**EXPERIMENT**

# Equilibrium constant

## Goal

The goal of this laboratory is to determine *the equilibrium constant* of a chemical reaction by using the *Lambert-Beer's law* to measure the concentration of the species in solution.

## Background

Most chemical reactions do not proceed to completion, proceeding only to the point where both reactants and products have constant concentration. This is because most reactions are reversible and they can run in both forward and reverse directions. The concentrations of the species involved in the equilibrium will achieve an *equilibrium state* when the reaction rates in both directions equalize. For a certain chemical reaction:

$$\mathrm{aA} \quad + \quad \mathrm{bB} \quad \rightleftharpoons \quad \mathrm{cC} \quad + \quad \mathrm{dD}$$

The equilibrium can be characterized by the expression:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where $K_c$ (capital letter) is the equilibrium constant in terms of molarity, the brackets represent the concentrations of the respective species and the exponents are their corresponding stoichiometric coefficients.

### Spectrophotometry

*Spectrophotometry* is a technique that measures the amount of light absorbed by a chemical substance, typically in solution, using the use of a *spectrophotometer*. Spectrophotometers display the absorbance, the amount of light absorbed by a sample. To properly measure the absorbance of a chemical in a water-based solution you need to set the blank by using a sample containing only the solvent without a solute. The blank establishes the baseline of the measurement, eliminating any absorbance caused by the solvent.

The spectrometer allows the measurement of absorbance at a single wavelength. Interestingly, for each substance, there is a wavelength of *maximum absorbance*, which allows us to differentiate among chemical substances with different maximum absorbances. For example, in the current experiment, you will analyze mixtures containing $Fe^{3+}_{(aq)}$, $SCN^{-}_{(aq)}$, and $Fe(SCN)^{2+}_{(aq)}$. However, only $Fe(SCN)^{2+}_{(aq)}$ will absorb radiation at $\lambda$=450 nm, and hence we can track the absorbance of this chemical only in the mixture.

### Lambert-Beer's law

Liquids *attenuated* the intensity of light passing through a colored solution. The effect can be comparable to a dirty window that attenuates the light passing through. The dirtier the window (higher concentration of dirt), the less one can see through it (because more light is absorbed, reflected, or refracted by the dirt). Lambert-Beer's law establishes the relationship between absorbance and concentration:

$$A = k_\lambda c$$

In this formula, $A$ stands for the *absorbance* (light absorbed by the liquid), $k_\lambda$ (lower case, not to be confused with the equilibrium constant, $K$) is a **proportionality constant**, which is specific to each compound and at the wavelength ($\lambda$) specified by the subindex, and $c$ is the solution concentration. Lambert-Beer's law is a linear function of the form $y = mx + b$. When graphing the absorbance ($y$-axes) versus the concentration ($x$-axes), the slope of the line corresponds to Lambert-Beer's proportionality constant. This line should cross the origin as there should be no absorbance when the concentration is null.

# The experiment

The experiment today is divided into 2 parts: determining Lambert-Beer's constant $k$ and determining the equilibrium constant $K$.

### Part A. Determining Lambert-Beer's constant $k$.

This experiment studies the reaction between iron(III) and thiocyanate to give an iron-thiocyanate complex:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$$

Interestingly, $Fe^{3+}$ in solution is yellow and becomes red when reacting with thiocyanate to produce the $(FeSCN)^{2+}$ complex. This intense red coloration allows us to use spectrophotometry to measure the $(FeSCN)^{2+}$ concentration and hence, of all the species in equilibrium.

The first part of this experiment requires the determination of Lambert-Beer's constant, $k_\lambda$. However, here we deal with a chemical reaction. According to the equilibrium, $Fe(SCN)^{2+}$ in solution will follow the reverse reaction forming iron(III) and thiocyanate ions. The shift due to the equilibrium makes the concentration of $Fe(SCN)^{2+}$ unknown.

To solve this problem $Fe^{3+}$ ion will be added in excess (0.0025 M) while adding only small amounts of $SCN^-$ ($10^{-4}$ M). This trick will displace the equilibrium to the right: according to Le Châtelier's, the equilibrium shifts to the products when one reactant is added. Hence, if one of the reactants is added in overwhelming excess, the other reactant will be consumed almost to exhaustion forming the product. Therefore, the $FeSCN^{2+}$ concentration can be calculated using the concentration of $SCN^-$.

