

Equilibrium Constant Determination

INTRODUCTION

Every chemical reaction has a characteristic condition of equilibrium at a given temperature. If two reactants are mixed, they will tend to react to form products until a state is reached where the amounts of reactants and products no longer change. Under such conditions the reactants and products are in chemical equilibrium and will remain so until the system is altered in some way. Associated with the equilibrium state there is a number called the *equilibrium constant*, K_{eq} , that expresses the necessary condition on the concentrations of reactants and products for the reaction. Consider the following idealized reaction, where a, b, c and d represent coefficients and A, B, C and D represent reactants and products.



The expression for the equilibrium constant is as follows.

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (2)$$

Concentrations of solutes in solution are expressed in terms of molarity. The equilibrium constant will have a fixed value for the reaction at any given temperature. If A, B, C and D are mixed in arbitrary amounts in a container they will tend to react until their concentrations satisfy equation 2. Depending upon the magnitude of K_{eq} and the amounts of species used initially, reaction 1 will proceed to the right or to the left until equilibrium is attained.

In this experiment we will study the equilibrium properties of the reaction between the iron(III) ion and thiocyanic acid (HSCN):



When solutions containing Fe^{3+} ion and thiocyanic acid are mixed, reaction 3 occurs to some extent, forming the $FeSCN^{2+}$ complex ion, which has a deep blood red color, and H^{+} ion. As a result of the reaction, the equilibrium amounts of Fe^{3+} and HSCN will be less than they would have been if no reaction had occurred; for every mole of $FeSCN^{2+}$ that is formed, one mole of Fe^{3+} and one mole of HSCN will react. According to the general law, K_{eq} for reaction 3 takes the following form.

$$K_{eq} = \frac{[FeSCN^{2+}][H^{+}]}{[Fe^{3+}][HSCN]} \quad (4)$$

Our purpose in the experiment will be to evaluate K_{eq} for the reaction by determining the equilibrium concentrations of the four species in equation 4 in several solutions made up in different ways. The equilibrium constant for the reaction has a convenient magnitude and the color of the $FeSCN^{2+}$ ion makes for an easy analysis of the equilibrium mixture.

The solutions will be prepared by mixing solutions containing known concentrations of iron(III) nitrate and thiocyanic acid. The color of the $FeSCN^{2+}$ ion formed will allow us to determine its equilibrium concentration by spectroscopy. Knowing the initial composition of the solution and the equilibrium concentration of $FeSCN^{2+}$, we can calculate the equilibrium concentrations of the rest of the pertinent species and then calculate K_{eq} .

Since the calculations that are necessary to find K_{eq} may not be apparent, let us consider a specific example. Assume that we prepare our solution by mixing 10.0 mL of 2.00×10^{-3} M $Fe(NO_3)_3$ with 10.0 mL of 2.00×10^{-3} M HSCN under conditions which keep $[H^+]$ equal to 0.500 M. The Fe^{3+} in the iron(III) nitrate reacts with the HSCN to produce some red $FeSCN^{2+}$ complex ion. By spectroscopy and Beer's Law, it is found that $[FeSCN^{2+}]$ at equilibrium is 1.50×10^{-4} M.

To find K_{eq} for the reaction from these data, it is convenient first to determine how many moles of reactant species were initially present before a reaction occurred. By the definition of the molarity of a species A,

$$M_A = \frac{\text{moles A}}{\text{Liters A}} \text{ or moles A} = M_A V$$

where V is the volume of the solution in liters. (Remember that 1000 mL = 1 L.)

$$\begin{aligned} \text{initial moles } Fe^{3+} &= (M_{Fe^{3+}})(V_{Fe^{3+}}) = 2.00 \times 10^{-3} \text{ mol/L (0.0100 L)} \\ &= 2.00 \times 10^{-5} \text{ mol } Fe^{3+} \end{aligned}$$

$$\begin{aligned} \text{initial moles HSCN} &= (M_{HSCN})(V_{HSCN}) = 2.00 \times 10^{-3} \text{ mol/L (0.0100 L)} \\ &= 2.00 \times 10^{-5} \text{ mol HSCN} \end{aligned}$$

The number of moles of $FeSCN^{2+}$ present at equilibrium is found from the molarity and the volume of the solution (10.0 mL + 10.0 mL = 20.0 mL).

$$\begin{aligned} \text{equilibrium moles } FeSCN^{2+} &= (M_{FeSCN^{2+}})(V_{FeSCN^{2+}}) = 1.50 \times 10^{-4} \text{ M (0.0200 L)} \\ &= 3.00 \times 10^{-6} \text{ mol } FeSCN^{2+} \end{aligned}$$

The $FeSCN^{2+}$ ion is produced as shown in equation 3.

