Experiment 4
Determining an Equilibrium Constant

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Name:

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Date:

Key Objectives

1. Understand the meaning of equilibrium as applied to chemical reactions
2. Review of spectroscopy, beers law, graphing, calibration curves and dilutions
3. Writing and using an equilibrium constant
4. Calculations using $M_1V_1 = M_2V_2$ and $y = mx + b$

Discussion

A complete discussion of Equilibrium can be found in McMurry Chapter 13 or your OER textbook Chapter 13. Reactions that have been studied so far proceed in one direction (from Reactants to Products) and the reaction arrow used ($\longrightarrow$) indicates the direction of the reactions.

Previous Reactions			**Equilibrium Reactions**		
Reactants	$\longrightarrow$	Products	Reactants	$\rightleftharpoons$	Products
0%		100%	50%		50%

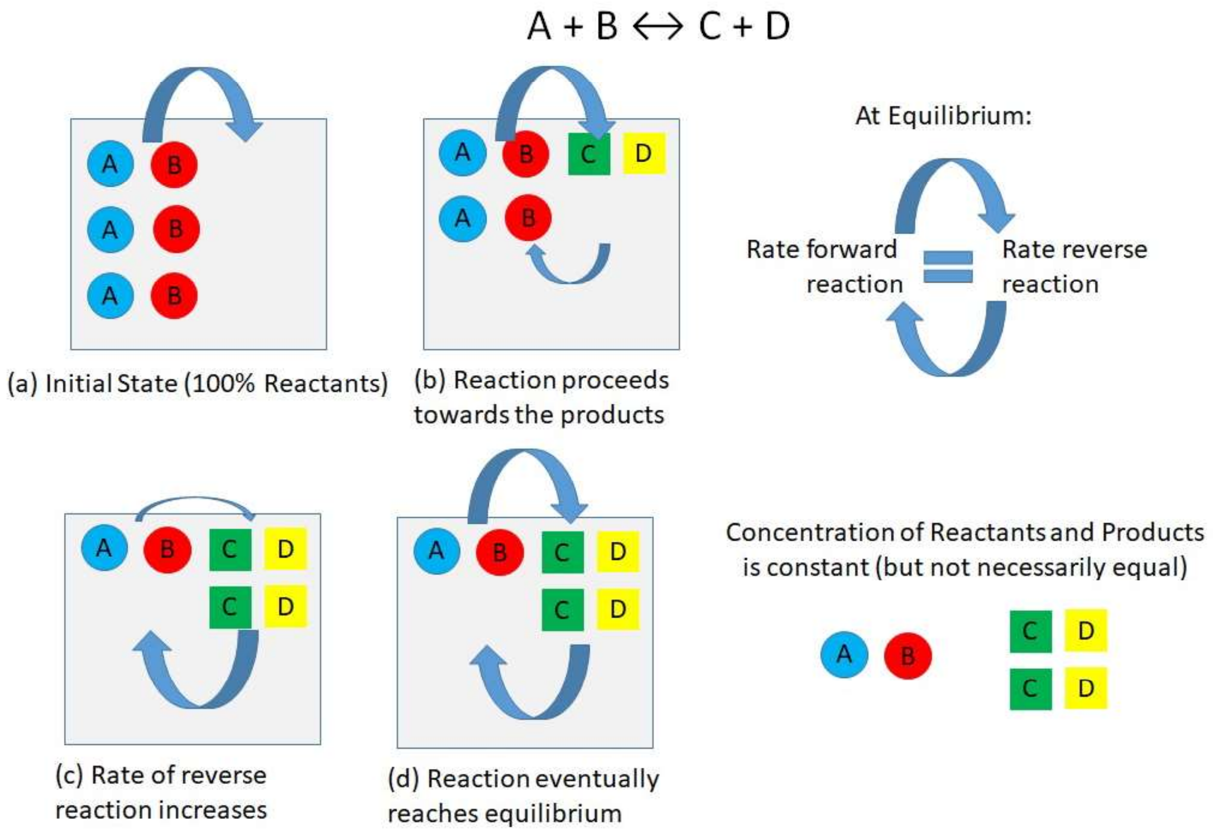
Figure 4.1: The difference between reactions that go to completion and equilibrium reactions.

