Iron(III) Thiocyanate Revisited

A Physical Chemistry Equilibrium Lab Incorporating Ionic Strength Effects

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A system's empirically observed equilibrium constant, K_{obs}, is related to the thermodynamic equilibrium constant, K_{therm}, by the ratio of activity coefficients, K_γ.

$$K_{obs} \cdot K_\gamma = K_{therm}$$

In moderate to high ionic strength solutions, the values of the activity coefficients can deviate significantly from 1; however, the majority of laboratory experiments designed to demonstrate the principles of equilibrium do so without addressing the effects of ionic strength. Gas-phase or dilute-solution systems are chosen so that ionic strength is not important, or an empirical equilibrium constant is measured but not related to the thermodynamic equilibrium constant. But high ionic strength solutions are a fact of life: industrial reactions are often carried out at high concentration for the sake of maximum productivity, waste tanks tend to be concentrated pools of ionic solutions, and some reactions must be carried out at very high or low pH—such as the iron(III) thiocyanate formation reaction

$$Fe^{3+} + SCN^- \rightleftharpoons Fe(SCN)^{2+}$$

which must be run in 0.5 M acid to prevent significant iron hydrolysis (*1*) via

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

The iron(III)–thiocyanate ion equilibrium has been used by several authors as a general chemistry laboratory experiment designed to demonstrate equilibrium principles (*2*). Reasons for its popularity include the striking red color of the iron(III) thiocyanate complex, the ease of handling of the aqueous solutions, and the low safety hazard involved. We have now found that this system also provides an excellent opportunity to demonstrate the effects of ionic strength on equilibrium. In our version of the laboratory exercise, the ionic strength of the solution is calculated as well as the equilibrium constant, and together these are used to calculate the thermodynamic equilibrium constant via the Davies extension of the Debye–Hückel theory. We have found that the procedure yields very satisfying results.

Prelab

Ramette's (*3*) graphical method for extracting K_{obs} is used, which is based on the equations developed by Frank and Oswalt (*4*). In this approach, the UV–vis absorption of the $FeSCN^{2+}$ complex in a thiocyanate solution (λ_{max} between 445 and 450 nm) is measured as a function of added $Fe(NO_3)_3$ and K_{obs} is calculated graphically. As a prelab, the students are told to use

$$A = ab[FeSCN^{2+}]$$
$$C_s = [SCN^-] + [FeSCN^{2+}] \qquad (1)$$
$$C_f = [Fe^{3+}] + [FeSCN^{2+}]$$

(where A is the measured absorbance, a is the absorptivity, b is the cell length, C_s is the initial concentration of thiocy-

anate, and C_f is the initial concentration of iron) along with

$$K_{obs} = \frac{\left[FeSCN^{2+}\right]}{\left[Fe^{3+}\right]\left[SCN^-\right]}$$

to show

$$K_{obs} = \frac{\dfrac{A}{ab}}{\left[C_f - \left(\dfrac{A}{ab}\right)\right]\left[C_s - \left(\dfrac{A}{ab}\right)\right]}$$

They are then asked to rearrange this expression into the standard form for a quadratic equation, $ax^2 + bx + c = 0$; that is,

$$\left(\frac{A}{ab}\right)^2 - \left(C_f + C_s + \frac{1}{K_{obs}}\right)\left(\frac{A}{ab}\right) + C_f C_s = 0$$

and use the method of reversion of series (*5*) to arrive at the expression

$$\frac{A}{ab} = \frac{C_f C_s}{C_f + C_s + \left(\dfrac{1}{K_{obs}}\right)} + \frac{\left(C_f C_s\right)^2}{\left[C_f + C_s + \left(\dfrac{1}{K_{obs}}\right)\right]^3}$$

The concentrations of iron and thiocyanate are small, so the second term of the above expression is dropped, resulting in an expression that can be rearranged to

$$\frac{C_f C_s}{A} = \frac{1}{abK_{obs}} + \frac{\left(C_f + C_s\right)}{ab} \qquad (2)$$

Plotting $C_f C_s / A$ vs. $C_f + C_s$ yields a straight line with a slope/intercept ratio equal to K_{obs}. It should be noted that this method for finding K_{obs} is independent of the absorptivity, a, and the cell length, b, and does not rely on the assumption that all the thiocyanate is converted to iron(III) thiocyanate at high iron concentrations, a necessary assumption for some other nongraphical methods (*6*).

Experiment

If the equipment is set out and the students have done their dilution calculations beforehand, the lab takes approximately 4 hours.

