Experiment 3: Equilibrium Constant for the Formation of $Fe(SCN)^{2+}$

What lab skills will you practice?

- Using volumetric glassware to prepare solutions
- Using a spectrophotometer
- Creating and applying calibration curves

What chemical concepts will you apply?

- Determining K_{eq} Silberberg: Chapter 15.2
- Effects of concentration on K_{eq} Chapter 15.5
- Complex ion equilibria Silberberg: Chapter 17.4
- Absorbance & colourimetry Experiment 2

What report writing skills will you use?

- Writing discussions for formal reports
- Interpreting statistical results
- Summarizing experimental results

Reminders:

- Complete the pre-lab quiz and flowchart at least **one hour before lab**
- Print & bring all Experiment 3 and Appendix H pages to lab

Objective

In this experiment, you will use absorbance measurements to determine the equilibrium constant for the formation of $Fe(SCN)^{2+}$ from iron and thiocyanate ions.

Introduction

Ferric thiocyanate, $Fe(SCN)^{2+}$, is a coloured species produced when a ferric ion, Fe^{3+}, reacts with a thiocyanate ion, SCN^-, in aqueous solution as shown in the chemical equation:

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq) \quad [1]$$

The **equilibrium constant**, *K*, for the reaction is given by the expression:

$$K = \frac{[Fe(SCN)^{2+}]_E}{[Fe^{3+}]_E[SCN^-]_E} \quad [2]$$

Where the subscript *E* indicates that the concentration is measured at equilibrium. In this experiment, you will measure these equilibrium concentrations so that *K* can be calculated. When you know the magnitude of the equilibrium constant *K* (for any reaction), you know how far the reaction proceeds. In equilibria involving complex ions, the equilibrium constant for the formation of complex ion is also called the formation constant, K_f.

To determine the equilibrium concentrations, you will measure **absorbance** of the complex ion $Fe(SCN)^{2+}$, which has a strong red-brown colour. Since the complex ion is the only colored compound in solution (the other species are colorless), Beer's Law for the solutions you will analyze becomes:

See the Introduction for Experiment 2 to review absorbance background.

$$A = \epsilon \ell [Fe(SCN)^{2+}] \quad [3]$$

By measuring the absorbance of the reaction solutions at equilibrium, you can use a calibration plot to determine $[Fe(SCN)^{2+}]_E$ (the complex ion concentration at equilibrium). Since the initial amounts of Fe^{3+} and SCN^- used in the reaction are known, the principles of equilibrium (and ICE tables) can be used to determine the equilibrium concentrations of these species in each solution.

In Part 1 of the experiment, you will generate a calibration curve in order to determine $\epsilon\ell$ for this reaction. In order to ensure that the $[Fe(SCN)^{2+}]$ for these calibration solutions is accurately known, a large excess of SCN^- is used, so that the equilibrium for these solutions lies heavily to the products, and we can assume all of the Fe^{2+} added becomes $Fe(SCN)^{2+}$. In Part 2, you will observe solutions prepared with various initial reactant concentrations in order to determine K_{eq} for the formation of iron(III) thiocyanate.

See information on D2L and in the Introduction chapter for details on 'blue books' and appropriate lab attire.

Preparing for Lab

Before coming to lab, make sure you have:

- Read Experiment 3 and Appendix H (print and bring both to lab)
- Completed the online pre-lab quiz – *at least one hour before lab*
- Completed the procedure flow chart on Page 9 of this experiment
- Obtained a "blue book" lab report notebook and prepared tables for entering your raw data as described below
- Prepared yourself by wearing appropriate clothing and lab coat.

Tables for Raw Data

On the **last two pages** of your "blue book", prepare **neat, labelled tables** to use for entering your raw data during lab. Remember to include units and titles for all tables.

Part 1: Calibration

Provide space to record the precise concentrations of all reagents used.

Use the guidelines from Experiment 2, and Table 1 in the Procedure section below to create a table to record your raw data for the calibration measurements.

Part 2: Equilibrium Measurements

Provide space to record the precise concentrations of all reagents used. (Not all are the same as Part 1!)

Prepare a table with columns for "Sample number" and "Absorbance", and space for 5 measurements.

