EXPERIMENT 11

EQUILIBRIUM CONSTANT OF IRON THIOCYANATE

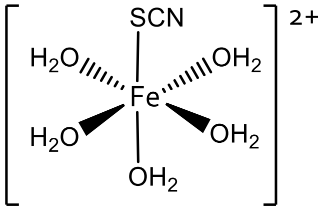
Objectives:

The objective of this experiment is to determine the value of the equilibrium constant for the equilibrium system of iron (III) ion and thiocyanate ion forming the iron-thiocyanate complex ion. The complex ion is highly colored therefore spectrophotometry will be used to determine the concentration of the complex in solution. Students will identify whether the reaction is endothermic or exothermic by evaluating the effect of temperature on the equilibrium constant.

Background:

In this procedure the equilibrium constant, K, for the iron (III) ion, thiocyanate ion, iron thiocyante complex ion system is determined at room temperature. The equilibrium reaction equation is written using half arrows in the forward and reverse direction (⇌) to indicate that the reaction system is dynamic and does not proceed fully to completion.

$Fe^{3+}(aq)$	+	$SCN^{-}(aq)$	⇌	$FeSCN^{2+}(aq)$
colorless		colorless		red-brown solution



The equilibrium constant is equal to the ratio of the equilibrium concentrations of the products to the equilibrium concentrations of the reactants raised to their stoichiometric coefficients. For the system being investigated the equilibrium constant expression is

$$K = \frac{[\mathrm{FeSCN}^{2+}]_{eq}}{[Fe^{3+}]_{eq}[SCN^{-}]_{eq}}$$

The value of the equilibrium constant does not depend on the initial concentrations of reactants and products but is calculated using equilibrium concentrations of the chemical species involved. It depends only upon the temperature and reaction environment of the equilibrium system.

The magnitude of the equilibrium constant gives insight to the composition of the equilibrium solution. When K=1, the solution in equilibrium consists equally of reactants and products (i.e. numerator and denominator in the above equation are equivalent). But if the value of K is very small or very large the equilibrium is said to lie to the left or right, respectively. For example, if the equilibrium constant is a very small value the equilibrium system will lie towards the left and the solution in equilibrium will contain mostly starting reagents and very little product. This solution can also be described as the equilibrium "favoring the reactants". Likewise, if the equilibrium constant is a very large value the equilibrium system will lie towards the right and the solution in equilibrium will contain mostly products and very little starting reactants. This solution can also be described as the equilibrium "favoring the products".

In this procedure three equilibrium solutions having different initial concentrations of reactants are investigated. In each of the three runs the system is allowed to reach equilibrium and the equilibrium concentrations of the product and reactants are determined. These equilibrium concentrations are then used to evaluate the value of the equilibrium constant. It should be noted that equilibrium is a thermodynamic effect. The rate at which a system reaches equilibrium is a kinetic effect and is dependent on the magnitude of the activation energy for the reaction. Because of this, it is important to allow the equilibrium solutions proper time to reach equilibrium, in this case 10-15 minutes.

Spectrophotometry is used to determine its equilibrium concentration in each of the three equilibrium solutions because the product complex ion, $FeSCN^{2+}$, has a characteristic red-brown color in solution. First the wavelength of maximum absorbance, λ_{max}, is determined and then the absorbance of each of the equilibrium solutions is compared to the absorbance of a standard to determine the concentration of the complex ion.

The preparation of the standard in this procedure involves the application of Le Chatelier's Principle to the equilibrium system to produce a solution of known concentration. A very large amount of thiocyanate ion is added to a system driving the equilibrium entirely to the product side. This allows the calculation of the concentration of the iron thiocyanate ion directly from the initial concentration of the iron(III) ion.

$$Fe^{3+}_{(aq)} + \underset{\text{large excess}}{SCN^{-}_{(aq)}} \rightarrow FeSCN^{2+}_{(aq)}$$

Le Chatelier's principle can also be applied to a system where temperature has been changed. For an equilibrium system where the formation of the product is **endothermic**, the system must absorb heat from the surroundings. Therefore "heat" can essentially be added as a reactant in the reaction equation. If the temperature of the equilibrium solution is increased then the equilibrium will shift toward the products to alleviate the stress of the excess heat on the equilibrium. The effect of the equilibrium shift will result in a higher value for the equilibrium constant, K.

$$\text{(increased heat) + reactants} \xrightarrow{\text{Shift to the right}} \text{products}$$

Likewise, for an equilibrium system where the formation of the product is **exothermic**, the system will release heat to the surroundings. Therefore "heat" is added as a product in the reaction equation. If the temperature of the equilibrium solution is increased then the equilibrium will shift toward the reactants to alleviate the stress of the excess heat on the equilibrium. The effect of the equilibrium shift will result in a lower value for the equilibrium constant, K.

$$\text{reactants} \xleftarrow{\text{Shift to the left}} \text{products + (increased heat)}$$

Analyzing the trend in the value of K as temperature of an equilibrium solution is increased will allow the reaction to be classified as an endothermic or exothermic reaction.

