THE FORMATION CONSTANT FOR A COMPLEX ION BY COLORIMETRY

INSTRUCTOR RESOURCES

The CCLI Initiative

Learning Objectives

The objectives of this experiment are to . . .

- illustrate how colorimetric measurements are made using the ***MicroLAB*** interface.
- use Beer's Law to measure the equilibrium concentration of a complex ion.
- calculate the equilibrium constant for the formation of a complex ion.

Procedure Overview

- a set of standard solutions is prepared.
- the ***MicroLAB*** colorimeter is used to determine the absorbency of the five standard solutions and the molar absorptivity constant for $FeSCN^{2+}$.
- the ***MicroLAB*** spreadsheet is used to calculate the equilibrium concentrations of Fe^{3+}, HSCN, and H^+ from the equilibrium concentration of $FeSCN^{2+}$.
- the value of K_f is calculated for the complex formation reaction from the collected data.

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Report Sheet

Determining the Molar Absorptivity of FeSCN

The following solution mixtures will be measured on the ***MicroLAB*** Colorimeter to determine the Molar absorptivity (ϵ) of the FeSCN.

	# 1	# 2	# 3	# 4	# 5
mL $Fe(NO_3)_3$	5.00	5.00	5.00	5.00	5.00
mL HSCN	1.00	2.00	3.00	4.00	5.00
mL HNO_3	4.00	3.00	2.00	1.00	0.00
Total mL	10.00	10.00	10.00	10.00	10.00
Initial [HSCN]	1.00×10^{-3} *M*				
Initial [Fe^{3+}]	2.00×10^{-4} *M*				

Average molar absorptivity (ϵ) __________

Standard Deviation on (ϵ) __________

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Report Sheet (page 2)

Determining the K_f of FeSCN from Equilibrium Measurements

The following equilibrium mixtures will be measured on the ***MicroLAB*** Colorimeter, and you will then determine the **K_f** for each equilibrium mixture.

	#1	#2	#3	#4	#5
ml Fe(NO3)3	5.00	5.00	5.00	5.00	5.00
ml HSCN	1.00	2.00	3.00	4.00	5.00
ml HNO3	4.00	3.00	2.00	1.00	0.00
Total ml	10.00	10.00	10.00	10.00	10.00
Initial [Fe3+]	1.00 x 10-3 *M*				
Initial [HSCN]	2.00 x 10-4 *M*				
Initial [H+]					
Equil. [Fe3+]					
Equil. [$FeSCN^{2+}$]					
Equil. [HSCN]					
Equil. [H+]					
K_f					

K_f average : __________

Std.Dev. K_f : _________

Calculations:

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Report Sheet (page 3)

Give equations used to determine each of the following in the spreadsheet program.

Absorbance (A)(Assuming I is proportional to transmittance):

$[FeSCN]^{2+}$ equil. =

$[H^+]$ equil. =

[HSCN] equil. =

$[Fe^{3+}]$ equil. =

Kf =

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Determination of the Value of an Equilibrium Constant

Questions/Problems

1. Consider the rection

$$A + B ==> C + 3D$$

A solution was prepared by mixing 50.0 ml of 1.00×10^{-3} *M* of A, 100.0 ml of 2.00×10^{-3} *M* of B, 10.0 ml of 1.0 *M* of C, and 75.0 ml of 1.50×10^{-3} *M* of D. At equilibrium the concentration of D was measured and found to be 6.0×10^{-4} *M*.

Calculate to two significant figures:

a. the equilibrium concentrations of **A, B, C** and **D**.

b. the value of the equilibrium constant for the reaction.

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Questions/Problems (page 2)

2. Consider the reaction

$$X + 3Y <==> 2N + 4Z$$

A solution was prepared by mixing 200.0 ml of 3.56 x 10^{-3} ***M*** of **X** and 100.0 ml of 5.78 x 10^{-3} ***M*** of **Y**. After the system had come to equilibrium, the absorbance, **A**, of the solution was measured at a wavelength (600 nm) where only **Z** absorbs light. The value of **A** was found to be 0.733 in a 1.00 cm cell.

The following data were also collected for known solutions of pure **Z** at 600 nm using a 1.00 cm cell.

[Z]	[A]
2.00 x 10^{-4} *M*	0.100
5.00 x 10^{-4} *M*	0.240
8.00 x 10^{-4} *M*	0.390
1.80 x 10^{-3} *M*	0.880

a. Calculate the equilibrium concentrations of **X**, **Y**, **Z**, and **N** in the solution

b. prepared in part A. Calculate the value of **K** for the reaction.

