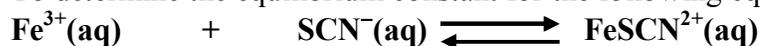


EXPERIMENT 3 THE EQUILIBRIUM CONSTANT

PURPOSE:

1. To examine the effect of changing reactant concentrations on a chemical equilibrium.
2. To determine the equilibrium constant for the following equilibrium:



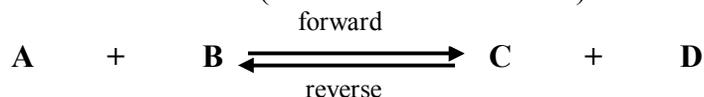
PRINCIPLES:

When chemical reactions occur, reactants are used up and products are formed.

For many reactions, this process is **irreversible** (reaction goes to completion) and products form to the extent of 100%. The net result is that **only products** and no reactants **are present in the system**. These types of irreversible changes often happen when an insoluble solid forms (precipitation reactions) or when one of the products is a gas.



For other chemical changes, the products can react to reform the original reactants. These type of reactions are said to be reversible. In this situation, both the forward reaction (formation of products) and the reverse reaction (reformation of reactants) are occurring simultaneously.



These two simultaneous processes continue to occur until equilibrium is reached. At equilibrium **both reactants and products are present in the system** (A, B, C, D) but not necessarily in the same amounts.

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction:

$$\text{Rate of Forward Reaction} = \text{Rate of Reverse Reaction}$$

The rate of any reaction is proportional to the concentration of the reacting species. It follows that :

$$\text{Rate of Forward Reaction} = k_f [\text{A}] [\text{B}] \qquad \text{Rate of Reverse Reaction} = k_r [\text{C}] [\text{D}]$$

where: k_f and k_r are proportionality constants called **Rate Constants**.

Since chemical equilibrium is defined as the state of the system in which the Rate of the Forward Reaction is equal to the of the Reverse Reaction, then the following must be true:

$$k_f [\text{A}] [\text{B}] = k_r [\text{C}] [\text{D}]$$

This equation can be rewritten by collecting all the reactant and product concentrations on the same side of the equation and the Rate Constants on the other side:

| |
|---|
| $\frac{k_f}{k_r} = \frac{[\text{C}] [\text{D}]}{[\text{A}] [\text{B}]} = K_{\text{eq}} = \text{Equilibrium Constant}$ |
|---|

EXPERIMENT 3 THE EQUILIBRIUM CONSTANT

In this experiment you will determine the numerical value of the K_{eq} (the equilibrium constant) for the reaction between the ferric ion (Fe^{3+}) and the thiocyanate ion (SCN^-) to form the red-orange colored $FeSCN^{2+}$ complex ion:



The $Fe^{3+}(aq)$ ions are derived from an aqueous solution iron (III) nitrate, $Fe(NO_3)_3$, and the $SCN^-(aq)$ ions are derived from an aqueous solution of sodium thiocyanate, $NaSCN$.

The **nitrate ions**, NO_3^- and the **sodium ions**, Na^+ are **spectator ions**, and as such they do not participate in the reaction.

Note that for this equilibrium:

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

You will determine the effect of increasing the concentration of $[Fe^{3+}]$ on the extent of formation of the red-orange colored complex of $FeSCN^{2+}$.

To determine the concentration of the red-orange colored complex of $FeSCN^{2+}$ at equilibrium, an instrument called a spectrophotometer is used.

The spectrophotometer is an instrument that measures numerically the color intensity of solutions by measuring how much light is absorbed (Absorbance, A) and/or transmitted (Transmittance, T) by a colored solution.

The higher the color intensity of a solution (higher concentration), the higher the Absorbance, A of the solution (more light is absorbed by the solution) and the lower the Transmittance, T of the solution (less light is transmitted through the solution).

