use several different initial concentrations of the reactants to determine whether the equilibrium constant has the same numerical value when the complex is formed under different conditions.

Chemicals

Iron(III) nitrate, $Fe(NO_3)_3$, 0.20 M, in nitric acid, HNO_3, 0.50 M

Iron(III) nitrate, $Fe(NO_3)_3$, 2.0×10^{-3} M, in nitric acid, HNO_3, 0.50 M

Potassium thiocyanate, KSCN, 2.0×10^{-3} M, in nitric acid, HNO_3, 0.50 M

Nitric acid, HNO_3, 0.50 M

Baking soda, $NaHCO_3$

Equipment

5 Test tubes, 18- × 150-mm, and test tube rack

4 Burets, clamps and stands, or pipets

Stirring rod

Spectrophotometer and cuvettes

5 volumetric flasks with stoppers, 100-mL

Procedure

Safety Alert

All solutions contain nitric acid which is very corrosive to skin and eyes. Wash spills off yourself with lots of water. Neutralize spills on the lab table with baking soda.

Solutions are toxic; so wash your hands before you leave the lab.

If pipets are used to measure solutions, always use a pipet bulb. Never pipet by mouth.

Wear Chemical Splash Goggles and a Chemical-Resistant Apron.

1. **Prepare Standard Solutions**

Note: The complex ion $FeSCN^{2+}$ slowly decomposes in nitric acid solution. Do not prepare the solutions for this experiment unless you can measure their absorbance values within one hour.

In order to know the relation between the absorbance of a solution and its concentration, it is necessary to prepare a calibration graph of the molar concentration of $FeSCN^{2+}$ vs. Absorbance. The problem associated with this is that since the reaction is an equilibrium reaction, it does not go to completion, and the concentration of $FeSCN^{2+}$ in solution is difficult to determine.

We will "force" the reaction to go almost to completion by adding a large excess (over 200 times that needed) of Fe^{3+} ions to a small quantity of HSCN. According to LeChatelier's principle, this should cause the reaction to go essentially to completion. In these solutions we can assume that all the HSCN present has reacted to form $FeSCN^{2+}$, so the $FeSCN^{2+}$ concentration can be calculated.

The test solutions will be prepared using a mixture of KSCN, $Fe(NO_3)_3$, and HNO_3 solutions. KSCN ionizes into K^+ and SCN^-, and in the presence of the H^+ ion supplied by nitric acid, the H^+ and SCN^- will combine to form the weak acid HSCN. Since there is a large excess of nitric acid compared to KSCN, we can assume that all of the SCN^- will be in the form of HSCN.

Using a buret or pipets, measure 2.0, 3.0, 4.0, 5.0, and 6.0 mL of 2.0×10^{-3} M KSCN in 0.50 M HNO_3 into 100-mL volumetric flasks. Dilute to 100 mL with 0.20 M $Fe(NO_3)_3$ in 0.50 M HNO_3 and mix well. Two solutions of $Fe(NO_3)_3$ in 0.50 M HNO_3 with different concentrations are needed for this experiment. Be sure you use the correct concentration. Calculate the concentration of $FeSCN^{2+}$ in each flask, assuming that all of the SCN^- has reacted.

Generally, spectrophotometers are used as follows: Turn the instrument on and allow it to warm up for 15 minutes. Set the wavelength at 445 nm. With no light passing through the instrument to the phototube, set the percent transmittance to zero with the "zero" control. Handle cuvettes at the top so no fingerprints are in the light path. Polish cuvettes with a tissue. Place a cuvette which is about 2/3 full of distilled water into the sample holder and set the percent transmittance to 100% with the appropriate control (not the zero control). Fill a cuvette about 2/3 full of a test solution, place it in the spectrophotometer and read the absorbance. Consult the instrument manual for details on its use.

Measure the absorbance of each of the standard solutions at 445 nm, using distilled water as the reference in the spectrophotometer. If absorbance is difficult to measure precisely on the meter because it is in the high range where the numbers are close together, measure percent transmittance and calculate the absorbance for each solution. Absorbance = –log T, where T is transmittance expressed as a decimal.

