CHEM 0012

Lab 4: Determination of an Equilibrium Constant using Spectroscopy

- Determination of the equilibrium constant of the following equilibrium system at room temperature.

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

Iron (III) cation thiocyanate ion iron thiocyanate complex

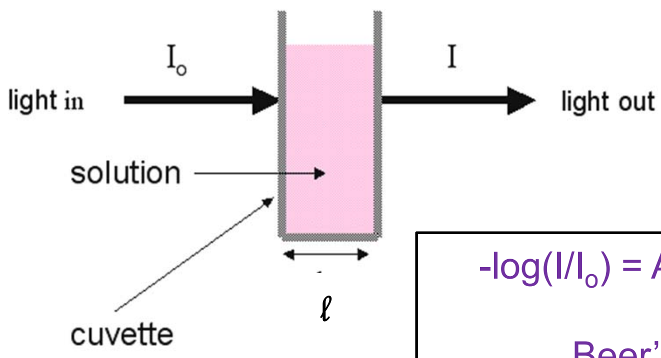
Experimental Procedure Overview

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

- Equilibrium concentrations of product and reactant will be determined from five different starting points.
- The equilibrium concentration of the red-brown product will be determined using a spectrophotometer.
- The equilibrium concentrations of the reactants will be calculated.

Determine Solution Concentrations by Spectrophotometry

Spectrophotometric Analysis



-log(I/I_o) = Absorbance

Beer's Law
Absorbance = $\varepsilon \times \ell \times c$

Measure concentration of a Solute by its absorbance of light.

- Nature of the solute
- Wavelength of light
- Distance light travels through the solution
- Concentration of the solute

where

ε - molar absorptivity

ℓ – distance light travels through the solution

c – concentration of the absorbing solute

Plot of "Absorbance versus Concentration" is a straight line of slope $\varepsilon\ell$. This is called a **Beer's-Law** plot.

Experimental Procedure - Steps

- Part A
  - Prepare 6 solutions to determine the calibration curve for $[Fe(SCN)^{2+}]$.
  - Measure the absorbance at wavelength, λ = 447 nm.
  - Plot a calibration curve and get the equation of the best fit line.

- Part B
  - Prepare 5 solutions + 1 blank and allow equilibrium to establish from 5 different starting points.
  - Measure the absorbance of the 5 equilibrium solutions at wavelength, λ = 447 nm
  - Determine the equilibrium $[FeSCN^{2+}]$ from the calibration curve from Part A.
  - Determine the equilibrium $[Fe^{3+}]$ and $[SCN^{-}]$ from the ICE table.
  - Calculate K

Prepare Solutions

- Work with partners
- Half the groups start with Part A and half with Part B
- $Fe(NO_3)_3$ - source of Fe^{3+}
  - from bottle-top dispenser
  - 0.150 M $Fe(NO_3)_3$ in Part A
  - 0.00150 M $Fe(NO_3)_3$ in Part B
- KSCN – source of SCN^-
  - from bottle-top dispenser
  - 0.000500 M SCN^- in Part A
  - 0.00300 M SCN^- in Part B
- Prepare 12 solutions – (2 blanks)
  - Total volume 25.00 mL using volumetric flasks
  - Follow recipe for Part A and Part B
  - Top up with 0.10 M nitric acid

Measure Absorbance at wavelength=447 nm

- Solutions transferred in cuvettes. Check cuvettes for:
  - Fingerprints
  - Scratches
  - Air bubbles
  - Use one cuvette only rinsing each time with solution to be analyzed

Part A - Determine absorbance of standard solution

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

- 25.00 mL volumetric flask
- Using the 0.150 M $Fe(NO_3)_3$
  - $[Fe^{3+}] > 300\ [SCN^-]$
  - Shifts equilibrium almost entirely to right.
  - Essentially all SCN^- converted to $Fe(SCN)^{2+}$
- Absorbance at $\lambda = 447$ nm
- Measure blank with only $Fe(NO_3)_3$ in acid.

Determine absorbance of all equilibrium solutions

- 10 solutions + 2 blanks
- Absorbance at $\lambda = 447$ nm
- Use one cuvette only rinsing each time with solution to be analyzed
- Check cuvettes for:
  - Fingerprints
  - Air bubbles
  - scratches

Discard of waste solutions:

- Use a 400 mL beaker and discard all liquid waste at your bench top.
- Discard your waste beaker content in the waste container provided.

Calculations:
Part A – Calibration Curve

$$[Fe(SCN)^{2+}] = \frac{(\text{Volume } SCN^- \text{ (L)})(\text{Concentration } SCN^- \text{ (M)})}{\text{Total volume (L)}}$$

