

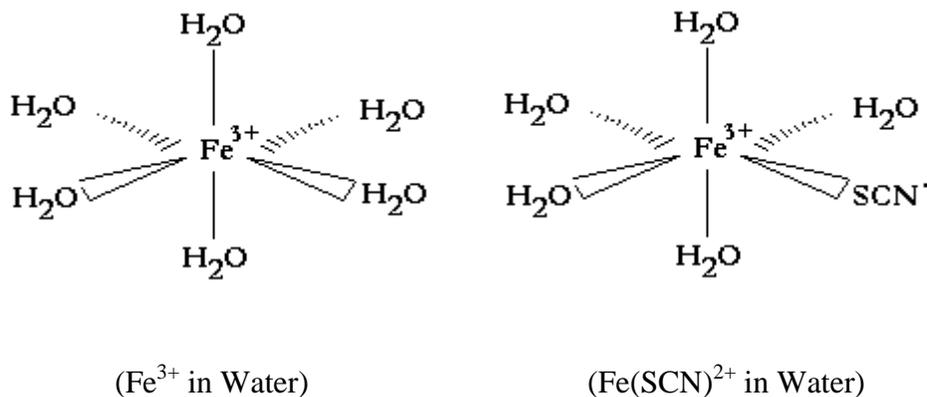
## Determination of the Equilibrium Constant for Ferric Thiocyanate

- To learn about Chemical Equilibrium.
- To learn about the Ferric Thiocyanate system.
- To learn about Absorbance Spectroscopy.

In this laboratory exercise, we will determine the Equilibrium Constant for the reaction between Ferric Ion ( $\text{Fe}^{3+}$ ) and Thiocyanate Ion ( $\text{SCN}^-$ ), which produces a Ferric Thiocyanate Ion ( $\text{Fe}(\text{SCN})^{2+}$ ) complex:

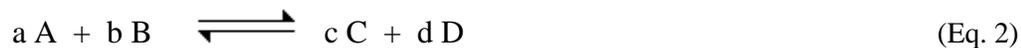


Ferric Thiocyanate is a brick-red Complex Ion which is stable in an aqueous environment. In an aqueous environment, the Ferric Ion ( $\text{Fe}^{3+}$ ) actually exists as a hydrated octahedral complex ion, more correctly denoted  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ . In the presence of Thiocyanate Ion ( $\text{SCN}^-$ ), one of the water molecules is displaced and the Ferric Thiocyanate Ion ( $\text{Fe}(\text{H}_2\text{O})_5\text{SCN}^{2+}$ ) is produced:



We will make use of the highly colored nature of this product to measure its equilibrium concentration, which will in turn allow us to determine the Equilibrium Constant  $K_c$  for the reaction of interest; (Eq. 1).

Recall that for a generalized reaction:



the Equilibrium Constant  $K_c$  is defined as:

$$K_c = \frac{([C]_{eq}/c^\circ)^c ([D]_{eq}/c^\circ)^d}{([A]_{eq}/c^\circ)^a ([B]_{eq}/c^\circ)^b} \quad (\text{Eq. 3})$$

where  $[i]_{eq}$  is the molar concentration of Species  $i$  once the reaction has come to equilibrium and  $c^\circ$  is the standard concentration of any Species in solution.

Since the solution Standard Concentration  $c^\circ$  is numerically equal to  $1M$ , this is notationally dropped from (Eq. 3). We also drop the "eq" notation as it is understood that since we are dealing with an Equilibrium Constant all the concentrations involved will be equilibrium concentrations. Thus, we can generally write the Equilibrium Constant expression as:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (\text{Eq. 4})$$

For the Ferric Thiocyanate system, the Equilibrium Constant expression is:

