# Activity of Solutions:
# Equilibrium and Ionic Strength Effects

## Purpose and Background

You will examine the effects that varying ionic strength have on the thermodynamic equilibrium constant the reaction between iron(III)ion and thiocyanate ion to form iron(III)-thiocyanate.

$$\mathbf{Fe^{3+}\,(aq)\ +\ SCN^{-}\,(aq)\ \rightleftharpoons\ FeSCN^{2+}\,(aq)}$$

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

$$\mathrm{aA\ +\ bB\ \rightleftharpoons\ cC} \qquad K = \frac{[C]^c}{[A]^a[B]^b} \qquad \mathbf{(1)}$$

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

$$K_{TRUE} = \frac{a_C^c}{a_A^a a_B^b} = \frac{\gamma_C^c}{\gamma_A^a \gamma_B^b} \cdot \frac{[C]^c}{[A]^a[B]^b} = K_\gamma \cdot K_{obs} \qquad \mathbf{(2)}$$

In Equation (2), activity coefficients have explicitly been incorporated, defined by $\mathbf{a_X = \gamma_X\,[X]}$. In ideal solutions, the activity coefficient approaches unity and thus the ratio $\mathbf{K_\gamma \approx 1}$ 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 enough then $\mathbf{K_\gamma}$ departs significantly from unity. It should be noted that even those ions that do not participate in the reaction drive the system away from ideality when their concentrations are not dilute.

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.

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq) \qquad \textbf{(3)}$$

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

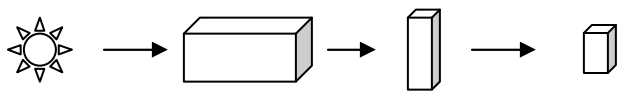
$$Fe^{3+}(aq) + 3\,H_2O(l) \rightleftharpoons Fe(OH)_3(aq) + 3\,H^{+}(aq) \qquad \textbf{(4)}$$

The second reaction can be minimized by increasing the acidity of the reaction mixture, which, according to LeChâtelier's principle, drives this equilibrium to the left. The added acid (and the other ions that will be added) will force this system far from ideality. Spectrophotometric methods will be used to measure $K_{obs}$ (the concentration equilibrium constant).

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

$K_{obs}$ will be calculated by first determining the concentrations of all species at equilibrium. The concentration of $FeSCN^{2+}$ will be measured and the concentrations of $Fe^{3+}$ and $SCN^{-}$ will be calculated. Because $FeSCN^{2+}$ is a colored complex, it absorbs visible radiation and we will use this absorption to measure its concentration.

You will use a spectrophotometer to measure the intensity of radiation that is absorbed by $FeSCN^{2+}$. A spectrophotometer is an instrument that measures the amount of radiation transmitted through a sample. A typical instrument has a schematic:



In the Spectronic 20, the source is a tungsten lamp; the dispersion element that separates white light into its different wavelengths is a grating; and the detector is a small phototube that detects photons and converts photon energy into electrical current that is displayed on a meter.

The Spectronic 20 measures the light absorbed through the sample, called the absorbance of a solution, A, according to Beer's Law:

$$A = \varepsilon bc = \varepsilon b[FeSCN^{2+}] \qquad \textbf{(5)}$$

where ε is the molar absorptivity ($M^{-1}cm^{-1}$), b is the pathlength of the cuvette and c is the concentration, here $[FeSCN^{2+}]$.

| | $Fe^{3+}$ (aq) + $SCN^-$ (aq) $\rightleftharpoons$ $FeSCN^{2+}$ (aq) | | |
|---|---|---|---|
| start | $[Fe^{3+}]_{initial}$ | $[SCN^-]_{initial}$ | - |
| Δ | -x | -x | + x |
| equil. | $[Fe^{3+}]_{initial}$ - x | $[SCN^-]_{initial}$-x | x |

$$K_{obs} = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{x}{([Fe^{3+}]_{initial} - x)([SCN^-]_{initial} - x)} \qquad \textbf{(6)}$$

