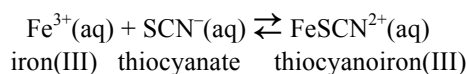


## CHEMICAL EQUILIBRIUM: FINDING A CONSTANT, $K_{eq}$

### INTRODUCTION

Chemical reactions occur to reach a state of equilibrium. The equilibrium state can be characterized by quantitatively defining its equilibrium constant,  $K_{eq}$ . In this experiment, you will determine the value of  $K_{eq}$  for the reaction between iron (III) ions and thiocyanate ions,  $SCN^-$ .



When  $Fe^{3+}$  and  $SCN^-$  are combined, equilibrium is established between these two ions and the product  $FeSCN^{2+}$  ion. The equilibrium constant expression for this reaction is

$$K_{eq} = \frac{[FeSCN^{2+}]_{eq}}{[Fe^{3+}]_{eq}[SCN^-]_{eq}} \quad (1)$$

To find the value of  $K_{eq}$ , which depends only upon temperature, it is necessary to determine the molar concentration of each of the three species in solution at equilibrium. You will determine these concentrations by measuring light that passes through a sample of the equilibrium mixture, with the product,  $[FeSCN^{2+}]$  producing solutions with a redish/orange color absorbing blue light very well. The amount of light absorbed by a colored solution is proportional to its concentration. By comparing the absorbance of each equilibrium system, Abs, to the absorbance of a standard calibration curve (Beer's Law) you can determine  $[FeSCN^{2+}]$  in each of the four solutions.

$$Abs = \epsilon[FeSCN^{2+}] + offset \quad (2)$$

Where  $\epsilon$  is a proportionality constant (slope), and the offset is the y-intercept. A calibration curve has already been prepared for you (below), since the standards for this system are difficult to prepare accurately.

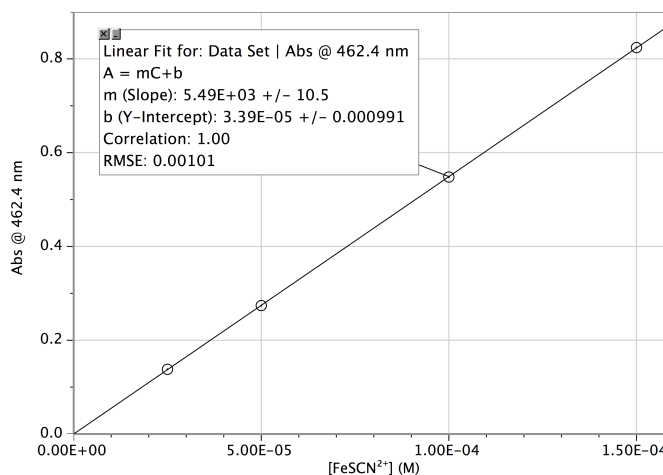
You will prepare a series of solutions that have varied initial concentrations of the  $Fe^{3+}$  ions and the  $SCN^-$  ions, with a constant concentration of  $H^+$  ions. The excess of  $H^+$  ions will ensure that  $Fe^{3+}$  engages in no side reactions (to form  $FeOH^{2+}$ , for example). The  $FeSCN^{2+}$  complex forms slowly, taking at least one minute for the color to develop. It is best to take absorbance readings after a specific amount of time has elapsed, between two and four minutes after preparing the equilibrium mixture. Do not wait much longer than four minutes to take readings, however, because the mixture is light sensitive and the  $FeSCN^{2+}$  ions will slowly decompose. You will use the equilibrium absorbance of each solution to calculate the equilibrium concentrations of each species (product and reactants) in solution at equilibrium.



### MATERIALS

LabQuest System  
SpectroVis Spectrometer  
1 3-mL plastic cuvette  
three small beakers or flasks  
0.00200 M thiocyanate,  $SCN^-$  (KSCN)  
0.00200 M iron (III) nitrate,  $Fe(NO_3)_3$ , prepared in 1.0 M  $HNO_3$   
5-mL autopipet with tips  
tissues (preferably lint-free)

Calibration Curve for  $FeSCN^{2+}$



## Procedure

1. Obtain and wear goggles.
2. Obtain  $\approx 5$  mL 0.0020 M  $\text{Fe}(\text{NO}_3)_3$  and  $\approx 5$  mL of 0.0020 M  $\text{SCN}^-$  in small beakers or flasks. Label each solution!  
**CAUTION:**  $\text{Fe}(\text{NO}_3)_3$  solutions in this experiment are prepared in 1.0 M  $\text{HNO}_3$  and should be handled with care.
3. Obtain a small beaker of distilled water.
4. Plug the SpectroVis spectrometer into the standard USB port of the LabQuest. The LabQuest should default to absorbance measurements.
5. Copy the data table below in your notebook **DATA PAGE**.