In this part, a set of solutions will be added to a clean cuvette, and absorbance at $\lambda$=450 nm will be measured using the spectrophotometer. With the 5 points obtained and the origin of the coordinates, a graph will be plotted to calculate the slope of the line. Notice again that in this linear representation, the line must pass through the origin by definition, since at concentration=0, absorbance must be 0.

### Parts B. Determining the equilibrium constant $K_c$.

Using the absorbance measured and the value of $k_{450nm}$, in this second part of the experiment you will calculate the concentration in equilibrium of all species involved in the equilibrium. First, the concentration of the product will depend on the absorbance, and will be given by the formula below:

$$A = k_{450nm}[Fe(SCN)^{2+}] \qquad [Fe(SCN)^{2+}] = \frac{A}{k_{450nm}}$$

An ICE chart given below will be used to calculate the equilibrium concentration of reactants, where 3 is calculated from the absorbance, and 2 and 1 are recalculated from the initial concentrations:

| | $[Fe(NO_3)_3]$ | [KSCN] | $[Fe(SCN)^{2+}]$ |
|---|---|---|---|
| Initial | 1 | 2 | 0 M |
| Change | −3 | −3 | +3 |
| Equilibrium | 1 − 3 | 2 − 3 | 3 |

# Procedure

### Preparing a diluted KSCN solution

☐ *Step 1:* – Clean 5 large test tubes and the matching stoppers and set them upside down on a rack. Number the test tubes from 1 to 5.

☐ *Step 2:* – Obtain a 100.0 mL volumetric flask and a Mohr pipette.

☐ *Step 3:* – Obtain about 15 mL of 0.0025 M KSCN in a 50 mL beaker. Rinse the Mohr pipette a couple of times with a small amount of this solution. Always discard the rinsing liquid. Then, transfer 4.00 mL into the volumetric flask.

☐ *Step 4:* – In a clean 100 mL beaker, obtain about 100 mL of distilled water. Carefully add water to the volumetric flask directly from the beaker and stop adding before you reach the 100.0 mL mark. Use a plastic dropper to level the water to the mark, drop by drop. This is the diluted KSCN solution.

☐ *Step 5:* – Rinse the Mohr pipette with the diluted solution of KSCN again.

**Good Lab Practice**

✍ Pipettes are always used together with a suction bulb or a syringe. **Never** suck a chemical using the mouth!

✍ **Never** leave a pipette lying on the table **while connected to the syringe**. Remaining liquid can leak into the syringe. The syringe will be damaged and the liquid will return to the pipette contaminated.

✍ Always wash pipettes with distilled water and rinse them using the same product to be measured. Suck a small volume, disconnect the syringe and move the liquid about, displacing the distilled water. Discard the rinsing liquid as waste. Rinse twice.

## Part A. Determining Lambert-Beer's constant $k$. Preparing the mixtures

☐ *Step 1:* – Following the Table in the description of Part A, add 1.00 mL of the diluted KSCN solution to jumbo test tube 1, 2.00 mL to test tube 2, 3.00 mL to test tube 3, 4.00 mL to test tube 4 and 5.00 mL to test tube 5. You will use jumbo test tubes throughout the experiment.

☐ *Step 2:* – Rinse the pipet with distilled water. Obtain about 50 mL of 0.25 M $Fe(NO_3)_3$ in a 100 mL beaker. Rinse the pipette with the solution of $Fe(NO_3)_3$ from the beaker.

☐ *Step 3:* – Add 5.0 mL of 0.25 M $Fe(NO_3)_3$ in each test tube.

☐ *Step 4:* – Rinse the pipette with distilled water. Obtain about 40 mL of 0.1 M $HNO_3$ in a 50 mL beaker. Rinse the pipette with the solution of $HNO_3$ from the beaker.

☐ *Step 5:* – Following the Table below, add 4.00 mL of the $HNO_3$ solution to test tube 1; 3.00 mL to test tube 2, 2.00 mL to test tube 3, and 1.00 mL to test tube 4.