Equilibrium reactions are a class of reactions that do not go from reactants to products completely but instead proceed in both directions at the same time resulting in a reaction in which both the reactants and products are present in appreciable amounts. This is indicated with a double sided arrow ($\rightleftharpoons$). The final concentration of Reactants and Products is **NOT** $50/50$ as indicated in Figure 4.1 below, but can have any values such as $25/75$ or $60/40$.

Chemical reactions are driven by two forces, Enthalpy and Entropy. Reactions are spontaneous when the change in enthalpy is negative (exothermic reactions) and when the change in entropy is positive (an increase in entropy). If both the change in enthalpy and entropy are favorable in the forward direction a reaction will go to completion, all reactants will be converted to products.

If the change in enthalpy and entropy are favorable in opposites directions, than the reaction will not go to completion, but will reach an equilibrium, where the rate of the reaction in the forward direction and in the reverse direction are the same and the concentrations of the reactants and products are present in a fixed ratio.

Equilibrium can be expressed mathematically in the form of an Equilibrium Constant (K$_{eq}$) describing the final concentration of the reactants and products in a reaction.



(a) Initial State (100% Reactants)

(b) Reaction proceeds towards the products

(c) Rate of reverse reaction increases

(d) Reaction eventually reaches equilibrium

Figure 4.2: Process by which a reaction reaches equilibrium. credit: author

$$\mathrm{aA + bB \rightleftharpoons cC + dD} \tag{22}$$

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{\text{Products}}{\text{Reactants}} \tag{23}$$

The concentrations of the Reactants and Products at equilibrium can vary depending on the initial concentration of reactants and products at the beginning of a reaction. However, the ratio of the Reactants and Products is a constant as long as the reaction has reached equilibrium. Thus, the Equilibrium Constant can be calculated if the concentrations of the reactants and products at equilibrium are known.

’ICE’ Tables

One method to help keep track of the **I**nitial, **C**hange and **E**quilibrium concentrations is the use of an "ICE" table. For example assume one has a reaction A $+$ B $\longrightarrow$ C and the initial concentrations (designated by the subscript 0 are $[A]_0$ = 0.05 M, $[B]_0$ = 0.15 M. After the reaction has reached equilibrium (designated with the subscript eq) the concentration of $[C_{eq}]$ = 0.006 M. One can create the following "ICE" table to aid in calculating the Equilibrium Consant.

Reaction:	**A**	**B**	$\longrightarrow$	**C**
I	0.05 M	0.15 M		0
C	- 0.006 M	-0.006 M		+0.006 M
E	0.044 M	0.144 M		0.006 M

Figure 4.3: ICE Tables - Initial, Change, and Equilibrium Concentrations

Temperature Dependence of the Equilibrium Constant

The Equilibrium Constant (much like rate constants) is a constant only at a specific temperature. We will not have time to explore the temperature dependence of the Equilibrium Constant in this experiment.

Thiocynate Equilibrium Reaction

The reaction studied in the experiment will be the equilibrium that occurs when Iron (III) ions (Fe^{+3}) react with thiocynate ions (SNC^-) to form a stable "complex" ion in solution. The reaction is shown in Figure 4.4 and is chosen due to the color change that occurs.

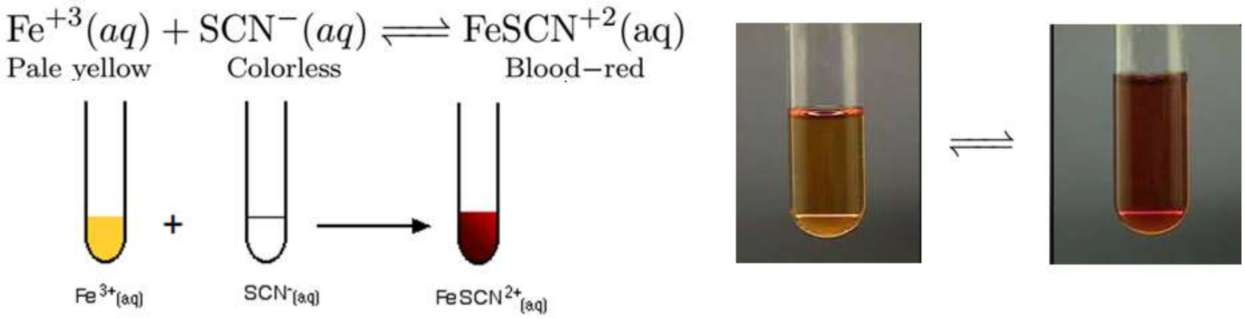


Figure 4.4: Iron thiocynate equilibrium reaction studied in this lab. The difference in color of the solutions can be measured to determine the concentration of the reactants and products. credit: author