Tasks to be completed:

1. A standard solution of iron (III) thiocyanate complex ion is prepared volumetrically.
2. Three equilibrium solutions are prepared in test tubes by dispensing reactants from burets.
3. Absorbance of room temperature solutions are measured at the wavelength of maximum absorbance to calculate the equilibrium constant for the reaction.
4. Absorbance of one equilibrium solution is evaluated at elevated and lower temperature to evaluate the thermodynamics of the equilibrium reaction.

Experimental Procedure: To be completed individually but reagents will be shared.

I. Prepare reagent burets. (This is enough reagent for two students to share.)

1. Before preparation of burets with reagents. Rinse both with deionized water.
2. Using a clean, dry 50 mL beaker obtain 45 mL 0.00150 M $Fe(NO_3)_3$, the source of the iron (III) ion. Obtain a 50 mL buret. Using about 5 mL of the $Fe(NO_3)_3$ solution carefully rinse with the buret and stopcock area. Fill the buret to the 10.00 mL marking. Maintain an organized work area and keep the solution labeled.
3. Using a clean, dry 100 mL beaker obtain 50 mL of 0.00150 M KSCN, the source of the thiocyanate ion. Obtain a second 50 mL buret. Using about 5 mL of the KSCN solution carefully rinse with the buret and stopcock area. Fill the buret to the 5.00 mL marking. Maintain an organized work area and keep this solution identified.

II. Prepare a standard solution of the iron thiocyanate complex ion (To be prepared individually)

1. Deliver 3.00 mL of 0.00150 M iron(III) nitrate solution directly into a 100 mL volumetric flask.
2. Add approximately 0.5 gram of solid KSCN and approximately 50-70 mL deionized water to the flask. Swirl the flask gently until all solid is dissolved.
3. Once the solid is completely dissolved dilute to the mark with deionized water. Mix the solution well by inverting and shaking ten times.
4. **Allow at least 10 minutes** for the solution to reach equilibrium before analyzing.

III. Prepare equilibrium solutions (To be prepared individually)

1. Prepare three equilibrium solutions in clean, DRY, test tubes as per the table below. Take care to keep work organized and to deliver exact volumes from the burets directly into the test tubes.
2. Mix each solution well using Parafilm so the concentrations are consistent throughout the solution.
3. **Allow at least 10 minutes** for the solutions to reach equilibrium before analyzing.

Equilibrium solution Run #	**1**	**2**	**3**
Volume, mL 0.00150 M $Fe(NO_3)_3$	4.00	5.00	6.00
Volume, mL 0.00150 M KSCN	8.00	7.00	6.00

IV. Prepare the Spectrophotometer and determine λ_{max}

Spectrophotometers will be shared during this experiment. Only one of the two students using the spectrophotometer will need to complete the spectrophotometer set up.

1. Connect a SpectroVis spectrophotometer to a computer equipped with LoggerPro software. Open the LoggerPro software.

2. Blank (calibrate) the spectrophotometer using deionized water.

   a. *Open the Experiment menu and select Calibrate → (Spectrometer)*. The following message appears in the Calibrate dialog box: "*Waiting ··· seconds for the device to warm up.*" After 60 seconds, the message changes to: "*Warm-up complete.*"

   b. Place a cuvet ¾ filled with deionized water into the cuvet holder of the spectrophotometer. If using a cuvet with frosted sides, align the cuvet so that the clear sides are in line with the light source of the spectrophotometer. Click "*Finish Calibration*", and then click OK.

3. Configure the software to measure solution absorbance at the wavelength of maximum absorbance.

   a. Place a cuvet ¾ filled with the standard solution in the spectrophotometer. Obtain an absorption spectrum. Select ▶ Collect, when the spectrum appears select ■ Stop.

   b. Select the Configure Spectrometer Data Collection icon, , on the toolbar

   c. Select the *Abs vs Concentration* collection mode.

   d. Verify that the wavelength of maximum absorbance is selected. Click OK to proceed. Select "No" in the dialog box that appears concerning the storing of the latest run.

   e. The absorbance of the standard solution at the wavelength of maximum absorbance should now appear in the bottom left corner of the screen. Record the wavelength of maximum absorbance and the absorbance of the standard solution on the Data Sheet. **Share the wavelength of maximum absorbance with the other student using the spectrophotometer as the absorbance of all solutions will be examined at this wavelength, regardless of who prepared them.**

IV. Spectrophotometric analysis of the solutions

1. Obtain the temperature of the standard solution using a thermometer submerged in the volumetric flask. Record this value on the Data Sheet as the temperature for all solutions at room temperature.