☐ *Step 6:* – At this point, all your test tubes should have the same volume of liquid. If not, repeat the ones that diverge.

☐ *Step 7:* – Put the stoppers in the test tubes and mix the solutions.

| Part A | $Fe(NO_3)_3$ 0.25 M | KSCN $10^{-4}$ M | $HNO_3$ 0.1 M | $v_{total}$ |
|---|---|---|---|---|
| Test Tube 1 | 5.0 mL | 1.0 mL | 4.0 mL | 10.0 mL |
| Test Tube 2 | 5.0 mL | 2.0 mL | 3.0 mL | 10.0 mL |
| Test Tube 3 | 5.0 mL | 3.0 mL | 2.0 mL | 10.0 mL |
| Test Tube 4 | 5.0 mL | 4.0 mL | 1.0 mL | 10.0 mL |
| Test Tube 5 | 5.0 mL | 5.0 mL | 0.0 mL | 10.0 mL |

## Part A. Determining Lambert-Beer's constant $k$. Measuring absorbance

☐ *Step 1:* – Start the spectrophotometer. The bulb needs time to heat up to a stable temperature.

☐ *Step 2:* – Get a 250 mL beaker for waste. Refill the 100 mL beaker with distilled water.

☐ *Step 3:* – Using the plastic dropper, fill the cuvette 3/4 full with distilled water.

☐ *Step 4:* – Insert the cuvette into the spectrophotometer, set the wavelength to 450 nm, and press "blank" or "zero".

☐ *Step 5:* – Use a new cuvette. Fill the cuvette 3/4 full with the solution from test tube 1.

☐ *Step 6:* – Insert the cuvette into the spectrophotometer to measure the absorbance. Record the result.

☐ *Step 7:* – Repeat for test tubes 2, 3, 4, and 5, always using new cuvettes for each measurement.

☐ *Step 8:* – Plot absorbance (7) vs. concentration (6) in order to obtain the Lambert-Beer's constant $k$.

**Good Lab Practice**

✍ For best results, use the same cuvette, with the same orientation, for all the measurements.

✍ Keep the outer walls of the cuvette clean. Do not touch them. Wipe them with a piece of optical paper.

✍ Rinse the cuvette at the same time as you rinse the pipette.

### Part B. Determining the equilibrium constant $K$. Preparing a different set of mixtures

☐ *Step 1:* – Prepare a new set of mixtures based on the proportions reported in the Table below.

☐ *Step 2:* – Make sure you use the 0.0025 M $Fe(NO_3)_3$ solution and not the 0.25M.

☐ *Step 3:* – The 0.0025 M KSCN solution to be used has already been prepared at the lab.

☐ *Step 4:* – Measure the absorbance for the new set of mixtures.

| Part B | $Fe(NO_3)_3$ 0.0025 M | KSCN 0.0025 M | $HNO_3$ 0.1 M | $v_{total}$ |
|---|---|---|---|---|
| Test Tube 6 | 1.0 mL | 5.0 mL | 1.0 mL | 7mL |
| Test Tube 7 | 1.0 mL | 4.5 mL | 1.5 mL | 7mL |
| Test Tube 8 | 1.0 mL | 4.0 mL | 2.0 mL | 7mL |
| Test Tube 9 | 1.0 mL | 3.5 mL | 2.5 mL | 7mL |
| Test Tube 10 | 1.0 mL | 3.0 mL | 3.0 mL | 7mL |
| Test Tube 11 | 2.0 mL | 4.0 mL | 1.0 mL | 7mL |
| Test Tube 12 | 2.0 mL | 3.5 mL | 1.5 mL | 7mL |
| Test Tube 13 | 2.0 mL | 3.0 mL | 2.0 mL | 7mL |
| Test Tube 14 | 2.0 mL | 2.5 mL | 2.5 mL | 7mL |
| Test Tube 15 | 2.0 mL | 2.0 mL | 3.0 mL | 7mL |

## Calculations

(1) This is the volume of $Fe(NO_3)_3$ added.

(2) This is the volume of KSCN added.

