

Experiment 34: An Equilibrium Constant

Background Information

Transmittance (T) is the fraction (a decimal) of light transmitted through sample.

T equals transmitted light (I_t) divided by incident light (I_o): $T = \frac{I_t}{I_o}$

Can also be expressed as a percentage: $\%T = T \times (100\%)$

Absorbance is a measure of light absorbed, and is **directly proportional to concentration**.

This is seen in **Beer's law** as $A = abc$, as follows:

a = **molar absorptivity** in L/(mol-cm), constant for a particular frequency

b = the light's **path length** in cm, also a constant

c = the **concentration** in mol/L

So, the plot of A versus concentration is a **straight line**.

A is also related to T, as follows:

$$A = \log\left(\frac{1}{T}\right) = -\log(T) \quad \text{and} \quad A = \log\left[\frac{100}{\%T}\right] = 2 - \log(\%T)$$

Procedure Notes

Part A

- A large excess of $[\text{Fe}^{+3}]$ will be used. LeChatelier's principle tells us that addition of a reactant drives the equilibrium to the right (forward reaction). As a result, assume that **all** SCN^{-1} will be converted to FeNCS^{+2} , so $[\text{FeNCS}^{+2}]_{\text{Eqm}} = [\text{SCN}^{-1}]_o$. This means $A_4 = A_3$.
- A_3 can be found by rearranging $M_1V_1 = M_2V_2$ as follows:
 $A_3 = (0.001 \text{ M}) \times (\text{ml in A1}) \div (25.0 \text{ ml})$
- A known concentration of the product will be used to create a **standardization curve**, which is a graph of A versus concentration.
- Note that all three solutions have $[\text{HNO}_3] = 0.1 \text{ M}$. The separate 0.1 M HNO_3 solution is only used to dilute the mixtures in order to maintain constant volume (25 ml) and constant $[\text{HNO}_3]$.
- Also, note that "dilute to 25 ml" means the new **total volume** is 25 ml. This does **not** mean that an additional 25 ml of 0.1 M HNO_3 is added.

Parts B and C

- The equilibrium constant can be determined once all three concentrations are known.
- The following equilibrium table can be used to set up the equation for Kc

	Fe^{+3}	+	SCN^{-1}	\rightleftharpoons	FeNCS^{+2}
Initial Molarity	B2		B4		0
Change in Molarity	- C1		- C1		+ C1
Equilibrium Molarity	(B2 - C1)		(B4 - C1)		(C1)

- Calculate B2 and B4 in mol/L, rather than moles, by rearranging $M_1V_1 = M_2V_2$ so that $M_2 = M_1V_1/V_2$ as follows:
B2 = $[\text{Fe}^{+3}]_o = (0.002 \text{ M})(\text{Fe}^{+3} \text{ ml used}) / (10 \text{ ml})$
B4 = $[\text{SCN}^{-1}]_o = (0.002 \text{ M})(\text{SCN}^{-1} \text{ ml used}) / (10 \text{ ml})$
- C1 = $[\text{FeNCS}^{+2}]_{\text{Eqm}}$ and is determined from the standardization curve (part A).
- C5 = B2 - C1
- C8 = B4 - C1
- Skip C2, C3, C4, C6, and C7.
- $C9 = Kc = \frac{[\text{FeNCS}^{+2}]}{[\text{Fe}^{+3}][\text{SCN}^{-1}]} = \frac{C1}{(B2 - C1)(B4 - C1)} = \frac{C1}{(C5)(C8)}$

Pre-Lab Hints

1. See Beer's law above ($A = abc$). In this experiment, a and b are both constants.
2. a. The molar concentration is initial moles of SCN^{-1} divided by new total volume.
b. Use stoichiometric ratios from equation 34.4.
3. Refer to Figure 34.5 and the paragraph above the figure.
Also, refer to **part A** notes above about SCN^{-1} .
4. Consider the similarity of both the blank and the DI water to the solutions analyzed.
See the **right margin** next to **Part A step 2** in the lab manual's procedure.
5. a. Plot a graph that is similar to Figure 34.4.
Use graph paper or excel, do not use the pre-lab's grid.
Use only identical regular intervals on both x and y axes.
The result needs to be a straight line.
b. **Note that there is another problem just below the data table.**
Use the equation in the background information above (or eqn 34.2) to find A from %T. Then, find concentration from graph using A.
6. Show your calculations!
B2 Find moles of Fe^{+3} as $\text{Fe}(\text{NO}_3)_2$ concentration (mol/L) times $\text{Fe}(\text{NO}_3)_2$ volume (in L).
B4 Find moles of SCN^{-1} as NaSCN concentration (mol/L) times NaSCN volume (in L).
C2 Find moles of FeNCS^{+2} as its concentration (C1) times its volume (convert to L).
C3 and C6 Same as moles of FeNCS^{+2}
C4 and C7 Subtract moles reacted (C3 and C6) from moles initial (B2 and B4)
C5 and C8 Divide equilibrium moles (C4 and C7) by the volume (convert to L).
Skip 6b.

Lab Questions

1. Review Fig 22.27 in Ebbing and Gammon (our classroom text). The wavelength for the spectrophotometer in experiment 34 is set at 447 nm. What spectrophotometer setting can be varied to find the best indicator of $[\text{FeNCS}^{+2}]$ concentration? What variable can be observed as a result of changing that setting? Which setting gives the best results?
2. Review equations 34.5, 34.6, 34.7, and 34.8. Suppose the spectrophotometer is miscalibrated in Part A only, so that a **higher** absorbance corresponds to a particular concentration. The **correct** absorbance in Part B would then correspond to a **lower** concentration for $[\text{FeNCS}^{+2}]$. How would this, in turn, change $[\text{Fe}^{+3}]$ and $[\text{SCN}^{-1}]$? What would be the overall effect on the Kc value?
3. Suppose that the graph for Part A has a **lower slope** than the correct line. Make a rough graph which compares the incorrect line with the correct line. Observe how the slope has changed, and which way the x-variable went. How is $[\text{FeNCS}^{+2}]$ affected in Part B? What would be the overall effect on the Kc value?
4. Review the equations in the Background Information section of this handout to see the relationships between A and T, as well as between A and the complex ion concentration. Also, review equations 34.5, 34.6, 34.7, and 34.8. Now, suppose there are fingerprints on the cuvet in Part B. Fingerprints prevent light from being transmitted, and this **lowers T** (transmission). How is $[\text{FeNCS}^{+2}]$ affected? How would this change $[\text{Fe}^{+3}]$ and $[\text{SCN}^{-1}]$? What would be the overall effect on the Kc value?
5. Review the Part A notes in this handout about how HNO_3 is used. Now, suppose the 1.0 ml of 0.1 M HNO_3 is omitted from trial 9. How is $[\text{FeNCS}^{+2}]$ affected? How is Absorbance (A) affected? What would be the overall effect on the Kc value?