Spectrophotometric Determination of an Equilibrium Constant

INSTRUCTOR RESOURCES

The CCLI Initiative

Computers in Chemistry Laboratory Instruction

Learning Objective

- to determine the equilibrium constant governing the formation of $Fe(SCN)^{2+}$ from iron(III) and thiocyanic acid by using the ***MicroLAB*** **Colorimeter** to measure the concentration of $Fe(SCN)^{2+}$.

Procedure Overview

- colorimetric measurements for the absorbance of four different solutions of a complex ion, $[Fe(SCN)^{2+}]$, are made using the ***MicroLAB*** Interface.
- the equilibrium constant for the formation of the complex is determined.

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SPECTROPHOTOMETRIC DETERMINATION OF AN EQUILIBRIUM CONSTANT

Report Sheet

Data Table

Complete the table while performing each trial.

	Col. A	Col. B	Col. C	Col. D	Col. E	Col. F	Col. G
Trial	Volume (H+)	Volume (HSCN)	Volume (Fe^{3+})	Conc. [HSCN]	Conc. [Fe^{3+}]	Abs.	Conc. [$Fe(SCN)^{2+}$]
1							
2							
3							
4							

Stock [H^+] (c1) =

Stock [HSCN] c2 =

Stock [Fe^{3+}] c3 =

Temperature =

Provide a sample calculation used to determine the initial concentrations of [HSCN] and [Fe^{3+}].

Calculations

1. Complete the "Table of Equations" with the missing equations.

TABLE OF EQUATIONS

CALCULATIONS	H^+	HSCN	Fe^{3+}	$Fe(SCN^{2+}$
Initial Concentration	$c1^+$	c2	c3	0
Initial Volume	V1	V2	V3	0
Initial Moles		c2V2		0
Equilibrium Moles		c2V2 - cV		cV
Equilibrium Volume	V	V	V	V
Equilibrium Concentration	(c1V1/V+c	(c2V2 / V) - c		c

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SPECTROPHOTOMETRIC DETERMINATION OF AN EQUILIBRIUM CONSTANT

Report Sheet (page 2)

2. Provide the equations used to calculate the absorbance (from I and I_o), equilibrium concentrations and equilibrium constant.

Abs =

$[Fe(SCN)2+]_{eq}$ =

$[H+]_{eq}$ =

$[HSCN]_{eq}$ =

$[Fe3+]_{eq}$ =

K =

3. List your K values and calculate the average K and the standard deviation for your four trials.

K1	K2	K3	K4	Kave	Std. Dev.

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SPECTROPHOTOMETRIC DETERMINATION OF AN EQUILIBRIUM CONSTANT

Questions/Problems

1. What effect does a dirty vial (caused by fingerprints, water spots, or lint) have on the absorbance reading for a $Fe(SCN)^{2+}$ solution? Does this error cause the reported K to be too high or too low? Explain.

2. Compare the K values obtained for the different trials. Assuming a constant temperature, how would you expect the K values to compare?

3. Compare the absorbance values of your four samples. Do the values of absorbance suggest the presence of a limiting reagent in the initial solution? Explain your answer.

4. Discuss your absorbance values in relation to the concentrations of Fe(SCN)2+. Can you find a relationship? Explain.

Questions/Problems (page 2)

5. A mixture of 2.0 ml of 2.0 *M* HCl, 5.0 ml of 0.0033 *M* HSCN and 3.0 ml of 0.0033 *M* Fe^{3+}gave a transmission current of 55 mA (It). A blank solution gave a transmission current of 82 mA (Io). The calibration equation for the colorimeter used in the experiment was

$$(\text{Absorbance}) = 1400\,[Fe(SCN)^{2+}] + 0.011$$

Using this equation and the Table of Equations, calculate the equilibrium concentrations of $Fe(SCN)^{2+}$, H+, HSCN and Fe^{3+} and then use these concentrations to calculate K.

SPECTROPHOTOMETRIC DETERMINATION OF AN EQUILIBRIUM CONSTANT

Tips and Traps

Calibration of the *MicroLAB* Colorimeter

1. Students should be instructed that the solutions of the complex are stable for a limited time; depending on the concentration. The half life, $t_{½}$, is approximately 1.5 hours, so they should proceed as quickly as prudent. The calibration procedure is described in the **BACKGROUND.** Known concentrations of the complex are obtained by reacting a large excess of $[Fe^{3+}]$ with HSCN. The following amounts are recommended.