3 This is the total volume of the mixtures.

4 This is the initial Iron(III) concentration in the mixtures:

$$[Fe^{+3}]_0 = \frac{v_{Fe^{+3}} \cdot c_{Fe^{+3}}}{v_{total}} = \frac{1 \cdot 0.25}{3}$$

5 This is the initial thiocyanide concentration in the mixtures:

$$[SCN^-]_0 = \frac{v_{SCN^-} \cdot c_{SCN^-}}{v_{total}} = \frac{2 \cdot 10^{-4}}{3}$$

6 This is the concentration of $Fe(SCN)^{+2}$ in the mixture:

$$[Fe(SCN)^{+2}] = [SCN^-] = 5$$

7 This is the measured absorbance of the mixture.

8 This step is needed to calculate numerically the Lambert-Beer's constant $k$:

$$[Fe(SCN)^{+2}] \cdot A = 6 \cdot 7$$

9 This step is needed to calculate numerically the Lambert-Beer's constant $k$:

$$[Fe(SCN)^{+2}]^2 = 6^2$$

10 This step is needed to calculate numerically Lambert-Beer's constant $k$, and results from adding all values of 8 .

11 This step is needed to calculate numerically Lambert-Beer's constant $k$, and results from adding all values of 9 .

12 This step the Lambert-Beer's constant $k$:

$$k = \frac{\sum [Fe(SCN)^{+2}] \cdot A}{\sum [Fe(SCN)^{+2}]^2} = \frac{10}{11}$$

13 This is the volume of $Fe(NO_3)_3$ added.

14 This is the volume of KSCN added.

15 This is the total volume of the mixtures.

16 This is the initial Iron(III) concentration in the mixtures:

$$[Fe^{+3}]_0 = \frac{v_{Fe^{+3}} \cdot c_{Fe^{+3}}}{v_{total}} = \frac{13 \cdot 0.0025}{15}$$

17 This is the initial thiocyanide concentration in the mixtures:

$$[SCN^-]_0 = \frac{v_{SCN^-} \cdot c_{SCN^-}}{v_{total}} = \frac{14 \cdot 0.0025}{15}$$

(18) This is the measured absorbance of the mixture.

(19) This is the concentration of $Fe(SCN)^{+2}$ in equilibrium:

$$[Fe(SCN)^{+2}]_{eq} = \frac{A}{k} = \frac{(18)}{(12)}$$

(20) This is the concentration of $Fe^{+3}$ in equilibrium:

$$[Fe^{+3}]_{eq} = [Fe^{+3}]_0 - [Fe(SCN)^{+2}]_{eq} = (16) - (19)$$

(21) This is the concentration of $SCN^-$ in equilibrium:

$$[SCN^-]_{eq} = [SCN^-]_0 - [Fe(SCN)^{+2}]_{eq} = (17) - (19)$$

(22) This is the equilibrium constant:

$$K = \frac{[Fe(SCN)^{+2}]_{eq}}{[Fe^{+3}]_{eq} \cdot [SCN^-]_{eq}} = \frac{(19)}{(20) \cdot (21)}$$

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**Pre-lab Questions**

# Equilibrium constant

1. You prepare a solution by following the procedure described next. You first obtain about 15 mL of 0.0025 M KSCN in a 50 mL beaker. Then you transfer 4.00 mL into the volumetric flask. In a clean 100 mL beaker, you obtain about 100 mL of distilled water, and carefully add water to the volumetric flask directly from the beaker stopping before reaching the 100.0 mL mark. Finally, you use a plastic dropper to level the water to the mark, drop by drop. Calculate the molarity of the solution you prepared.

2. You mix 1mL of $Fe(NO_3)_3$ 0.25 M with 5mL of KSCN $10^{-4}$ M and 1mL of $HNO_3$ 0.1 M. Calculate the initial concentration of $Fe^{3+}$ in the mixture.

3. Write down the formula for the equilibrium constant in terms of concentration for the equilibrium below:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$$

4. A set of absorbances, $A$, for different concentrations, $c$, are given below.

(a) Plot $A$ vs. $c$ in the graph below.