Plot molar concentration of $FeSCN^{2+}$ vs. absorbance as shown in Figure 1, and draw the best fitting straight line through the data points. Include the origin (zero absorbance for zero concentration) as a valid point.

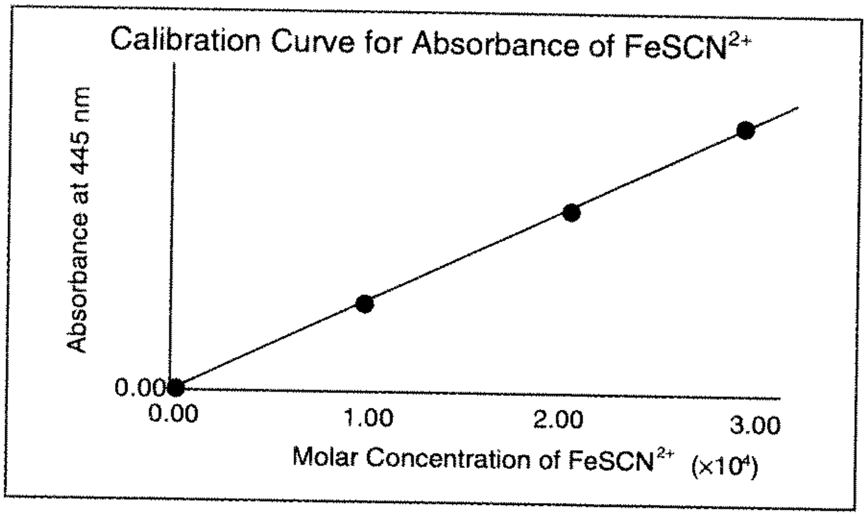


Figure 1. Graph of Absorbance versus Concentration of $FeSCN^{2+}$

2. Prepare and Measure Absorbance of Test Solutions

The standard solutions contained a large excess of Fe^{3+} over HSCN. The test solutions will contain concentrations of Fe^{3+} and HSCN that are close to one another. Under these conditions, there should be fairly large percentages of all species present at equilibrium.

Use a buret or pipets to measure the quantities listed in Table 1 into five 18- × 150-mm test tubes. Mix the solutions well with a glass rod, and measure the absorbance of each at 445 nm, using distilled water as a reference.

Solution	2.0×10^{-3} M $Fe(NO_3)_3$ in 0.50 HNO_3	2.0×10^{-3} M KSCN in 0.50 M HNO_3	0.50 M HNO_3
1	5.0 mL	1.0 mL	4.0 mL
2	5.0 mL	2.0 mL	3.0 mL
3	5.0 mL	3.0 mL	2.0 mL
4	5.0 mL	4.0 mL	1.0 mL
5	5.0 mL	5.0 mL	0.0 mL

Table 1. Quantities of Reagents Needed to Prepare Test Solutions

Disposal

Consult the *Flinn Chemical Catalog/Reference Manual*, suggested disposal method #24b. See the appendix.

3. Data and Calculations

Standard Solutions

Prepare a table in your laboratory notebook like Table 2 in which you can record your measured and calculated values. Show an example of each type of calculation.

Solution	mL 2.0×10^{-3} M KSCN in 0.50 M HNO_3	% Transmittance (if needed)	Absorbance	Concentration $FeSCN^{2+}$, M
1				
2				
3				
4				
5				

Table 2. Absorbance and Concentration of Standard Solutions

Record the absorbance of each solution. Calculate the concentration of $FeSCN^{2+}$ in each of the standard solutions, assuming that all of the SCN^- present is combined in the complex ion. Use the equation:

$$V_{\text{concentrated}} \times M_{\text{concentrated}} = V_{\text{dilute}} \times M_{\text{dilute}}$$

where V and M refer to the volumes and molarities of the solutions. Show a sample calculation.

Plot the data as suggested. Use a ruler to draw the best fitting straight line through the points. The point at zero absorbance for zero concentration is a valid point.

Test Solutions

Set up a chart like the one in Table 3 in which you can record your data and calculations. Show a sample of each type of calculation in your lab report.

