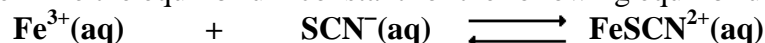


EXPERIMENT 2
THE EQUILIBRIUM CONSTANT

PURPOSE:

- To determine the equilibrium constant for the following equilibrium:



- To examine the effect of changing the initial concentration of one of the reactants on the chemical equilibrium.

PRINCIPLES:

Irreversible chemical reactions are reactions that go to completion.

In this type of reactions the reactants are used up and products form to the extent of 100%.

The net result is that only products and no reactants are present in an irreversible system.

These types of irreversible changes often happen when an insoluble solid forms or when one of the products is a gas.



Reversible chemical reactions are reactions in which the products can react to reform the original reactants. In this situation, both the forward reaction (formation of products) and the reverse reaction (reformation of reactants) occur simultaneously, and both directions continue until equilibrium is reached.



At equilibrium:

- both reactants and products are present in the system (A, B, C, D), although not necessarily in the same amounts.
- the rate of the forward reaction is equal to the rate of the reverse reaction.

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

As the previous experiment demonstrated, the rate of any reaction is proportional to the concentration of the reacting species.

$$\text{Rate of Forward Reaction} = k_f [\text{A}] [\text{B}]$$

$$\text{Rate of Reverse Reaction} = k_r [\text{C}] [\text{D}]$$

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 Rate of the Reverse Reaction, then the following must be true:

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

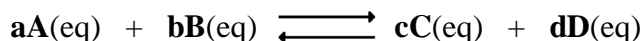
This equation can be rewritten as:

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

EXPERIMENT 2
THE EQUILIBRIUM CONSTANT

The equilibrium constant, is calculated from the stoichiometry of the equation and the equilibrium concentrations of the reactants and products.

For example:



A and **B** are reactants

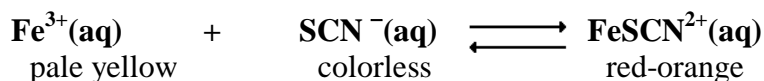
C and **D** are products

a, **b**, **c**, and **d** are the stoichiometric coefficients.

$$K_{\text{eq}} = \frac{[\mathbf{C}_{\text{eq}}]^c [\mathbf{D}_{\text{eq}}]^d}{[\mathbf{A}_{\text{eq}}]^a [\mathbf{B}_{\text{eq}}]^b}$$

This relationship is referred to as the “**Law of Mass Action**”

The numerical value of the equilibrium constant (K or K_{eq}) quantifies the concentrations of the reactants and products at equilibrium. In this experiment the numerical value of the equilibrium constant, K_{eq} , will be determined for the reaction between the ferric ion (Fe^{3+}) and the thiocyanate ion. (SCN^-) forming the red-orange colored FeSCN^{2+} complex ion:



- The $\text{Fe}^{3+}(\text{aq})$ ions are provided by an aqueous solution of iron (III) nitrate, $\text{Fe}(\text{NO}_3)_3$
- The $\text{SCN}^-(\text{aq})$ ions are provided by an aqueous solution of sodium thiocyanate, NaSCN
- The **nitrate ions**, NO_3^- and the **sodium ions**, Na^+ are **spectator ions**, and do not participate in the reaction

Since the coefficients of the reactants and the product in the balanced chemical equation are equal to 1, the expression of the Equilibrium Constant does not contain exponents (i.e. the exponents are 1)

As such, the expression of the Equilibrium Constant (K_{eq}) for this equilibrium system is as follows:

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

This experiment will determine the effect of the increase of the initial concentration of $[\text{Fe}^{3+}]_0$ ions on the equilibrium concentration of red-orange colored complex ions of $[\text{FeSCN}^{2+}]_{\text{eq}}$

A **spectrophotometer** will be used to determine the concentration of the red-orange colored complex of FeSCN^{2+} at equilibrium. The spectrophotometer numerically determines the color intensity of colored solutions, by measuring how much light is absorbed by the colored solution (Absorbance, A). As more light is absorbed, less light is transmitted through the colored solution.

EXPERIMENT 2 THE EQUILIBRIUM CONSTANT

The higher the concentration of a colored solution, the higher the color intensity of the solution, and the higher the Absorbance value (A) will be for that solution. Absorbance readings will be used to calculate the equilibrium concentration of several colored solutions containing varying concentrations of the red-orange colored FeSCN^{2+} complex ions.

As light passes through the red-orange colored solution of FeSCN^{2+} , it interacts 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 perceive as the color of the solution.