(b) Compute the slope of the graph by using the formula:

$$k = \frac{\sum c \cdot A}{\sum c^2}$$

| $c$ (M) | $A$ | $c \cdot A$ (M) | $c^2$ ($M^2$) |
|---|---|---|---|
| 0.0120 | 0.681 | | |
| 0.00960 | 0.540 | | |
| 0.00720 | 0.389 | | |
| 0.00480 | 0.270 | | |
| 0.00240 | 0.133 | | |
| Sum | | | |
| $k$ ($M^{-1}$) | | | |

(c) After calculating $k$, now write down the formula for absorbance in the form: $A = k \cdot c$

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**Results**
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# Equilibrium constant

**Parts A. Determining Lambert-Beer's constant $k$.**

| | $Fe(NO_3)_3$ 0.25M (1) | KSCN $10^{-4}$M (2) | $HNO_3$ 0.1M | $v_{tot}$ (3) | $[Fe^{+3}]_0$ (4) | $[SCN^-]_0$ (5) | $[FeSCN^{+2}]$ (6) | A (7) | $[FeSCN^{+2}]\cdot A$ (8) | $[FeSCN^{+2}]^2$ (9) |
|---|---|---|---|---|---|---|---|---|---|---|
| Test Tube 1 | 5mL | 1mL | 4mL | 10mL | ____ | ____ | ____ | ____ | ____ | ____ |
| Test Tube 2 | 5mL | 2mL | 3mL | 10mL | ____ | ____ | ____ | ____ | ____ | ____ |
| Test Tube 3 | 5mL | 3mL | 2mL | 10mL | ____ | ____ | ____ | ____ | ____ | ____ |
| Test Tube 4 | 5mL | 4mL | 1mL | 10mL | ____ | ____ | ____ | ____ | ____ | ____ |
| Test Tube 5 | 5mL | 5mL | 0mL | 10mL | ____ | ____ | ____ | ____ | ____ | ____ |
| Origin | | | | | | | 0 | 0 | 0 | 0 |
| | | | | | | | | | (10) | (11) |
| | | | | | | | | Sum= | ____ | ____ |

(12) $k =$ ____________

### Parts B. Determining the equilibrium constant $K$.

| Test Tube | $Fe(NO_3)_3$ 0.0025M (13) | KSCN 0.0025M (14) | $HNO_3$ 0.1M | $v_{tot}$ (15) | $[Fe^{3+}]_0$ (16) | $[SCN^-]_0$ (17) | A (18) | $[Fe(SCN)^{2+}]_{eq}$ (19) | $[Fe^{3+}]_{eq}$ (20) | $[SCN^-]_{eq}$ (21) | K (22) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 1mL | 5.0mL | 1.0mL | 7.0mL | ______ | ______ | ______ | ______ | ______ | ______ | ______ |
| 7 | 1mL | 4.5mL | 1.5mL | 7.0mL | ______ | ______ | ______ | ______ | ______ | ______ | ______ |
| 8 | 1mL | 4.0mL | 2.0mL | 7.0mL | ______ | ______ | ______ | ______ | ______ | ______ | ______ |
| 9 | 1mL | 3.5mL | 2.5mL | 7.0mL | ______ | ______ | ______ | ______ | ______ | ______ | ______ |
| 10 | 1mL | 3.0mL | 3.0mL | 7.0mL | ______ | ______ | ______ | ______ | ______ | ______ | ______ |
| 11 | 2mL | 4.0mL | 1.0mL | 7.0mL | ______ | ______ | ______ | ______ | ______ | ______ | ______ |
| 12 | 2mL | 3.5mL | 1.5mL | 7.0mL | ______ | ______ | ______ | ______ | ______ | ______ | ______ |
| 13 | 2mL | 3.0mL | 2.0mL | 7.0mL | ______ | ______ | ______ | ______ | ______ | ______ | ______ |
| 14 | 2mL | 2.5mL | 2.5mL | 7.0mL | ______ | ______ | ______ | ______ | ______ | ______ | ______ |
| 15 | 2mL | 2.0mL | 2.0mL | 7.0mL | ______ | ______ | ______ | ______ | ______ | ______ | ______ |