The value for K_{eq} can be determined experimentally by mixing known concentrations of the reactants and measuring the concentration of the $FeSCN^{+2}$ ion at equilibrium by the formation of the blood-red color. The equation for the the Equilibrium Constant for the reaction is given in Equation 24.

$$K_{eq} = \frac{[\mathrm{FeSCN}^{+2}]}{[\mathrm{Fe}^{+3}][\mathrm{SCN}^{-}]} \tag{24}$$

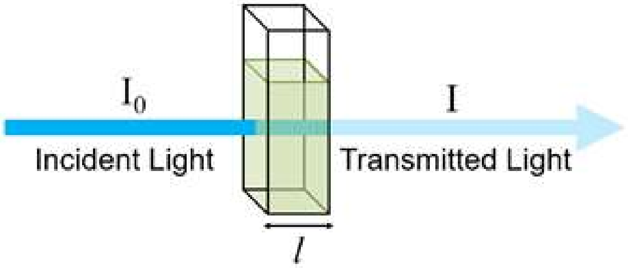
Using a Spectrometer and Beer's Law, the concentration of $FeSCN^{+2}$ ions can be measured by the intensity of the blood-red color formed.

Review and Flashback

A complete discussion of Spectrometers and Beer's Law was given last semester in lab, you may wish to review the lab. Since no one is likely to remember the lab (or have kept it), the relevant portions are included here.

Spectrometers

If we consider light of only one wavelength being transmitted through a solution we can define two quantities. Transmittance (T) is the ratio of the initial intensity of light, I_0 and the light that leaves the solution as I. Absorbance (A) is a related quantity defined as the negative log of the transmittance as shown in Figure 4.7.



Transmittance (T) $T = \frac{I}{I_0}$

Absorbance (A) $A = -\log T$

Figure 4.5: Measuring the absorption or transmission of light through a sample. credit: author

The device used to measure Transmittance and Absorbance is called a spectrometer. The device functions by splitting light into its component wavelengths and measuring the intensity before and after it passes through a solution. Spectrometers come in a variety of shapes, sizes, and most importantly for us price.

Absorption Spectrum

Given a colored substance dissolved in a colorless liquid (water), the colored substance will absorb different wavelengths of light. Using a spectrometer one can measure the Absorbance at many different wavelengths to produce an Absorption Spectrum. Figure 4.6 shows data and a typical absorption spectra. Note the Absorption Maximum marked in the data and on the graph. This is the most sensitive part of the spectrum to changes in concentration. In the lab you will measure the spectrum of your compound and determine the Absorption Maximum for it.

Wavelength (λ) (nm)	Absorbance (A)
300	0.002
325	0.017
350	0.152
375	0.360
400	0.610
425	0.719
450	0.589
475	0.297
500	0.097
525	0.033
550	0.004
575	0.001

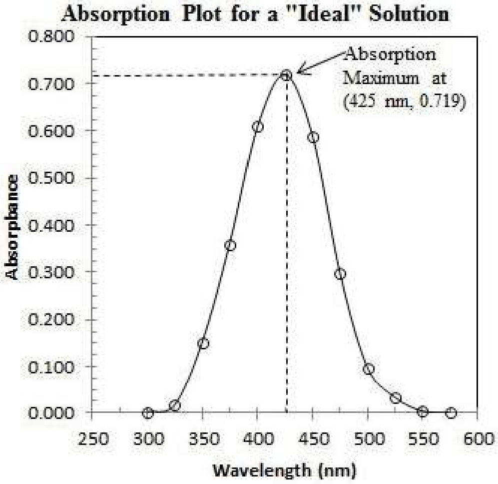


Figure 4.6: Ideal absorbance data and spectrum. Measurements in lab will NOT look this nice. credit: author

For a series of solutions (discussed below) we see that the Absorption Maximum decreases as the concentration of the solution decreases as shown in Figure 4.8 below.

