Experiment 23B

FV 2/4/04

DETERMINATION OF THE EQUILIBRIUM CONSTANT FOR A DISSOCIATION REACTION

MATERIALS: 50 mL and 25 mL graduated cylinders, two 50 mL beakers, two plastic Pasteur pipets, four 250 mL Erlenmeyer flasks, 50 mL buret, standard KBr solution, 0.010 M $AgNO_3$ in autoburet, 2.0 M NH_3 solutions.

PURPOSE: The purpose of this experiment is to determine the equilibrium constant for the dissociation of $Ag(NH_3)_2^+$ (aq) into Ag^+ (aq) and NH_3 (aq).

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Use a pipet and buret correctly.
2. Perform titrations accurately and precisely.
3. Calculate the molarity of components in a solution from stoichiometry information.
4. Calculate the equilibrium constant of a reaction from measured concentrations.
5. Apply ICE tables to solve equilibrium problems.

DISCUSSION:

A *complex ion* is formed when neutral molecules or anions attach to a metal cation. Usually, the metal cation is a transition metal, such as Ag^+ or Fe^{3+}. The molecules or anions attached to the central cation are called *ligands*. The number of bonds from the ligands to the metal cation is the *coordination number* of the metal. In this experiment, we will be examining the complex formed between silver cation and ammonia ligands. The formation of this complex ion can be represented by the equation:

$$Ag^+ (aq) + 2\,NH_3 (aq) \rightleftharpoons Ag(NH_3)_2^+ (aq)$$

Since two ammonia molecules are attached to the silver ion, the coordination number of the silver ion in this system is two. The equilibrium constant expression for this reaction as written is:

$$K_1 = \frac{\left[Ag(NH_3)_2^+\right]_{eq}}{\left[Ag^+\right]_{eq}\left[NH_3\right]_{eq}^2} \qquad (1)$$

where the concentrations of all species are equilibrium concentrations. The equilibrium constant for this reaction is very large. Therefore, when a relatively small amount of silver ion is combined with a large excess of ammonia, we can assume that all of the silver is converted to the diammine silver complex product, $Ag(NH_3)_2^+$, and that the concentration of this complex equals the concentration of Ag^+ added to the original solution. Since the ammonia is used in excess, the concentration of the ammonia changes very little as the reaction occurs and $[NH_3]_{eq}$ is essentially equal to the initial concentration of ammonia, $[NH_3]_{initial}$.

In general, chemists are concerned with the stability of a complex ion and, therefore, it is more common to study the reverse of this reaction, the dissociation of $Ag(NH_3)_2^+$, shown as:

$$Ag(NH_3)_2^+ (aq) \rightleftharpoons Ag^+ (aq) + 2\,NH_3 (aq)$$

Like all equilibrium reactions, the extent to which this dissociation occurs can be expressed through its equilibrium constant, K. The equilibrium constant expression for this reaction as written is:

$$K_2 = \frac{\left[Ag^+\right]_{eq}\left[NH_3\right]_{eq}^2}{\left[Ag(NH_3)_2^+\right]_{eq}} \qquad (2)$$

where the concentrations of all species refer to equilibrium concentrations.

To determine the value for the equilibrium constant for the dissociation, the equilibrium concentrations must be known for all species. It is not necessary, however, to be able to measure the concentration of each. If the initial concentrations of all species are known and the equilibrium concentration of ONE species can be measured, stoichiometry can be used to determine the remaining concentrations. These calculations are often shown in the form of an ICE table[1]. The ICE table for the dissociation reaction is shown below. The ICE table includes our assumptions about concentrations explained earlier.

	$Ag(NH_3)_2^+$ (aq) $\rightleftharpoons$	**Ag^+ (aq)**	**+ 2 NH_3 (aq)**
Initial Concentration	$[Ag(NH_3)_2^+]_{init}$	0	$[NH_3]_{init}$
Change	-x	+x	+2x
Equilibrium Concentration	$([Ag(NH_3)_2^+]_{init}$ - x)	x	$([NH_3]_{init}$ + 2x)

While measuring any one of the equilibrium values would allow us to complete the ICE table and calculate K, experimental considerations determine which is easiest to measure accurately and precisely. For the dissociation we are studying, the easiest equilibrium concentration to measure is that of the silver cation.