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Tips and Traps

1. FeSCN is very strongly absorbing at 472 nm, so it is important to use the very dilute solutions for determining the molar absorptivity constant. Even at those dilute concentrations, the best fit for the data is a third order polynomial. However, a linear fit is sufficient to get a good value for the absorptivity coefficient.

2. At the higher concentrations, the third order polynomial data fit gives very good values for the concentrations and for K_f.

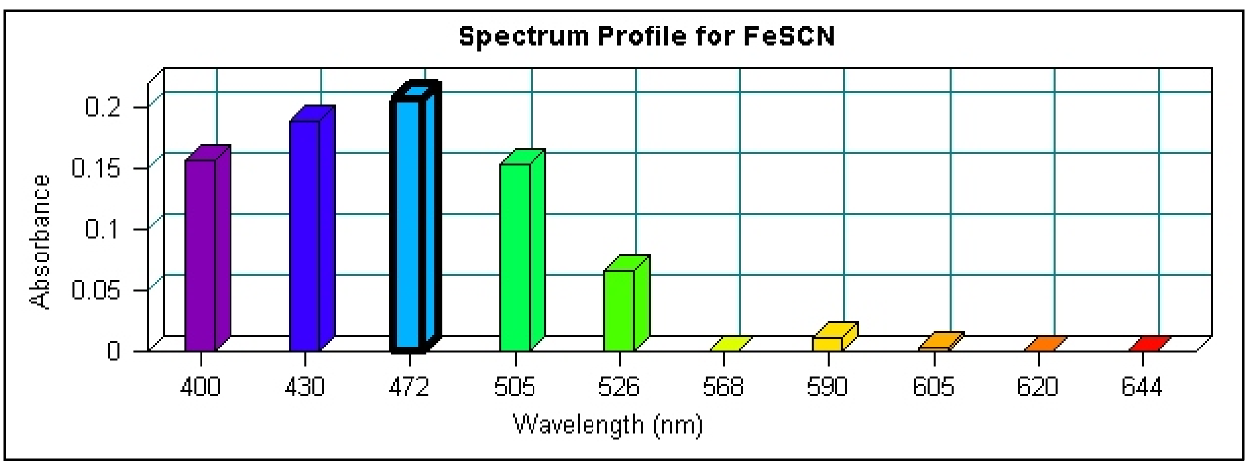
3. Care must be taken that the pipetting is done accurately or the calibration curve will be inaccurate.

4. Solutions must be well mixed for accurate readings.

5. There are ***two*** different $Fe(NO_3)_3$ solutions and ***two*** different HSCN solutions. Labels should be clear to avoid confusion and student error.

6. Initial concentrations of HSCN must be calculated prior to running the program since you will need this information when running each sample. This can be set up in the HAND ENTER mode for the spreadsheet, entering the necessary values in the spreadsheet, then using the **Add Formula** function to do the calculation.

FeSCN Absorbance Spectrum Profile



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Sample Data

Standard Solutions

	# 1	# 2	# 3	# 4	# 5
ml $Fe(NO_3)_3$	**25.00**	**25.00**	**25.00**	**25.00**	**25.00**
ml HSCN	**5.00**	**10.00**	**15.00**	**20.00**	**25.00**
ml HNO_3	**70.00**	**65.00**	**60.00**	**55.00**	**50.00**
Total ml	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**
Initial [HSCN]	**3.00×10^{-5} *M***	**6.00×10^{-5} *M***	**9.00×10^{-5} *M***	**1.20×10^{-4} *M***	**1.50×10^{-4} *M***

Molar absorptivity constant = 1750 cm^{-1}

Equilibrium Measurements

	#1	#2	#3	#4	#5
ml $Fe(NO_3)_3$	**5.00**	**5.00**	**5.00**	**5.00**	**5.00**
ml HSCN	**1.00**	**2.00**	**3.00**	**4.00**	**5.00**
ml HNO_3	**4.00**	**3.00**	**2.00**	**1.00**	**0.00**
Total ml	**10.00**	**10.00**	**10.00**	**10.00**	**10.00**
Initial [Fe^{3+}]	**1.00×10^{-3} *M***	**1.00×10^{-3} *M***	**1.00×10^{-3} *M***	**1.00×10^{-3} *M***	**1.00×10^{-3} *M***
Initial [HSCN]	**2.00×10^{-4} *M***	**4.00×10^{-4} *M***	**6.00×10^{-4} *M***	**8.00×10^{-4} *M***	**1.00×10^{-3} *M***
Initial [H+]	**5.0×10^{-1} *M***	**5.0×10^{-1} *M***	**5.0×10^{-1} *M***	**5.0×10^{-1} *M***	**5.0×10^{-1} *M***
Equil. [Fe^{3+}]	**9.73×10^{-4} *M***	**9.46×10^{-4} *M***	**9.26×10^{-4} *M***	**8.99×10^{-4} *M***	**8.74×10^{-4} *M***
Equil. [$FeSCN^{2+}$]	**2.74×10^{-5} *M***	**5.40×10^{-5} *M***	**7.44×10^{-5} *M***	**1.01×10^{-4} *M***	**1.26×10^{-4} *M***
Equil. [HSCN]	**1.73×10^{-4} *M***	**3.46×10^{-4} *M***	**5.26×10^{-4} *M***	**6.99×10^{-4} *M***	**8.74×10^{-4} *M***
Equil. [H+]	**5.0×10^{-1} *M***	**5.0×10^{-1} *M***	**5.0×10^{-1} *M***	**5.0 x 10-1 *M***	**5.0×10^{-1} *M***
Kf	**79.4**	**78.1**	**70.8**	**72.4**	**72.3**