2.0 M HCl (V2) ml Column A	0.0033 M HSCN(V2) ml Column B	0.20 M Fe^{3+} (V3) ml Column C	Water ml	Total Volume ml
0 (Blank)	0	2	8	10
2	1	2	5	10
2	2	2	4	10
2	3	2	3	10
2	4	2	2	10

2. The***MicroLAB*** **Hand Entered Spreadsheet** is used to set up the calculations as follows:

Columns:	**Item**	**Column**	**Item**
A	**Vol H^+ (v1)**	**B**	**Vol HSCN (v2)**
C	**Vol Fe^{3+} (v3)**	**D**	**Calc [HSCN]**
E	**Calc [Fe^{3+}]**	**F**	**Absorbance (from colorimeter)**
G	**Equil [$Fe(SCN)^{2+}$]**	**H**	**Calc Keq.**
Average Keq.			
Std. Dev.			

3. plot a linear regression graph.

Column F:	(Abs)	y-axis
Column G:	$[Fe(SCN)^{2+}]$	x-axis

4. The calibration equation is quite stable and can be averaged for all the boxes used.

5. The calibration equation provided in the **BACKGROUND** section works well.

SPECTROPHOTOMETRIC DETERMINATION OF AN EQUILIBRIUM CONSTANT

Sample Data (Page 2)

Calculations

1. Complete the "Table of Equations" with the missing equations.

TABLE OF EQUATIONS

CALCULATIONS	H^+	HSCN	Fe^{3+}	$Fe(SCN^{2+}$
Initial Concentration	$c1^+$	c2	c3	0
Initial Volume	V1	V2	V3	0
Initial Moles	c1V1	c2V2	c3V3	0
Equilibrium Moles	c1V1+ eV	c2V2 - cV	c3V3-eV	cV
Equilibrium Volume	V	V	V	V
Equilibrium Concentration	(c1V1/V) + c	(c2V2 / V) - c	(c3V3/V) -c	c

2. Provide equations used to calculate the absorbance, equilibrium concentrations and equilibrium constant in the Spreadsheet.

Abs = **$\log(I_o/I)$ = F**

$[Fe(SCN)^{2+}]_{eq}$ = **(Abs - intercept)/ 2.54/ϵ (Slope of calibration curve) = G**

$[H+]_{eq}$ = **4/10 + G = 0.4**

$[HSCN]_{eq}$ = **D - G**

$[Fe3+]_{eq}$ = **E - G**

K = **G * (0.4 + G) / (E-G) / (D-G)**

3. List your K values and calculate the average K for your four trials.

K1	K2	K3	K4	Kave	Std. Dev.
39.69	**39.70**	**39.63**	**40.41**	**39.86**	**0.37**

Sample Data (Page 2)

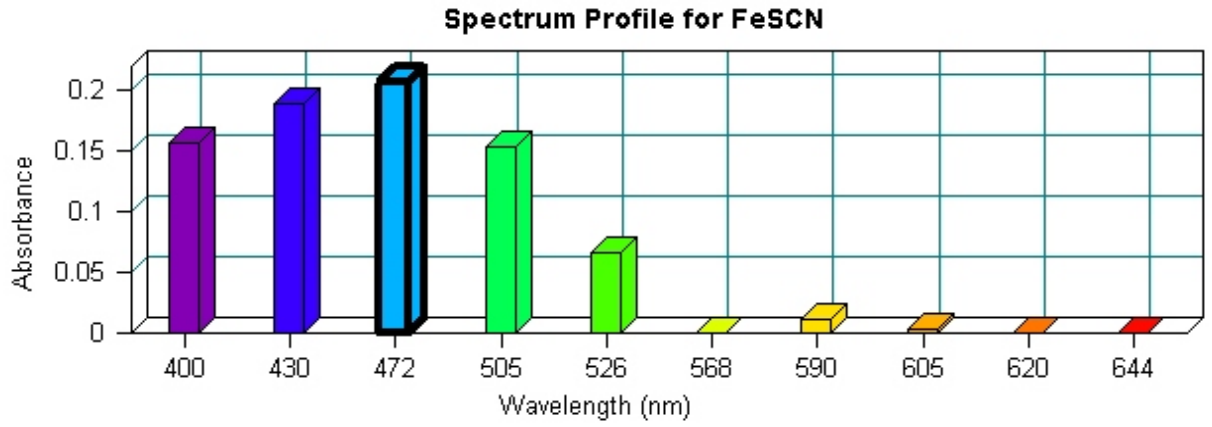

Figure 2. Spectrum Profile for $FeSCN^{2+}$ solution.

