Determination of an Equilibrium Constant, $K_{eq}$

- Equilibrium
- Equilibrium Constant
- Data Collection and Calculation
- Beer’s Law
- Calibration Curve/Working curve
Learning Objectives

• Practice colorimetric measurement

• Use Beer’s Law to determine concentration of FeSCN$^{2+}$

• Calculate equilibrium constant, $K_{eq}$, for the formation of FeSCN$^{2+}$
Equilibrium Constant

- General expression:

\[ aA + bB \rightleftharpoons cC + dD \quad K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

- Specific expression for this lab:

\[ \text{Fe}^{3+}(aq) + \text{HSCN}(aq) \rightleftharpoons \text{H}^+(aq) + \text{FeSCN}^{2+}(aq) \]

\[ K_{eq} = K_f = \frac{[\text{H}^+] [\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}] [\text{HSCN}]} \]

The numbers on the right side of the formula are concentrations at equilibrium. Therefore:

\[ K_{eq} = K_f = \frac{[\text{H}^+]_{eq} [\text{FeSCN}^{2+}]_{eq}}{[\text{Fe}^{3+}]_{eq} [\text{HSCN}]_{eq}} \]
Calculations
(to determine equilibrium concentrations)

Important formula to remember:

For dilutions:

\[ C_2 V_2 = C_1 V_1 \]

\[ C_2 = \frac{C_1 V_1}{V_2} \]

- \( C_1 \) = Concentration of a species at the beginning of dilution
- \( V_1 \) = Volume of a species at the beginning of dilution
- \( C_2 \) = Concentration of a species at the end of dilution
- \( V_2 \) = Volume of a species at the end of dilution
Important formula to remember: For dilutions: \( C_2 = \frac{C_1 V_1}{V_2} \)
Here: \( C_1 = 6.0 \times 10^{-4} \) M (for HSCN)

Table 1: Standard curve (working curve) table

<table>
<thead>
<tr>
<th>mL Fe(NO_3)_3</th>
<th># 1</th>
<th># 2</th>
<th># 3</th>
<th># 4</th>
<th># 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>mL HSCN</td>
<td>5.00</td>
<td>10.00</td>
<td>15.00</td>
<td>20.00</td>
<td>25.00</td>
</tr>
<tr>
<td>mL HNO_3</td>
<td>70.00</td>
<td>65.00</td>
<td>60.00</td>
<td>55.00</td>
<td>50.00</td>
</tr>
<tr>
<td>Total mL</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>Initial [HSCN]</td>
<td>3.0 \times 10^{-5} M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Important formula to remember: For dilutions: \( C_2 = \frac{C_1V_1}{V_2} \)

Here: \( C_1 = 2.00 \times 10^{-3} \text{ M (for Fe(NO}_3\text{)}_3 \text{ or Fe}^{3+} \text{ for short)} \)

or \( C_1 = 2.00 \times 10^{-3} \text{ M (for HSCN)} \)

<table>
<thead>
<tr>
<th></th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
</tr>
</thead>
<tbody>
<tr>
<td>mL ( \text{Fe(NO}_3\text{)}_3 )</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>mL HSCN</td>
<td>1.00</td>
<td>2.00</td>
<td>3.00</td>
<td>4.00</td>
<td>5.00</td>
</tr>
<tr>
<td>mL HNO\textsubscript{3} \</td>
<td>4.00</td>
<td>3.00</td>
<td>2.00</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total mL</td>
<td>10.00</td>
<td>10.00</td>
<td>10.00</td>
<td>10.00</td>
<td>10.00</td>
</tr>
<tr>
<td>Initial ( [\text{Fe}^{3+}]_0 )</td>
<td>( 1.00 \times 10^{-3} \text{ M} )</td>
<td>( 1.00 \times 10^{-3} \text{ M} )</td>
<td>( 1.00 \times 10^{-3} \text{ M} )</td>
<td>( 1.00 \times 10^{-3} \text{ M} )</td>
<td>( 1.00 \times 10^{-3} \text{ M} )</td>
</tr>
<tr>
<td>Initial ( [\text{HSCN}]_0 )</td>
<td>( 2.00 \times 10^{-4} \text{ M} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