K_f average = **74.6**

K_f Std.Dev. = **3.9**

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Sample Data (page 3)

Give equations used to determine each of the following in the spreadsheet program.

Absorbance (A): **log (Io/I)**

$[FeSCN^{2+}]$ equil. = **A/ϵl**

$[H^+]$ equil. = $\mathbf{[H^+]_i}$

[HSCN] equil. = $\mathbf{[HSCN]_i - [FeSCN^{2+}]_{eq}}$

$[Fe^{3+}]$ equil. = $\mathbf{[Fe^{3+}]_I - [FeSCN^{2+}]_{eq}}$

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

1. Consider the reaction

$$A + B \Longrightarrow C + 3D$$

A solution was prepared by mixing 50.0 mL of 1.00 x 10^{-3} *M* of **A**, 100.0 mL of 2.00 x 10^{-3} *M* of **B**, 10.0 mL of 1.0 *M* of **C**, and 75.0 mL of 1.50 x 10^{-3} *M* of **D**. At equilibrium the concentration of **D** was measured and found to be 6.0 x 10^{-4} *M*.

Calculate to two significant figures.

(a) the equilibrium concentrations of **A, B, C** and **D**.

[A] = 1.7 x 10^{-4} M; [B] = 8.1 x 10^{-4} M;

[C] = 4.3 x 10^{-2} M; [D] = 6.0 x 10^{-4} M

(b) the value of the equilibrium constant for the reaction.

$$K = \frac{[C][D]^3}{[A][B]} = \frac{(4.3 \times 10^{-2})(6.0 \times 10^{-4})^3}{(1.7 \times 10^{-4})8.1 \times 10^{-4})}$$

$$= \frac{(4.3 \times 10^{-2})(2.16 \times 10^{-10})}{(1.7 \times 10^{-4})8.1 \times 10^{-4})}$$

$$= 6.7 \times 10^{-5}$$

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Suggested Answers to Questions/Problems (page 2)

2. Consider the reaction

$$X + 3Y \quad 2N + 4Z$$

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The following data were also collected for known solutions of pure **Z** at 600 nm using a 1.00 cm cell.

[Z]	[A]
2.00×10^{-4} M	0.100
5.00×10^{-4} M	0.240
8.00×10^{-4} M	0.390
1.80×10^{-3} M	0.880

Calculate the equilibrium concentrations of **X, Y, Z,** and **N** in the solution prepared in part A. Calculate the value of **K** for the reaction.

$[X] = 2.00 \times 10^{-3}$

$[Y] = 8.05 \times 10^{-4}$

$[N] = 7.50 \times 10^{-4}$

$[Z] = 1.50 \times 10^{-3}$

$K = 2.74 \times 10^{-6}$

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Laboratory Preparation (per student station)

Equipment

- colorimeter
- colorimeter vials
- 100 ml volumetric flasks (5)
- 25 ml pipet
- 5 ml pipet, graduated
- 10 ml pipet
- 10 ml beaker
- wash bottle

Supplies

- paper towels
- Kimwipes

Chemicals

- 0.50 *M* HNO_3 (350 ml)
- 0.200 *M* $Fe(NO_3)_3$ in 0.50 *M* HNO_3 (25 ml)
- 2.00×10^{-3} *M* HSCN in 0.50 *M* HNO_3 (15 ml)
- 2.00×10^{-3} *M* $Fe(NO_3)_3$ in 0.50 *M* HNO_3 (125 ml)
- 6.0×10^{-4} *M* HSCN in 0.50 *M* HNO_3 (75 ml)
- a 50% excess of solutions is recommended

Safety and Disposal

- no special precautions are needed