Chemical Equilibrium: Determination of K_f for the iron-thiocyanate complex ion

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

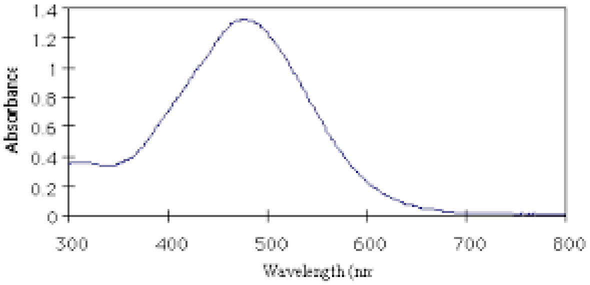
$$K_f = \frac{[\mathrm{FeSCN^{2+}}]}{[\mathrm{Fe^{3+}}][\mathrm{SCN^{-}}]}$$

$[\mathrm{FeSCN^{2+}}]$, obtain from the absorption of visible light

Beer's Law, $A = \varepsilon l c$ absorbance = (molar absorptivity)(path length)(concentration)

$A \propto c$ at λ of maximum absorption

note: at appropriate λ, reactants do not absorb light



need A for a known $[\mathrm{FeSCN^{2+}}]$ standard solution

all trials, use 2.0×10^{-4} M KSCN

<u>trial 1</u>: use a large excess of $\mathrm{Fe^{3+}}$ (0.20 M)
Le Chatelier's principle: shift the equilibrium to the right, assume all the $\mathrm{SCN^{-}}$ reacts, so $[\mathrm{SCN^{-}}] = [\mathrm{FeSCN^{2+}}]$ (note dilution for concentrations)

<u>trials 2-6</u>

$$[\mathrm{FeSCN^{2+}}]_n = \overset{\text{trial 1}}{[\mathrm{FeSCN^{2+}}]_1} \times \frac{A_n}{A_1} \quad \begin{matrix}\text{other trials}\\ \text{trial 1 (test tube 1)}\end{matrix}$$

$[\mathrm{Fe^{3+}}]_{\text{equil}} = [\mathrm{Fe^{3+}}]_{\text{initial}} - [\mathrm{FeSCN^{2+}}]_n$

$[\mathrm{SCN^{-}}]_{\text{equil}} = [\mathrm{SCN^{-}}]_{\text{initial}} - [\mathrm{FeSCN^{2+}}]_n$ note dilution

calculate K_f for trials 2-6, get the average K_f

<u>Procedure:</u>

add 5 mL of 2.0×10^{-4} M KSCN to each of the six test tubes

$\mathrm{Fe(NO_3)_3}$ solutions, use a disposable pipet and graduated cylinder

Note, above reactants already in 0.50 M $\mathrm{HNO_3}$

test tube #1: add 5 mL of 0.20 M $Fe(NO_3)_3$, large excess, standard solution

test tubes 2-6:

add 10.0 mL of 0.20 M $Fe(NO_3)_3$ to the 25 mL graduated cylinder,
add deionized water to get 25 mL of solution (0.080 M Fe^{3+})

add 5.0 mL of this solution (0.080 M Fe^{3+}) to test tube #2

discard all but 10.0 mL of the rest of the solution in the graduated cylinder

to the 10.0 mL of remaining solution, add deionized water to get 25.0 mL of solution (0.032 M Fe^{3+})

add 5.0 mL of this solution to test tube #3

repeat procedure for test tubes 4, 5, and 6.

Ocean Optics spectrophotometer
use 1 cuvette only for all the solutions (place in holder the same way each time (V mark))
wipe cuvette with chemwipe (no fingerprints)

first calibrate the spectrophotometer with a blank solution (0.50 M HNO_3)
do not skip warm up set for the lamp

scan all six solutions from 390-700 nm (change scanning range)

want to record the absorption at the top of the curve (record both the wavelength and the absorption value), try to be consistent in recording the absorption for each solution at approximately the same maximum wavelength value

example:

test tube #1: 5.0 mL 2.0×10^{-4} M KSCN mix together
5.0 mL 0.2 M $Fe(NO_3)_3$

$[KSCN] = 1.0 \times 10^{-4}$
$[Fe^{3+}] = 0.10$ M remember dilution

$[FeSCN^{2+}] = 1.0 \times 10^{-4}$

at λ_{max}, A = 0.470 for the standard

test tube #2: 5.0 mL 2.0×10^{-4} KSCN
5.0 mL 0.080 M Fe^{3+} mix together

$[SCN^-] = 1.0 \times 10^{-4}$
$[Fe^{3+}] = 0.040$ M initial concentrations (after dilution)

$$[FeSCN^{2+}]_{unknown} = [FeSCN^{2+}]_{standand} \times \frac{A_{unknown}}{A_{standard}}$$

$[FeSCN^{2+}] = 1.0 \times 10^{-4} \times 0.426/0.470 = 9.06 \times 10^{-5}$ M

$[Fe^{3+}]_{equil} = 0.040 - 9.06 \times 10^{-5} = 0.040$

$[SCN^{-}]_{equil} = 1.0 \times 10^{-4} - 9.06 \times 10^{-5} = 9.4 \times 10^{-6}$

$$K_f = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^{-}]} = \frac{9.06 \times 10^{-5}}{(0.040)(9.4 \times 10^{-6})} = 241$$

K_f experimental data:

Test Tube Absorbance

1. **Standard 0.452**
2. **0.434**
3. **0.398**
4. **0.298**
5. **0.185**
6. **0.096**

Calculations:

1. Determine the initial concentrations of Fe^{3+} and SCN^- upon mixing the solutions together. Remember that there is a dilution factor present for the calculation of the initial concentrations as the solutions were made.

Trial (Test Tube)	$[Fe^{3+}]$ initial	$[SCN^-]$ initial
2		
3		
4		
5		
6		

2. Determine the concentration of $FeSCN^{2+}$ in the various solutions using the following equation:

$$[FeSCN^{2+}]_{\text{unknown}} = [FeSCN^{2+}]_{\text{standard}} \times \frac{\text{absorbance unknown}}{\text{absorbance standard}}$$

where standard refers to the standard solution (test tube #1) and unknown refers to the other 5 test tubes. For test tube #1 ($[FeSCN^{2+}]_{\text{standard}}$), assume that all the initial thiocyanate ion (SCN^-) has been converted to the iron-thiocyanate complex ion ($FeSCN^{2+}$).

3. Calculate the concentration of Fe^{3+} and SCN^- present at equilibrium in tubes 2 - 6 by subtracting the amount reacted based on the complex ion formed from the initial values in each test tube.

$$[Fe^{3+}]_{\text{equil}} = [Fe^{3+}]_{\text{initial}} - [FeSCN^{2+}]$$

$$[SCN^-]_{\text{equil}} = [SCN^-]_{\text{inital}} - [FeSCN^{2+}]$$

Equilibrium concentrations

Trial (test tube)	[$FeSCN^{2+}$] (M)	[Fe^{3+}] (M)	[SCN^-] (M)
2			
3			
4			
5			
6			

3. Calculate K_f for trials 2 - 6, and calculate the average K_f for the complex ion equilibrium.

K_f

Trial 2 __________________

Trial 3 __________________

Trial 4 __________________ Average K_f = ___________________

Trial 5 __________________

Trial 6 __________________

Show the K_f calculation for one of the trials.