2. Measure the absorbance of the equilibrium solutions in Runs #1-3 at the wavelength of maximum of absorbance, λ_{max}.

   a. Use the same cuvet for all measurements. Between each solution analysis completely empty the cuvet into a waste beaker, rinse with deionized water from a wash bottle and rinse the cuvet twice with the next solution to be analyzed**, discarding rinses into the waste beaker**, before filling with the new solution to be analyzed.

   b. Fill the cuvet ¾ full and make certain there are no air bubbles in the solution nor fingerprints on the cuvet. **Do not discard the last solution analyzed.**

3. Prepare a small ice bath in a 50 ml beaker taking care to keep the ice/water depth less than the height of a cuvet.
   a. Place the solution filled cuvet in the ice bath being careful to prevent any water from entering the cuvet and altering the solution concentration holding the cuvet if necessary.
   b. Allow five minutes for the temperature of the solution in the cuvet to reach the ice bath temperature then remove the cuvet from the ice bath, carefully and quickly dry it and place it in the spectrophotometer.
   c. **Quickly read the absorbance of the solution at this lower temperature.** The absorbance reading will change as the solution warms so note and record the initial reading. Record the temperature of the ice bath.

4. Next place the solution filled cuvet in the elevated temperature bath provided in the lab.
   a. Allow five minutes for the temperature of the solution in the cuvet to reach the elevated temperature.
   b. After five minutes remove the cuvet from the water bath, carefully and quickly dry it and place it in the spectrophotometer. **Quickly read the absorbance of the solution at this higher temperature.** The absorbance reading will change as the solution cools so note and record the initial reading.
   c. Record the temperature of the water bath and the initial absorbance of the solution at this elevated temperature.

Waste Handling and Clean Up:

- Dispose of all waste solutions in the properly marked waste containers.
- Dispose of used cuvets in the waste can.
- Rinse burets with deionized water. Wash volumetric flasks and cap with soap and tap water, rinse with DI water.
- Unplug cord from the spectrophotometer. Leave spectrophotometer, cord, Kim-wipes, and cuvet holder neatly at the workstation.

Data Analysis:

Concentrations of Standard Solution

Because the system was flooded with KSCN all of the iron(III) ion introduced with the iron (III) nitrate solution was converted to iron thiocyanate ion then diluted to 100.00 mL. Therefore, the concentration of the product in the standard solution can be directly calculated.

$$(molarity\ Fe(NO_3)_3)(0.00300\ L)\left(\frac{1\ mole\ Fe^{3+}}{1\ mole\ Fe(NO_3)_3}\right)\left(\frac{1\ mole\ FeSCN^{2+}}{1\ mole\ Fe^{3+}}\right) = moles\ FeSCN^{2+}$$

$$\frac{moles\ Fe(SCN)^{2+}}{0.10000\ L} = concentration\ FeSCN^{2+}\ standard, M$$

Initial concentrations of Fe^{3+} and SCN^- in equilibrium solutions

Calculate the initial concentration of each ion in each equilibrium dividing the moles of reactant by the total volume of solution in each test tube. The total volume in each test tube is 12.00 mL.

$$\frac{(volume\ of\ reactant\ solution, L)(molarity\ of\ reactant\ solution)}{0.01200\ L} = [reactant]_{initial}$$

Equilibrium concentration of $Fe(SCN)^{2+}$ in each equilibrium solution

Beer-Lambert law is used to relate concentration and absorbance of the standard to concentration and absorbance of each solution.

$$A = \varepsilon bc$$

A = absorbance
ε = molar absorptivity, liter/(mole cm) (a characteristic of the substance being analyzed)
b = path length, cm (distance through which the light travels through the substance)
c = concentration, mole/liter

The Beer-Lambert law can be written for both the standard (std) solution and equilibrium (eq) solution. Because the pathlength and molar absorptivity components are equal for both solutions they will cancel when the two equations are added together. A simplified equation shows how to calculate the equilibrium concentration of the complex ion for each equilibrium solutions.

Simplified equation: $c_{eq} = (A_{eq})\left(\frac{c_{std}}{A_{std}}\right)$

Equilibrium solutions: $[\mathrm{FeSCN}^{2+}]_{eq} = (A_{\mathrm{FeSCN}^{2+}eq})\left(\frac{c_{\mathrm{FeSCN}^{2+}\,\mathrm{std}}}{A_{\mathrm{FeSCN}^{2+}\mathrm{std}}}\right)$

Equilibrium concentrations of Fe^{3+} and SCN^- in each equilibrium solution

Calculate the equilibrium concentrations of reactants in each equilibrium solution. The relationships are best illustrated using a standard ICE box.