The total **Absorbance** (A) is the sum of the absorbance the solute (FeSCN^{2+}), the absorbance of the solvent (**water**), and the absorbance of the container (called a “**cuvette**”), used to hold the colored solution.

Light absorbed by FeSCN^{2+} (the solute)	+	Light absorbed by water (the solvent)	+	Light absorbed by cuvette (the container)	=	Total Light Absorbed
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The Absorbance, A , of water and of the cuvette are automatically corrected for, when the spectrophotometer is “auto-zeroed”. The concentration of the FeSCN^{2+} in the solution 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:

$$\boxed{A \propto C}$$

A simple application of Beer’s Law will be used in this experiment to calculate the unknown equilibrium concentrations of the red-orange solutions containing the FeSCN^{2+} complex ions.

The Absorbance, A , is measured at the wavelength of the maximum absorbance of FeSCN^{2+} , which is 449 nm. A reference standard will be prepared that has the maximum known concentration of FeSCN^{2+} (C_{ref}) and its absorbance value, A_{ref} will be measured and recorded.

$A_{\text{ref}} = \text{Constant} \times C_{\text{ref}}$	Rearrange to:	$\text{Constant} = \frac{A_{\text{ref}}}{C_{\text{ref}}}$	where C_{ref} is the max concentration of $\text{FeSCN}^{2+} = 2.00 \times 10^{-4} \text{ M}$
--	---------------	---	--

For a solution of unknown concentration (such as C_1 for Solution 1), A_1 is determined experimentally. Applying Beer’s Law yields:

$A_1 = \text{Constant} \times C_1$	Rearrange to:	$\text{Constant} = \frac{A_1}{C_1}$	where C_1 is unknown
------------------------------------	---------------	-------------------------------------	------------------------

It follows that:

$\text{Constant} = \frac{A_{\text{ref}}}{C_{\text{ref}}} = \frac{A_1}{C_1}$	Rearrange to:	$C_1 = C_{\text{ref}} \times \frac{A_1}{A_{\text{ref}}}$
---	---------------	--

EXPERIMENT 2
THE EQUILIBRIUM CONSTANT


Example:


The absorbance at 449 nm of the Reference Standard: $A_{\text{ref}} = 0.90$
 The known concentration of the Reference Standard: $C_{\text{ref}} = 2.00 \times 10^{-4} \text{ M}$
 The absorbance of a solution of unknown concentration: $A_x = 0.61$
 The unknown concentration of solution x: $C_x = ?$


$$C_x = C_{\text{ref}} \times \frac{A_x}{A_{\text{ref}}} = 2.00 \times 10^{-4} \text{ M} \times \frac{0.61}{0.90} = \mathbf{1.4 \times 10^{-4} \text{ M}}$$

If the initial concentrations of the reactants are known, and the equilibrium concentration of the red-orange complex of FeSCN^{2+} has been determined by Absorbance measurements, then the equilibrium concentrations of the reactants ($\text{Fe}^{2+}_{\text{eq}}$ and $\text{SCN}^{-}_{\text{eq}}$) can be calculated, as shown:

	$\text{Fe}^{3+}(\text{aq})$	+	$\text{SCN}^{-}(\text{aq})$	\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	$- 1.4 \times 10^{-4} \text{ M}$		$- 1.4 \times 10^{-4} \text{ M}$		$+ 1.4 \times 10^{-4} \text{ M}$
Equil. Conc's:	$80.0 \times 10^{-4} \text{ M}$ $-1.4 \times 10^{-4} \text{ M}$		$2.00 \times 10^{-4} \text{ M}$ $-1.4 \times 10^{-4} \text{ M}$		0 $+ \mathbf{1.4 \times 10^{-4} \text{ M}}$


 $\mathbf{[\text{Fe}^{3+}]_{\text{eq}} = 78.6 \times 10^{-4} \text{ M}}$


 $\mathbf{[\text{SCN}^{-}]_{\text{eq}} = 0.6 \times 10^{-4} \text{ M}}$


 $\mathbf{[\text{FeSCN}^{2+}]_{\text{eq}} = 1.4 \times 10^{-4} \text{ M}}$

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

$$K_{\text{eq}} = \frac{[\text{FeSCN}^{2+}]_{\text{eq}}}{[\text{Fe}^{3+}]_{\text{eq}} [\text{SCN}^{-}]_{\text{eq}}} = \frac{\mathbf{1.4 \times 10^{-4} \text{ M}}}{(\mathbf{78.6 \times 10^{-4} \text{ M}}) (\mathbf{0.6 \times 10^{-4} \text{ M}})} = \mathbf{3 \times 10^2 \text{ M}^{-1}} \text{ (1 Significant Figure)}$$