Range for the Absorbance: $A = 0.0 - 2.0$ (dimensionless number)

Range for Transmittance, $T = 100 - 0\%$ (expressed as a percent or as a decimal)

Note that when all of the light is absorbed ($A = 2.0$), no light is transmitted ($T = 0\%$)

Conversely, when no light is absorbed ($A = 0.0$), all of the light is transmitted ($T = 100\%$)

Absorbance, A , and Transmittance, T are related by the following relationship:

$$A = \log \frac{1}{T}$$

T is expressed as a decimal in this equation !

The above relationship is useful, since Transmittance, T , readings are easier to read from the spectromotometer than Absorbance, A , readings. However, the quantity that is directly related to the concentration of a colored solution is the Absorbance. In this experiment you will be reading the Transmittance of solutions of different unknown concentrations, and then will convert your Transmittance reading to Absorbance readings.

EXPERIMENT 3 THE EQUILIBRIUM CONSTANT

The Absorbance readings will then be used to calculate the concentrations. As light passes through the red-orange colored solution of FeSCN^{2+} , it interact with the FeSCN^{2+} ions. These ions will absorb light of a certain wavelength (λ in nanometers). The light that is not absorbed by the FeSCN^{2+} ions is transmitted through the colored solution and is seen by the eye. This transmitted light has a characteristic color which we call the color of the solution. The total **Absorbance, A** is determined by both the **solute (FeSCN^{2+})** and the **solvent (water)**. In addition, **the container** (called a “**cuvet**”), used to hold the colored solution for the Absorbance measurements, also absorbs light.

$$\boxed{\begin{array}{c} \text{Total} \\ \text{Light} \\ \text{Absorbed} \end{array}} = \boxed{\begin{array}{c} \text{Light absorbed} \\ \text{by} \\ \text{FeSCN}^{2+} \end{array}} + \boxed{\begin{array}{c} \text{Light absorbed} \\ \text{by} \\ \text{Water} \end{array}} + \boxed{\begin{array}{c} \text{Light absorbed} \\ \text{by} \\ \text{cuvet} \end{array}}$$

The Absorbance, A, of water and of the cuvet are automatically corrected for during the measurements (see Procedure)

The concentration of the FeSCN^{2+} can be calculated from Absorbance measurements using Beer's Law.

Beer's Law states that the Absorbance, a, of a colored solution is directly proportional to the concentration, C, of the colored solution: $\boxed{A \propto C}$

The Absorbance, A, is measured at the wavelength of the **maximum absorbance of FeSCN^{2+}** , which is **449 nm**.

A simple application of Beer's Law will be used in this experiment to calculate the unknown concentrations of the red-orange FeSCN^{2+} complex in your solutions. You will prepare a reference standard that has the **Maximum Concentration** of FeSCN^{2+} (C_{ref}) and record its absorbance value, A_{ref} .

$$A_{\text{ref}} = \text{Constant} \times C_{\text{ref}} \quad \text{where } C_{\text{ref}} = \text{Maximum Concentration of } \text{SCN}^{2+} = 2.00 \times 10^{-4} \text{ M}$$

For solution of unknown concentration, C_1 (Example Solution 1), A_1 is determined experimentally. Applying Beer's Law:

$$A_1 = \text{Constant} \times C_1 \quad \text{where } C_1 \text{ is unknown}$$

$$\text{Constant} = \frac{A_{\text{ref}}}{C_{\text{ref}}} = \frac{A_1}{C_1} \quad \text{Rearranging to find the unknown: } \boxed{C_1 = C_{\text{ref}} \times \frac{A_1}{A_{\text{ref}}}}$$

For example:

| | |
|--|--|
| The absorbance at 449 nm of the Reference Standard: | $A_{\text{ref}} = 0.901$ |
| The concentration of the Reference Standard: | $C_{\text{ref}} = 2.00 \times 10^{-4} \text{ M}$ |
| The absorbance of a solution of unknown concentration: | $A_x = 0.612$ |
| The concentration of solution x: | $C_x = ?$ |