See Table on page 43 of lab manual
### The Third table

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Trial #1</th>
<th>Trial #2</th>
<th>Trial #3</th>
<th>Trial #4</th>
<th>Trial #5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial $[\text{Fe}^{3+}]_0$</td>
<td>$1.00 \times 10^{-3}$ M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial $[\text{HSCN}]_0$</td>
<td>$2.00 \times 10^{-4}$ M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial $[\text{H}^+]_0$</td>
<td>0.5 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{H}^+]_{eq}$</td>
<td>0.5 M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{FeSCN}]_{eq}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Fe}^{3+}]_{eq}$</td>
<td>$1.00 \times 10^{-3} - [\text{FeSCN}]_{eq}$ M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{HSCN}]_{eq}$</td>
<td>$2.00 \times 10^{-4} - [\text{FeSCN}]_{eq}$ M</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$[\text{Fe}^{3+}]_0$ Determined from initial solution preparation (see the table on page 43).
$[\text{HSCN}]_0$ Determined from initial solution preparation (see the table on page 43).
$[\text{H}^+]_0$ Determined from initial solution preparation, $[\text{H}^+]_0 = 0.5$ M.
$[\text{H}^+]_{eq} = [\text{H}^+]_0 = 0.5$ M (because $\text{H}^+$ balance and $\text{H}^+$ is always in excess amount).
$[\text{FeSCN}]_{eq}$ Determined from colorimetry (see below).

$[\text{Fe}^{3+}]_{eq} = [\text{Fe}^{3+}]_0 - [\text{FeSCN}]_{eq}$ (because of Fe balance: $[\text{Fe}^{3+}]_0 = [\text{Fe}^{3+}]_{eq} + [\text{FeSCN}]_{eq}$)

$[\text{HSCN}]_{eq} = [\text{HSCN}]_0 - [\text{FeSCN}]_{eq}$ (because HSCN balance: $[\text{HSCN}]_0 = [\text{HSCN}]_{eq} + [\text{FeSCN}]_{eq}$)

Therefore, the key of the experiment is to determine $[\text{FeSCN}]_{eq}$
How to determine \([\text{FeSCN}]_{eq}\)?

**Use the Beer’s Law**

- \(\text{FeSCN}^{2+}\) is a deep red colored complex.

- The more \(\text{FeSCN}^{2+}\) in solution, the darker the solution appears.

- There is a direct relationship between the color of \([\text{FeSCN}^{2+}]\) and its absorbance.

August Beer (July 31, 1825 - November 18, 1863), German physicist.

Pierre Bouguer (February 16, 1698 – August 15, 1758), French mathematician.
Spectronic 20 Spectrophotometer
**Beer’s Law**

\[ A = \log \left( \frac{I_0}{I} \right) = \varepsilon bc \]

- **A**: absorbance
- **I₀**: Intensity of incident light = photocell current of the blank solution
- **I**: Intensity of transmitted light = photocell current of your sample
- **ε**: molar absorptivity constant
- **b**: path length (= 1 cm in our experiment)
- **c**: concentration of the sample

The slope of the absorbance vs. concentration graph is:

\[ \text{Slope} = \varepsilon = \frac{A}{c} \]

when **b** = 1 cm
Calibration Curve (Working Curve)

Number of Student vs Number of Sandwich

Beer's Law

Absorbance vs Concentration (mol/L)

Standard 1
Standard 2
Standard 3
Standard 4
Concentration of Unknown
• Cuvettes should be handled on the FROSTED side only (and with finger cots).
• All solutions should be made using volumetric techniques.
• You must take a reading immediately after making the solution (the solution degrades).
• There are two different stock solutions of different concentrations for each chemical. Make sure you use the right one!
• Set up your NetFiles account in order to save your data!
Review and Preview

- Review today’s lecture:
  - Read Lab 4 (pages 37-46)
- Preview next lecture (Determination of the Solubility of Calcium Sulfate)
  - Read Lab 5 (pages 47-55)
  - Prepare and submit pre-Lab