Equation 6 can be rearranged to produce Equation 7.

$$x^2 - \left([Fe^{3+}]_{initial} + [SCN^-]_{initial} + \frac{1}{K_{obs}}\right)x + [Fe^{3+}]_{initial} + [SCN^-]_{initial} = 0 \qquad \textbf{(7)}$$

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

$$x = \frac{\left[Fe^{3+}\right]_{initial} \cdot \left[SCN^{-}\right]_{initial}}{\left[Fe^{3+}\right]_{initial} + \left[SCN^{-}\right]_{initial} + \frac{1}{K_{obs}}} + \frac{\left(\left[Fe^{3+}\right]_{initial} \cdot \left[SCN^{-}\right]_{initial}\right)^2}{\left(\left[Fe^{3+}\right]_{initial} + \left[SCN^{-}\right]_{initial} + \frac{1}{K_{obs}}\right)^3} \cong \frac{\left[Fe^{3+}\right]_{initial} \cdot \left[SCN^{-}\right]_{initial}}{\left[Fe^{3+}\right]_{initial} + \left[SCN^{-}\right]_{initial} + \frac{1}{K_{obs}}} \quad \textbf{(8)}$$

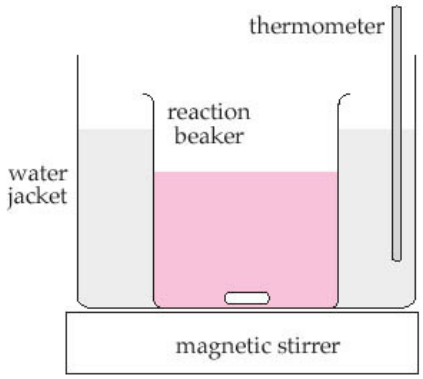
We have used the fact that the second term in the expansion above is negligible since the concentrations are small. From Equation 5 we can readily see that **x =A/εb** .Therefore,we obtain the following expression:

$$\frac{\left[Fe^{3+}\right]_{initial} \cdot \left[SCN^{-}\right]_{initial}}{A} = \frac{1}{\varepsilon b}\left(\left[Fe^{3+}\right]_{initial} + \left[SCN^{-}\right]_{initial}\right) + \frac{1}{\varepsilon b K_{obs}} \quad \textbf{(9)}$$

Plotting $([Fe^{3+}]_{initial} \cdot [SCN^{-}]_{initial})/A$ *vs.* $([Fe^{3+}]_{initial} + [SCN^{-}]_{initial})$ yields a straight line with a slope/intercept ratio equal to $\mathbf{K_{obs}}$ .An interesting facet of this method for determining $\mathbf{K_{obs}}$ is that it is independent of absorptivity **a** and cell length **b** .

**Procedure**

Set up the apparatus as shown below. Since the equilibrium constant, and the activity coefficients 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.




Turn on the spectrophotometer and allow it to warm up for 15minutes before using. Before taking measurements (at 450 nm, which is the $\lambda_{max}$ for this system), you will need to blank the spectrophotometer with the iron solution.

Measurements should be obtained in the following manner:

1. Prepare the following solutions 25 mL each of 0.5 M $HNO_3$ , 0.1M $Fe(NO_3)_3 \cdot 9\ H_2O$ in

0.5 M $HNO_3$, 0.02 M KSCN and 2.0 M $HNO_3$.
Record the exact mass of each substance weighed in order to calculate the exact concentrations of each solution.

2. Into a 100-mL volumetric flask, pipet (using volumetric pipets!)1mL of 0.02 M KSCN and 25-mL of 2.0 M $HNO_3$ mix well and dilute with distilled water to the mark. For precision, make sure you use the exact concentrations of all solutions as you prepared them.

3. 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).