Dilutions

Dilutions can best be thought of as taking a concentrated solution and making a less concentrated solution from it. Similar to the way that one can take frozen OJ (the juices, not the football player) and add water to it. When making concentration measurements, it is often necessary to make a series of solutions of different concentrations to make a calibration curve. This process is best accomplished by taking a solution of known concentration and performing a series of dilutions to make less concentrated solutions. The following formula is most often used:

$$M_1V_1 = M_2V_2$$

M_1 = Molarity of Initial Solution
V_1 = Volume of Initial Solution
M_2 = Molarity of Final Solution
V_2 = Volume of Final Solution

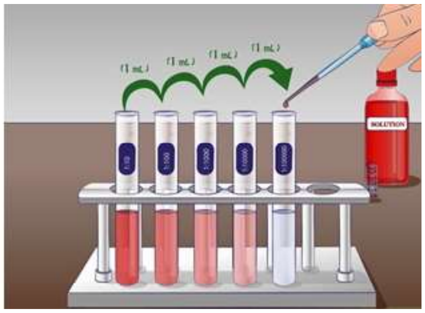


Figure 4.7: Serial dilution - taking a concentrated solution and diluting it to create less concentrated solutions. credit: `https://en.wikipedia.org/wiki/Serial_dilution#/media/File:Logarithmic_dilution.png`

Note that V_2 is the final volume of the solution, for example to calculate the Molarity of Solution 2 in the table below, you take 4 mL of the concentrated solution, and add 1 mL of water, the final volume (V_2) would be 5 mL.

For Solution 2:

$M_1V_1 = M_2V_2$
(0.0120 M)(4.0 mL) = M_2(5.0 mL)
M_2 = 0.00960 M

M_1 = 0.0120 M
V_1 = 4.0 mL
M_2 = Molarity of Final Solution
V_2 = 5.0 mL

The table in Figure 4.8 summarizes a series of 4 dilutions. Figure 4.8 also shows the absorption spectra for five solutions, the original, and four dilutions. Note that the Absorption Maximum decreases as the concentration of the solutions decreases.

Beer's Law

Beer's Law (not the one you are probably thinking of) states that the absorbance at a given wavelength is directly proportional to the molar concentration of the substance. The proportionality constant is often termed the molar absorptivity constant. Note that because absorbance is a unitless, the units for the proportionality constant (k) are simply the inverse of normal concentration units. The constant is specific to each substance and specific to a given wavelength.

A = kM

A = Absorbance
k = molar absorptivity constant (L/mol or M^{-1})
M = Molarity of the solution (mol/L or M)

Solution Number	M_1 (M)	V_1 (mL)	M_2 (M)	V_2 (mL)	Final Conc. (
1	0.0120	-	-	-	-
2	0.0120	4	x	5	0.0096
3	0.0120	3	x	5	0.0048
4	0.0120	2	x	5	0.0028
5	0.0120	1	x	5	0.0024

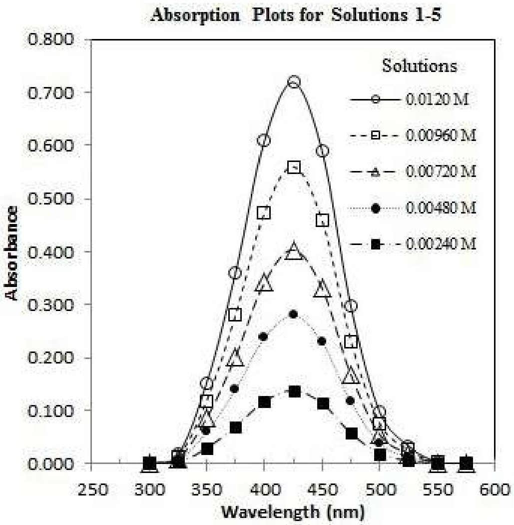


Figure 4.8: Absorption curves for Solutions 1-5. credit: author

Note that the equation for Beer's Law has the same form as that of a straight line. Given a series of solutions with known concentration plotting Concentration vs. Absorbance should yield a straight line whose slope is the molar absorptivity, and the equation of the line allows calculation of the concentration of an unknown concentration.