EXPERIMENT 3
THE EQUILIBRIUM CONSTANT

$$C_x = C_{\text{ref}} \times \frac{A_x}{A_{\text{ref}}} = 2.00 \times 10^{-4} \text{ M} \times \frac{0.612}{0.901} = \mathbf{1.36 \times 10^{-4} \text{ M}}$$

Once the equilibrium concentration of the red-orange complex of FeSCN^{2+} is known, the equilibrium concentrations of the reactants ($\text{Fe}^{2+}_{\text{eq}}$ and $\text{SCN}^{-}_{\text{eq}}$) can be calculated, as it is shown below:

| | | | | | |
|--------------------|--|---|--|----------------------|---|
| | $\text{Fe}^{3+}(\text{aq})$ | + | $\text{SCN}^{-}(\text{aq})$ | \rightleftharpoons | $\text{FeSCN}^{2+}(\text{aq})$ |
| Initial Conc's: | $80.0 \times 10^{-4} \text{ M}$ | | $2.00 \times 10^{-4} \text{ M}$ | | 0 |
| Change: | $- 1.36 \times 10^{-4} \text{ M}$ | | $- 1.36 \times 10^{-4} \text{ M}$ | | $+ 1.36 \times 10^{-4} \text{ M}$ |
| Equil. Conc's: | $80.0 \times 10^{-4} \text{ M} -$ $1.36 \times 10^{-4} \text{ M}$ | | $2.00 \times 10^{-4} \text{ M} -$ $1.36 \times 10^{-4} \text{ M}$ | | $0 +$ $1.36 \times 10^{-4} \text{ M}$ |
| | \Downarrow | | \Downarrow | | \Downarrow |
| | $78.6 \times 10^{-4} \text{ M}$ | | $0.64 \times 10^{-4} \text{ M}$ | | $1.36 \times 10^{-4} \text{ M}$ |

Once, the equilibrium concentrations are known, the Equilibrium Constant, K_{eq} can be easily calculated:

$$\begin{aligned} [\text{Fe}^{3+}]_{\text{eq}} &= \mathbf{78.6 \times 10^{-4} \text{ M}} \\ [\text{SCN}^{-}]_{\text{eq}} &= \mathbf{0.64 \times 10^{-4} \text{ M}} \\ [\text{FeSCN}^{2+}]_{\text{eq}} &= \mathbf{1.36 \times 10^{-4} \text{ M}} \end{aligned}$$

$$K_{\text{eq}} = \frac{[\text{FeSCN}^{2+}]_{\text{eq}}}{[\text{Fe}^{3+}]_{\text{eq}} [\text{SCN}^{-}]_{\text{eq}}} = \frac{\mathbf{1.36 \times 10^{-4} \text{ M}}}{(\mathbf{78.6 \times 10^{-4} \text{ M}}) (\mathbf{0.64 \times 10^{-4} \text{ M}})} = \mathbf{270 \text{ M}^{-1}} \text{ (2 Sig Figs)}$$

EXPERIMENT 3
THE EQUILIBRIUM CONSTANT

PROCEDURE:

I. Turning on the spectrophotometer.

1. Make sure that the sample compartment is empty
2. Press “VIS” on the spectrophotometer (DO NOT PRESS “UV”). The lamp will turn on
3. Let the lamp warm up for at least 10 minutes.

II. Preparation of Reaction Mixtures

1. Thoroughly clean five (5) test tubes (18mm x 150 mm).
2. Rinse with deionized water and allow to drain as dry as possible.
3. Label the tubes: 1, 2, 4, 8, and XS (excess)
4. Add the reagents according to the table below:

Preparation of mixtures of Fe^{3+} and SCN^- in a final volume of 15.0 mL

| Tube label | Relative $[\text{Fe}^{3+}]$ | $\text{Fe}(\text{NO}_3)_3$ (6.00×10^{-2} M) | NaSCN (6.00×10^{-4} M) | HNO_3 (0.10 M) |
|------------|-----------------------------|--|--|----------------------------|
| 1 | x 1 | 1.00 | 5.00 | 9.00 |
| 2 | x 2 | 2.00 | 5.00 | 8.00 |
| 4 | x 4 | 4.00 | 5.00 | 6.00 |
| 8 | x 8 | 8.00 | 5.00 | 2.00 |