EXPERIMENT 2
THE EQUILIBRIUM CONSTANT

PROCEDURE:**I. Preparation of Reaction Mixtures**

1. Thoroughly clean five vials with deionized water.
2. Allow the vials to drain as dry as possible.
3. Label the vials as follows: 1, 2, 4, 8, and XS (excess)
4. Add the reagents according to the table below:

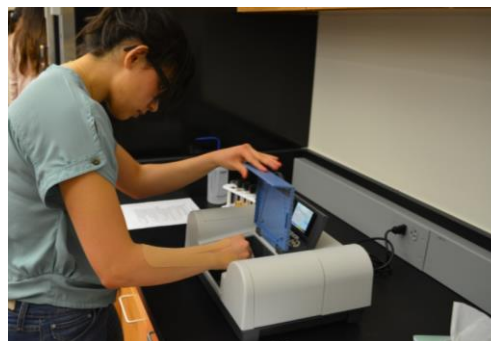
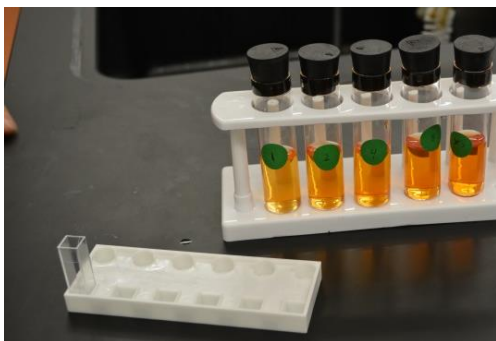
Mixtures of Fe^{3+} and SCN^- (final volume of 15.0 mL)

Vial 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 mL	5.00 mL	9.00 mL
2	x 2	2.00 mL	5.00 mL	8.00 mL
4	x 4	4.00 mL	5.00 mL	6.00 mL
8	x 8	8.00 mL	5.00 mL	2.00 mL

Mixture containing an excess of Fe^{3+}

Vial 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 mL	5.00 mL	0.00 mL

5. Seal vials with #4 stoppers and mix the contents of the vials by inverting the vials several times. Do not spill. If you spill, discard the solution and make a new solution.
6. Place the five vials in the test tube rack
7. Continue to the next step within 10 minutes since the solutions are not stable.

**II. Absorbance Readings****1. Prepare a cuvette**

- Rinse the cuvette with deionized water and fill it 2/3 full with deionized water.
- Dry the outside of the cuvette with tissue paper, and only hold it with tissue paper (fingerprints affect the Absorbance reading)

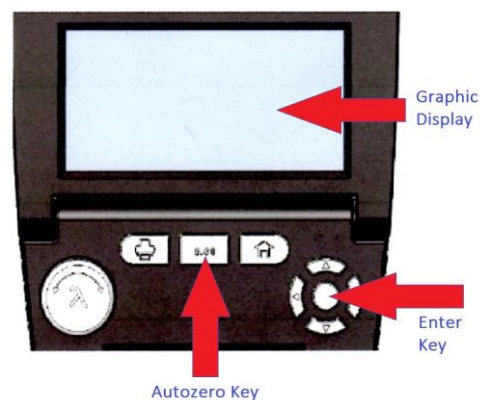
2. Prepare the spectrophotometer for Absorbance readings

- Turn on the Spectronic 200 Version 1.12 (the spectrophotometer needs 10 minutes to warm up), set the wavelength to 449 nm, and select "Absorbance" as the Measurement Mode
- The spectrophotometer has an 8 key soft touch keypad and a color graphics display, as shown on the next page.

EXPERIMENT 2 THE EQUILIBRIUM CONSTANT

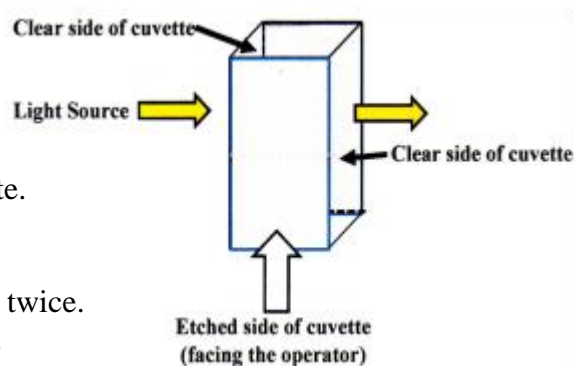
3. Autozero (calibrate) the spectrophotometer.