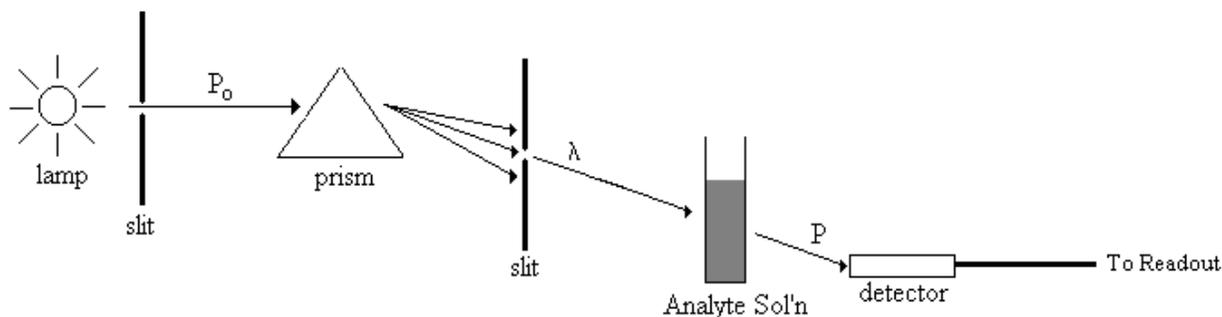
$$K_c = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} \quad (\text{Eq. 5})$$

To measure this Constant, we must be able to measure the concentration of each Species in the mixture at the Equilibrium Point. This is not always a trivial matter! However, if we know the Initial Concentrations of each Species, and measure the Equilibrium Concentration of any other single Species, the reaction stoichiometry will determine the equilibrium concentrations of all the other Species. This reduces the complexity of the experimental problem to finding the equilibrium concentration of a single Species.

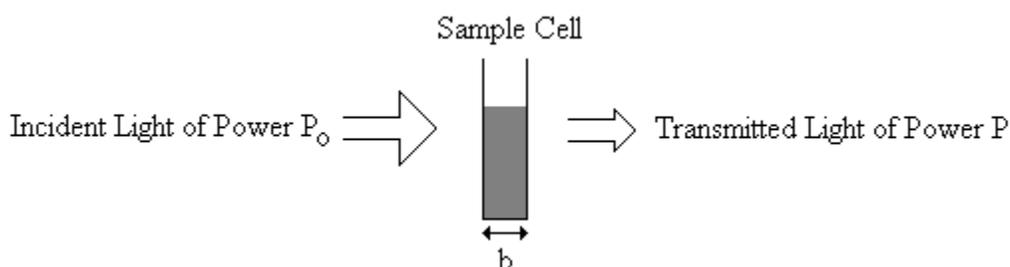
Since the Ferric Thiocyanate ( $Fe(SCN)^{2+}$ ) product is brick-red, and all the other Species are colorless, we can measure its equilibrium concentration by measuring the intensity of the color of the equilibrium solution. Knowing the Initial Concentrations of the  $Fe^{3+}$  and  $SCN^-$  will then allow us to determine their Equilibrium Concentrations via the reaction stoichiometry of (Eq. 1).

We will quantify the intensity of the color of the solution by measuring the Absorbance of light by the solution. Absorbance Spectroscopy involves measuring, via a Spectrometer, the intensity of light after it passes through a colored solution. The deeper the color, the more light will be absorbed.

A UV-Vis Spectrometer consists of a White Light source, dispersive optics to separate the wavelengths of the light, a sample compartment and a detector.



Light from the source passes through an Entrance Slit and is focused on the dispersive element, such as a diffraction grating or prism. This separates out the various wavelengths comprising the White Light into a rainbow of colors. The desired wavelength is selected by rotating the dispersive element such that the desired color passes through an Exit Slit, through the Sample and then onto a detector.



The Transmittance of the light is then defined as:

$$T = \frac{P}{P_o} \quad (\text{Eq. 6})$$

which is related to the Absorbance by:

$$A = -\log T \quad (\text{Eq. 7})$$

Besides the Concentration ( $c$ ) of the absorbing Species, two other factors determine the Absorbance of a sample solution. The further light must travel through a solution, the so-called pathlength  $b$ , the greater is the Absorbance. The ability of the molecule to absorb light at the given wavelength, known as the extinction coefficient  $\epsilon$ , a quantum mechanical effect, will also determine the Absorbance. The relationship between these influences and the Absorbance is given by the Beer-Lambert Law:

$$A = \epsilon b c \quad (\text{Eq. 8})$$

Note the Absorbance is directly proportional to each factor.

