Physical Chemistry Laboratory, I
CHEM 445
Experiment 5
Formation Constant for Monothiocyanatoiron (III)
$K_F\{FeSCN^{2+}\}$
(Revised, 01/09/06)

The blood red complexes of Fe^{+++}/SCN^- have been known for many years and have been used for the determination of trace amounts of Fe(III) in aqueous solutions.[1] In very dilute solutions, $FeSCN^{2+}$ is formed as the dominant species; and with larger concentrations of SCN^-, higher complexes, $Fe(SCN)_n^{3-n}$ are formed.[2] Some $Fe(SCN)_3$ is formed at high concentrations of SCN^-, which can be partially extracted into ether.[1,3] The hexathiocyanatoferrate(III) ion, $Fe(SCN)_6^{3-}$, is well established in coordination chemistry.[4] It has also been known for many years that the intensity of the color of $FeSCN^{2+}$ or higher complexes in solution decreases when inert electrolytes are added to the solution.[5,6]

The chemical reaction of interest in this experiment may be written as

$$Fe(H_2O)_6^{3+} + SCN^- \rightarrow Fe(H_2O)_5SCN^{2+} \quad \text{or} \quad Fe^{3+} + SCN^- \rightarrow FeSCN^{2+}$$

Or the reaction may be written to indicate that each species is hydrated in solution, $SCN^-(aq)$, etc. K_{F1}, in Eq. (1), below, represents the activity formation constant or activity equilibrium constant for the formation of the $FeSCN^{2+}$ complex – a true constant; therefore, the concentration formation constant, $Q_1 = \dfrac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$, is a function of ionic strength.

(1) $$Fe^{3+}(aq) + SCN^-(aq) = FeSCN^{2+} \qquad K_{F1} = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}\left(\frac{\gamma\{FeSCN^{2+}\}}{\gamma\{Fe^{3+}\} * \gamma\{SCN^-\}}\right)$$

As predicted from Debye-Hückel theory, the concentration formation constant, $Q\{FeSCN^+\}$, decreases with increasing ionic strength[2,7,8].

Aqueous solutions of iron(III) or Fe^{3+} are somewhat acidic because $Fe(H_2O)_6^{3+}$, or the hydrated ferric ion, acts as a Brønsted acid in water,

(2) $$Fe(OH)_6^{3+} + H_2O \Leftrightarrow Fe(H_2O)_5OH^{2+} + H_3O^+ \qquad K_A = 0.006$$

In addition, $Fe(OH)_3$ or $Fe_2O_3.xH_2O$ (a hydrous oxide of ill-defined composition) is very insoluble. The very low solubility of rust is well known, although the acidity of the hydrated ferric ion is not so well known.

If $Fe(H_2O)_5OH^{2+}$ and/or $Fe(OH)_3$ were present in the system, the actual concentration of Fe^{3+} in solution would be unknown and less than the concentration of Fe^{3+} from preparation. In order to keep Fe^{3+} in solution and to reduce the extent of formation of $Fe(H_2O)_5OH^{2+}$ it is necessary that the solution be strongly acidic: pH ≤ 1.0. If, for example, $[H_3O^+] = 0.20$ M, then the ratio,$[Fe(H_2O)_5OH^{2+}]/[Fe(H_2O)_6^{3+}] = 0.006/0.20 = 0.03$. That is, about 3 % of the total iron is present as the dissociated species, $Fe(H_2O)_5OH^{2+}$, and ~ 97% is present as $Fe(H_2O)_6^{3+}$, the hydrated Fe(III) ion. This small extent of hydrolysis (or ionization) can be neglected in our analyses.

As mentioned initially, spectrophotometry is used to determine the concentration of Fe(III) as a{Fe/SCN} complex. For chemical analysis, one would use a large excess of SCN^- to ensure that the Fe(III) was overwhelmingly in the form of a complex – perhaps $Fe(SCN)_6^{3-}$, prepare a calibration curve of absorbance, A, *vs.* concentration, and then analyze an unknown sample.

However, in this experiment, we wish to measure the first formation constant and cannot add a large excess of SCN^- or of Fe^{3+} and be sure that the $FeSCN^{2+}$ complex is the only complex formed. In order to form the monothiocyanato complex as the predominant species in solution, the concentrations of Fe^{3+} and SCN^- must be roughly comparable, with $[Fe^{3+}] > [SCN^-]$. Consequently,

[$FeSCN^{2+}$] cannot be determined directly from a calibration curve in the usual manner by assuming that all Fe^{3+} or all SCN^- have been converted to the $FeSCN^{2+}$ complex.