TABLE 1

| Solution | 0.0020 M $\text{Fe}^{3+}$ (mL) | 0.0020 M $\text{SCN}^-$ (mL) | Distilled water (mL) | Abs of $\text{FeSCN}^{2+}$ |
|----------|--------------------------------|------------------------------|----------------------|----------------------------|
| BLANK    | 1.00                           | —                            | 2.00                 | —                          |
| 1        | 1.00                           | 2.00                         | —                    |                            |
| 2        | 1.00                           | 1.50                         | 0.50                 |                            |
| 3        | 1.00                           | 1.00                         | 1.00                 |                            |
| 4        | 1.00                           | 0.50                         | 1.50                 |                            |

1. Prepare the blank according to the table. Using a 5-mL autopipet to transfer each solution directly into the 3-mL plastic cuvette. Make sure you use the correct tip! Cap and invert the solution to mix.
2. Align the cuvette so the clear sides of the cuvette are facing the light source (east-west).
3. **Choose Sensors ► Calibrate ► USB:Spectrometer.** There may be a slight delay before the calibrate screen appears. When warm-up is complete, select **Finish Calibration**. After the message “Calibration Completed” appears, **tap OK**. Remove the blank cuvette.

### GENERATING A FULL ABSORBANCE SPECTRUM – SETTING THE WAVELENGTH OF MAXIMUM ABSORBANCE

1. The data collection mode should be Full Spectrum. If not, tap the **Mode:** window and set to **Full Spectrum**. Use the default parameters as listed.
2. Shake dry as completely as possible your cuvette. Prepare the first solution by pipetting directly into the plastic cuvette. Cap the cuvette and invert twice to mix. This solution will first be used to find the wavelength of maximum absorbance.
3. Insert solution 1 into the spectrometer. **Tap the green start arrow** to collect a spectrum. The Spectrometer will display a real-time absorbance spectrum of the product:  $\text{FeSCN}^{2+}$ . **Tap the red Stop button to stop. DO NOT REMOVE THE CUVETTE.**
4. The LabQuest will automatically identify the wavelength of maximum absorbance,  $\lambda_{\text{max}}$ . **Record this wavelength in your notebook. It should be between 450-470 nm.**

### MEASURING THE EQUILIBRIUM SOLUTIONS

1. **Tap the Meter tab.** On the meter screen tap **Mode**.
2. Change the mode to **Events with Entry**. Enter a **Name** (e.g. *Solution*) and **Units** (*none*).
3. **Select Average over 10 seconds. Select OK.**
4. A message will appear warning you to either save or discard the Full Spectrum run. Select Discard.
5. Using solution 1 that is still in the cuvette, start data collection by **tapping the green start arrow**. A graph should appear with the real-time absorbance being shown on the graph and also displayed in the window on the right side of the LabQuest. After the absorbance reading stabilizes, **tap KEEP**. After the ten-second averaging is complete enter the solution number into the LabQuest. **Select OK.**
6. Empty the cuvette contents into your waste container. Shake dry as completely as possible your cuvette.
7. Repeat the previous steps using solutions 2, 3 and 4.
8. After solution 4 is measured, **Tap the red Stop button to stop**. Empty the cuvette contents into your waste container.
9. Using the list view on the LabQuest, record the absorbance values for each solution into your notebook.
10. Clean-up and dispose of all unused reagents and waste in the appropriate waste container.

## REPORT SHEET

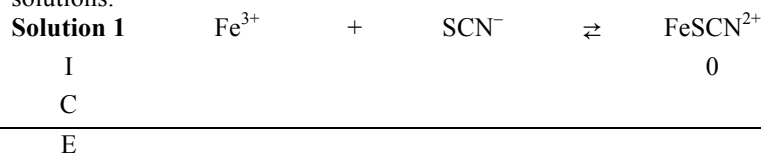
### ICE TABLES for each Solution and Calculation of $K_{eq}$