Therefore, for every mole of FeSCN^{2+} present in the equilibrium mixture, one mole Fe^{3+} and one mole HSCN are reacted. We can see then that

$$\begin{aligned} \text{equilibrium moles Fe}^{3+} &= \text{initial moles Fe}^{3+} - \text{equilibrium moles FeSCN}^{2+} \\ \text{equilibrium moles Fe}^{3+} &= 2.00 \times 10^{-5} \text{ mol} - 3.00 \times 10^{-6} \text{ mol} = 1.70 \times 10^{-5} \text{ mol Fe}^{3+} \end{aligned}$$

Similarly for HSCN,

$$\text{equilibrium moles HSCN} = 2.00 \times 10^{-5} \text{ mol} - 3.00 \times 10^{-6} \text{ mol} = 1.70 \times 10^{-5} \text{ mol HSCN}$$

Knowing the number of moles of Fe^{3+} and HSCN present in the equilibrium mixture and the volume of the mixture, we can easily find the concentrations of those two species.

$$\begin{aligned} [\text{Fe}^{3+}] &= \frac{\text{mol Fe}^{3+}}{\text{L solution}} = \frac{1.70 \times 10^{-5} \text{ mol}}{0.0200 \text{ L}} = 8.50 \times 10^{-4} \text{ M} \\ [\text{HSCN}] &= \frac{\text{mol HSCN}}{\text{L solution}} = \frac{1.70 \times 10^{-5} \text{ mol}}{0.0200 \text{ L}} = 8.50 \times 10^{-4} \text{ M} \end{aligned}$$

To organize all the initial and final numbers of moles and the final (equilibrium) molarities,

	$\text{Fe}^{3+}_{(\text{aq})}$	+	$\text{HSCN}_{(\text{aq})}$	\leftrightarrow	$\text{FeSCN}^{2+}_{(\text{aq})}$	+	$\text{H}^{+}_{(\text{aq})}$
Initial moles	2.00×10^{-5}		2.00×10^{-5}		0		Concentration kept constant at 0.500 M
Change	-3.00×10^{-6}		-3.00×10^{-6}		$+3.00 \times 10^{-6}$		
Final moles	1.70×10^{-5}		1.70×10^{-5}		3.00×10^{-6}		
Final volume	0.0200 L		0.0200 L		0.0200 L		
Final M	8.50×10^{-4}		8.50×10^{-4}		1.50×10^{-4}		

We can now substitute into equation 4 to find the equilibrium constant for this reaction:

$$K_{\text{eq}} = \frac{[\text{FeSCN}^{2+}][\text{H}^{+}]}{[\text{Fe}^{3+}][\text{HSCN}]} = \frac{(1.50 \times 10^{-4} \text{ M})(0.500 \text{ M})}{(8.50 \times 10^{-4} \text{ M})(8.50 \times 10^{-4} \text{ M})} = 104$$

(The data in this calculation correspond to a different temperature than the one at which you will be working, so the actual value of K_{eq} you will obtain will not be the one found above.)

Methods of analysis have been developed to determine the $[\text{FeSCN}^{2+}]$ in the equilibrium mixtures. A very precise method makes use of a spectrophotometer, which measures the amount of light absorbed by the red complex at 450 nm, the wavelength at which the complex most strongly absorbs. The absorbance, A , of the complex is proportional to its concentration, c , according to Beer's Law ($A=mc$). (Check the Beer's Law lab if you need more information.)

In order to use Beer's Law to determine the equilibrium concentration of FeSCN^{2+} you will have to prepare a calibration curve by measuring the absorbance of a series of standard solutions of known FeSCN^{2+} molarity. The slope, m , of this curve is then used to find the $[\text{FeSCN}^{2+}]$ of a series of equilibrium solutions.

PROCEDURE

All the HSCN and $\text{Fe}(\text{NO}_3)_3$ solutions were prepared using 0.500 M HNO_3 in place of distilled water to maintain the $[\text{H}^+]$ at 0.500 M at all times.