However, using the mathematical analysis of Frank and Oswalt[2] and subsequently Ramette[9], one can determine K_F and the concentrations of the species from the absorption of several solutions of known total concentrations of Fe(III) and of thiocyanate at a given wavelength.

In dilute solutions, $Fe(H_2O)_6^{3+}$ and SCN^- do not absorb in the visible region and $FeSCN^{2+}$ does. Consequently, the absorbance at wave lengths from 400 – 500 nm (4000 – 5000 Å) is due only to the complex. If the Beer-Lambert-Bouget law applies to these solutions, then

(3) $A_\lambda = k_\lambda[FeSCN^{2+}]$,

where A_λ is the absorbance at a given wavelength, λ; [$FeSCN^{2+}$] is the concentration of $FeSCN^{2+}$ in mol/L; and k_λ is the proportionality constant {= (path length)*(molar absorptivity)}. However, as noted in the paragraph above, the constant k_λ cannot be determined from a calibration curve directly.

One writes the species balance equations for the total concentration, $C_T\{Fe^{3+}\}$ and/or $C_T\{SCN^-\}$ as the following:

(4) $C_T\{Fe^{3+}\} = [Fe^{3+}] + [FeSCN^{2+}]$

(5) $C_T\{SCN^-\} = [SCN^-] + [FeSCN^{2+}]$

In these equations C_T represents the total concentration of Fe^{3+} or of SCN^- from preparation of the solution and is known for each species in each experiment. One assumes that there are no other complexes or species containing either Fe^{3+} or SCN^- in the solution.

The concentration equilibrium constant for the formation of $FeSCN^{2+}$ is given above and in Eq. (6)

$$(6)\qquad Q = \frac{\left[FeSCN^{2+}\right]}{\left[Fe^{3+}\right]\left[SCN^-\right]} = \frac{\left[FeSCN^{2+}\right]}{\left(C_T\{Fe^{3+}\} - \left[FeSCN^{2+}\right]\right) * \left(C_T\{SCN^-\} - \left[FeSCN^{2+}\right]\right)}$$

$C_T\{Fe^{3+}\}$ and $C_T\{SCN^-\}$ are known from the preparation of the solutions. $\left[FeSCN^{2+}\right]$ is not known directly, but may be obtained from Eq. (3) and substituted into Eq. (6) to give

$$(7)\qquad Q = \frac{\frac{A_\lambda}{k_\lambda}}{\left(C_T\{Fe^{3+}\} - \frac{A_\lambda}{k_\lambda}\right) * \left(C_T\{SCN^-\} - \frac{A_\lambda}{k_\lambda}\right)}$$

In Eq. (7), A_λ is the experimental absorbance at wavelength, λ, for a solution of known total concentrations, $C_T\{Fe^{3+}\}$ and $C_T\{SCN^-\}$. Q is the concentration equilibrium constant, which is to be determined and k_λ is the slope of the calibration curve, which is also to be determined. Q and k_λ cannot be determined from a single measurement; but if several solutions are analyzed, average values for Q and k_λ can be obtained.

Eq. (7) may be expanded into a second order equation in A_λ.

$$(8)\qquad \left(\frac{A_\lambda}{k_\lambda}\right)^2 - \left(\frac{A_\lambda}{k_\lambda}\right)\left(C_T\{Fe^{3+}\} + C_T\{SCN^-\} + \frac{1}{Q}\right) = -C_T\{Fe^{3+}\} * C_T\{SCN^-\}$$

Eq. (8) does not suggest anything that can be plotted to determine k and Q. However, if one changes this power series in A_λ into another power series (reversion of series, *CRC Handbook of Chemistry and Physics*) by expanding Eq. (8) into a power series in $C_T\{Fe^{3+}\}*C_T\{SCN^-\}$, then a useful equation can be obtained that can be plotted to give the two needed values.[2]

For the reversion of series, if one has a power series of the form (9a) in one variable, then one can change this power series into a power series in the other variable, (9b).

