CHEM 0012

Lab 7: Determination of an Equilibrium Constant using Spectroscopy
Determination of the equilibrium constant of the following equilibrium system at room temperature.

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

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

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**

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

\[-\log(I/I_o) = \text{Absorbance}\]

**Beer’s Law**

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

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 **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, \(\lambda = 447\ nm\).
  - 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, \(\lambda = 447\ nm\).
  - 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(NO$_3$)$_3$ - source of Fe$^{3+}$
  - from the 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 10 mL burets
  - 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 \( \text{Fe(NO}_3\text{)}_3 \)
  - \([\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(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

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

- Volume SCN\(^{-}\) (L) = refer to Table 7-1
- Concentration SCN\(^{-}\) (M) = refer to Table 7-1
- 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 7-2
- Concentration Fe(NO$_3$)$_3$ (M) = refer to Table 7-2
- 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 7-2
- Concentration SCN$^-$ (M) = refer to Table 7-2
- Total volume (L) = Volume of volumetric flask in liter
Calculations: Equilibrium concentration of Reactants

<table>
<thead>
<tr>
<th></th>
<th>$[\text{Fe}^{3+}]$</th>
<th>$[\text{SCN}^-]$</th>
<th>$[\text{Fe(SCN)}^{2+}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{I}]$</td>
<td>$[\text{Fe}^{3+}]_{\text{initial}}$</td>
<td>$[\text{SCN}^-]_{\text{initial}}$</td>
<td>0</td>
</tr>
<tr>
<td>$[\text{C}]$</td>
<td>- $X$</td>
<td>- $X$</td>
<td>+ $X$</td>
</tr>
<tr>
<td>$[\text{E}]$</td>
<td>$[\text{Fe}^{3+}]_{\text{initial}} - X$</td>
<td>$[\text{SCN}^-]_{\text{initial}} - X$</td>
<td>$X$ (known from absorbance)</td>
</tr>
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</table>
Calculate $K$ for Solutions 8 to 12 and calculate the average $K$. 

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