Standard Solutions

Label three 25 mL volumetric flasks 1 through 3. Pipet 0.50 mL of 0.00200 M HSCN into flask #1, 1.0 mL into flask #2, and 1.5 mL into flask #3. Fill each flask to the mark with **0.200 M $\text{Fe}(\text{NO}_3)_3$** . Stopper and mix well. Measure the absorbance of each of these three solutions at 450 nm after calibrating the spectrophotometer with distilled water for 100% transmission.

Equilibrium Solutions

Label five 10 mL volumetric flasks 1 through 5. Pipet 1 mL of 0.00200 M HSCN into flask #1, 2 mL into flask #2, 3 mL into flask #3, 4 mL into flask #4, and 5 mL into flask #5. Add 5 mL of **0.00200 M $\text{Fe}(\text{NO}_3)_3$** to flasks 1, 2, 3, and 4. Fill flask 5 to the mark with **0.002000 M $\text{Fe}(\text{NO}_3)_3$** . Fill flasks 1-4 to the mark with 0.500 M HNO_3 . Each flask will now contain 10.0 mL of total solution. Stopper each flask and mix well.

Measure the absorbance of each solution in the spectrophotometer at 450 nm.

DISPOSE ALL IRON SOLUTIONS IN THE HEAVY METAL WASTE CONTAINER.

Name: _____

DATA

Standard Solutions

Volume HSCN (mL)	[FeSCN ²⁺] (M)	Absorbance
0.00	0.00	0.00
0.50		
1.00		
1.50		

Equilibrium Solutions

#	Volume (mL)			Absorbance	[FeSCN ²⁺] (M)
	Fe(NO ₃) ₃	HSCN	HNO ₃		
1	5.00	1.00	4.00		
2	5.00	2.00	3.00		
3	5.00	3.00	2.00		
4	5.00	4.00	1.00		
5	5.00	5.00	0.00		

Name: _____

CALCULATIONS

Calibration Curve

Calculate the concentrations of $[\text{FeSCN}^{2+}]$ in your three standard solutions. Since the $[\text{Fe}^{3+}]$ is so much greater (100x) than the $[\text{HSCN}]$, one can safely assume that all the HSCN has been changed to FeSCN^{2+} . That is the $[\text{FeSCN}^{2+}]$ in the final solutions equals the $[\text{HSCN}]$ in the final solutions after the original $[\text{HSCN}]$ has been diluted to 25 mL with the Fe^{3+} solution.

$$(\text{Initial } [\text{HSCN}])(\text{mL HSCN Used}) = (\text{Final } [\text{HSCN}])(25.00 \text{ mL})$$

Using a computer graphing program such as Excel or Graphical Analysis, plot Absorbance vs. Concentration. Have the computer put the best straight line and the equation of the line on the graph and evaluate the slope, m . Include the graph with the report.

Equilibrium Reactions

Calculate K_{eq} assuming the reaction: $\text{Fe}^{3+}_{(\text{aq})} + \text{HSCN}_{(\text{aq})} \leftrightarrow \text{FeSCN}^{2+}_{(\text{aq})} + \text{H}^{+}_{(\text{aq})}$. This calculation is most readily carried out by completing the following tables as follows.

1. Knowing the initial concentrations and volumes of Fe^{3+} and HSCN used, calculate the initial number of moles of these species.
2. Calculate $[\text{FeSCN}^{2+}]$ at equilibrium using $A = mc$. From the absorbance, A , and the slope of the calibration, m , calculate c , which is $[\text{FeSCN}^{2+}]$ ($c = A/m$).
3. Realizing that 1 mole of FeSCN^{2+} is formed at the expense of 1 mole of Fe^{3+} and 1 mole of HSCN, calculate the number of moles of Fe^{3+} and HSCN at equilibrium.
4. Knowing the number of moles of Fe^{3+} and HSCN at equilibrium and the volume (10.0 mL), calculate $[\text{Fe}^{3+}]$ and $[\text{HSCN}]$.
5. Use equation 4 to calculate K_{eq} .