(9a) $Y = aX + bX^2$

(9b) $X = AY + BY^2 + CY^3 + DY^4 + ...$

Substitute the expression for X from (9b) into the initial expression for Y in (9a) and then equate terms in the power series to get A, B, C, etc in terms of a and b.

(10) $Y = a\left(AY + BY^2 + CY^3 + Dy^4 + ...\right) + b\left(AY + BY^2 + CY^3 + DY_4 + ...\right)^2$

From the first power terms,

(11) $1 = aA \quad \text{and} \quad A = 1/a$

Because there is no term in Y^2, the coefficient in Eq (10) is 0 and

(12) $aB + bA^2 = 0 \quad \text{and} \quad B = -A^2\left(\frac{b}{a}\right) = -\left(\frac{1}{a}\right)^2\left(\frac{b}{a}\right) = -\frac{b}{a^3}$

For the third coefficient in the X equation from the third power terms, because c = 0 in (9a):

$C = \frac{2b^2}{a^5}$. The reversed series, to three terms, is

(13) $X = \left(\frac{1}{a}\right)Y - \left(\frac{b}{a^3}\right)Y^2 + \left(\frac{2a^2}{b^5}\right)Y^3$

For the expansion of Eq. (8), $Y = -C_T\{Fe^{3+}\} * C_T\{SCN^-\}$ and $X = A_\lambda/k$. In this expansion, $Y = -C_T\{Fe^{3+}\} * C_T\{SCN^-\}$ will be small and we can neglect all terms past the first order to get the following approximation.

(14) $$\left(\frac{A_\lambda}{k_\lambda}\right) = \frac{-C_T\{Fe^{3+}\} * C_T\{SCN^-\}}{-\left(C_T\{Fe^{3+}\} + C_T\{SCN^-\} + \frac{1}{Q}\right)}$$

Eq. (14) doesn't look useful either, but it can be rearranged to get an equation in which one experimental variable (parameter) is plotted against another.

(15) $$\frac{C_T\{Fe^{3+}\} * C_T\{SCN^-\}}{A} = \frac{C_T\{Fe^{3+}\} + C_T\{SCN^-\}}{k_\lambda} + \frac{1}{k_\lambda Q}$$

The left hand side of Eq. (15) contains only experimental numbers and can be plotted against $C_T\{Fe^{3+}\}+C_T\{SCN^-\}$, also experimental numbers, to get a straight line whose intercept is $1/k_\lambda Q$ and whose slope is $1/k_\lambda$. Microsoft Excel, or other data analysis program, can fit data to this equation and determine the constants.

This graphical analysis was used in the original work to determine Q {and eventually K}.[2] With modern computational facilities, one can use Eq. (7) or Eq. (8) with the Solver Function in Excel (or another data analysis program) to obtain values for k_λ and Q from experimental data on several solutions. {An example of the use of the Excel Solver Function is given in Harris, Quantitative Chemical Analysis, 6th Ed., p. 435.}

Rearrange Eq. (7) to get

(16) $$Q - \frac{\frac{A_\lambda}{k_\lambda}}{\left(C_T\{Fe^{3+}\} - \frac{A_\lambda}{k_\lambda}\right) * \left(C_T\{SCN^-\} - \frac{A_\lambda}{k_\lambda}\right)} = 0$$

Make initial guesses for Q and k_λ, using values obtained from Eq. (15) and minimize the square of the left hand side using the Solver function in Excel to get new values for Q and k_λ. You may obtain

somewhat different values for Q and k_λ. Analyzing the data using different methods and getting different values gives one a more realistic idea of the reliability of the results.

You will use the HP8453 UV-VIS spectrophotometer to determine the absorption of solutions of different total concentrations of Fe^{3+} and SCN^- from which you will determine numerical values for Q and k_λ.

Experimental Procedure:

The operating instructions for the use of the HP8453 UV-VIS spectrophotometer are available at the station (in the adjacent room).

The instrument should be turned on to warm up, perhaps for half an hour. You will have plenty of time for the instrument to warm up while preparing your solutions.

You will be provided with a stock solution of Fe^{3+} and a stock solution of SCN^- from which you are to prepare your solutions in ***50 mL volumetric flasks*** by adding accurate volumes of each solution and then diluting to the mark with distilled water and mixing well.

All of the solutions should be at least 0.20 M in HNO_3, prepared by adding a 5.00 mL aliquot (volumetric pipet) of 2.0 M HNO_3 to each 50.0 mL volumetric flask.