One last point needs to be addressed; different colored solutions absorb different wavelengths of light. The color of the light absorbed is directly related to the color of the light transmitted; i.e., the color we see. The color absorbed is the Complement of the color we see:

| Color Absorbed  | Wavelength (nm) | Color Observed  |
|-----------------|-----------------|-----------------|
| Red             | 650-780         | Bluish-Green    |
| Orange          | 595-650         | Greenish-Blue   |
| Yellow          | 580-595         | Blue            |
| Yellowish-Green | 560-580         | Violet          |
| Green           | 500-560         | Purple          |
| Bluish-Green    | 490-500         | Red             |
| Greenish-Blue   | 480-490         | Orange          |
| Blue            | 435-480         | Yellow          |
| Violet          | 380-435         | Yellowish-Green |

This simply means our spectrometer must be set to a wavelength corresponding to the maximal absorbance of the compound. For our brick-red  $\text{Fe}(\text{SCN})^{2+}$  compound, we will measure the absorbance in the blueish region of the spectrum at  $\lambda = 447\text{nm}$ .

So, the measured absorbance of the Equilibrium solution provides us with the Equilibrium Concentration of  $[\text{Fe}(\text{SCN})^{2+}]_e$ . To obtain the Equilibrium Concentrations of  $[\text{Fe}^{3+}]_e$  and  $[\text{SCN}^-]_e$  we apply the reaction stoichiometry:



Thus, if we know the Initial Concentrations of each reagent,  $[\text{Fe}^{3+}]_o$  and  $[\text{SCN}^-]_o$ , the amount present at equilibrium is simply the initial amount minus the amount of  $\text{Fe}(\text{SCN})^{2+}$  produced. This, then, gives us all the desired concentrations:

$$[\text{Fe}(\text{SCN})^{2+}]_e = A / \epsilon b \quad (\text{Eq. 11})$$

$$[\text{Fe}^{3+}]_e = [\text{Fe}^{3+}]_o - [\text{Fe}(\text{SCN})^{2+}]_e \quad (\text{Eq. 12})$$

$$[\text{SCN}^-]_e = [\text{SCN}^-]_o - [\text{Fe}(\text{SCN})^{2+}]_e \quad (\text{Eq. 13})$$

Thus, we can now calculate the desired equilibrium constant  $K_c$ .

So, we will prepare solutions of  $\text{Fe}^{3+}$  and  $\text{SCN}^-$ , mix them and allow the reaction to come to Equilibrium. The Equilibrium Concentration of the product will be measured using Absorbance Spectroscopy. This will allow us to calculate the Equilibrium Concentrations of  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  via the reaction stoichiometry. Once the Equilibrium Concentrations of each Species is known, the Equilibrium Constant can be determined.

### Pre-Lab Safety Questions

1. Why is Nitric Acid referred to as an Oxidizing Acid? What are some particular safety concerns when handling Nitric Acid, as opposed to other strong acids?
2. The SDS for KSCN suggests; "Use only in a chemical fume hood." Why can we ignore this admonition during this laboratory exercise?
3. Should we wear gloves when performing this experiment? Why or why not?

## Procedure

We will be performing this experiment 5 times; using different initial concentrations of each reagent in each trial. We will do this by using different volumes of each reagent drawn from the stock solution, keeping the total volume of all the reagents constant at 10mL. The average equilibrium constant will be calculated using the results for each individual trial. This allows us to obtain a more accurate value for the equilibrium constant.

