**Equilibrium and Ionic Strength Effects**

**Objectives**

You will determine the thermodynamic equilibrium constant for the reaction between iron(III) ion and thiocyanate ion to form iron(III)-thiocyanate.

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

**Introduction**

In general chemistry courses, students are typically taught that the equilibrium constant for solution-based reactions is simply the equilibrium ratio of the molarities\(^1\) of products and reactants raised to the power of their stoichiometric coefficients.

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

In fact, the true equilibrium constant of the system is actually calculated using the equilibrium activities of the reaction participants rather than equilibrium concentrations:

\[
K_{\text{true}} = \frac{aC}{aA^a b^b} = \frac{\gamma_C}{\gamma_A^a \gamma_B^b} \cdot \frac{[C]^c}{[A]^a[B]^b} = K_{\gamma} \cdot K_{\text{obs}}
\]

In Equation (2), we have explicitly incorporated the activity coefficient, defined by

\[
a_X = \gamma_X[X].
\]

Note that the equilibrium constant is unitless; each concentration is divided by the standard concentration. In solution chemistry, it is most common to use a 1.0 M standard state. In ideal solutions, the activity coefficient approaches unity and thus the ratio \(K_{\gamma} = 1\) and the observed equilibrium constant matches the true value. In the case of aqueous reactions involving ionic species, ionic strength affects the activities greatly. If the ionic strength is high, \(K_{\gamma}\) departs significantly from unity. It should be noted that all ions in the solution, not just those that do participate in the reaction, drive the system away from ideality.

High ionic strength reactions are found all around us, from industrial reactions that are carried out at high concentrations to ensure increased productivity to biochemical processes that occur at low or high pH. Indeed, practically every solution-based reaction of importance deviates from ideality to some extent. In this experiment we will explicitly factor in the effect of ionic strength on equilibrium and introduce analysis of nonideal electrolyte chemistry.

The interaction between iron(III) cation and the thiocyanate anion is a well-known complexation reaction, which produces the striking red color of the iron(III)-thiocyanate complex-ion.

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

A competing reaction, the hydrolysis of iron, decreases the availability of free iron.

\[
\text{Fe}^{3+}(aq) + 3\text{H}_2\text{O}(l) \rightleftharpoons \text{Fe(OH)}_3(aq) + 3 \text{H}^+(aq)
\]

The second reaction can be suppressed by increasing the acidity of the reaction mixture, which, according to LeChatelier's principle, drives this equilibrium to the left. The added acid (and the

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\(^1\)Equilibrium constants are unitless. In both equations we must plug in the dimensionless concentration; that is, the concentration divided by the standard-state concentration.
other ions present) will force this system far from ideality. In this experiment we will use UV-visible spectrophotometry to measure $K_{obs}$ (the concentration based equilibrium constant) and then we will use Debye-Hückel-Davies theory to calculate the ionic strength $I$, $K_\gamma$, and $K_{true}$.

**Theory**

**Calculation of $K_{obs}$**

Beer's Law tells us that the absorbance of this solution is related to the concentration of thiocyanate ion (since the other ions are essentially colorless) by:

$$A = ab[FeSCN^{2+}]$$

where $a$ is the absorptivity and $b$ is the cell length. If we designate $x$ as the molarity of FeSCN$^{2+}$ at equilibrium, we can construct the following reaction chart.

<table>
<thead>
<tr>
<th></th>
<th>Fe$^{3+}$</th>
<th>SCN$^-$</th>
<th>FeSCN$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Init</td>
<td>$M_F$</td>
<td>$M_S$</td>
<td>0</td>
</tr>
<tr>
<td>Equil</td>
<td>$M_F - x$</td>
<td>$M_S - x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

The observed equilibrium constant at the specified conditions can then be calculated from a single spectrophotometric measurement.

$$K_{obs} = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{x}{(M_F - x)(M_S - x)}$$

Equation 6 can be rearranged to produce Equation 7.

$$x^2 - \left(M_F + M_S + \frac{1}{K_{obs}}\right)x + M_F M_S = 0$$

Using the method of reversion of series $^2$, Equation 7 can be expanded to give the following.

$$x = \frac{M_F M_S}{M_F + M_S + 1/K_{obs}} + \frac{(M_F M_S)^2}{(M_F + M_S + 1/K_{obs})^3} = \frac{M_F M_S}{M_F + M_S + 1/K_{obs}}$$

We have used the fact that the second term in the expansion above is negligible since the concentrations are small. From Equation 5 we can readily see that $x = A/ab$. Therefore, we obtain the following expression:

$$\frac{M_F M_S}{A} = \frac{1}{ab} \left(\frac{1}{M_F + M_S} + \frac{1}{ab K_{obs}}\right)$$
Given equation 9, determine the correct plot to extract the value of $K_{\text{obs}}$.

*Calculation of Ionic Strength and Activity Coefficients*

An atmosphere of solvent molecules and other ions surrounds an ion in solution. On average, each positive ion will have more negative ions than positive ions in its immediate vicinity. This contributes to the nonideality of the solution and the activity coefficients are related to the ionic strength of the solution, which is defined by the following equation:

$$I = \frac{1}{2} \sum z_i^2 m_i$$  \hspace{1cm} (10)

where $z_i$ is the charge number (e.g., $z = 2$ for Ca$^{2+}$ and $z = -3$ for PO$_4^{3-}$) and $m_i$ is the molality of ion $i$. In practice, however, the molarity is more convenient to use and when aqueous solutions are reasonably dilute, Equation 10 becomes:

$$I = \frac{1}{2\rho} \sum z_i^2 [i]_i$$  \hspace{1cm} (11)

where $\rho$ is the density of the solution (on the order of 1.02 g/mL for our experiment, so the correction is not large). Remember that all ions appreciably present in solution will contribute to the ionic strength whether inert or not. In fact, there are seven terms in the summation in Equation (11) for this system (Can you identify them?).