**Solution 1:** Equilibrium Absorbance Reading \_\_\_\_\_

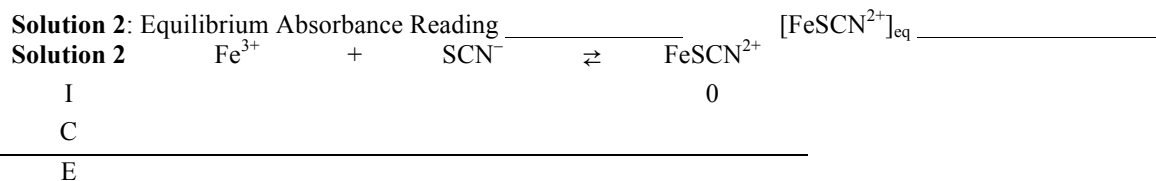
Convert the equilibrium absorbance into an equilibrium concentration of  $FeSCN^{2+}$  using the calibration graph and eqn 2. Use **3 sig figures for the  $[FeSCN^{2+}]_{eq}$  concentration.**

$$[FeSCN^{2+}]_{eq} =$$

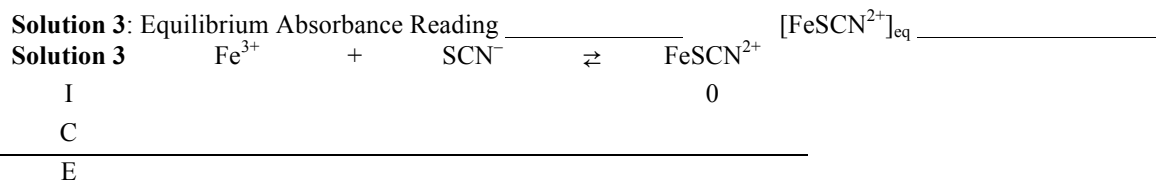
Complete the following ICE Table. You will need to calculate the initial concentration of each reactant by knowing the volumes pipetted (Table 1) and the STOCK molarities of each reactant. Check the label. This is a dilution problem. The equilibrium concentration of product for each ICE table comes from the previous calculation. Repeat for the remaining 3 solutions.



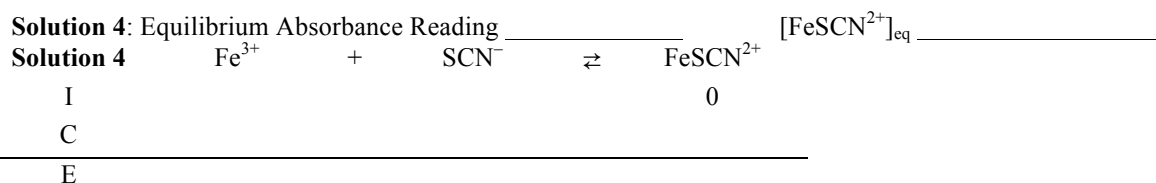
Use the equilibrium concentrations to calculate  $K_{eq}$  for this solution (eqn 1):



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Average equilibrium constant (3 sig figs),  $K_{eq}$  \_\_\_\_\_

**Follow-up Questions**

1. If the equilibrium concentrations of  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  are  $1.0 \times 10^{-2}$  M and  $3.0 \times 10^{-3}$  respectively, what must be the equilibrium concentration of  $\text{FeSCN}^{2+}$ ?

2. What is the value of  $K_{\text{eq}}$  for the reverse reaction,  $\text{FeSCN}^{2+}(\text{aq}) \rightleftharpoons \text{Fe}^{2+}(\text{aq}) + \text{SCN}^-(\text{aq})$ ?

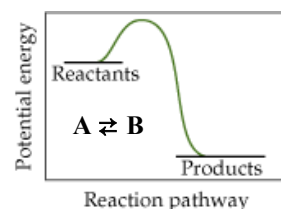
3. Based on the following energy profile answer the following questions for **a system at equilibrium**.

a) Is the **kinetic rate constant** for the forward or reverse reaction is greater?

b) How do the forward and reverse **rates of reaction** compare at equilibrium?

c) At equilibrium, do you expect to have more reactants than products or more products than reactants?

d) Predict whether the equilibrium constant for the process is greater than 1 or less than 1.



4. In thermodynamics we spend a considerable amount of time determining the energetics of reactions that begin at “standard conditions” of concentration/pressure. Standard conditions of concentration are exactly 1 M for all aqueous reactants or products and exactly 1 atm pressure for all gaseous reactants or products.