1. Obtain ~40 mL of  $\text{Fe}(\text{NO}_3)_3$  solution in a small beaker. Do the same for ~25 mL KSCN solution. And, ~ 20 mL  $\text{HNO}_3$ .
2. Use 5 different clean, dry large test tubes. Label them 1 - 5. Using a different pipet for each solution, pipet the following amounts of each reagent into the given test tube. (The  $\text{HNO}_3$  acts to prevent the degradation of the reagents and can be considered inert in this reaction.) Mix each solution thoroughly.

| Trial | $\text{Fe}(\text{NO}_3)_3$ Solution<br>( $2 \times 10^{-3}$ M) | KSCN Solution<br>( $2 \times 10^{-3}$ M) | $\text{HNO}_3$ Solution |
|-------|--|--|-------------------------|
| 1     | 5 mL   | 1 mL                                     | 4 mL                    |
| 2     | 5 mL   | 2 mL                                     | 3 mL                    |
| 3     | 5 mL   | 3 mL                                     | 2 mL                    |
| 4     | 5 mL   | 4 mL                                     | 1 mL                    |
| 5     | 5 mL   | 5 mL                                     | 0 mL                    |

3. Record your observations.
4. Fill a spectrometer cuvette ~2/3 full with each of these solutions. Do the same for an  $\text{HNO}_3$  blank solution. **Do not touch the faces of the cuvettes; handle them from the edges. Use a Kimwipe to clean the faces of the cuvettes before making any readings.**
5. Proceed to the instrument room to make the absorbance measurements.
6. Use the Shimadzu UV-2550 scanning UV-VIS spectrometer to measure the absorbance of each solution at 447 nm. Use your  $\text{HNO}_3$  "blank" to first "zero" the instrument. (Your lab instructor will assist you in making these measurements. The Shimadzu spectrometer is a scanning, double-beam instrument. We will be using it to make single wavelength measurements, so will only be using a fraction of its capabilities.)

## Data Analysis

1. Set-up a Table such as that below and calculate the Initial Concentration of  $[\text{Fe}^{3+}]_o$  and  $[\text{SCN}^-]_o$  for each Trial:

| Trial | $[\text{Fe}^{3+}]_o$ (M) | $[\text{SCN}^-]_o$ (M) |
|-------|--------------------------|------------------------|
| 1     |                          |                        |
| 2     |                          |                        |
| 3     |                          |                        |
| 4     |                          |                        |
| 5     |                          |                        |

2. Now use your Absorbance measurements to calculate  $[\text{Fe}(\text{SCN})^{2+}]_e$  for each Trial using (Eq. 11). Use (Eqs. 12 and 13) to calculate  $[\text{Fe}^{3+}]_e$  and  $[\text{SCN}^-]_e$ . Finally, calculate  $K_c$  for each Trial. For our sample cell  $b = 1.0$  cm. The extinction coefficient for Ferric Thiocyanate  $\epsilon = 5030 \text{ M}^{-1}\text{cm}^{-1}$  under these experimental conditions.

| Trial | $[\text{Fe}(\text{SCN})^{2+}]_e$ (M) | $[\text{Fe}^{3+}]_e$ (M) | $[\text{SCN}^-]_e$ (M) | $K_c$ |
|-------|--------------------------------------|--------------------------|------------------------|-------|
| 1     |                                      |                          |                        |       |
| 2     |                                      |                          |                        |       |
| 3     |                                      |                          |                        |       |
| 4     |                                      |                          |                        |       |
| 5     |                                      |                          |                        |       |

3. Now calculate the Average & Standard Deviation for  $K_c$ .

## Post Lab Questions

Complete all the questions in the “*Titration* Fundamentals” appendix.

## Appendix - Titrator Fundamentals

Solving chemical equilibrium problems for the concentrations of each chemical species, after equilibrium has been established, can be quite complex.