4. Pipet 1.00-mL of the0.1M iron(III) solution into the reaction beaker. Wait at least 5 minutes for the reaction to react thoroughly and mix well. You should note that each pipetting increases the total volume by 1 mL, something you will need to consider later in your data analysis.

5. Using a transfer pipet, carefully transfer some of the solution to the cuvette and measure the absorbance of the solution.

6. Return the cuvette's contents back into the reaction beaker after the measurement.

7. Repeat steps 3 through 5 until ten absorbance measurements have been obtained.

8. 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.

**Data Analysis**

The data are best analyzed by a computer spreadsheet program because there are several calculations.

DO NOT FORGET: The concentration for each absorbance measurement must be corrected for dilution (since the volume changes with each aliquot of iron added).

Your report you will need to include tables with the following data:

mL added ,Absorbance (A), $[Fe^{3+}]_{initial}$, $[SCN^-]_{initial}$, $([Fe^{3+}]_{initial} \cdot [SCN^-]_{initial})/A$ , $[Fe^{3+}]_{initial} / [SCN^-]_{initial}$, $[Fe^{3+}]_{initial} + [SCN^-]_{initial}$, $[FeSCN^{2+}]$, $[Fe^{3+}]$, $[SCN^-]$, $[K^+]$, $[NO_3^-]$, $[H^+]$, $[NO_3^-]$, $\mu$ (ionic strength), $\gamma_{Fe^{3+}}$, $\gamma_{SCN^-}$, $\gamma_{FeSCN^{2+}}$, $K_{obs}$, $K_\gamma$, and $K_{true}$.

$$[FeSCN^{2+}] = \frac{K_{obs}[Fe^{3+}]_{initial} \cdot [SCN^-]_{initial}}{1 + ([Fe^{3+}]_{initial} + [SCN^-]_{initial}) \cdot K_{obs}}$$

$$[Fe^{3+}] = [Fe^{3+}]_{initial} - [FeSCN^{2+}] \qquad \textbf{(10)}$$

$$[SCN^-] = [SCN^-]_{initial} - [FeSCN^{2+}]$$

μ is the ionic strength of the solution. 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 ionic strength summation for this system.

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.

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

It should be noted that the parameters in the Davies equation are only accurate for 25°C and vary significantly with temperature. The activity coefficient ratio $\boldsymbol{K}_\gamma$ can then be calculated, followed by the true equilibrium constant $\boldsymbol{K}_{true}$.

1. Plot $([Fe^{3+}]_{initial} \cdot [SCN^-]_{initial})/A$ vs. $([Fe^{3+}]_{initial} + [SCN^-]_{initial})$. Perform a linear regression analysis on the data. Add linear trendline to the plot, calculate the value of $K_{obs}$. Determine the standard error (at the 95% confidence interval) [reporting your answer as $K_{obs}$ ± the standard error] and plot the residuals (label axes). What is the purpose of plotting the residuals? What does the appearance of the plot tell you about your experimental data? [This step can be easily done with Excel. In Excel click on the Tools button, and chose Add-Ins, click on Data Analysis, chose regression.]

2. Determine the $K_{true}$ values by multiplying each $K_\gamma$ by $K_{obs}$. Report the average $K_{true}$ at the 95% confidence interval. ($K_{true}$ ± confidence interval).

3. After the confidence intervals have been calculated, use the significance test, determine if $K_{obs}$ and $K_{true}$ are the same or different within experimental uncertainty at 95% and 99% confidence intervals.

4. Plot the $K_{true}$ vs. the ionic strength. What does this graph tell you about the relationship between the equilibrium constant and the ionic strength of a solution?

**References**

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2.*CRC Standard Mathematical Tables* ,25th ed;Beyer,W.H.,Ed;CRC:L Boca Raton,FL, 1973;p.385.

3.Atkins,P.*Physical Chemistry* ,6 th ed.WH Freeman;New York,1997,p249