The students are provided with 0.005 M Na_2EDTA and 0.02 M KSCN solutions (labeled with their concentrations and respective uncertainty) and asked to make up 2.0 M $HClO_4$ from concentrated $HClO_4$; 0.5 M $HClO_4$ from the 2.0 M $HClO_4$; 0.002 M KSCN from the provided 0.02 M KSCN;

and approximately 0.1 M $Fe(NO_3)_3 \cdot 9H_2O$ in 0.5 M $HClO_4$. This last solution is standardized by titration with 0.005 M Na_2EDTA, using variamine blue as indicator (*7*): 1 mL of 0.1 M $Fe(NO_3)_3$ in $HClO_4$ solution is diluted with distilled water to 50 mL to bring the pH up to 2, one drop of indicator is added, and approximately 20 mL of Na_2EDTA is added via buret until the yellow endpoint is reached.

The spectrometer is zeroed using the iron solution as the blank. A 0.0002 M thiocyanate solution in 0.5 M $HClO_4$ is prepared by adding 10 mL of the 0.002 M KSCN to a 100-mL volumetric flask along with 25 mL of 2.0 M $HClO_4$ and distilled water to the mark. This is mixed well and poured into a 250-mL beaker. Successive 1-mL portions of the iron solution are added by pipet, the solution is mixed, and the absorbance is measured. After each absorbance measurement the solution is returned to the 250-mL beaker and the next portion of iron is added. Ten absorbance measurements at different concentrations are generally enough to obtain good results.

Results

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. We illustrate such a spreadsheet here with 4 points from a typical run: 1-, 3-, 5-, and 7-mL iron solution additions.

The variables for the linear plot are calculated as shown in Spreadsheet 1. A graph of $C_f C_s / A$ vs. $C_f + C_s$ is made, the best-fit line is found, and the slope/intercept ratio is used to calculate K_{obs}. In this particular run, the observed equilibrium constant was found to be 146, a value that agrees well with recent measurements made by other methods (*8*).

The next step is to relate K_{obs} to K_{therm}. Using eqs 1 and 2 above, students derive an expression for the equilibrium concentration of iron(III) thiocyanate using K_{obs}: $[FeSCN^{2+}]$ = $K_{obs} C_f C_s / [1 + (C_f + C_s) K_{obs}]$. The equilibrium concentration of $FeSCN^{2+}$ is then used to calculate equilibrium concentrations of other ions in solution. These concentrations, along with the acid-ion concentrations and the potassium and nitrate spectator-ion concentrations, are used to calculate the ionic strength via

$$I = \frac{1}{2} \sum_i z_i^2 m_i$$

where z_i is the charge on the ith ion and m_i is the molality. To convert from molarity to molality, the ionic strength is multiplied by the density of the final solution, which is on the order of 1.02 g/mL, not a large correction. The results of these calculations are shown on Spreadsheet 2.

To correct for the effects of ionic strength, an expression for γ, the activity coefficient, must be found for each species. In dilute solutions, the Debye–Hückel limiting law provides a method for calculating activity coefficients, but this approach generally fails for solutions with an ion concentration greater than 0.1 *m*. More recent theories have been developed that reportedly work well for solutions up to 3 *m*, but these generally require some knowledge of the structure of the ion in solution (*9*). Davies (*10*), on the other hand, found an empirical relationship that works well for high ionic strength solutions and is quite adequate for this experiment. According to the Davies formulation, in H_2O at 25 °C

$$\log \gamma = -0.509\, z^2 \left\{ \frac{\left(\dfrac{I}{m^\circ}\right)^{1/2}}{1 + \left(\dfrac{I}{m^\circ}\right)^{1/2}} - 0.30\left(\dfrac{I}{m^\circ}\right) \right\}$$

where m° is the standard concentration of 1 *m*. Using this expression, K_γ and K_{therm} are calculated for each dilution, as shown on Spreadsheet 3. The thermodynamic equilibrium constant for the iron(III) thiocyanate formation reaction derived from tabulated values (*11*) of ΔG_f° at 298.15 K is 9.2×10^2.

Error Analysis

In a typical run, there is only about a 1% error in the K_{obs} value as calculated from the standard deviation of the slope and intercept. The experimental sources of error that contribute equally to all points on the graph are on the order of 6%, most of this being attributable to the error in the absorbance measurement. The uncertainty in K_{therm} is $\pm 0.4 \times 10^2$ as estimated from the reported number of significant figures in ΔG_F° and the uncertainty in the temperature.