Preparation of mixture containing an excess of Fe^{3+}

| Tube label | Relative $[\text{Fe}^{3+}]$ | $\text{Fe}(\text{NO}_3)_3$ (0.10 M) | NaSCN (6.00×10^{-4} M) | HNO_3 (0.10 M) |
|------------|-----------------------------|---|--|----------------------------|
| XS | excess | 10.00 | 5.00 | 0.00 |

5. Cover (seal) each test tube with a piece of saran wrap or parafilm
6. Mix the contents of each tube by inverting tubes several times.
7. **Go to the next step IMMEDIATELY!**

NOTE:

Read the Absorbance of the solutions within 10 minutes. The solutions are not stable so you cannot “store” the solution beyond that time period.

III. Absorbance Readings

1. Preparing the cuvet

- (a) Obtain a cuvet and hold it with tissue paper (your fingerprints would affect your readings).
- (b) Rinse the cuvet thoroughly with deionized water and fill it 2/3 full with deionized water.
- (c) Set a large beaker for waste next to the spectrophotometer and place your wash bottle nearby.

EXPERIMENT 3
THE EQUILIBRIUM CONSTANT

2. Zeroing

- (a) Wipe the outside of the cuvet gently with a KimWipe to remove any excess water.
- (b) Lift the door of the sample compartment of the spectrophotometer and place the cuvet in the sample compartment in the proper orientation.
ASK YOUR INSTRUCTOR ABOUT THE PROPER ORIENTATION OF THE CUVET.
Close the sample compartment.
- (c) Set the wavelength (λ) on the spectrophotometer to 449 nm.
Note: your lab instructor may have already done this for you.
- (d) Press "CALIB" and wait until "0.000" appears on the Absorbance display. (100 % T)
Press "CALIB" again if the number appears to drift. Wait until further drift stops and press "CALIB" .
NOTE: Depending on the type of spectrophotometer available this step may be slightly different; However, keep in mind that the purpose of this step is to automatically correct the Absorbance, A , of **water and** of the **cuvet** for further measurements.
As such, after completing this step, the spectrophotometer should read:
Absorbance = 0.000 and **Transmittance = 100%**
- (e) Lift the door of sample compartment and remove the cuvet. Close door.
- (f) Pour the water out into the waste beaker and shake any excess out of the cuvet.

3. Measuring the Absorbance of the solutions

- (a) Using solution 1 (with the least amount of color), carefully pour the solution into the cuvet to 2/3 full.
Pour this back into the tube and repour the solution into the cuvet to 2/3 full. This will mix in and dilute any traces of water left in the cuvet.
- (b) Wipe the outside of the cuvet gently with a KimWipe to remove any excess solution. This is a precaution in case you accidentally spilled solution on the outside of the cuvet or touched them with your hands.
- (c) Lift the door of the sample compartment and place the cuvet in it in the proper orientation. Close the sample compartment.
DO NOT PRESS ANY KEYS!
- (d) Record the Absorbance of the solution.
If you spectrophotometer you are using has a digital read-out, read the Absorbance directly. If there is no digital read-out, read the Transmittance in % and convert it to Absorbance readings (See page 2)
- (e) Repeat steps (a) through (d) with the other solutions.
- (f) Remove the cuvet from the spectrophotometer.
- (g) Show your Absorbance (transmittance) readings to your instructor.

EXPERIMENT 3
THE EQUILIBRIUM CONSTANT

NAME: _____
PARTNER: _____

REPORT FORM

Part I: Calculating the Initial Concentration of the Reactants in the 15.0 mL Reaction Mixture

For each test tube, calculate the Initial Concentrations of the two reactants (Fe^{3+} and SCN^-)

Use exponential notation and express all of your calculated concentrations in: # x 10⁻⁴ M

Use proper significant figures.