In your results section of your lab report, you will also need a table with columns for: $[Fe^{3+}]_0$, $[SCN^-]_0$, $[Fe(SCN)^{2+}]_E$, $[Fe^{3+}]_E$, $[SCN^-]_E$, and K. You can also include these columns in your data-collection table if you like (they should be included in your Results section either way).

Experimental Procedure

For this experiment you will work in pairs.
Each partner must submit an individually written lab report.

Before beginning, sign out a *Supplementary Equipment Tray* from your TA, containing:

- 1 digital stopwatch
- 1 digital thermometer
- 2 13×100 mm spectrophotometer cuvettes
- 5 18×150 mm test tubes with rubber stopper

By 'signing out' this equipment, you are responsible for it (similar to the equipment in your drawer) until you and your TA sign it back in at the end of lab.

Potassium thiocyanate, KSCN, causes **respiratory tract, eye and skin irritation**. All test tubes with reaction mixtures must be **stoppered** whenever the absorbance is not being measured. Any skin contact, inhalation and ingestion must be avoided.

Part 1: Calibration

Record the actual concentrations (from the bottle labels) of all reagents used.

1. **Prepare dilute $Fe(NO_3)_3$.** Use this diluted solution in Part 1 only.
   - ↪ Label a 10 mL graduated pipet "#1".
   - ↪ Rinse pipet #1 twice with RO water, then twice with 0.0025 M $Fe(NO_3)_3$ stock solution.
   - ↪ Transfer 4.0 mL of 0.0025 M $Fe(NO_3)_3$ stock solution into a clean 100 mL volumetric flask and add RO water to the mark.
   - ↪ Mix the solution well by inverting the stoppered flask several times.
2. **Prepare your solutions**. You will prepare 5 solutions according to the volumes in Table 1 below.
   - ↪ Mark clean and dry test tubes with identification numbers 1-5.
   - ↪ Rinse pipet #1 twice with RO water, then twice with the **dilute** $Fe(NO_3)_3$ solution you just prepared.
   - ↪ Use pipet #1 to transfer the volumes of dilute $Fe(NO_3)_3$ solution described in Table 1 into test tubes 1-5.
   - ↪ Label a second 10 mL graduated pipet "#2". Rinse it twice with RO water and with 0.1 M HNO_3.
   - ↪ Use pipet #2 to deliver the required amounts of 0.1 M HNO_3 into each of test tubes 1-5, as outlined in Table 1.
   - ↪ ⚠ Clean a 5 mL volumetric pipet with RO water, and rinse it with **1.0 M KSCN** solution.
   - ↪ Use this 5 mL volumetric pipet to add 5.00 mL of 1.0 M KSCN to test tubes 1-5.
   - ↪ Immediately cap all test tubes with clean and dry rubber stoppers, and swirl to mix.

TABLE 1: COMPOSITION OF CALIBRATION MIXTURES

Test tube #	**Dilute** $Fe(NO_3)_3$ (mL)	0.1 M HNO_3 (mL)	**1.0 M** KSCN (mL)
1	1.0	4.0	5.00
2	2.0	3.0	5.00
3	3.0	2.0	5.00
4	4.0	1.0	5.00
5	5.0	0.0	

3. **Measure the absorbance.**
   - ↪ Rinse your two cuvettes with 0.1 M HNO_3.
   - ↪ Fill one cuvette half-full of 0.1 M HNO_3 and use it as your blank when setting up the spectrophotometer.
   - ↪ Rinse the second cuvette with a small amount (1-2 mL) of solution from Test tube #1, then fill the cuvette halfway with Solution 1 and measure its' absorbance.
   - ↪ Repeat this procedure (rinse, fill, measure) for the solutions in test tubes 2-5. *Always rinse the cuvette with the solution to be measured.*
   - ↪ After taking all 5 measurements, wash and dry all test tubes and stoppers before moving to Step 4.
   - ↪ Rinse cuvettes with RO water, but do not dry them (to avoid damaging them).

Use a waste beaker to collect **all** discarded solutions for proper disposal.

Never pipet directly from a volumetric flask! Pour some solution into a clean beaker, and pipet from there.

All test tubes should contain a total of 5 mL at this point.

There are **two concentrations** of KSCN available on the back bench. Make sure you use the right one!