Standard ICE box for calculation of equilibrium concentrations			
	$[Fe^{3+}]$	$[SCN^-]$	$[FeSCN^{2+}]$
Initial concentration	$[Fe^{3+}]_{initial}$	$[SCN^-]_{initial}$	0
Change in concentration	-x	-x	+x
Equilibrium concentration	$[Fe^{3+}]_{initial}$- x therefore, $[Fe^{3+}]_{eq}$ = $[Fe^{3+}]_{initial}$ - $[FeSCN^{2+}]_{eq}$	$[SCN^-]_{initial}$- x therefore, $[SCN^-]_{eq}$ = $[SCN^-]_{initial}$ - $[FeSCN^{2+}]_{eq}$	$[FeSCN^{2+}]_{eq}$ = x

Equilibrium constant from each solution

Calculate the equilibrium constant <u>for each</u> equilibrium solutions by substituting the equilibrium concentrations into the equilibrium constant expression.

$$K = \frac{[\mathrm{FeSCN}^{2+}]_{eq}}{[Fe^{3+}]_{eq}[SCN^-]_{eq}}$$

Determination of exothermic/endothermic nature of reaction

Le Chatlier's principle predicts that with an increase in temperature the equilibrium of an endothermic reaction system will shift to the product side, increasing the value of the equilibrium constant. A temperature increase will shift an exothermic reaction system to the reactant side, decreasing the value of the equilibrium constant.

Reactants + heat $\rightleftharpoons$ products	$\uparrow$ T $\uparrow$ K	endothermic
Reactants $\rightleftharpoons$ products + heat	$\uparrow$ T $\downarrow$ K	exothermic

Evaluate the influence of temperature on the equilibrium constant and identify the formation of the complex ion as an endothermic or exothermic process. Arrange K values by increasing temperature.

$$K_{\text{ice bath}} \rightarrow K_{\text{room temperature}} \rightarrow K_{\text{warm bath}}$$

Data Sheet

Name:______________________________

Date: _______

CHM123L section___ Instructor________________

Analysis of Standard Solution

Wavelength of maximum absorbance, λ_{max} _______________

Absorbance of standard solution, $A_{\mathrm{Fe(SCN)^{2+}}std}$ _______________

Analysis of Equilibrium Solutions

Room Temperature Analysis

Run #	Temperature	Absorbance, $A_{\mathrm{FeSCN^{2+}}eq}$
1		
2		
3		

Elevated / Decreased Temperature Analysis

Run #	Temperature	Absorbance, $A_{\mathrm{FeSCN^{2+}}eq}$
3		
3		

Report Sheet

Name:______________________________________

Date: _______

CHM123L section___ Instructor__________________

Analysis of Standard Solution

1. Concentration of Standard Solution, $c_{\mathrm{FeSCN^{2+}\ std}}$ (Show work)

Equilibrium Constant Analysis at Constant Temperature

2. Calculate the **initial concentration** of Fe^{3+} and SCN^{-} in the equilibrium solutions.

Run #	$[Fe^{3+}]_{initial}$, mol/L	$[SCN^{-}]_{initial}$, mol/L
1		
2		
3		

Report Sheet, cont.

3. Calculate **equilibrium concentration** of $FeSCN^{2+}$, Fe^{3+} and SCN^- in each of the equilibrium solutions and enter them into the table. Show a sample calculation for Run 1 below in a-c.

Run	$[FeSC)^{2+}]_{eq}$ M	$[Fe^{3+}]_{eq}$ M	$[SCN^-]_{eq}$ M	K
1				
2				
3				
			Average K	

Sample Calculation of Run 1:

a. Calculate the equilibrium concentration of the product $FeSCN^{2+}$ in Run 1 from Beer-Lambert Law.

b. Calculate the equilibrium concentration of Fe^{3+} and SCN^- in Run 1 from ICE analysis.

c. Calculate the equilibrium constant for Run 1 based on the equilibrium concentrations of reactants and product.

Report Sheet

Name:_______________________________________

Date: _______

CHM123L section___ Instructor__________________

Equilibrium Constant Analysis at Varying Temperature

4. Calculate **equilibrium concentration** of $FeSCN^{2+}$, Fe^{3+} and SCN^- in Run 3 at varying temperatures. Use initial concentrations for Run 3 calculated on page 11-11.

Temperature	$[FeSCN^{2+}]_{eq}$ M	$[Fe^{3+}]_{eq}$ M	$[SCN^-]_{eq}$ M	K

5. From the variable temperature study, report if the formation of the complex ion is an endothermic or exothermic process. It is helpful to arrange the equilibrium constant for Run 3 from cold to warm temperature. **Include room temperature data in your analysis**. Explain your conclusion.