For an extremely simple example, consider the dissociation of Dinitrogen Tetroxide:



This reaction has an equilibrium constant of  $K_c = 0.00461$ . Suppose we start with a flask charged with 0.0240 M  $\text{N}_2\text{O}_4$ , determining equilibrium concentrations for this system involves first defining the equilibrium concentrations in terms of a progress variable  $x$ ;

|               | <u><math>\text{N}_2\text{O}_4</math></u> | <u><math>2 \text{NO}_2</math></u> |
|---------------|--|-----------------------------------|
| Initial Conc. | 0.0240                                   | 0                                 |
| Change        | $-x$                                     | $+2x$                             |
| Equilibrium   | $0.0240 - x$                             | $2x$                              |

The Equilibrium Constant expression is written using the above defined progress variable:

$$0.00461 = \frac{4x^2}{(0.0240 - x)} \quad (\text{Eq. 15})$$

and then translated into a polynomial:

$$4x^2 + 0.00461x - 0.0001106 = 0 \quad (\text{Eq. 16})$$

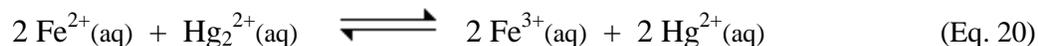
Solving the polynomial gives us the progress variable  $x$ , which then gives us the desired equilibrium concentrations:

$$x = 0.00471 \text{ M} \quad (\text{Eq. 17})$$

$$[\text{N}_2\text{O}_4] = 0.0240 - 0.00471 = 0.0193 \text{ M} \quad (\text{Eq. 18})$$

$$[\text{NO}_2] = 2(0.00471) = 0.00942 \text{ M} \quad (\text{Eq. 19})$$

The polynomials which must be solved can be of higher order. For instance, the equilibrium established when Ferrous Ion is oxidized by Mercuric Ion:



potentially involves solving a 4<sup>th</sup>-Order polynomial. This is more difficult, but not impossible, to solve.

However, a considerable step-up in problem complexity occurs when multiple equilibrium problems are coupled together via common species. For instance, the solubility of Lead Fluoride

(PbF<sub>2</sub>) is coupled to the Basic reaction of Fluoride Ion (F<sup>-</sup>) with Water, which in turn is coupled to the Autoionization of Water:



The Solubility Equilibrium (Eq. 21) is coupled to the Acid-Base Rxn (Eq. 22) via the Fluoride Ion and the Acid-Base reaction is coupled to the Autoionization of Water (Eq. 23) via the Hydroxide Ion (OH<sup>-</sup>).

Clearly the pH of the solution will influence the Solubility of the PbF<sub>2</sub>. For instance, at low pH's the H<sup>+</sup> concentration will be high. This will cause the Autoionization equilibrium (Eq. 23) to shift left; lowering [OH<sup>-</sup>]. The lowering of the Hydroxide Ion concentration will cause the equilibrium of (Eq. 22) to shift right; lowering [F<sup>-</sup>]. Finally, the lowered Fluoride Ion concentration will cause the Solubility equilibrium (Eq. 21) to shift right; increasing the solubility of PbF<sub>2</sub>. How to quantify all this?

Solving these coupled systems can be tedious at best, intractable at worst. For the Lead Fluoride system, we have to solve for six equilibrium concentrations:



And, for starters, we have only identified three equations constraining the solution; K<sub>sp</sub> for PbF<sub>2</sub>, K<sub>b</sub> for F<sup>-</sup>, and K<sub>w</sub> for H<sub>2</sub>O. (These equations must be supplemented with equations balancing the charges of all the ionic species and balancing the concentrations of species that are stoichiometrically linked.)

In the modern age, tedious computational problems should be solved using appropriate software packages. For simple aqueous equilibrium problems, the software package *Titration* can be employed to solve the desired equilibrium problem. This is a software package that is capable of quickly and repeatedly solving complex coupled equilibrium problems. In the current exercise, we will introduce the *Titration* interface and use the software to solve some simple equilibrium problems.

First, to the interface. This computational package distinguishes between system Species and Components. Species are all the "stoichiometrically distinct chemical entities"; Fe<sup>3+</sup>, SCN<sup>-</sup> and FeSCN<sup>2+</sup> for the Ferric Thiocyanate system. Components are "a subset of the species that form a Basis Set for the construction of all other species." In other words, the Components are the minimum number of species whose concentrations must be determined in order to determine all the other species. Fe<sup>3+</sup> and SCN<sup>-</sup> are used to form the species FeSCN<sup>2+</sup>, so they can be chosen as Components for our system. This choice is not unique, but some choices are better than others.