The previous experiments used very dilute solutions of SCN^-, total concentration ~ $3*10^{-4}$ M, with Fe^{3+} solutions of ~ 0.5 - $5*10^{-3}$ M.

The stock solution of KSCN will be approximately 0.004 M (the exact value will be provided on the bottle). Use a 5.00 mL aliquot of the stock SCN^- solution for each experiment.

The stock solution of Fe^{3+} will be 0.0179 M, 1000 ± 10 ppm {Fisher}, which is also 0.032 M in HNO_3. Remember to include this concentration of nitric acid in calculating the total ionic strength of the solution.

Determination of Q and k

Prepare **6 solutions** containing different accurately known total concentrations of Fe^{3+} and of SCN^- using volumetric pipets.

Do not prepare all of the solutions at the same time. Prepare one or two solutions from 5.00 mL of 2.0 M HNO_3, 5.00 mL of SCN^- solution, and X.YY mL of Fe^{3+} and measure the absorbance of these solutions to determine the concentrations that you need for other determinations. The absorbance readings should be in the range of 0.05 – 1.0 for reliable results.

Do not contaminate the stock solutions by using the same pipet for Fe^{3+} and SCN^- or by touching the tip of the pipet to the top of the volumetric flask.

Use a 0.00179 M Fe^{3+} solution (a 1.00 mL to 10.00 mL dilution of the stock solution of Fe^{3+}) in 0.20 M HNO_3 as the blank for each measurement. You may use the same blank for all experiments.

You may use the spectrometer to measure the absorbance over than range from 350 – 500 nm and then tabulate the absorbance at 3 wave lengths (400 nm, 455 nm, and 500 nm are reasonable choices). Or you may set up the instrument to measure the absorbance at these three wavelengths. You must use the same wavelengths for each measurement on each solution.

Rinse the reference sample holder (cuvette) with a little of the solution to be analyzed. Wipe carefully to remove any liquid on the outside and any fingerprints.

Tabulate your data in a well-organized fashion in Table 1 (with an appropriate heading, and footnotes containing any additional necessary information): columns containing volume of Fe^{3+} solution added, $C_T\{Fe^{3+}\}$, $C_T(SCN^-\}$, $(C_T\{Fe^{3+}\}+ C_T(SCN^-\})$, A_λ (three columns, indicating each wavelength used), and $(C_T\{Fe^{3+}\}*C_T(SCN^-\})/A_\lambda$, at each wavelength. This table contains all of the data needed for the plot of Eq. (15).

Plot your data in Fig. 1 (with an appropriate heading) at each wavelength: $(C_T\{Fe^{3+}\}*C_T(SCN^-\})/A_\lambda$ on the vertical axis *vs.* $(C_T\{Fe^{3+}\}+ C_T(SCN^-\})$ on the horizontal axis. If the data at each wavelength do not create a "reasonable" straight line (some scatter will always occur), prepare additional solutions and complete additional measurements. {Check your results either before the second week or in lab during the second week for the experiment.} Use Excel, or another data analysis program, to calculate the slope and intercept of each curve. From the slope and intercept of each curve, calculate k_λ and Q for each wavelength.

Analysis of data is frequently subjective, regardless of our best intentions. If there is a point that is well off the line of the other points, you may omit that point in your analysis, but you should always say so in your analysis and should **not** discard the point without comment or not include the point in your data. If several of your points don't fit a line, you can't omit them.

Use the Problem Solver Function in Excel to obtain k_λ and Q from Eq. (16), as discussed earlier. The values will be similar by the two methods, but they may not be identical. The Problem Solver Function fits the data to the equation by adjusting two variables to give a "best" fit, as indicated by a minimum in the sum of squares of deviations. There may be more than one good or best fit, depending on the initial choice of the two parameters.

Present these results for Q and k_λ in a well-organized (heading, column labels, etc.) table, Table 2. Compare the values obtained by the two procedures.