Name: _____

CALCULATIONS

#	Initial Moles		Equilibrium Moles		
	Fe^{3+}	HSCN	FeSCN^{2+}	Fe^{3+}	HSCN
1					
2					
3					
4					
5					

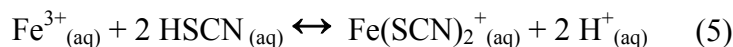
Equilibrium Molarities

#	$[\text{Fe}^{3+}]$ (M)	[HSCN] (M)	$[\text{FeSCN}^{2+}]$ (M)	$[\text{H}^+]$ (M)	K_{eq}
1				0.500	
2				0.500	
3				0.500	
4				0.500	
5				0.500	

Name: _____

Calculations

In calculating K_{eq} above, we assumed that the formula of the complex ion was $FeSCN^{2+}$. It is by no means obvious that this is the case, and one might have assumed, for instance, that $Fe(SCN)_2^+$ was the species formed. The reaction would then have been:



If we analyzed the equilibrium reaction assuming that reaction 8 occurred rather than reaction 3, we would probably obtain nonconstant values of K_{eq} . Using the same kind of procedure as above, calculate K_{eq} for solutions 1, 3 and 5 on the basis that $Fe(SCN)_2^+$ formed by reaction between Fe^{3+} and HSCN. Because of the procedure used for calibrating the system by this method, $[Fe(SCN)_2^+]$ will equal one-half the $[FeSCN^{2+}]$ obtained for each solution above. Note that 2 moles of HSCN are needed to form one mole $Fe(SCN)_2^+$ according to reaction 8. This changes not only the relative numbers of moles from the previous case but also the expression for K_{eq} . (See the prestudy, question 3b and fill in the expression below)

$$K_{eq} = \text{_____}$$

#	Initial Moles		Equilibrium Moles		
	Fe^{3+}	HSCN	$Fe(SCN)_2^+$	Fe^{3+}	HSCN
1					
3					
5					

Equilibrium Molarities

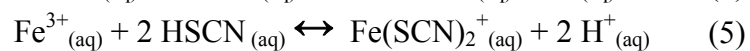
#	$[Fe^{3+}]$ (M)	$[HSCN]$ (M)	$[Fe(SCN)_2^+]$ (M)	$[H^+]$ (M)	K_{eq}
1				0.500	
3				0.500	
5				0.500	

Name: _____

Questions

The correct reaction should have K_{eq} values that are truly constants (within experimental error). An incorrect K_{eq} expression from an incorrect equation will lead to nonconstant K_{eq} values.

1. Based on your results, which equation, 3 or 5, leads to constant K_{eq} values? Justify your answer.



2. What is the correct formula of the iron(III)-thiocyanate complex ion?

Name: _____

Equilibrium Constant Determination

PRESTUDY

Include a separate piece of paper showing your calculations.

1. (2) a. When Fe^{3+} and HSCN react to form an equilibrium with FeSCN^{2+} and H^+ , what happens to the concentration of Fe^{3+} ?

b. How are the numbers of moles of FeSCN^{2+} produced and the number of moles of Fe^{3+} used up related to each other?

2. (6) In an experiment similar to the one you will be doing, the FeSCN^{2+} equilibrium concentration was found to be 3.20×10^{-5} M in a solution made by mixing 5.00 mL of 1.00×10^{-3} M $\text{Fe}(\text{NO}_3)_3$ with 5.00 mL of 1.00×10^{-3} M HSCN. The H^+ concentration is maintained at 0.500 M at all times since the HSCN and Fe^{3+} solutions were prepared using 0.500 M HNO_3 in place of distilled water.

a. How many moles FeSCN^{2+} are present at equilibrium? _____

b. How many moles each of Fe^{3+} and HSCN were initially present? _____

c. How many moles Fe^{3+} remained unreacted in the equilibrium mixture? _____

d. How many moles of HSCN remained unreacted? _____

e. What are $[\text{Fe}^{3+}]$ and $[\text{HSCN}]$ in the equilibrium solution? _____

f. Calculate K_{eq} for the reaction. _____

3. (2) In this experiment, we assume that the complex ion formed is FeSCN^{2+} . It would be possible, however, to form $\text{Fe}(\text{SCN})_2^+$ under certain conditions.

a. Write the equation for the reaction between Fe^{3+} and HSCN in which $\text{Fe}(\text{SCN})_2^+$ is produced. (Hint: Look in the previous pages!)

b. Formulate the expression, analogous to equation 4, for the equilibrium constant, K_{eq} , associated with the reaction in part a.