Chemistry 112

SPECTROPHOTOMETRIC DETERMINATION OF AN EQUILIBRIUM CONSTANT

INTRODUCTION:

The principle underlying a spectrophotometric method of analysis involves the interaction of electromagnetic radiation with matter. The most common regions of the electromagnetic spectrum used for analysis are the ultraviolet, visible, and infrared. In this experiment you will be making experimental measurements involving absorption in the visible portion.

When electromagnetic radiation strikes an atom or molecule, only the energy that corresponds exactly to the difference between two energy levels in that atom or molecule will be absorbed.

We observe that substances are colored because they absorb light at one or more of the wavelengths or frequencies in the visible portion of the spectrum. A few examples that you have already encountered in your Chem. 112 career thus far are the aqua blue color of the hydrated copper (II) ion, $Cu(H_2O)_4^{+2}$, the yellow color of the chromate ion, CrO_4^{-2}, containing solutions, and of course the dark purple solutions containing the permanganate ion, MnO_4^-.

Several factors control the amount of "light" that is absorbed by a sample:

1. The concentration of the absorbing substance

2. The pathlength of the cuvet containing the absorbing species.

3. The probability of light absorption by the absorbing substance (called the molar absorptivity coefficient or extinction coefficient).

In this experiment, a source of electromagnetic radiation will be used to determine the concentration of an absorbing substance in an aqueous solution. The wavelength at which a maximum absorption of electromagnetic radiation for this substance occurs will be set on the spectrophotometer, an instrument that is used to measure light intensities with a photosensitive call at specific (but variable) wavelengths.

Table I Visual Response of Color

Color Absorbed	Wavelength, nm	Observed Color
Ultraviolet	Less than 380	Colorless
Violet	380 – 435	Yellow-green
Blue	435 – 480	Yellow
Greenish-blue	480 – 490	Orange
Bluish-green	490 – 500	Red
Green	500 – 560	Purple, rose, magenta
Yellow-green	560 – 580	Violet
Yellow	580 – 595	Blue
Orange	595 – 650	Greenish-blue
Red	650 – 780	Bluish-green
Infrared	Greater than 780	Colorless

The ratio of the intensity of the incident light, I, to the transmitted light, I_o, is related to the concentration of the absorbing substance (Figure 4) by the following equation:

$$\text{Log } \frac{I_o}{I_t} = a \cdot b \cdot c \qquad \text{Eqn. 1}$$

where "a" is called the molar absorptivity coefficient, "b" is the thickness of the absorbing substance in centimeters, and "c" is the concentration of the absorbing substance expressed in moles per liter.

The quantity log $\frac{Io}{I_t}$ is generally referred to as the aborbance, A. Equation (1) then becomes:

$$A=abc \qquad \text{Eqn. 2}$$

The equation is commonly referred to as Beer's law. From Equation (2) the absorbance, "A," is directly proportional to the molar concentration, "c," of the absorbing substance, provided that the same spectrophotometric cell is used for all measurements and that wavelength of the light is the same.

The magnitude of the equilibrium constant, K_c, expresses the position of equilibrium for a chemical system. For example, a large equilibrium constant indicates the position of the equilibrium to be far to the right and a small value indicates the position of the equilibrium to be far to the left. At a given temperature the value of K is constant for a given chemical system. In this experiment you will be determining K_c for the equilibrium system represented by the following equation:

$$Fe(H_2O)_6^{+3} + SCN^- \rightleftharpoons FeSCN(H_2O)_5^{+2} + H_2O$$

In a dilute aqueous solution the concentration H_2O is essentially constant. As a result, the water of hydration can be neglected and the equation becomes

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

for which the equilibrium expression is

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

The equilibrium system will be prepared by mixing known concentrations of Fe^{+3} and SCN^{-}. In that the $FeSCN^{+2}$ complex is a deep blood-red color with an absorption maximum at about 447 nm, its concentration can be determined spectrophotometrically. By knowing the initial concentrations of Fe^{+3} and SCN^{-} and by measuring the $FeSCN^{+2}$ equilibrium concentration spectrophotometrically, the equilibrium concentrations of Fe^{+3} and SCN^{-} can be determined and K_c for the system can be calculated.