Average $K$= ______

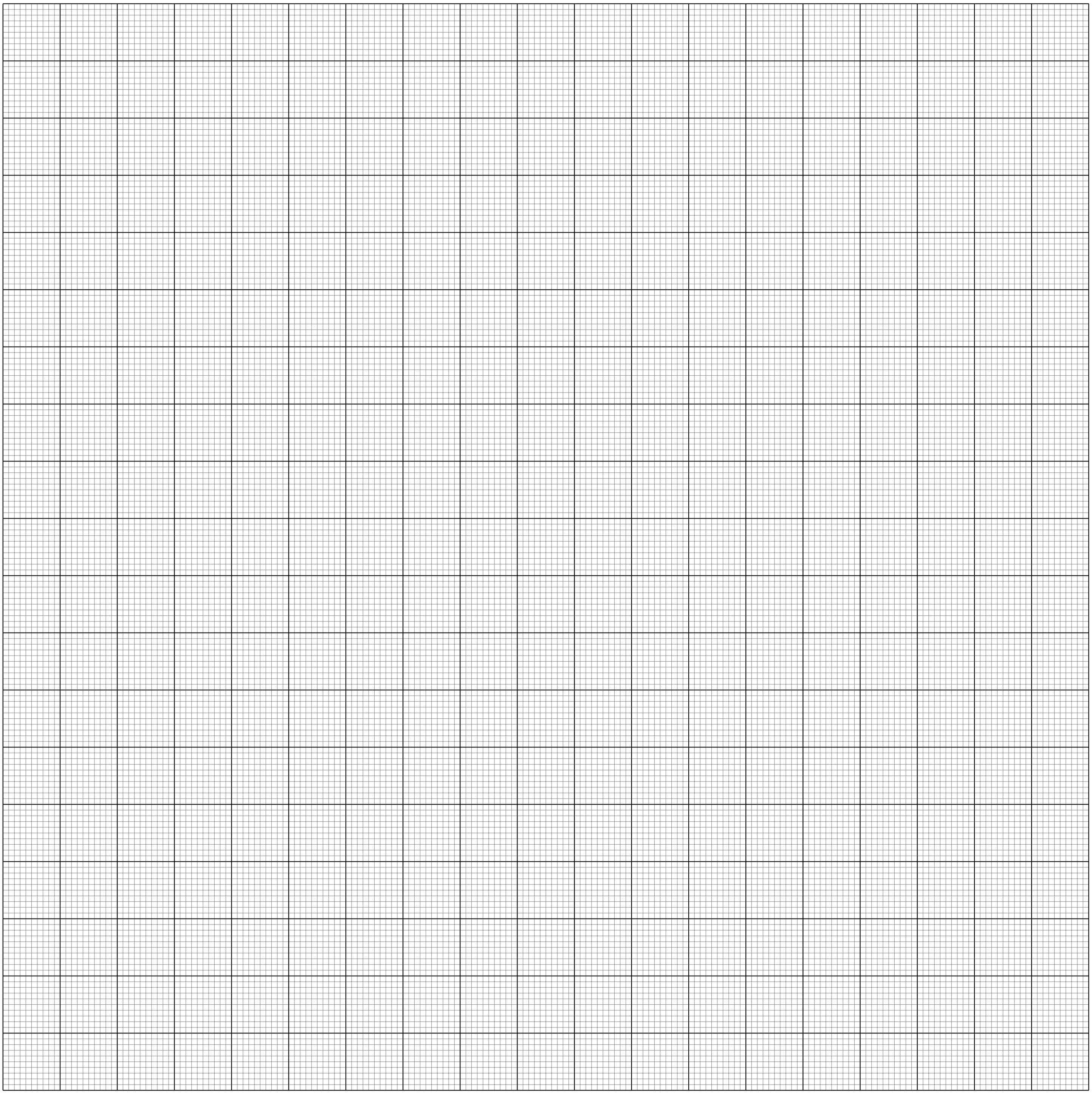

Figure 1: Column 6 [$Fe(SCN)^{+2}$] (X axis) vs. A Column 7 (Y axis)