Next, *Titration* distinguishes between Components with known Total and Free concentrations. Specifying a component has a Total concentration is typical when the species concentration is given as a Formal (Initial) concentration. On the other hand, a Free concentration is specified when the concentration of a species is fixed; as will be the case for H<sub>2</sub>O in an aqueous system where all other species are present in small amounts.

Finally, when *Titration* is launched, a screen allowing for the entry of Components and Species comes up.

Each can be entered by *clicking* on the *cell* under the *Type* column. Editing mistakes is accomplished by *clicking* on this same *cell*. After *clicking* on this *cell* a data entry *window* will open. Enter the data and *click* the *Accept* button. Once all the Components and Species have been entered, *click* on *Solve this system* to solve for the equilibrium concentrations.

Now, let us specify the Ferric Thiocyanate system for *Titration*. Begin with the components:

| Component        | Type  | Total M | Guess Log Free M | Charge |
|------------------|-------|---------|------------------|--------|
| Fe <sup>3+</sup> | Total | 0.001   | 0                | +3     |
| SCN <sup>-</sup> | Total | 0.0002  | 0                | -1     |

The concentrations used are consistent with Trail 1 of our laboratory exercise. Finish by specifying the remaining species:

| Species             | Dissolved/Ppt | logK | $\Delta H$       | $\Delta S$ |
|---------------------|---------------|------|------------------|------------|
| $\text{FeSCN}^{2+}$ | Dissolved     | 2    |                  |            |
| Coefficients:       |               |      | $\text{Fe}^{3+}$ | +1         |
|                     |               |      | $\text{SCN}^-$   | +1         |

I have used an Equilibrium Constant of  $K_c = 100$ , or  $\log K = 2$ , for illustrative purposes. Go ahead and solve the system.

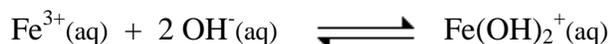
*Questions:*

- For this illustrative example, what are the equilibrium concentrations of each species?
- Confirm by explicit calculation the equilibrium concentrations determined by *Titrat* give us the correct equilibrium constant  $K_c = 100$ .
- Now change the initial concentration of  $\text{Fe}^{3+}$  over the range 0.001 to 0.005 M in 0.001 increments and determine the equilibrium concentration of  $\text{FeSCN}^{2+}$  for each case. Report these results. Are your results reasonable? Explain
- Now reset the initial concentration of  $\text{Fe}^{3+}$  to 0.001 M. Try changing the Equilibrium Constant itself. Suggested values are: 0.1, 1, 10, 100, 1000, 10000. For each case determine the equilibrium concentration of the  $\text{FeSCN}^{2+}$ . Report these results. Again, are the results reasonable? Explain

Now, we know our Ferric Thiocyanate reaction takes place in Water. Water itself auto-dissociates, producing  $\text{H}^+$  and  $\text{OH}^-$ . The resulting Hydroxide can then also react with the Ferric Ion,  $\text{Fe}^{3+}$ :



$$\log K = 14$$



$$\log K = 22.32$$

Although we are just getting started with all the reactions that will couple to this system, these additional reactions will be sufficient to illustrate the full power of *Titrat*.

We need to include these coupled equilibria in our *Titrat* definition.  $\text{Fe}^{3+}$  and  $\text{OH}^-$  are required to form  $\text{Fe}(\text{OH})_2^+$ , so they can be added to our component list.  $\text{Fe}(\text{OH})_2^+$  will then be a simple species.  $\text{H}_2\text{O}$  is required to form  $\text{H}^+$ , so it will be a component with a fixed Free concentration of 55.5M. (*Why this concentration?*)