First you will prepare a set of standard solutions containing known concentrations of the $FeSCN^{+2}$ complex. The absorbance of each will be plotted versus the $FeSCN^{+2}$ molar concentration to establish a calibration curve from which the concentration of $FeSCN^{+2}$ can be determined for the remaining systems. In the preparation of the standards, the Fe^{+3} concentration will be in large excess compared to the SCN^{-} concentration. The assumption is made that the $FeSCN^{+2}$ concentration approximates the original SCN^{-} concentration; i.e. it is assumed that the position of equilibrium is driven so far to the right that for all practical purposes, all of the SCN^{-} is complexed by the large excess of Fe^{+3} to form $FeSCN^{+2}$.

SAFETY:

Potassium Thiocyanate: Hazardous in case of ingestion. Slightly hazardous when spilled on the skin or splashed into your eyes. Eyes and skin must be rinsed with large volumes of water.

Dilute Nitric acid: can harm eyes, skin, and clothing. Handle with care. Hazardous in case of skin contact, of eye contact, of ingestion, of inhalation. Skin contact may produce burns. Any acid spilled on the skin or splashed into your eyes must be rinsed with large volumes of water.

EXPERIMENTAL PROCEDURE

This experiment is to be completed in ONE DAY. If you do not finish see your lab instructor so that if permission is graded by the stockroom, he/she can store your SPEC KIT for another period. Each pair of students is to check out a **SPEC KIT,** 25 ml pipet and 2 pi pumps from the stockroom. The glassware in the "SPEC" kit is already clean and does not need to be re-cleaned.

A. The Set of Standards Solutions

Pipet 2, 3, 5, 10, 15 ml. of 0.00200 M KSCN and 25.00 ml of .200 M $Fe(NO_3)_3$ solution into separate 100 ml volumetric flasks and dilute to the 100ml mark with 0.1 M HNO_3. Pipet no KSCN but 25.00 ml of .200M Fe $(NO_3)_3$ into another 100 ml volumetric flask and dilute to the 100ml mark with 0.1 MHNO_3 – this will be your blank. These solutions are to be used to establish a calibration curve for determining the equilibrium $FeSCN^{+2}$ concentration spectrophotometrically.

Composition of Test Solutions for Calibration Curve

Solution	0.200 M $Fe(NO_3)_3$ [in 0.1 M HNO_3)$_3$]	0.00200 M KSCN	0.1 M HNO_3
			dilute to:
Blank	25.00 ml	0.00 ml	100 ml
1	25.00 ml	2 ml	100 ml
2	25.00 ml	3 ml	100 ml
3	25.00 ml	5.00 ml	100 ml
4	25.00 ml	10.00 ml	100 ml
5	25.00 ml	15.00 ml	100 ml

SPECTROPHOTOMETER - VERNIER PROBE SETUP

1. Turn LabQuest 2 on and plug in the spectrophotometer, SpectroVis Plus
2. Click on the meter icon , File Sensors,  located on the top left corner.
3. Insert cuvette with the blank solution
4. Tap somewhere in the red rectangle with the **USB:ABS**
5. Select change wavelength and change the wavelength = 447nm. Hit "ok"
6. Tap again in the red rectangle with the **USB:ABS**
7. Select calibrate
    a. Wait until the lamp warms up
    b. Select finish calibration
    c. Select "ok"
8. Remove blank and insert cuvette with Solution #1
    a. Select play 
    b. Select discard (only if this window appears)
    c. Wait until the "thinking icon" is "done" and then select Stop 
    d. Record the abs for solution #1
9. Remove cuvette with Solution #1 and insert cuvette with Solution #2 and repeat the steps in 8.

Fill the cuvet halfway with your solution, and then wipe the outside with a clean Kim-wipe to remove water and fingerprints. Touch only the top of the cuvet thereafter. Any foreign substance on the outside of the cuvet will affect the intensity of the transmitted light. Record the Absorbance of each solution at 447 nm.

