CHEM 0012

Lab 4: Determination of an Equilibrium Constant using Spectroscopy
Determination of the equilibrium constant of the following equilibrium system at room temperature.

\[ \text{Fe}^{3+}{}_{(aq)} + \text{SCN}^-{}_{(aq)} \rightleftharpoons \text{Fe(SCN)}^{2+}{}_{(aq)} \]

Iron (III) cation     thiocyanate ion     iron thiocyanate complex
Experimental Procedure Overview

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

- 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

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

\[
\text{Absorbance} = \varepsilon \times \ell \times c
\]

where

\( \varepsilon \) - molar absorptivity
\( \ell \) – 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 \textbf{Beer’s-Law} plot.
Experimental Procedure - Steps

- **Part A**
  - Prepare 6 solutions to determine the calibration curve for \([\text{Fe(SCN)}^2+]\).
  - Measure the absorbance at wavelength, \(\lambda = 447\text{ nm}\).
  - 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, \(\lambda = 447\text{ nm}\).
  - Determine the equilibrium \([\text{FeSCN}^2+]\) from the calibration curve from Part A.
  - Determine the equilibrium \([\text{Fe}^{3+}]\) and \([\text{SCN}^-]\) from the ICE table.
  - Calculate \(K\).
Prepare Solutions

- Work with partners
- Half the groups start with Part A and half with Part B
- Fe(NO₃)₃ - source of Fe³⁺
  - from bottle-top dispenser
  - 0.150 M Fe(NO₃)₃ in Part A
  - 0.00150 M Fe(NO₃)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

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

- 25.00 mL volumetric flask
- Using the 0.150 M Fe(NO₃)₃
  - \([\text{Fe}^{3+}] > 300 \ [\text{SCN}^-]\)
  - Shifts equilibrium almost entirely to right.
  - Essentially all SCN\(^-\) converted to Fe(SCN)\(^{2+}\)
- Absorbance at \(\lambda = 447\) nm
- Measure blank with only Fe(NO₃)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

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

- 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 $[\text{Fe(SCN)}^{2+}]_{\text{equilibrium}} = 'X'$

- Use the Net Absorbance values for each solution.
Calculations:
Initial concentration of Reactants

Initial $[\text{Fe}^{3+}] = \frac{(\text{Volume Fe(NO}_3)_3 (\text{L})) (\text{Concentration Fe(NO}_3)_3 (\text{M}))}{\text{Total volume (L)}}$

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

- 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

<table>
<thead>
<tr>
<th></th>
<th>[Fe(^{3+})]</th>
<th>[SCN(^{-})]</th>
<th>[Fe(SCN)(^{2+})]</th>
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<tbody>
<tr>
<td>[I ]</td>
<td>[Fe(^{3+})](_{\text{initial}})</td>
<td>[SCN(^{-})](_{\text{initial}})</td>
<td>0</td>
</tr>
<tr>
<td>[ C ]</td>
<td>- X</td>
<td>- X</td>
<td>+ X</td>
</tr>
</tbody>
</table>
| [ E ] | [Fe\(^{3+}\)]\(_{\text{initial}}\) - X | [SCN\(^{-}\)]\(_{\text{initial}}\) - 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.