Thus, our new *Titration* definition will appear as:

| Component        | Type  | Total M | Guess | Log Free M | Charge |
|------------------|-------|---------|-------|------------|--------|
| Fe <sup>3+</sup> | Total | 0.001   | 0     |            | +3     |
| SCN <sup>-</sup> | Total | 0.0002  | 0     |            | -1     |
| H <sub>2</sub> O | Free  | 55.5    | 0     |            | 0      |
| OH <sup>-</sup>  | Total | 0       | -7    |            | -1     |

| Species                          | Dissolved/Ppt | logK          | ΔH               | ΔS  |
|----------------------------------|---------------|---------------|------------------|-----|
| FeSCN <sup>2+</sup>              | Dissolved     | 2             |                  |     |
|                                  |               | Coefficients: | Fe <sup>3+</sup> | +1  |
|                                  |               |               | SCN <sup>-</sup> | +1  |
| Fe(OH) <sub>2</sub> <sup>+</sup> | Dissolved     | 22.32         |                  |     |
|                                  |               | Coefficients: | Fe <sup>3+</sup> | +1  |
|                                  |               |               | OH <sup>-</sup>  | +2  |
| H <sup>+</sup>                   | Dissolved     | -14           |                  |     |
|                                  |               | Coefficients: | OH <sup>-</sup>  | -1* |
|                                  |               |               | H <sub>2</sub> O | +1  |

\*Since OH<sup>-</sup> is on the right-hand side of the chemical equation involved in “forming” H<sup>+</sup>, its stoichiometric coefficient will be negative.

*Questions:*

- Compare the equilibrium concentration of FeSCN<sup>2+</sup> for this case with that of the uncoupled case. Explain any difference.
- What impact will this have on our determination of K<sub>c</sub> for the Ferric Thiocyanate system?

Further, suppose we wish to know how the pH affects the equilibrium concentrations for this system. *Titration* is capable of “sweeping” over a wide range of concentrations of OH<sup>-</sup> and repeatedly solving the system for the equilibrium concentrations; we don’t “sweep” the H<sup>+</sup> concentration because it is not a component.

To do this, *click* on “Sweep”. Select OH<sup>-</sup> as the “Component to Sweep” and 0.0001 as the sweep “Increment”. Finally, 100 points should be sufficient for “Number of Points”. *Click* “Sweep” and the “Results” table should fill. Plot H<sup>+</sup> and FeSCN<sup>2+</sup> as Species 2 and 3 in the “Sweep Results” graph.

*Questions:*

- At what pH does the FeSCN<sup>2+</sup> concentration begin to fall-off rapidly?
- Why does the FeSCN<sup>2+</sup> concentration fall-off at high pH’s?
- What happens to the Fe<sup>3+</sup> equilibrium concentration at high pH’s? Explain this behavior.

## Addendum

### The Principle of Le Chatelier

When a chemical system at equilibrium is perturbed by some external change, it must respond so as to reestablish an equilibrium state. This is similar to what might happen if two kids are sitting on a teeter-totter that is perfectly balanced and someone adds a bag of sand to one side. The children will readjust themselves so the teeter-totter can again come to a balance. In chemical systems, this means concentrations of reactants and products will readjust themselves so as to again balance at the  $K_c$  value.

This chemical “readjustment” was postulated by Henri-Louis Le Chatelier to be such that:

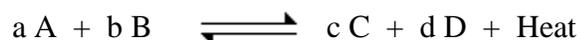
*The system will shift its equilibrium position so as to counteract the effect of the disturbance.*

This means that if additional reactant is added, say more  $A$  in the general case:



the reaction will proceed forward so as to reduce this perturbation; meaning more product is produced. On the other hand, if reactant  $A$  is somehow removed, by adding another species with which it reacts, for instance, the reaction will proceed in reverse until equilibrium is reestablished. A similar analysis holds for changes in product concentrations.

If the temperature is adjusted, these concentration changes will actually cause the  $K_c$  value to change. If the reaction is Exothermic:



the  $K_c$  value will decrease when the temperature is increased. This means the system will readjust itself by shifting toward reactants. The reverse will happen if the reaction is Endothermic.

In this short exercise we will perturb several equilibrium systems to as to directly observe Le Chatelier’s Principle.

#### Procedure

**Perform all Addendum reactions in a Fume Hood!!!**

