Section ___ Name ________________________

EXPERIMENT 5: PHOTOMETRIC DETERMINATION OF AN EQUILIBRIUM CONSTANT

The following preparatory questions should be answered before coming to class. They are intended to introduce you to several ideas important to aspects of the experiment. You must turn–in your work to your teaching assistant before you will be allowed to begin the experiment. Be sure to bring a calculator and paper to laboratory.

l. The equilibrium constant, K_c, for the reaction

$$A(g) + B(g) \rightleftharpoons AB(g)$$

is 115 at 25 °C. If 1.580×10^{-1} mol of A and 4.721×10^{-5} mol of B are introduced into a 1.00 liter vessel at 25 °C, calculate the equilibrium concentration of all species.

2. Answer the following questions regarding problem #1:

a) How does the amount of B reacting compare to initial amount of B?

b) How does the amount of AB at equilibrium compare to the initial amount of B?

c) What is it about the initial conditions that might explain your answer in 2 b)?

Section ___ Name ________________________

3. The equilibrium constant, K_C, for the reaction

$$C(g) + D(g) \rightleftharpoons CD(g)$$

is unknown at 25 °C. If 1.934×10^{-1} mol of C and 7.315×10^{-5} mol of D are introduced into a 1.00 liter vessel at 25 °C, calculate the equilibrium concentration of CD.

Discuss any assumptions you made in arriving at your answer.

4. a) This experiment is separated into parts I and II. What are the $[Fe^{3+}]$ and $[SCN^-]$ before mixing in each part?

Part I	Part II
$[Fe^{3+}]$ =	$[Fe^{3+}]$ =
$[SCN^-]$ =	$[SCN^-]$ =

b) Briefly, explain why the concentrations of the Fe^{3+} and SCN^- are different in the two parts of the experiment.

c) How are you going to keep from mixing the wrong combinations when you are doing the experiment?

Section ___ Name ______________________

EXPERIMENT 5: PHOTOMETRIC DETERMINATION OF AN EQUILIBRIUM CONSTANT

The purpose of this experiment is to determine the equilibrium constant for a chemical reaction.

To begin the experiment obtain 10 mL samples of $Fe(NO_3)_3$ and KSCN from the reagent bottles marked "stock solution" from the center lab bench. Complete the following table:

Stock Solution	Color of Solution	Cation & Color	Anion & Color
$Fe(NO_3)_3$			
KSCN			

Mix the two 10 mL samples and record your observations.

Obs. #1

Write the ionic and net ionic equation that best describes the reaction that occurred when the two solutions were mixed. In the net ionic equation indicate the color of all species.

Equ. #1 and #2

The equilibrium constant expression for the net ionic reaction is:

Expl. #1

The equilibrium constant, K_c, can be calculated if the equilibrium concentration of all species, in the equilibrium expression above, are known.

Section ___ Name ________________________

In the experiment, known amounts of the reactants Fe^{3+} and SCN^{-} (thiocyanate ion) will be allowed to react to form the product $FeSCN^{2+}$. If there were a method of determining the amount of $FeSCN^{2+}$ at equilibrium it would be possible to stoichiometrically calculate the equilibrium concentration of the reactants. Substituting into the equilibrium expression above would yield the equilibrium constant.

Fortunately, because $FeSCN^{2+}$ is colored, a light measuring device called a Spectronic 20 can be used to determine, quantitatively, the concentration of $FeSCN^{2+}$ formed at equilibrium. The Spectronic 20 measured the amount of light absorbed by the colored species, $FeSCN^{2+}$. Mathematically the amount of light absorbed by the $FeSCN^{2+}$ is directly proportional to the concentration of $FeSCN^{2+}$, according to the equation:

$$\text{Absorbance (A)} = a \cdot b \cdot [FeSCN^{2+}]$$

where 'a' and 'b' are constants unique to the colored compound and the experiment.

The experiment consists of two parts. In Part I the absorbance of samples of known concentration of $FeSCN^{2+}$ will be measured. This data will be plotted on a sheet of graph paper to obtain a calibration line. In Part II the absorbance of samples containing an unknown concentration of $FeSCN^{2+}$ will be measured.

Briefly, discuss the importance of the Part I experiment and how the results of Part I will be used in Part II.

Expl. #2

Section ___ Name ________________________

Experimental Procedure: Work in pairs

Checkout: 1 – 10 mL Mohr pipet
(per pair) 5 – 18 x 150 mm test tubes
5 – Spectronic 20 test tubes (note: these Spec 20 test tubes are very expensive.)

Part I. Calibration Line (*Note: The concentration of reagents vary in Part I and Part II*)

A. Preparing Solutions:

Place the five 18 x 150 mm test tubes in a test tube rack and clearly label them A through E. Obtain 60 mL of the 0.200 M $Fe(NO_3)_3$ solution in a 100 mL beaker, 20 mL of 9.00 x 10^{-4} M KSCN in a 50 mL beaker and 40 mL of 0.500 M HNO_3 in another 50 mL beaker. Write the chemical equations which indicate the ions that are in these three solutions.

Equ. #1, #2 and #3

When solutions A – E are prepared, extreme care must be exercised to insure that the exact amount of each reagent is added to each test tube. To do this use the Mohr pipets to dispense the specific volume. **(DO NOT MOUTH PIPET.)** Follow your TA's instructions on how to properly use a Mohr pipet. Practice with it before beginning the mixing of solutions A – E. A few minutes of practice could prevent having to repeat the experiment. If at any time during the preparation of the mixtures a solution in a Mohr pipet turns brownish red, then the pipet is contaminated. It must be cleaned and the solution for that test tube prepared again. Suggestion: add one of the reagents to all the test tubes, clean the Mohr pipet and add another reagent to the test tube, etc.

Pipet into each test tube the amount of each reagent specified in Table I. Carefully mix the solution so the color is homogeneous.

Table I

Test Tube	mL of .200 M $Fe(NO_3)_3$	mL of 9.00 x 10^{-4} M KSCN	mL of .500 M HNO_3
A	10.00	5.00	5.00
B	10.00	4.00	6.00
C	10.00	3.00	7.00
D	10.00	2.00	8.00
E	10.00	0.00	10.00

Solution E is termed the "blank."

Section ___ Name ________________________

B. Calibrating Spectronic 20 and Measuring Sample Absorption of Solutions A–D.

The blank (Solution E) will be used to standardize the spectrophotometer. After the Spectronic 20 has warmed up for 30 minutes, adjust the wavelength dial to 480 nanometers (nm). Before inserting the blank, adjust the meter reading to 0% transmittance using the left knob. To read the meter, superimpose the needle with its reflection. Insert Solution E into the Spectronic 20 sample chamber so the line on the test tube matches the line in the Spectronic 20 sample chamber, and adjust the meter reading to 100% transmittance using the right knob. Remove the blank and check the meter reading to be sure it is at 0% again. If it is not a 0%, readjust the needle using the left knob and place the blank in the sample chamber and use the right knob to adjust the needle to 100%. Repeat until the Spectronic 20 reads 0% without the blank and 100% with the blank. When the Spectronic 20 is standardized do not touch the calibrating knobs.

Fill the remaining Spectronic 20 test tubes with solutions A – D (are they labeled?). Use a Kim–wipe and clean the outside of the Spectronic 20 test tube, then place the tube in the sample chamber and record the absorbance and % transmittance for the solution on the data page. Clean off the tube for each of the remaining solutions and make the remaining absorbance measurements.

Table II
Calibration Line Absorbance Data

Test Tube	% Transmittance	Absorbance
A		
B		
C		
D		

Using the data in Table I, several calculations must be performed at this point in the experiment. First, the initial concentrations of the reactant ions must be determined. Table I provides the concentrations of the 'stock' solutions of each ion and the volumes in each test tube. Using this data complete Table III. Note: Be sure to take into account the dilution effect.

After completing Table III, plot the data on a piece of graph paper which you can obtain from your teaching assistant. The calibration line is prepared by plotting absorbance (y–axis) versus [$FeSCN^{2+}$] (x–axis). The calibration line will be needed to complete Table VII.

Section ___ Name ________________________

Table III
Calibration Line Concentration Data

Test Tube	Fe^{3+} Before Mixing	Fe^{3+} After Mixing[1]	SCN^{-} Before Mixing	SCN^{-} After Mixing[1]	$FeSCN^{2+}$ at Equilibrium	Absorbance
A	.200		9.0×10^{-4}			
B	.200		9.0×10^{-4}			
C	.200		9.0×10^{-4}			
D	.200		9.0×10^{-4}			

Work Space: (Show sample calculation for one of these tube).

[1] After mixing means after combining the three solutions. Calculate the new concentrations in the solutions prior to the reaction occurring.

Section ___ Name ________________________

Sheet of Graph Paper

Section ___ Name ________________________

Part II. Determination of K_c

A. Preparing Solutions:

Clean the test tubes containing solutions A–D and re–label as solutions F through I. Do not throw away Solution E. Fill each test tube with the amounts of each reagent specified in Table IV and carefully mix each solution so the color is homogeneous. As in Part I, be as accurate as possible when using the Mohr pipet to prepare the Solutions F–I.

Table IV

Test Tube	mL of 1.00×10^{-2} M Fe^{3+}	mL of 1.13×10^{-3} M SCN^{-}
F	2.50	2.50
G	2.50	5.00
H	5.00	2.50
I	5.00	1.00

Before measuring the absorbances of Solutions F–I, check the calibration of the Spectronic 20 using the blank (Solution E).

Measure and record the absorbance[2] and % transmittance of Solutions F–I in the data table below (Table V). Remember to wash the Spectronic 20 test tube with a small amount of the solution to be measured before filling the test tube. Also clean the outside of the test tube using the Kim–wipes.

Table V
Equilibrium Absorbance Data

Test Tube	% Transmittance	Absorbance
F		
G		
H		
I		

[2] In the event that the % transmittance data is more accurate than the absorbance data, the following equation may be used to convert to % transmittance data to absorbance:

$$A = 2 - \log \%T$$

Section ___ Name ________________________

Complete Tables VI and VII to calculate the equilibrium constant, K_c, for the reaction.

Table VI
Equilibrium Concentration Data

Test Tube	Fe^{3+} Before Mixing	Fe^{3+} After Mixing	SCN^- Before Mixing	SCN^- After Mixing	Absorbance
F	1.0×10^{-2}		1.13×10^{-3}		
G	1.0×10^{-2}		1.13×10^{-3}		
H	1.0×10^{-2}		1.13×10^{-3}		
I	1.0×10^{-2}		1.13×10^{-3}		

Work Space: (Show sample calculation for one of the test tubes).

Section ___ Name ________________________

Table VII
Equilibrium Constant Calculation

at Equilibrium[3]	at Equilibrium	$FeSCN^{2+}$ at Equilibrium	Fe^{3+} K_c	SCN^- Tube	Test Absorbance
F					
G					
H					
I					

Work Space: (Show sample calculation for one of the test tubes).

[3] The equilibrium concentration of $FeSCN^{2+}$ is obtained from the Part I calibration line.

Section ___ Name ________________________

Additional problems to be turned in with the laboratory write-up. SHOW ALL CALCULATIONS.

1. In the reaction

$$A(g) + 2B(g) \text{ ä } 3C(g)$$

initially 1.80 mol of A, 4.20 mol of B and 1.00 mol of C are placed in a 3.00 liter container. Analysis shows 4.50 mol of B at equilibrium. Calculate the equilibrium constant for the reaction.

2. In the space below enter the concentrations of Fe^{3+} and SCN^{-} in test tube 'C'.

Fe^{3+} = ______________ M

SCN^{-} = ______________ M

absorbance = ______________

When a few drops of Fe^{3+} are added to test tube 'C' the absorbance of the solution does not change significantly. Briefly, explain this observation.

When a few drops of SCN^{-} are added to test tube 'C' the absorbance of the solution does change. Briefly, explain this observation.

Section ___ Name ________________________

3. Consider Problem #1 on page 1 of the experiment. What would be the percentage error if we assumed the equilibrium concentration of AB was equal to the initial concentration of B?

The equilibrium constant, K_c, for the reaction

A(g) + B(g) ä AB(g)

is 115 at 25 °C. If 1.580×10^{-1} mol of A and 4.721×10^{-5} mol of B are introduced into a 1.00 liter vessel at 25 °C, calculate the equilibrium concentration of all species.

4. If, while preparing solutions A in Part I, the solution in the pipet turns brownish red, explain what has happened and why it is necessary to repeat the preparation of that test tube.