Make all absorbance measurements (Parts 1 & 2) at **450 nm.**

Your plot should have a y-intercept of 0. (*why?)*

4. **Plot your data.** Using the graph paper in your blue book, plot the data from Part 1 immediately after finishing. You may use pencil or erasable pen *for plotting this graph only*. Draw a line of best fit through your data, determine the slope (see Calculations section) and have your TA review and initial your graph **before moving on to Part 2.**

Part 2: Equilibrium Measurements

Record the actual concentrations (from the bottle labels) of all reagents used.

1. **Prepare your solutions.** You will prepare 5 solutions according to the volumes in Table 2 below.
   - ↪ Re-number the cleaned and dry test tubes as # 6-10.
   - ↪ Rinse pipet #1 with **0.0025 M** $Fe(NO_3)_3$ stock solution (not your dilute solution!).
   - ↪ Use pipet #1 to deliver the required volume of the 0.0025 M $Fe(NO_3)_3$ solution into each of test tubes 6-10.
   - ↪ Use pipet #2 to add 0.1 M HNO_3 according to the volumes in Table 2 to each of test tubes 6-10.

There are **two concentrations** of KSCN available on the back bench. Make sure you use the right one!

   - ↪  Obtain a third graduated pipet from your drawer. Rinse it with RO water and a small amount of **0.0025 M KSCN** solution. Label this pipet #3.
   - ↪ Use pipet #3 to deliver **0.0025 M** KSCN according to the volumes in Table 2 to each of test tubes 6-10.
   - ↪ Immediately close each test tube with a clean and dry stopper, and swirl to mix the solution.

TABLE 2: COMPOSITION OF REACTION MIXTURES

Test tube #	**0.0025 M** $Fe(NO_3)_3$ (mL)	0.1 M HNO_3 (mL)	**0.0025 M** KSCN (mL)
6	1.0	7.0	2.0
7	1.0	6.5	2.5
8	1.0	6.0	3.0
9	2.0	7.0	1.0
10	2.0	6.5	1.5

2. **Measure the absorbance**.
   - ↪ Place the cuvette in the spectrophotometer. **Use the same instrument** that you used in Part 1 or your $\epsilon\ell$ value may be invalid. You should not need to re-blank the spectrophotometer.
   - ↪ Rinse a cuvette with a small amount (1-2 mL) of solution from Test tube #6, then fill the cuvette halfway with Solution 6 and measure its' absorbance.
   - ↪ Repeat this procedure (rinse, fill, measure) for the solutions in test tubes 7-10. *Always rinse the cuvette with the solution to be measured.*
   - ↪ After taking all 5 measurements, wash and dry all test tubes and stoppers before moving to Step 4.

Do not put the thermometer into the cuvette. Use a beaker or test tube.

   - ↪ For at least one sample, measure the solution temperature after taking the absorbance.
   - ↪ Rinse cuvettes, but do not dry them (to avoid damaging them).

After all measurements have been completed, dispose of all solutions properly, clean all your glassware and tidy your bench. Return all supplementary equipment to your TA and sign for its return.

Calculations

Graphs for Part 2 may be done on a computer using Excel or similar software, if you like. The calibration curve for Part 1 is completed during lab. Remember to show sample calculations for **each** type of calculation in Part 1 and 2 in your blue book.

Calibration (*done during lab*)

From the measurements of Solutions 1-5, make a plot of A vs. $[Fe(SCN)^{2+}]$ using the graph paper included in your blue book, and use a ruler to hand-draw a line of best fit through your data. Use the same formatting guidelines as given for Experiment 2 when preparing your graph.

From your line of best fit, determine the slope of your plot (and so $\varepsilon\ell$). Mark the points that you used for the slope calculation. Label the slope **on your plot.** You can show your sample calculation on the plot or with your other sample calculations, as long as it is clearly labelled.

Equilibrium Constant Determination (*done after lab*)

Use the $\varepsilon\ell$ value you found during lab to determine the $[Fe(SCN)^{2+}]_E$ from each absorbance measurement of Solutions 6-10. Equation [3] will help you.

From the *actual* concentrations of the stock solutions used, determine the $[Fe^{3+}]_0$ and $[SCN^-]_0$ in each test tube 6-10.