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**Post-lab Questions**

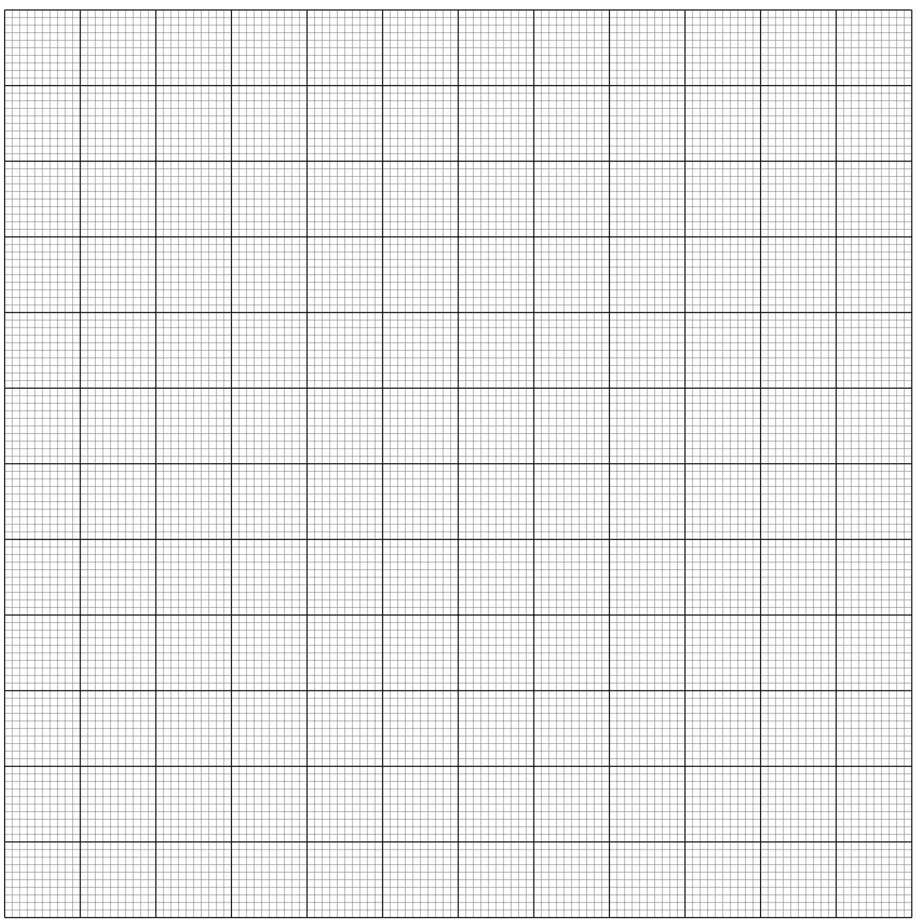
# Equilibrium constant

1. The absorbance of a colored substance in a colorless liquid is measured at each of a series of wavelengths, and the data is given below:

| $\lambda$(nm) | 325 | 350 | 375 | 400 | 425 | 450 | 475 | 500 | 525 |
|---|---|---|---|---|---|---|---|---|---|
| $A$ | 0.016 | 0.144 | 0.341 | 0.578 | 0.681 | 0.558 | 0.281 | 0.092 | 0.031 |

(a) Plot $A$ vs. $\lambda$ in the graph below.

(b) Calculate the $\lambda$ value that gives a maximum $A$.



$\lambda(A_{max})$ = ______________________________

2. In parts A and B you use different iron and thiocyanate solutions: in part, A you use a 0.25M-$Fe(NO_3)_2$ solution and a $10^{-4}$M-KSCN solution, whereas on part B you use a 0.0025M-$Fe(NO_3)_2$ solution and a 0.0025M-KSCN solution. Explain why you do this.

3. You mix 5mL of $Fe(NO_3)_3$ 0.25 M with 2mL of KSCN $10^{-4}$ M and 3mL of $HNO_3$ 0.1 M. Calculate the initial concentration of $SCN^-$ in the mixture.

4. You mix 5mL of $Fe(NO_3)_3$ 0.25 M with 4mL of KSCN $10^{-4}$ M and 1mL of $HNO_3$ 0.1 M. Calculate the concentration of $FeSCN^{2+}$ in the mixture.