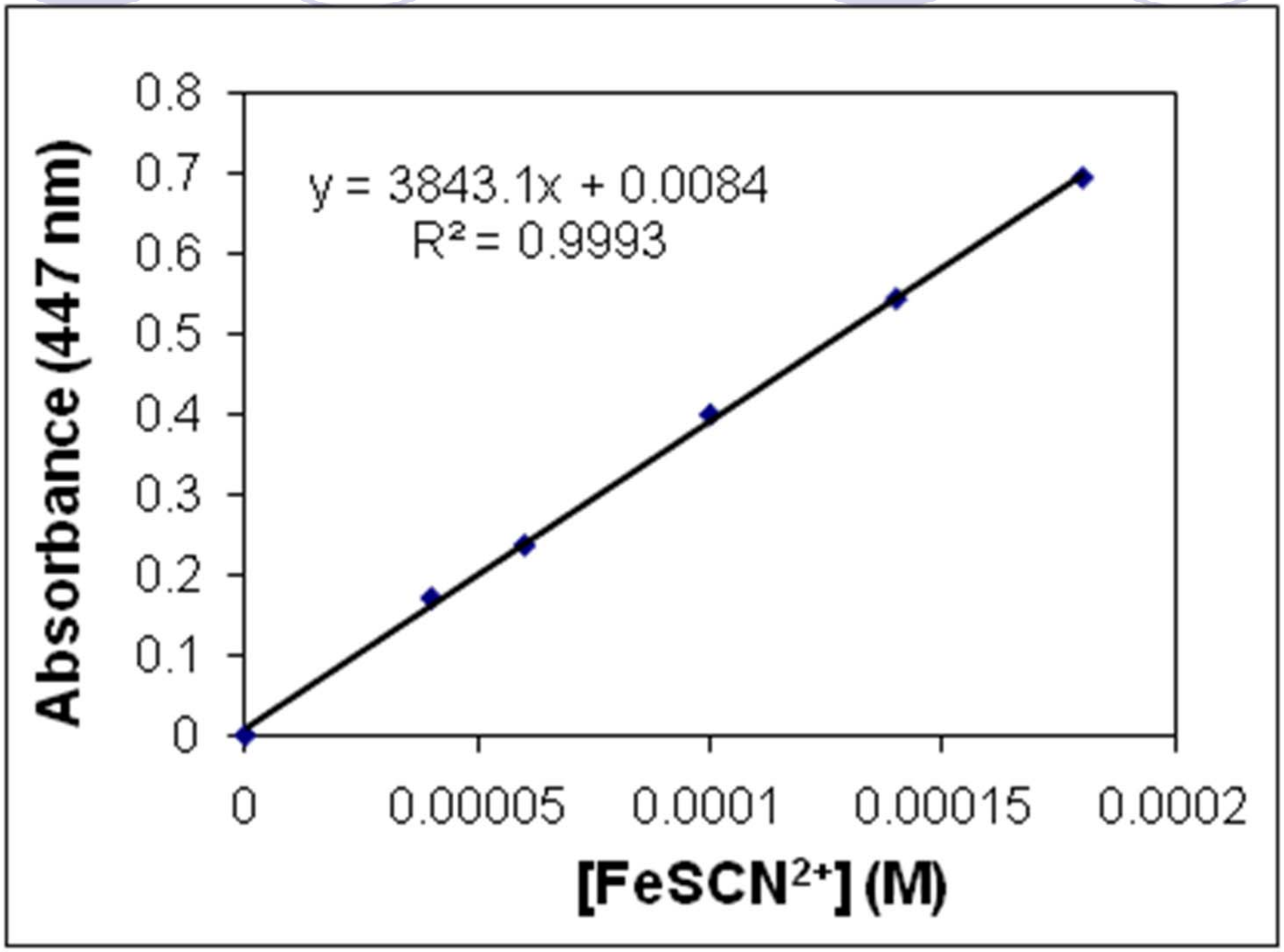
- Volume SCN^- (L) = refer to Table 4-1
- Concentration SCN^- (M) = refer to Table 4-1
- Total volume (L) = Volume of volumetric flask in liter

Calibration Curve:

Plot Absorbance Versus $[Fe(SCN)^{2+}]$

- Use the net absorbance column
- Include (0,0) on the graph
- Get the best fit line from Excel

Calibration Curve



Used to determine $[FeSCN^{2+}]$ in equilibrium solutions in Part B

Calculations:

Part B - Equilibrium concentration of $Fe(SCN)^{2+}$

- For Solutions 8 – 12, $[Fe(SCN)^{2+}]$ is determined from the calibration curve. This is $[Fe(SCN)^{2+}]_{equilibrium}$ = 'x'

- Use the Net Absorbance values for each solution.

Calculations:
Initial concentration of Reactants

Initial $[Fe^{3+}]$ = $\dfrac{(\text{Volume } Fe(NO_3)_3 \text{ (L)})(\text{Concentration } Fe(NO_3)_3 \text{ (M)})}{\text{Total volume (L)}}$

- Volume $Fe(NO_3)_3$ (L) = refer to Table 4-2
- Concentration $Fe(NO_3)_3$ (M) = refer to Table 4-2
- Total volume (L) = Volume of volumetric flask in liter

Initial $[SCN^-]$ = $\dfrac{(\text{Volume } SCN^- \text{ (L)})(\text{Concentration } SCN^- \text{ (M)})}{\text{Total volume (L)}}$

- Volume SCN^- (L) = refer to Table 4-2
- Concentration SCN^- (M) = refer to Table 4-2
- Total volume (L) = Volume of volumetric flask in liter

Calculations:
Equilibrium concentration of Reactants

	$[Fe^{3+}]$	$[SCN^{-}]$	$[Fe(SCN)^{2+}]$
[I]	$[Fe^{3+}]_{initial}$	$[SCN^{-}]_{initial}$	0
[C]	- X	- X	+ X
[E]	$[Fe^{3+}]_{initial}$ - X	$[SCN^{-}]_{initial}$ - X	X (known from absorbance)

Data Analysis - Equilibrium Constant

$$K = \frac{[FeSCN^{2+}]_{equilibrium}}{[Fe^{3+}]_{equilibrium}\,[SCN^{-}]_{equilibrium}}$$

$$K = \frac{x}{([Fe^{3+}]_{initial} - x)([SCN^{-}]_{initial} - x)}$$

$$where\ x = [FeSCN^{2+}]_{equilibrium}\ determine\ by\ absorption\ measurement$$

Calculate K for Solutions 8 to 12 and calculate the average K.