Use an ICE table to determine $[Fe^{3+}]_E$ and $[SCN^-]_E$ for each of solutions 6-10. An example is partially filled out for you below:

	Fe^{3+}	+	SCN^-	⇌	$Fe(SCN)^{2+}$
Initial	$[Fe^{3+}]_0$		$[SCN^-]_0$		0
Change	$-x$		$-x$		$+x$
Equilibrium	$[Fe^{3+}]_E$ $= [Fe^{3+}]_0 - x$		$[SCN^-]_E$ $= [SCN^-]_0 - x$		$[Fe(SCN)^{2+}]_E$ $= 0 + x = x$

From the equilibrium concentrations you have found, determine the equilibrium constant *K* for each of Solutions 6-10. Equation [2] will help.

From your five *K* values, determine the standard deviation *s* for your data set. Determine whether any values should be rejected (refer to Appendix E), and determine the value of *K* you will report.

From the source provided, find the literature values for *K* at 20°C and 25°C. Use these literature values and the van't Hoff equation (below) to determine the standard enthalpy (ΔH^0) for this reaction.

$$\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Use the enthalpy of reaction and either of the literature values to predict the value of *K* at the observed room temperature in the laboratory.

Calculate a % error for your experimental value, based on your predicted *K* value.

It is possible that none of your data points lie exactly on your line of best fit. Calculate slope from points that are **actually on** the best-fit line. (they do not have to be measured data points)

Hint: Solutions 6-10 each have a total volume of 10.0 mL.

You can complete these calculations on the computer (attach a printout of the table) – but you still need to show a sample calculation for each, handwritten in your blue book.

Reference (also on D2L):

Lister, M.; Rivington, D.; *Can. J. Chem.* **1955** 33, p. 1572-1590

Lab Report

You will have **one week** to complete your formal lab report. Your report must be handwritten in a blue lab notebook (with the exception of graphs and tables, as noted above – these can be hand-drawn in pencil or plotted by computer and stapled into the book).

Submit your completed report to your lab section's dropbox outside SA 116. If your report Is late, hand it in to the *Late Report Box* outside SA 116, and notify your TA and the Lab Coordinator when you have submitted it. Marks will be deducted for late reports: ½ mark per half-day and 1 mark per weekend day.

Marks Breakdown

The general marking scheme for the lab report is as follows:

Criteria	Marks
Introduction Objective is clear, techniques and analyses are described	2
Procedure Statement of procedure, including additions or changes.	1
Data Data tables copied neatly into Results section and formatted appropriately	1
Data: Plots Graph for Part 1 has correct formatting, displays relevant information, and any values used are clearly labelled	2
Data: Results & Calculations Sample calculations are shown for all steps (including ICE table), all calculated values tabulated, final results clearly shown	3
Discussion Major results are re-stated and placed in context of the techniques used. Format and general writing quality are appropriate.	2
Discussion Accuracy and reproducibility of results are evaluated, with numeric support for each.	2
Discussion At least two appropriate sources of error are discussed in the context of the results. (at least one non-"human error")	1
Conclusion & References Objectives, results, and their reliability are summarized. Reference list is consistently formatted, includes all required sources, and makes use of in-text citations.	2

Refer to the lab manual Introduction chapter for details on formal reports.

Specific Guidelines

A sample discussion section (for Experiment 1) is posted on D2L to help you write your discussion for this lab. Use this sample and the types of questions asked in Experiments 1 and 2 to guide your writing for Experiment 3.

Since this is your first time writing a discussion for Chem 209, you will be given the opportunity to rewrite the Discussion section (after it is graded and returned) in order to improve your writing skills and the mark received on this section.

To submit your Discussion for re-grading:

- Attach your new introduction to your original lab report, *including* the gradesheet.
- Submit this package to your lab section's dropbox **within 24 hours** of the lab period where your reports were returned.
- A maximum of **half of the grades originally 'lost'** on your Introduction section may be returned in increments of 0.5 points, based on your TA's assessment.

Procedure Flow Chart – Pre-Lab Assignment

Fill in the flowchart below with all relevant experimental details (use the flowcharts in Experiments 1 & 2 as a guide):

Safety Precautions:

Part 1: Calibration

1. Dilute $Fe(NO_3)_3$

2. Prepare Solutions

3. Measure Absorbance

4. Plot Data

Part 2: Equilibrium

1. Prepare Solutions

2. Measure Absorbance

Cleanup:

Solution disposal in:

Items checked in to Supplemental Equipment Kit:

Attach this flowchart to the inside cover of your lab report.