Answer the following questions assuming we begin ( $Q_1$ ) with **standard conditions for all reactants and products**.

a) Calculate  $Q_1$  under standard conditions of concentration \_\_\_\_\_

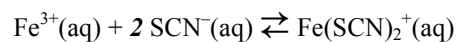
b) Is the system at equilibrium? (Compare  $Q_1$  to your average  $K_{\text{eq}}$ ) \_\_\_\_\_

c) In what direction (if any) will a net reaction take place (fwd. or rev.)? \_\_\_\_\_

d) Use a reaction table to find the equilibrium concentrations of reactants and products if we begin at standard conditions. Note, to solve for final concentrations you will need to use a quadratic equation or the SOLVE function of your TI calculator. **Use your average  $K_{\text{eq}}$  in the calculation.**

**Advanced Analysis of the Data**

In this part of the analysis we will use equilibrium theory to show that the stoichiometry of the reaction CANNOT be 1:2 for the reactants:



If 1:2 is the correct equilibrium stoichiometry, then  $K_{\text{eq}}$  will be defined as follows (*the [SCN<sup>-</sup>] is now squared*):

$$K_{\text{eq}} = \frac{[\text{Fe}(\text{SCN})_2^{+}]_{\text{eq}}}{[\text{Fe}^{3+}]_{\text{eq}}[\text{SCN}^{-}]_{\text{eq}}^2} \quad (3)$$

Repeat your ICE tables from the last page using a 1:2 reactant stoichiometry. For these calculations the initial reactant concentrations are the same as in the previous tables. The  $[\text{Fe}(\text{SCN})_2^{+}]_{\text{eq}}$  is also the same as in your previous tables. The only change will be for  $\Delta[\text{SCN}^{-}]$ . This will be double the previous value since the stoichiometry is 1:2.

|                   |                  |   |                    |                      |                               |  |
|-------------------|------------------|---|--------------------|----------------------|-------------------------------|--|
| <b>Solution 1</b> | $\text{Fe}^{3+}$ | + | $2 \text{SCN}^{-}$ | $\rightleftharpoons$ | $\text{Fe}(\text{SCN})_2^{+}$ | Use the equilibrium concentrations to calculate $K_{\text{eq}}$ for this solution (eqn 3): |
| I                 |                  |   |                    |                      | 0                             |  |
| C                 |                  |   |                    |                      |                               |  |
| E                 |                  |   |                    |                      |                               |  |
| <hr/>             |                  |   |                    |                      |                               |  |
| <b>Solution 2</b> | $\text{Fe}^{3+}$ | + | $2 \text{SCN}^{-}$ | $\rightleftharpoons$ | $\text{Fe}(\text{SCN})_2^{+}$ | Use the equilibrium concentrations to calculate $K_{\text{eq}}$ for this solution (eqn 3): |
| I                 |                  |   |                    |                      | 0                             |  |
| C                 |                  |   |                    |                      |                               |  |
| E                 |                  |   |                    |                      |                               |  |
| <hr/>             |                  |   |                    |                      |                               |  |
| <b>Solution 3</b> | $\text{Fe}^{3+}$ | + | $2 \text{SCN}^{-}$ | $\rightleftharpoons$ | $\text{Fe}(\text{SCN})_2^{+}$ | Use the equilibrium concentrations to calculate $K_{\text{eq}}$ for this solution (eqn 3): |
| I                 |                  |   |                    |                      | 0                             |  |
| C                 |                  |   |                    |                      |                               |  |
| E                 |                  |   |                    |                      |                               |  |
| <hr/>             |                  |   |                    |                      |                               |  |
| <b>Solution 4</b> | $\text{Fe}^{3+}$ | + | $2 \text{SCN}^{-}$ | $\rightleftharpoons$ | $\text{Fe}(\text{SCN})_2^{+}$ | Use the equilibrium concentrations to calculate $K_{\text{eq}}$ for this solution (eqn 3): |
| I                 |                  |   |                    |                      | 0                             |  |
| C                 |                  |   |                    |                      |                               |  |
| E                 |                  |   |                    |                      |                               |  |

Look at your four  $K_{\text{eq}}$  values are they the same? Your answer should be no! They should be continuously increasing from solution 1 to 4 and change by over a factor of three. Why? Because the equilibrium stoichiometry was defined as 1:2, *which is not correct*. With the incorrect stoichiometry the equilibrium constant will not be a “constant”. The equilibrium concentrations we measure in lab will conform to only one balanced chemical reaction, the correct balanced reaction!