Solution	(a) mL 2×10^{-3} M Fe^{3+} in 0.50 M HNO_3	(b) mL 2×10^{-3} M SCN^- in 0.50 M HNO_3	(c) % Transmittance (if needed)	(d) Absorbance	(e) Initial moles Fe^{3+}
1					
2					
3					
4					
5					

Table 3. Data and Calculated Values for Test Solutions

Solution	(f) Initial moles SCN^-	(g) Concentration $FeSCN^{2+}$, M	(h) Moles $FeSCN^{2+}$ at Equilibrium	(i) Moles Fe^{3+} at Equilibrium	(j) Moles HSCN at Equilibrium
1					
2					
3					
4					
5					

Table 3, continued. Data and Calculated Values for Test Solutions

Solution	(k) Concentration HSCN at Equilibrium, M	(l) Concentration Fe^{3+} at Equilbrium, M	(m) Concentration H^+ at Equilibrium, M	(n) Equilibrium Constant K_c
1	______	______	______	______
2	______	______	______	______
3	______	______	______	______
4	______	______	______	______
5	______	______	______	______

Table 3, Concluded. Data and Calculated Values for Test Solutions

(a) (b) Record the volume of Fe^{3+} and SCN^- solutions in each test solution.

(c) (d) Measure the absorbance of each test solution. If the needle of the meter is in the high absorbance range, measure %T and calculate A. A = –logT, where T is transmittance expressed as a decimal value.

(e) Calculate the total number of moles of Fe^{3+} initially present in each solution.

(f) Calculate the total number of moles of SCN^- initially present in each solution.

(g) Use your calibration curve to find the concentration of $FeSCN^{2+}$ in each solution.

(h) Calculate the number of moles of complex ion, $FeSCN^{2+}$, present in each solution based on the concentration found in step (g) and the total solution volume.

(i) Find the moles of uncomplexed Fe^{3+} in each solution by subtracting the number of complexed moles of Fe^{3+} (h) from the initial moles of Fe^{3+} (e).

(j) Find the moles of SCN^- which are not complexed with Fe^{3+} by subtracting the number of complexed moles (h) from the initial moles (f). Since HSCN is a weak acid, the high concentration of nitric acid will cause any SCN^- not combined with Fe^{3+} to combine with H^+ and form HSCN.

(k) Convert the number of moles of HSCN found in (j) to molarity.

(l) Convert the moles of free Fe^{3+} found in (i) to molarity.

(m) Calculate the concentration of H^+ initially present in each of the solutions. The small amount of H^+ that combines with the SCN^- will not significantly change the concentration of H^+.

(n) For each experiment, calculate K_c for the reaction:

$$Fe^{3+}(aq) + HSCN(aq) \rightleftarrows FeSCN^{2+}(aq) + H^+(aq)$$

$$K_c = \frac{[FeSCN^{2+}]\,[H^+]}{[Fe^{3+}]\,[HSCN]}$$

Calculate the average value of K_c.

Discussion

1. In your laboratory report, show a sample of each type of calculation. Explain what is meant by an equilibrium constant. Was the value constant for all your experiments? Should it be constant?
2. What does the calculated value of the equilibrium constant, K_c, indicate regarding the degree of completeness of the reaction? In other words, at equilibrium, are there mostly products, reactants, or relatively large amounts of both?
3. When the calibration graph was prepared it was assumed that essentially all of the HSCN present was combined with Fe^{3+} to form the complex ion. Use the average value for K_c that you determined, and calculate the amount of HSCN that was not a part of the complex ion for the standard solution in which 5.0 mL of KSCN was used. Was the assumption valid?
4. Explain what a spectrophotometer is and what it measures. Describe how the "standard" solutions were obtained and used to determine concentrations of unknown solutions.
5. When you use a spectrophotometer, should you set the wavelength of light to be the same color as that of the solution, or would a different color be more appropriate? Explain. What was the color of light chosen for this experiment? What was the color of the $FeSCN^{2+}$ complex ion?
6. What degree of precision (how many significant figures) can you obtain with the spectrophotometer that was used? What is the major source of error in the experiment?
7. Suggest other experiments in which a spectrophotometer would be useful.