Since the total volume in each test tube is 15.0 mL, this volume must be taken into account in calculating the initial concentrations of the two reactants.

For example, in test tube 1, since the 1.00 mL of 6.00×10^{-2} M $\text{Fe}(\text{NO}_3)_3$ added reacts in a total volume of 15.00 mL, the initial concentration of $[\text{Fe}^{3+}]$ can be calculated to be:

$$[\text{Fe}^{3+}] = 6.00 \times 10^{-2} \text{ M} \times \frac{1.00 \text{ mL}}{15.00 \text{ mL}} = \mathbf{40.0 \times 10^{-4} \text{ M}}$$

Carry out similar calculations for all other initial values of $[\text{Fe}^{3+}]$ and $[\text{SCN}^-]$

| Tube Label | $[\text{Fe}^{3+}]$, M | $[\text{SCN}^-]$, M |
|---------------------|------------------------|--------------------------|
| 1 | | |
| 2 | | Same as in test tube # 1 |
| 4 | | Same as in test tube # 1 |
| 8 | | Same as in test tube # 1 |
| XS Fe^{3+} | | Same as in test tube # 1 |

EXPERIMENT 3
THE EQUILIBRIUM CONSTANT

Part II: Calculating the Equilibrium Concentration of the Product (FeSCN^{2+}) from Absorbance Readings

DATA TABLE # 2

| Tube Label | Transmittance (%) (if needed) | Absorbance | Calculations (see Page 3 for Sample Calculation) | Equilibrium Concentration of FeSCN^{2+} (M) # x 10^{-4} |
|-------------------|----------------------------------|------------|---|---|
| 1 | | | | |
| 2 | | | | |
| 4 | | | | |
| 8 | | | | |
| XS (reference) | | | | * |

* In the reference tube (excess Fe^{3+}), the large excess of Fe^{3+} speeds up the forward reaction and therefore shifts the equilibrium all the way to the right. All of the SCN^- present will be bound in the FeSCN^{2+} form.

Since the SCN^- is the limiting reagent, then: $[\text{SCN}^-]_{\text{initial}} = [\text{FeSCN}^{2+}]_{\text{equilibrium}}$

This is explained in the Equilibrium Table below:

| | $\text{Fe}^{3+}(\text{aq})$ Reactant in excess | + | $\text{SCN}^-(\text{aq})$ Limiting Reactant | \rightleftharpoons | $\text{FeSCN}^{2+}(\text{aq})$ |
|----------------|---|---|--|----------------------|--------------------------------|
| Initial Conc's | large excess | | X | | 0 |
| Change: | -X | | - X | | + X |
| Equil. Conc's | large excess -X | | 0 | | X |

EXPERIMENT 3
THE EQUILIBRIUM CONSTANT

Part III: Calculating the Equilibrium Concentration of the Reactants

1. Complete $[\text{Fe}^{3+}]_{\text{initial}}$, $[\text{SCN}^-]_{\text{initial}}$, and $[\text{FeSCN}^{2+}]_{\text{equil}}$ from data obtained in Part I and Part II (Data Table # 1 and Data Table # 2)

DATA TABLE # 3

| Tube Label | $[\text{Fe}^{3+}]_{\text{initial}}$ (M) | $[\text{SCN}^-]_{\text{initial}}$ (M) | $[\text{FeSCN}^{2+}]_{\text{equil}}$ (M) | $[\text{Fe}^{3+}]_{\text{equil}}$ (M) | $[\text{SCN}^-]_{\text{equil}}$ (M) |
|------------|--|--|---|--|--|
| 1 | | | | | |
| 2 | | | | | |
| 4 | | | | | |
| 8 | | | | | |
| XS | | | | | |