- Place the cuvette containing deionized water in the cuvette holder.
- Note that two of the sides of the cuvette are clear (opposite each other) and the other two sides are etched. Insert the cuvette in the cuvette holder so that the light source passes through the clear sides (not the etched sides).
- Close the compartment door and press the “Autozero” key (should read 0.00) to correct for the Absorbance of water and of the cuvette.
- Remove the cuvette containing the deionized water and close the compartment door.



4. Measure the Absorbance of a solution.

- Pour out the deionized water from the cuvette and shake out any excess water out of the cuvette.
- Pour solution # 1 into the cuvette to 2/3 full, then re-pour it back into its original vial, then re-pour it back into the cuvette. Repeat this step twice. The purpose of pouring back and forth is to mix and dilute any trace of water left in the cuvette.
- Place the cuvette containing solution # 1 into the spectrophotometer compartment and close the compartment door. **DO NOT PRESS ANY KEYS!** Read and record the Absorbance of the solution.
- Remove the cuvette from the cuvette holder and transfer the solution back into Vial # 1. This will ensure that the solution is available for a second Absorbance reading, in case the first Absorbance reading was in error. **Do not wash the cuvette with deionized water!**
- Use solution # 2 to pour back and forth from the vial to the cuvette several times, in order to mix and dilute any trace of solution # 1.
- Repeat the above steps to obtain the Absorbance readings of the remaining solutions.



5. Clean-up instructions:

- Report the Absorbance readings to your instructor. Your instructor will verify the validity of your experimentally determined Absorbance readings and will inform you if you have to repeat any or all steps of the experiment.
- Rinse the cuvette with deionized water and return the cuvette to your instructor.
- Discard all solutions.

Bibliography:

1. Jo A. Beran “Chemistry in the Laboratory”, First Edition
2. R.A.D. Wentworth “Experiments in General Chemistry”, Sixth Edition
3. James M. Postma & all, “Chemistry in the Laboratory”, Seventh Edition

EXPERIMENT 2
THE EQUILIBRIUM CONSTANT

REPORT FORM

NAME: _____ Date: _____ Partner: _____

Part I

Calculating the Initial Concentrations of Reactants in the Reaction Mixtures.

For each vial, calculate the Initial Concentrations of $[\text{Fe}^{3+}]_0$ and $[\text{SCN}^-]_0$ in the reaction mixture for each vial.

- Take into account that the total volume in each test tube is **15.0 mL**.
- Record all the calculated Initial Concentration as **# x 10⁻⁴ M**.
- Express your answers to the correct amount of significant figures.

For example, in vial 1, the 1.00 mL of $6.00 \times 10^{-2} \text{ M Fe(NO}_3)_3$ added is diluted to a total volume of 15.00 mL. The initial concentration of $[\text{Fe}^{3+}]$ in solution 1 can be calculated as shown in the first box:

DATA TABLE #1

Vial Label	$[\text{Fe}^{3+}]_0, \text{ M}$	$[\text{SCN}^-]_0, \text{ M}$
#1	$6.00 \times 10^{-2} \text{ M} \times \frac{1.00 \text{ mL}}{15.00 \text{ mL}} = 40.0 \times 10^{-4} \text{ M}$	
#2		Same as vial # 1
#4		Same as vial # 1
#8		Same as vial # 1
XS Fe^{3+}		Same as vial # 1

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THE EQUILIBRIUM CONSTANT

Part II

Calculate the equilibrium concentration of the product from Absorbance Readings.

DATA TABLE # 2

Vial Label	Absorbance (2 Significant Figures)	Calculations (for example calculations, see pages 3 & 4)	Equilibrium Concentration of $[\text{FeSCN}^{2+} \times 10^{-4}]_{\text{eq}}$ (2 Significant Figures)
#1			
#2			
#4			
#8			
XS (reference)			*2.00

* In the reference vial the large excess of Fe^{3+} speeds up the forward reaction and shifts the equilibrium system all the way to the right. As such, all of the SCN^- initially present will be bound in the FeSCN^{2+} form.

$$[\text{SCN}^-]_{\text{initial}} = [\text{FeSCN}^{2+}]_{\text{equilibrium}}$$

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 ($667 \times 10^{-4} \text{ M}$)		$2.00 \times 10^{-4} \text{ M}$		0
Change	$- 2.00 \times 10^{-4} \text{ M}$		$- 2.00 \times 10^{-4} \text{ M}$		$+ 2.00 \times 10^{-4} \text{ M}$
Equil. Conc's	$665 \times 10^{-4} \text{ M}$		0		$2.00 \times 10^{-4} \text{ M}^*$