Calculate the ionic strength of one solution – the middle concentration of Fe^{3+}. The ionic strength includes all ions in the solution, H_3O^+, NO_3^-, K^+, SCN^-, Fe^{3+}, $FeSCN^{2+}$. $[FeSCN^{2+}] = A/ k_\lambda$ and $[Fe^{3+}]$ and $[SCN^-]$ are calculated from C_T and Eq. (5) and (6). There are two sources of H_3O^+ and NO_3^-. Ionic strength, μ or I, is defined by $\mu = I = \frac{\sum_j m_j Z_j^2}{2}$, in which m_j = molality of each ion, j, with charge Z_j. We can neglect the difference between molality and molarity, because $m \cong M$ for these solutions. The ionic strength will be somewhat larger than 0.20.

Use the Debye-Hückel-Guggenheim (DHG) equation to calculate activity coefficients for Fe^{3+}, SCN^-, and $FeSCN^{2+}$ in this solution. The DHG equation is

$$\log\gamma_x = -\left(\frac{0.509 Z_x^{\,2}\sqrt{\mu}}{1+\sqrt{\mu}}\right) \qquad (16)$$

in which γ_x is the activity coefficient of the ion x, Z_x is the charge of the ion, x, and μ is the ionic strength, calculated from all ions in solution, not merely the ionic species, x. The value, - 0.509, applies to aqueous solutions at 25 ^oC.

Use these activity coefficients to calculate K, from the average value for Q, according to Eq. (1). Table 3 should contain the solution that you chose to analyze, the ionic strength, the activity coefficients of the needed species, Q, and K. Compare the calculated value for K with the experimental value for Q. Are they the same? Should they be the same?

Effect of Ionic Strength on Q:

The value of $k_\lambda\{FeSCN^{2+}\}$ (the slope of the calibration curve) was determined at three wavelengths in the previous section. If the value for k_λ { $FeSCN^{2+}$} is independent of ionic strength (although k_λ $\{FeSCN^{2+}\}$ depends on wavelength), then the absorbance, A, can be used to determine $[FeSCN^{2+}]$ in any solution.

Prepare two solutions of accurately known total concentrations of Fe^{3+} and SCN^-, as above, which also contain different concentrations of KNO_3. The amount of KNO_3 that you add is not critical, but you want to add enough to change the ionic strength significantly.

Measure the absorbance of each solution at the same three wavelengths used in the section above. Calculate [$FeSCN^{2+}$] from A and k_λ, and calculate [Fe^{3+}] and [SCN^-] from C_T and the species balance equations.

Use these values for concentrations of species in equilibrium to calculate Q at these two ionic strengths, from Eq. (7). Calculate the total ionic strength for each solution. Use the DHG equation to calculate the activity equilibrium constant, K, at these two ionic strengths. These data should be presented in Table 4.

Compare the three values of Q and the three values of K.

The following data were reported for solutions of Fe^{3+} and SCN^-.

Table I
Absorbance Data, Fe^{3+}/SCN^- Solutions
Ionic strength = 0.50

$C_T\{Fe^{3+}\}$,M	$C_T\{SCN^-\}$,M	A
0.0010	0.00030	0.130
0.0020	0.00030	0.255
0.0020	0.00030	0.236
0.0030	0.00030	0.327
0.0030	0.00030	0.321
0.0050	0.00030	0.463
0.0080	0.00030	0.602
0.0080	0.00030	0.588

Plot and analyze these data as you analyzed your data to calculate Q for the formation of $FeSCN^{2+}$ and $k\{FeSCN^{2+}\}$. Use the DHG equation to calculate activity coefficients for Fe^{3+}, $FeSCN^{2+}$and SCN^-, and the activity equilibrium constant K, Eq. (1). Compare this value with your value for K.

References:

[1]J. T. Woods and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.* **13**, 551 (1941), which gives a reference to an article from 1837.
[2]H. S. Frank and R. L. Oswalt, *J. Am. Chem. Soc.* **69**, 1321 (1947)
[3]C. A. Peters and C. L. French, *Ind. Eng. Chem., Anal. Ed.* **13**, 604 (1941)
[4]F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, 1962, p. 717.
[5]R. DuBois, J. Chem. Ed. 14, 324 (1937)
[6]D. C. Harris, *Quantitative Chemical Analysis*, **6th Ed.**, W. H. Freeman & Co., 2003, p. 366.
[7]C. L. Cobb and G. A. Love, *J. Chem. Ed.* **75**, 90 (1998)
[8]R. J. Stolzberg, *J. Chem. Ed.* **76**, 640 (1999)
[9]R. W. Ramette, *J. Chem. Ed.* **40**, 71 (1963)