2. Calculate $[\text{Fe}^{3+}]_{\text{equil}}$ and $[\text{SCN}^-]_{\text{equil}}$ from $[\text{Fe}^{3+}]_{\text{initial}}$, $[\text{SCN}^-]_{\text{initial}}$, and $[\text{FeSCN}^{2+}]_{\text{equil}}$ by using the Equilibrium Tables provided below (see Page 4 for an example)

| Tube # 1 | | | |
|-----------------------------|-----------------------------|---|---|
| | $\text{Fe}^{3+}(\text{aq})$ | + | $\text{SCN}^-(\text{aq}) \rightleftharpoons \text{FeSCN}^{2+}(\text{aq})$ |
| Initial: Conc's: | | | |
| Change: | | | |
| Equil Conc's: | | | |

| Tube # 2 | | | |
|-----------------------------|-----------------------------|---|---|
| | $\text{Fe}^{3+}(\text{aq})$ | + | $\text{SCN}^-(\text{aq}) \rightleftharpoons \text{FeSCN}^{2+}(\text{aq})$ |
| Initial: Conc's: | | | |
| Change: | | | |
| Equil Conc's: | | | |

EXPERIMENT 3
THE EQUILIBRIUM CONSTANT

| Tube # 4 | | | |
|---|--|--|--|
| $\text{Fe}^{3+}(\text{aq}) \quad + \quad \text{SCN}^{-}(\text{aq}) \rightleftharpoons \text{FeSCN}^{2+}(\text{aq})$ | | | |
| Initial: Conc's: | | | |
| Change: | | | |
| Equil Conc's: | | | |

| Tube # 8 | | | |
|---|--|--|--|
| $\text{Fe}^{3+}(\text{aq}) \quad + \quad \text{SCN}^{-}(\text{aq}) \rightleftharpoons \text{FeSCN}^{2+}(\text{aq})$ | | | |
| Initial: Conc's: | | | |
| Change: | | | |
| Equil Conc's | | | |

3. Enter your calculated values for $[\text{Fe}^{3+}]_{\text{equil}}$ and $[\text{SCN}^{-}]_{\text{equil}}$ in the appropriate Data Table # 3

Part IV: Calculating the Equilibrium Constant (K_{eq}) (See Page 4 for a sample calculation)

DATA TABLE # 4

| Tube Label | $[\text{Fe}^{3+}]_{\text{equil}}, \text{M}$ | $[\text{SCN}^{-}]_{\text{equil}}, \text{M}$ | $[\text{FeSCN}^{2+}]_{\text{equil}}, \text{M}$ | $K_{\text{equil}} (\text{M}^{-1})$ (2 Sig Figs allowed) (carry one additional Sig Fig to be dropped in the next step) |
|-----------------------|---|---|--|---|
| 1 | | | | |
| 2 | | | | |
| 4 | | | | |
| 8 | | | | |

EXPERIMENT 3
THE EQUILIBRIUM CONSTANT

Part V: Calculating the Average Value of the Equilibrium Constant (K_{eq})

Answer should be given in decimal notation (not exponential) and 2 Significant Figures!

PART VI: Interpreting the data in view of Le Chatelier's Principle

1. Complete the following table and the blanks below the table by entering: **increased**, **decreased**, **stayed the same**, **to the right**, **to the left**, as appropriate

Consider the trend given by your data in going from tube #1 \longrightarrow tube # 8

| | $Fe^{3+}(aq)$ | + | $SCN^{-}(aq)$ | \rightleftharpoons | $FeSCN^{2+}(aq)$ |
|---------------------------|---------------|---|---------------|----------------------|------------------|
| Stress (Change): | | X | | | |
| Equilibrium Shift: | | X | | | |
| New Equilibrium: | | X | | | |

2. How does the data from this experiment illustrate Le Chatelier's principle ?

Answer by completing the blanks.

(10)

As the concentration of _____ is _____ the equilibrium _____

As a result:

- The equilibrium concentration of _____ is _____
- The equilibrium concentration of _____ is _____
- The equilibrium concentration of _____ is _____
- The Equilibrium Constant, K_{eq} _____

EXPERIMENT 3
THE EQUILIBRIUM CONSTANT