Plot A versus [$FeSCN^{+2}$]. Draw the best straight line through the five points and the origin.

B. The Set of Equilibrium Solutions

Prepare the following set of solutions in 7-inch test tubes for the determination of the $[FeSCN^{+2}]$ in the equilibrium systems. Use pipets for the volumetric measurements. Stir each solution thoroughly with a clean and DRY stirring rod. Fill and then wipe the cuvet with a Kim-wipe as was done before.

Composition of Test Solutions for Determination of K_c

Solution	0.00200 M $Fe(NO_3)_3$ (in 0.1 M HNO_3)	0.00200 M KSCN	0.1 M HNO_3
Blank	5.00 ml	0 ml	5.00 ml
1	5.00 ml	2.00 ml	3.00 ml
2	5.00 ml	3.00 ml	2.00 ml
3	5.00 ml	4.00 ml	1.00 ml
4	5.00 ml	5.00 ml	--------

Record the Absorbance for each solution. Determine the **$FeSCN^{+2}$** equilibrium concentration for each solution. Be careful in handling the cuvets.

Name_____
(Last) (First)

SPECTROPHOTOMETRIC DETERMINATION OF AN EQUILIBRIUM CONSTANT

PURPOSE:

EQUATIONS:

MATERIAL AND EQUIPMENT TABLE:

SAFETY

PROCEDURE:

DATA:

A. Set of Standards Solutions
1. Molar concentration $Fe(NO_3)_3$ _____
2. Molar concentration KSCN _____

(Show the setups for each of the required calculations in the table below for Standard Solutions at the bottom of this page.)

3. Table:

Standard Solutions	1	2	3	4	5
Volume KSCN (ml)					
Moles $FeSCN^{2+}$					
$[FeSCN^{+2}]$					
Absorbance, A					

4. Sample Setups Molarity of SCN^-, $[SCN^-]$ in 100 mL KSCN

B. GRAPH (requires a full page)
Graph should be taped into the lab book page. The entire edge should be taped down onto the page.

C. Set of Equilibrium Solutions

1. Molar concentration $Fe(NO_3)_3$ _____
2. Molar concentration KSCN _____

3. Table:

Solutions	1	2	3	4
a. Volume $Fe(NO_3)_3$ (ml)				
b. Moles Fe^{3+}, initial				
c. Volume KSCN (ml)				
d. Moles SCN^-, initial				
e. Absorbance				

.

CALCULATIONS:

Show a sample calculation for each of the required calculations.

Solutions	1	2	3	4
1. $[FeSCN^{2+}]$, from calibration curve				
2. $[Fe^{3+}]$				
a. Moles $FeSCN^{2+}$ in solution at equilibrium				
b. Mole Fe^{3+} complexed				
c. Mole Fe^{3+} uncomplexed				
d. $[Fe^{3+}]$ at equilibrium, uncomplexed (mole/liter)				
3. $[SCN^-]$				
a. Moles SCN^- complexed				
b. Moles SCN^- uncomplexed				
c. $[SCN^-]$ at equilibrium, uncomplexed				
4. $K_f = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$				

5. Average K_f _____
6. Standard Deviation _____

Sample setups

3b. Moles Fe^{3+}, initial
d. Moles SCN^-, initial
} From data table C.3

2. $[Fe^{3+}]$
   a. Moles $FeSCN^{2+}$ in solution at equilibrium

   b. Moles Fe^{3+} complexed

   c. Moles Fe^{3+} uncomplexed

   d. $[Fe^{3+}]$ at equilibrium, uncomplexed (mole/liter)

3. $[SCN^-]$
   b. Moles SCN^- complexed

   c. Moles SCN^- uncomplexed

   d. $[SCN^-]$ at equilibrium, uncomplexed (mole/liter)

4. K_f

5. Average K_f

6. Standard deviation

QUESTIONS:

1. What effect would the use of a cuvet that has fingerprints and/or waterspots on it have on the absorbance reading for a $FeSCN^{+2}$ solution?

3. What effect would the error in question 1 have on the experimental value for the equilibrium constant?

SUMMARY: