

Determination of an Equilibrium Constant

NOTE: You will use the SpectraSuite Spectrophotometer. See additional handouts for more information about using this instrument.

INTRODUCTION

For a general chemical system at equilibrium:



The Law of Mass Action states that

$$\frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} = K_c$$

where K_c , the equilibrium constant, is a constant for a given temperature.

In this experiment you will study the equilibrium properties of the reaction between the iron (III) ion and the thiocyanate ion:



Because the FeSCN^{2+} ion has a deep red color, a spectrophotometer can be used at 447 nm wavelength to determine its concentration. The equilibrium concentrations of Fe^{3+} and SCN^{-} can be calculated from the initial concentration values and the amount of FeSCN^{2+} that has been formed. The equilibrium constant, K_c , is calculated from the equilibrium concentration values using the equation:

$$K_c = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^{-}]} \quad (2)$$

The purpose of the experiment is to calculate K_c of reaction (1) for several reaction mixtures with initially different concentrations of the reactants, in order to show that within experimental error, K_c , indeed has the same value in each mixture.

In the first part of the experiment, a Beer's Law calibration curve is obtained for FeSCN^{2+} by measuring the absorbance of standard solutions, that is, solutions with known concentrations. In the second part of the experiment the absorbance is measured for various reaction mixtures and the concentration of FeSCN^{2+} is calculated using the slope of the calibration curve.

EXPERIMENTAL PROCEDURE

Special equipment needed:

- one 50-mL volumetric flask and stopper
- four 25-mL volumetric flasks and stoppers
- two 5-mL graduated pipets
- one 5-mL volumetric pipet
- one 10-mL graduated pipet
- pipet bulb

Reagents:

For work at your workstation obtain about:

30 mL of 2.00×10^{-3} M KSCN (for Part A and B)

100 mL of 0.10 M $\text{Fe}(\text{NO}_3)_3$ prepared in 0.50 M HNO_3 (for Part A)

30 mL of 2.00×10^{-3} M $\text{Fe}(\text{NO}_3)_3$ prepared in 1.0 M HNO_3 (for Part B)

- Pour the solutions into the smallest possible clean dry beakers.
- The $\text{Fe}(\text{NO}_3)_3$ solutions have been prepared in HNO_3 so that the $[\text{H}_3\text{O}^+]$ is kept approximately constant in all mixtures used for this experiment.

Part A. Beer's law calibration curve

1. Measure carefully 6.00 mL of 2.00×10^{-3} M KSCN solution into the 50-mL volumetric flask. Dilute with deionized water(DW) to the mark, stopper and mix well. Use this KSCN solution for the next step.
2. Measure carefully 2.00, 4.00, 7.00, and 10.00 mL of the KSCN solution prepared in Step 1 successively into four 25-mL volumetric flasks.
3. Dilute each solution to the mark with 0.10 M $\text{Fe}(\text{NO}_3)_3$. Stopper the flasks and mix the solutions well.
4. Using an OceanOptics Spectrophotometer measure the absorbance of each solution at 447 nm wavelength. Use the 0.10 M $\text{Fe}(\text{NO}_3)_3$ solution as a blank.

Part A. Results and Calculations

1. Molar concentration of KSCN in a 50-mL volumetric flask = _____
2. In the mixtures used, SCN^- is the limiting reagent and essentially all of it reacts to form FeSCN^{2+} . Therefore use the number of moles of KSCN to calculate the concentration of FeSCN^{2+} in each solution prepared in Step 3.

3. Complete:

25-mL volumetric flask	1	2	3	4
Vol. of KSCN soln. mL	2.00	4.00	7.00	10.00
No. moles SCN^-				
No. moles FeSCN^{2+}				
[FeSCN^{2+}]				
Absorbance				

4. Plot a graph of A (absorbance) vs molar concentration of FeSCN^{2+} .
5. Using linear least squares find the slope of your graph. Slope = _____

Part B. Determination of K_c

1. Label five regular size test tubes 1 to 5 using a pencil.
2. **As precisely as you can**, measure the volumes of solutions into test tubes 1 to 5 according to the following table. The $\text{Fe}(\text{NO}_3)_3$ solution to be used here is the $2.00 \times 10^{-3} \text{ M}$ $\text{Fe}(\text{NO}_3)_3$ prepared in 1.0 M HNO_3 . **Note:** *This is not the same $\text{Fe}(\text{NO}_3)_3$ solution as was used for Part A.*

Test tube no.	1	2	3	4	5
$\text{Fe}(\text{NO}_3)_3$ mL	5.00	5.00	5.00	5.00	5.00
KSCN mL	1.00	2.00	3.00	4.00	5.00
H_2O mL	4.00	3.00	2.00	1.00	0.00

3. Mix each solution thoroughly with a glass stirring rod. Be sure to dry the stirring rod after mixing each solution.
4. Place a portion of the solution from test tube 1 into a spectrophotometer cuvette and measure the absorbance at 447 nm using the $2.00 \times 10^{-3} \text{ M}$ $\text{Fe}(\text{NO}_3)_3$ solution as the blank.
5. Repeat Step 4 for solutions 2 to 5.

Part B. Results and Calculations

1. Use the slope obtained for the calibration curve in Part A, to calculate the molar concentration, $[\text{FeSCN}^{2+}]$, for each solution at equilibrium:

$$[\text{FeSCN}^{2+}] = \text{absorbance/slope}$$

2. Complete the table:

Test tube no.	Absorbance	Equilibrium $[\text{FeSCN}^{2+}] \times 10^{-4}$
1		
2		
3		
4		
5		

3. Calculate the initial no. moles as $\text{Volume}_{\text{initial}} \times \text{Molarity}_{\text{initial}}$.

For example, for the mixture in test tube 1,

$$\text{initial no. moles } \text{Fe}^{3+} = 5.00 \times 10^{-3} \text{ L} \times 2.00 \times 10^{-3} \text{ mol/L} = 10.0 \times 10^{-6} \text{ mol}$$

$$\text{initial no. moles } \text{SCN}^- = 1.00 \times 10^{-3} \text{ L} \times 2.00 \times 10^{-3} \text{ mol/L} = 2.0 \times 10^{-6} \text{ mol}$$

- Calculate the other initial no. moles similarly.
- To calculate the no. of moles at equilibrium, first enter the equilibrium no. of moles of FeSCN^{2+} . These are calculated as:

equilibrium conc. value, $[\text{FeSCN}^{2+}]$, from the table above (step 3) x total volume of solution
 (= 0.0100 L for all trials)

Then calculate the equilibrium no. moles

$$\begin{aligned} \text{Fe}^{3+} &= \text{initial no. moles Fe}^{3+} - \text{no. moles Fe}^{3+} \text{ reacted} \\ &= \text{initial no. moles Fe}^{3+} - \text{no. moles FeSCN}^{2+} \text{ at equilibrium.} \end{aligned}$$

Similarly, equilibrium no. moles

$$\text{SCN}^- = \text{initial no. moles SCN}^- - \text{no. moles FeSCN}^{2+} \text{ at equilibrium.}$$

- Calculate the molar concentrations at equilibrium by dividing the no. of moles at equilibrium by the total volume of the solution, which was 0.0100 L for all trials.
- Calculate the equilibrium constant, K_c , value using the equilibrium molar concentrations and equation (2).
- Complete the table:

Mixture in test tube	Initial no. moles x 10^{-6}			Equilibrium no. moles x 10^{-6}			Equilibrium molar conc. x 10^{-4}			
	Fe^{3+}	SCN^-		Fe^{3+}	SCN^-	FeSCN^{2+}	Fe^{3+}	SCN^-	FeSCN^{2+}	K_c
1										
2										
3										
4										
5										

Average $K_c =$ _____