Sample Absorbance versus Concentration graph for $FeSCN^{2+}$ solution

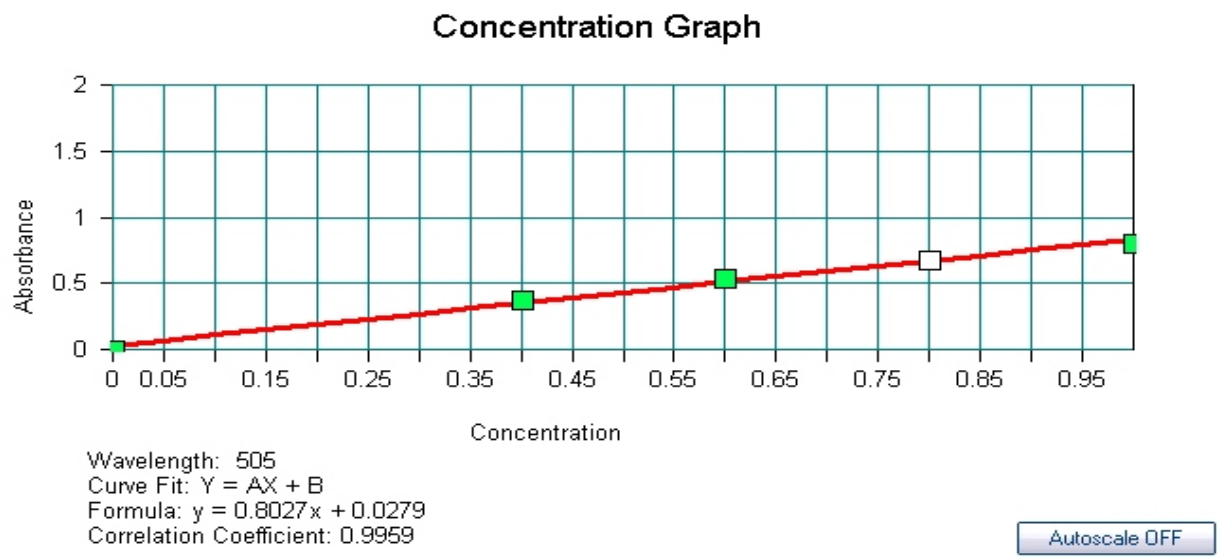

Figure 4. Sample Absorbance versus concentration graph for $FeSCN^{2+}$ solution at 472 nm wavelength. Using the coefficient of the X term in the formula, we can calculate the molar absorptivity for that wavelength.

SPECTROPHOTOMETRIC DETERMINATION OF AN EQUILIBRIUM CONSTANT

Suggested Answers to Questions/Problems

1. What effect does a dirty cuvette (caused by fingerprints, water spots, or lint) have on the absorbance reading for a Fe(SCN)2+ solution? Does this error cause the reported K to be too high or too low? Explain.

   Less light is transmitted to the detector; this increases the absorbance reading.
   The reported K will be too high. A larger absorbance indicates a higher [$Fe(SCN)^{2+}$], and also a larger K.

2. Compare the K values obtained for different trials. Assuming a constant temperature, how would you expect the K values to compare?

   All the K values should be similar if the temperature does not change.

3. Compare the absorbance values of your four samples. Do the values of absorbance suggest the presence of a limiting reagent in the initial solution? Explain your answer.

   Yes, the absorbance will increase if the limiting reagent increases because more [$Fe(SCN)^{2+}$] is produced (either HSCN or Fe^{3+} may become the limiting reagent).

4. Discuss your absorbance values in relation to the concentrations of $Fe(SCN)^{2+}$. Can you find a relationship? Explain.

   The absorbance increases if [$Fe(SCN)^{2+}$] increases, according to Beer's Law.

5. A mixture of 2.0 ml of 2.0 *M* HCl, 5.0 ml of 0.0033 *M* HSCN and 3.0 ml of 0.0033 *M* Fe^{3+} gave a transmission current of 55 mA (It). A blank solution gave a transmission current of 82 mA (Io). If the calibration equation for the colorimeter used in the experiment was

   $$\textbf{(Absorbance)} = \textbf{1400 [Fe(SCN)}^{2+}\textbf{]} + \textbf{0.011},$$

   Use this equation and the Table of Equations to calculate the equilibrium concentrations of $Fe(SCN)^{2+}$, H^+, HSCN and Fe^{3+} and then use these concentrations to calculate K.

   Abs = 0.17

   [HSCN] = 1.53×10^{-3} M

   [$Fe(SCN)^{2+}$] = 1.16×10^{-4} M

   [Fe^{3+}] = 8.7×10^{-4} M

   [H^+] = 0.40 M

   K = 35 (no units)

SPECTROPHOTOMETRIC DETERMINATION OF AN EQUILIBRIUM CONSTANT

Laboratory Preparation (per student station)

Equipment

- 250 ml beaker
- 10 ml Grad cylinder with stopper
- 4 plastic Beryl pipets
- cuvette
- wash bottle
- colorimeter box
- three, 25 or 50 ml burets
-

Supplies

- towel

Chemicals

Exact quantities needed are listed below. A minimum 50% excess is recommended.

- 20 ml of 0.0033 *M* KSCN
- 20 ml of 0.0033 *M* $Fe(NO_3)_3$ in 0.010 *M* HCl
- 10 ml of 2.0 *M* HCl
- 10 ml of 0.2 *M* $Fe(NO_3)_3$ in 0.010 *M* HCl for calibration

Safety and Disposal

- no special precautions necessary