Discussion

The iron thiocyanate reaction must be run in at least 0.5 M acid to prevent iron hydrolysis. At this high acid concentration, the ionic strength is essentially constant—which keeps K_{obs}

Spreadsheet 1. Calculation of Variables for Linear Plot

Point	A	C_f	C_s	$C_s C_f / A$	$C_f + C_s$
1	123	1.03E-03	1.99E-04	1.67E-09	1.23E-03
3	281	3.03E-03	1.95E-04	2.10E-09	3.23E-03
5	380	4.95E-03	1.92E-04	2.50E-09	5.14E-03
7	448	6.80E-03	1.88E-04	2.85E-09	6.99E-03

Spreadsheet 2. Calculation of Ionic Strength

Point	$\left[FeSCN^{2+}\right] = \dfrac{K_{obs} C_f C_s}{\left[1 + \left(C_f + C_s\right) K_{obs}\right]}$	$[Fe^{3+}] = C_f - [FeSCN^{2+}]$	$[SCN]^- = C_s - [FeSCN^{2+}]$	$I = 0.5 \left\{ \left(9 * [Fe^{3+}]\right) + \left(4 * [FeSCN^{2+}]\right) \right.$ $+ [NO_3^-] + [K^+] + [SCN^-]$ $\left. + [H^+] + [ClO_4^-] \right\}$ density
1	2.54E-05	1.00E-03	1.74E-04	5.16E-01
3	5.86E-05	2.97E-03	1.36E-04	5.29E-01
5	7.93E-05	4.87E-03	1.13E-04	5.40E-01
7	9.24E-05	6.71E-03	9.60E-05	5.52E-01

essentially constant—which allows K_{obs} to be calculated from the slope of a straight line. The method also produces acceptable results when the ionic strength is varied by lowering the pH as far as 0.15; however, at acid concentrations above 0.7 M the equilibrium

$$H^+ + SCN^- \rightleftharpoons HSCN$$

can begin to affect the iron thiocyanate equilibrium by reducing the available SCN^-. This additional equilibrium could possibly be accounted for by solving a system of simultaneous equilibria, but this correction would make for a much more complicated spreadsheet—beyond that which is normally required in an undergraduate laboratory exercise. For the above reasons, the practical acid range for this experiment is probably limited to 0.5–0.7 M acid, which does not provide much in the way of a test of the Davies equation. Therefore students should be cautioned that the estimation of activities at high ionic strength is a complicated matter—for which several approaches have been developed (see above)—and even though the Davies equation appears to work in this particular instance, other systems may require the use of a more detailed theory.

With the simpler spreadsheet for the 0.5 M acid system, given the relative error, students should find that the several values of K_{therm} calculated from the experimental K_{obs} agree well with literature values. Students may be asked to comment on the fact that their thermodynamic equilibrium "constant" appears to vary with concentration: they should readily recognize that their K_{obs} is actually an average over the concentration range and if a K_{obs} were found for each concentration, the values would vary as a function of ionic strength and the product $K_{obs} \cdot K_\gamma$ would be constant. The students may also be asked to comment on a popular iron(III) thiocyanate equilibrium classroom demonstration in which Fe^{3+}, NO_3^-, and SCN^- salts are added to a $FeSCN^{2+}$ solution and the observed color change is attributed to mass action (12). In light of the present experiment, students may be able to suggest an additional explanation. To help with this explanation, they can be requested to observe and explain the color changes of a $FeSCN^{2+}$ solution brought about by the addition of inert salts such as KCl. They can also be directed to a paper by DuBois (13) in which this decolorizing salt effect is analyzed in terms of ionic strength.

Conclusion

This restructuring and extension of the classic iron(III) thiocyanate equilibrium lab requires students to derive

	Spreadsheet 3. Calculation of K_{therm}				
Point	γFe^{3+}	γSCN^-	$\gamma FeSCN^{2+}$	K_γ	$K_{therm} = K_{obs} \cdot K_\gamma$
1	0.0624	0.735	0.291	6.34	926
3	0.0631	0.736	0.292	6.29	918
5	0.0631	0.736	0.292	6.29	918
7	0.0637	0.736	0.293	6.25	913

formulas, employ precise experimental techniques, and use error analysis to compare experimental results with literature values. In addition—and most importantly—it requires students to analyze a reaction carried out at high ionic strength. Given the prevalence of high ionic strength solutions in real-world situations, this experience should prove useful to them in their future work and could someday help them interpret what otherwise might appear to be anomalous results.

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