The activity coefficient of a particular solute may be related to the ionic strength by the *Davies Equation*, which is an extension of the Debye–Hückel limiting law for ionic solutions.

$$\log \gamma_i = -0.509z_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.30I \right)$$  \hspace{1cm} (12)

It should be noted that the parameters in the Davies equation are only accurate for 25°C and vary significantly with temperature. From this equation, the activity coefficients for Fe$^{3+}$, SCN$^-$ and FeSCN$^{2+}$ can be calculated. The activity coefficient ratio $K_r$ can then be calculated, followed by the true equilibrium constant $K_{\text{true}}$. 
Procedure

Set up the apparatus as shown to the right. The digital thermometer should be in the crystallization dish. Put magnetic stir bars in both the dish and the beaker. Since the equilibrium constant, the activity coefficient and the Davies parameters are all temperature-dependent, thermal regulation at 25°C is necessary. Addition of small amounts of ice or warm water to the water jacket will maintain this temperature, as the reaction is only slightly exothermic.

1. Always label all glassware before adding solutions.

2. Remember that one should not pipette directly from a shared stock solution; doing so could introduce a contamination. Instead, pour a little more than you need into a clean beaker, and pipette from there.

3. Into a 100-mL volumetric flask, pipette (using volumetric pipettes!) 1-mL of 0.02 M KSCN and 25-mL of 2.0 M HClO₄; mix well and dilute with distilled water to the mark. For precision, make sure you record the actual concentrations of all solutions as indicated on the containers.

4. Pour the solution carefully into the 250-mL beaker and adjust the magnetic stirrer so that it stirs thoroughly but not violently. Adjust the water jacket to 25°C and allow the system to thermally equilibrate (at least 10 minutes). While you are waiting, open the spectrophotometer software, SpectraSuite. Turn on the lamp by clicking on the “lamp enable” check box.

5. Use a transfer pipette to put a 1-2 mL aliquot of the reaction mixture into a cuvette. Put the cuvette in the cuvette holder in the spectrophotometer. Close any open spectra. Under File menu, choose “new absorbance measurement”; this opens the absorbance wizard. Check the “Enable Lamp” box and click on “set automatically” to set the integration time. Repeat until the integration time stops changing. The lamp spectrum should fill the window without being cut off at the top. If the integration time is more than 100 ms, check to make sure that the cuvette is oriented correctly. Set average to 5 and boxcar to 3. Next, store the reference spectrum by clicking on the light bulb button; be sure that you have the blank solution in the spectrophotometer and that the lamp is on during this step. Finally, after turning the lamp off (uncheck “lamp enable”) and inserting the black cuvette, collect and store a dark spectrum by pressing on the dark light bulb button. Turn the lamp back on and pour the contents of the cuvette back into the reaction vessel.

6. Use a micropipette to add a 1.00-mL aliquot of the iron solution into the reaction beaker. Wait at least 5 minutes for the reaction to react thoroughly and mix well. You should note that each addition increases the total volume by 1 mL, something you will need to consider later in your data analysis. Place the sample cuvette in the cuvette holder. Click
on the spectrum. A text box will appear at the bottom of the screen. Enter the wavelength that you would like to monitor (447 nm). The absorbance appears just to the right of the text box. Record the absorbance.

7. Repeat step 4 until ten absorbance measurements have been obtained. When you are done, pour the reaction mixture into the proper waste container. Wash all glassware, rinse it with DI water, and put it in the drainer.

7. Make sure to record or estimate the error in each volume-measuring device that you use. We will assume that the concentrations of the solutions used are exact for the purposes of error analysis.

Analysis

The data are best analyzed by a computer spreadsheet program because there are several calculations and the concentration for each absorbance measurement must be corrected for dilution (since the volume changes with each aliquot of iron added). In your report you will need to include tables with the following data:

\[ mL \text{ added}, A, M_F, M_S, M_{F+S}/A, M_F+M_S, [FeSCN^{2+}], [Fe^{3+}], [SCN^-], [K^+], [NO_3^-], [H^+], [ClO_4^-], I, \gamma_{Fe^{3+}}, \gamma_{SCN^-}, \gamma_{FeSCN}, K_g, \text{ and } K_{true} \]

You will need to calculate the error in each of the values above except for the activity coefficients and \( K_g \).

\[
\begin{align*}
[Fe^{3+}] &= M_F - [FeSCN^{2+}] \\
[SCN^-] &= M_S - [FeSCN^{2+}]
\end{align*}
\]

note: \( (13) \)

Required Report Elements

1. Abstract
2. Methods and Materials
3. An appendix with all of your error equations and regression data
4. Spreadsheet data tables (don’t forget errors)
5. Plot
6. Comparison of your \( K_{true} \) with the literature value
7. Data entry in LabPal

For items (1-3), refer to the Integrated Writing Guide.

References