Solution Number	Concentration (M)	Absorbance (at 425 nm)
1	0.0120	0.719
2	0.00960	0.560
3	0.00720	0.404
4	0.00480	0.280
5	0.00240	0.138

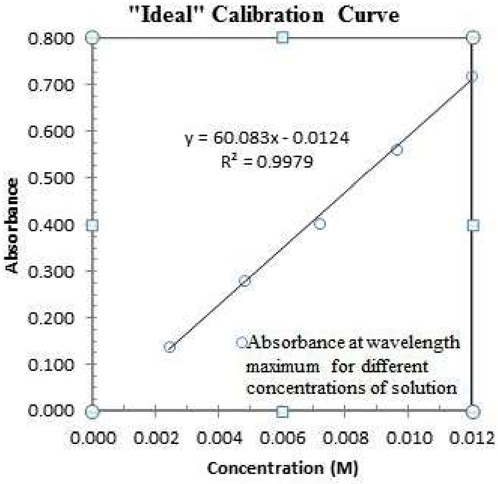


Figure 4.9: Example Beer's Law data and plot. credit: author

Procedure

The purpose of this experiment is to calculate the Equilibrium Constant (K_{eq}) and to test it under a variety of different conditions to determine if it is truly a constant.

There are two parts to the experiment, the first is to establish a calibration curve to measure the concentration of $FeSCN^{+2}$ ions. This will be accomplished by preparing solutions with a large excess of Fe^{+3} ions with a known amount of SCN^{-} ions. According to LeChatelier's Principle the large excess of ions will cause the equilibrium to shift almost 100% to the product side resulting in a known concentration of $FeSCN^{+2}$ equal to the concentration of the Fe^{+3} ions in the original solution. This will allow us to establish a calibration curve.

In the second part of the experiment a series of solutions will be prepared with different amounts of Fe^{+3} and SCN^{-} ions and the concentration of $FeSCN^{+2}$ measured. This will allow the calculation of the Equilibrium Constant (K_{eq}).

Solution Preparation for the Calibration Curve

1. Obtain 2 volumetric pipets, 5 test tubes and a test tube rack.
2. Rinse the volumetric pipet several times with the solution to be used, discarding the solution each time.
3. Using the table below prepare 5 test tubes by taking the required and mixing them. Do not use a stopper or your finger.
4. Calculate the concentration of $FeSCN^{+2}$ for each solution and enter the data in the Results section. In the space below the table in the Results section show work for Test Tubes 2 and 4.

Test Tube Number	mL of 0.20 M $Fe(NO_3)_3$	mL of 0.00020 M KSCN
1	8.0	2.0
2	7.0	3.0
3	6.0	4.0
4	5.0	5.0
5	4.0	6.0

Measuring the Absorption Spectra of Your Solutions

1. Connect the spectrometer to your computer. Fill an empty spectrometer cell with water. Place it in the spectrometer and under the Experiments Menu choose calibration.
2. Using a disposable pipet, fill a spectrometer cell with the sample to be tested.
3. Measure the absorption spectrum of the solution in each test tube.
4. Stop the data collection after a few seconds.
5. Copy and paste the raw data into an Excel spreadsheet and save your data for use later.

6. Plot the entire spectrum of Test Tube 1 for your lab report (Figure 4.6). Determine the Absorbance Maximum. (Attach the spectrum to the end of the Results section.)

7. In the results section, list the value of the maximum in the Data Table 1.

8. Using the Absorbance Maximum, determine the Absorbance for each of the test tubes at the maximum and record the data in the Results section.

9. Dispose of all solutions in the sink.

10. Make a calibration curve (Figure 4.9) for your sample and for the linear portion of the graph determine the equation of the line and the Molar Absorptivity constant. (Attach the calibration curve to the end of the Results section.)

11. Before you come to lab on day 2 be sure you have completed the previous section. If you have any bad data you will be allowed time to remeasure it.

Solution Preparation for Determining the Equilibrium Constant (K_{eq})

1. Obtain 3 volumetric pipets, 5 test tubes and a test tube rack.

2. Rinse the volumetric pipet several times with the solution to be used, discarding the solution each time.

3. Using the table below prepare 5 test tubes by taking the required and mixing them. Do not use a stopper or your finger.