EXPERIMENT 2
THE EQUILIBRIUM CONSTANT

Part III**Calculating the equilibrium concentrations of the reactants: $[\text{Fe}^{3+}]_{\text{eq}}$ and $[\text{SCN}^-]_{\text{eq}}$**

1. Enter in the four equilibrium tables the values of $[\text{Fe}^{3+}]_{\text{initial}}$, $[\text{Fe}^{3+}]_0$, $[\text{SCN}^-]_{\text{initial}}$, $[\text{SCN}^-]_0$ from Data Table #1 and $[\text{FeSCN}^{2+}]_{\text{equil}}$ from Data Table #2.
2. Complete the tables below for all four vials (#1, # 2, # 4 and # 8) and calculate the equilibrium concentrations of the reactants: $[\text{Fe}^{3+}]_{\text{eq}}$ and $[\text{SCN}^-]_{\text{eq}}$.
3. For a sample calculation, see page 4.
(for an example, see page 4)

Vial # 1

	$\text{Fe}^{3+}(\text{aq})$	+	$\text{SCN}^-(\text{aq})$	\rightleftharpoons	$\text{FeSCN}^{2+}(\text{aq})$
Initial Concentrations: [] ₀					
Change:					
Equilibrium Concentrations: [] _{eq}					

Vial # 2

	$\text{Fe}^{3+}(\text{aq})$	+	$\text{SCN}^-(\text{aq})$	\rightleftharpoons	$\text{FeSCN}^{2+}(\text{aq})$
Initial Concentrations: [] ₀					
Change:					
Equilibrium Concentrations: [] _{eq}					

Vial # 4

	$\text{Fe}^{3+}(\text{aq})$	+	$\text{SCN}^-(\text{aq})$	\rightleftharpoons	$\text{FeSCN}^{2+}(\text{aq})$
Initial Concentrations: [] ₀					
Change:					
Equilibrium Concentrations: [] _{eq}					

Vial # 8

	$\text{Fe}^{3+}(\text{aq})$	+	$\text{SCN}^-(\text{aq})$	\rightleftharpoons	$\text{FeSCN}^{2+}(\text{aq})$
Initial Concentrations: [] ₀					
Change:					
Equilibrium Concentrations: [] _{eq}					

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THE EQUILIBRIUM CONSTANT

Part IV**Calculating the Equilibrium Constant (K_{eq})**

1. Enter the Equilibrium Concentrations of the Reactants and of the Product in Data Table # 3
2. Calculate the equilibrium constant (K_{eq})
3. See page 4 for a sample calculation.

DATA TABLE # 3

Vial Label	$[\text{Fe}^{3+}]_{\text{equil}}$, M	$[\text{SCN}^-]_{\text{equil}}$, M	$[\text{FeSCN}^{2+}]_{\text{equil}}$, M	K_{equil} (M^{-1}) Although only 1 significant figure is allowed in these answers, carry one additional significant figure that will be dropped in the next step.
#1				
#2				
#4				
#8				

4. Calculate the average value of the equilibrium constant ($K_{\text{eq/ave}}$), and express your answer in 1 significant figure. Show calculations below:

EXPERIMENT 2
THE EQUILIBRIUM CONSTANT

Part V**Conclusions:**

1. What was the first purpose of this experiment?

Please state your conclusion below:

2. What was the second purpose of this experiment?

Before you state your conclusions, consider the followings:

(a) The ionic formulas of the two reactants are: _____ and _____

(b) In preparing the solutions in vials 1 through 8:

- The initial concentration of _____ _____
increased /decreased / remained the same
- The initial concentration of _____ _____
increased /decreased / remained the same

(c) Examine Data Table # 3 to obtain a conclusion for the second purpose of this experiment:

State your conclusion by completing the blanks below:

An _____ ^{increase / decrease} in the initial concentration of _____ ions had the following effect on the Equilibrium System:

- | | | |
|---|---|--|
| ➤ | The Equilibrium Concentration of _____ | _____ |
| | | increased /decreased / remained the same |
| ➤ | The Equilibrium Concentration of _____ | _____ |
| | | increased /decreased / remained the same |
| ➤ | The Equilibrium Concentration of _____ | _____ |
| | | increased /decreased / remained the same |
| ➤ | The Equilibrium <u>Constant</u>, K_{eq} _____ | _____ |
| | | increased /decreased / remained the same |

EXPERIMENT 2
THE EQUILIBRIUM CONSTANT