4. Calculate the molarity of each solution and enter the data in the Results section. In the space below the table in the Results section show work for Test Tubes 7 and 9.

5. After preparing the Test Tubes, make your Absorbance measurements and answer the questions in the lab.

6. Dispose of all solutions in the sink.

Test Tube Number	mL of 0.0020 M $Fe(NO_3)_3$	mL of 0.0020 M KSCN	mL H_2O
6	5.0	1.0	4.0
7	5.0	2.0	3.0
8	5.0	3.0	2.0
9	5.0	4.0	1.0
10	5.0	5.0	0.0

Name: ______________________________ Class: ______________________ Date: ______________________

Results

Data Table 1: Concentration and Absorption Measurements - Reference Solutions

Test Tube #	**Concentration [$FeSCN^{+2}$] M**	**Absorption @ ______________**
1		
2		
3		
4		
5		

Table 4.1: Results for the Reference Solutions

Attachments

1. Attach the absorption spectrum of test tube 3. Draw an arrow pointing to the Absorption Maximum, and label it. In the label include both the value of the wavelength and the value of the Absorption (Figure 4.6).
2. Attach the calibration curve and be sure to include the line fit (Figure 4.9).

Data Table 2: Concentration and Absorption Measurements - Test Solutions

Test Tube #	**Original [Fe^{+3}] M**	**Original [SCN^{-}] M**	**Absorption @ ______________**
6			
7			
8			
9			
10			

Table 4.2: Results for the Test Solutions

Show calculations for the concentrations of Fe^{+3} and SCN^{-} for test tubes 7 and 9.

Data Table 3: Calculating the Equilibrium Constant (K_{eq})

Test Tube #	**$[FeSCN^{+2}]_{eq}$ M**	**$[Fe^{+3}]_{eq}$ M**	**$[SCN^{-}]_{eq}$ M**	**Equilibrium Constant (K_{eq})**
6				
7				
8				
9				
10				

Table 4.3: Determining the Equilibrium Constant (K_{eq})

1. Complete Data Table 4.3. Show an example calculation for all columns for Test Tube 7.

2. Calculate the Mean (Average Value) and Standard Deviation for the Equilibrium Constant (K_{eq}) for Test Tubes 6-10.

3. Based on the results of the previous question, does the precision of your measurements indicate that the Equilibrium Constant is indeed a "constant" for the reaction? Explain.

4. Describe the possible sources of error in this experiment (2 sources) **AND** how they might effect the results. If you did the experiment over again, how could you control for those sources of error?

5. Based on the value of the Equilibrium Constant, does the reaction favor the Reactants or Products? (ie at equilibrium are there more reactants or products in the test tube?). Explain.

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Name: ____________________ Class: ________________ Date: ________________

Prelab Questions

Use the following information to answer the questions on the prelab.
The reaction of silver ions and ammonium molecules to form the "complex" diamminesilver ion is shown below.

$$\mathrm{Ag^+(aq) + 2NH_3(aq) \longrightarrow Ag(NH_3)_2{}^+(aq)}\cdot$$

1. Write the Equilibrium Constant equation for the reaction.

2. Students made several measurements of [$Ag(NH_3)_2{}^+$] vs Absorbance. Using the data make a (good looking) calibration plot and attach it to the pre-lab. Be sure to include the equation and the R^2 value of the line on the graph.

Test Tube #	[$Ag(NH_3)_2{}^+$] M	Absorption
1	1.0×10^{-2}	0.137
2	2.0×10^{-2}	0.188
3	3.0×10^{-2}	0.242
4	4.0×10^{-2}	0.294
5	5.0×10^{-2}	0.345

3. Assuming a test tube starts with initial concentrations [Ag^+]$_0$ = 3.6×10^{-2} M and [NH_3]$_0$ = 3.5×10^{-2} M and after reacting the measured absorbance is 0.2621. Calculate the concentration of [$Ag(NH_3)_2{}^+$] and enter the result in the table below. Explain.

4. Using experimental data above, complete the following Table. Show work in the space below. (Hint, create an ICE chart to help you.)

[Ag^+]$_{eq}$ M	[NH_3]$_{eq}$ M	[$Ag(NH_3)_2{}^+$]$_{eq}$ M	Equilibrium Constant (K_{eq})

Table 4.4: Pre-Lab

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