Because the complex ion is quite stable, only a very small amount of free silver ion is present at equilibrium. The exact concentration can be determined by titrating the silver with potassium bromide. Silver ions react with bromide ions to form an essentially insoluble compound, AgBr.

$$Ag^+ (aq) + Br^- (aq) \rightleftharpoons AgBr (s)$$

The formation of this compound is also an equilibrium reaction, with an equilibrium constant of 2.0×10^{12}. A white solid will be formed in the flask when the $[Ag^+][Br^-] = 1/2.0 \times 10^{12} = 5.0 \times 10^{-13}$. Rearranging this equation, we can see that:

$$[Ag^+]_{equil} = \frac{5.0 \times 10^{-13}}{[Br^-]} \qquad (3)$$

Measuring the volume of standard potassium bromide solution needed to cause some silver bromide solid to form allows us to calculate the amount of free Ag^+ present. Determining the amount of Ag^+ by titration adds one additional calculation step in setting up the ICE table. During the titration, the complex ion containing solution is being *diluted* by the solution being added. Since we are only interested in the concentrations present at the endpoint of the titration, our ICE table must be adjusted as shown below,

	$Ag(NH_3)_2^+$ (aq) $\rightleftharpoons$	**Ag^+ (aq)**	**+ 2 NH_3 (aq)**
Initial Concentration	0.00010 mol/V_f	0	y
Change	-x	+x	+2x
Equilibrium Concentration	(0.00010 mol/V_f - x)	x	(y + 2x)

where V_f is the volume in the flask at the endpoint (e.g., 0.0500 L + volume of KBr solution added), and y is the ammonia concentration at the endpoint. In this ICE table, the initial concentration of $Ag(NH_3)_2^+$ is determined by the amounts of $AgNO_3$ and NH_3 initially added to the solution (e.g., for Flask 1 in Table I of the procedure, 0.00010 moles $Ag(NH_3)_2^+$ will be present after mixing 10.0 mL of 0.010 M $AgNO_3$ with 5.0 mL of 2.0 M NH_3). The value of y can be calculated using the dilution equation $M_{init}V_{init} = M_{final}V_{final}$ and the initial volumes of ammonia found in the procedure. To allow for greater accuracy and precision, the value for K will be determined from four different initial concentrations of $Ag(NH_3)_2^+$ and the results will be averaged.

[1]*Chemistry, The Central Science*, Brown, LeMay and Bursten, pp. 570-571.

PROCEDURE:

Part A. Preparation of the Diammine Silver Complexes

1. Obtain four clean, dry 250 mL Erlenmeyer flasks. If your flasks are not perfectly clean, your results will be poor so give any flasks with white residues on the side to your instructor.

2. In the Data Section, record the actual concentration of the NH_3 solution to be used in this experiment.

3. Using the information in Table I below, set up a series of four flasks, each containing the appropriate amounts of the silver nitrate solution, ammonia solution, and distilled water. Use the autoburet to measure out the silver nitrate solution. Use graduated cylinders to measure out the ammonia and water. The total volume of each solution should be 50 mL.

Flask #	0.010 M $AgNO_3$	2.0 M NH_3	Distilled H_2O
1	10.0 mL	5.0 mL	35.0 mL
2	10.0 mL	8.0 mL	32.0 mL
3	10.0 mL	10.0 mL	30.0 mL
4	10.0 mL	15.0 mL	25.0 mL

Table I: Preparation of solutions containing diammine silver complexes

Part B. Titration of the Free Silver Ions with Potassium Bromide

1. In the Data Section, record the actual concentration of the standard potassium bromide solution.

2. Properly rinse and fill the buret with the potassium bromide solution.

3. Titrate each of the four solutions with the standard potassium bromide solution. The titration is complete when a very faint permanent cloud of silver bromide is present in the flask. A dark background behind the flask may aid in seeing the AgBr precipitate. Be sure to swirl the flask after each addition of reagent. Record your initial and final buret readings for each titration in the Data Section.

Clean up:

1. Place all solutions containing silver in the appropriate waste container in the hood. All other solutions may go down the sink.

2. Clean all glassware and rinse thoroughly with distilled water. Use a brush to remove any white residue from the Erlenmeyer flasks.

3. Return equipment to their original locations.

Name _____ Section _____

Partner _____ Date _____

DATA SECTION
Experiment 23B

Report all data with units and the correct number of significant figures.

Part A. Preparation of the Diammine Silver Complexes

Concentration of stock NH_3 solution _____

Part B. Titration of the Free Silver Ions with Potassium Bromide

Concentration of standard KBr solution _____

	Flask 1	Flask 2	Flask 3	Flask 4
Initial Volume of KBr				
Final Volume of KBr				
Volume of KBr added				

DATA TREATMENT
Experiment 23B

Be sure to include units and the correct number of significant figures in your final answers.

Part A. Preparation of the Diammine Silver Complexes

1. Calculate the number of moles of ammonia added to each of the four flasks. Show your work for the calculation for Flask 1. Since the ammonia is used in large excess, these values will be used to calculate the initial concentration of ammonia to insert in our ICE tables.

	Flask 1	Flask 2	Flask 3	Flask 4
moles of NH_3 added				

2. Calculate the number of moles of diammine silver complex formed. Use the assumption that all the silver ions added are converted to the complex. The calculated value is the same for all four flasks since the same amount of silver nitrate solution is added to each. This value will also be used to calculate the initial concentration of the complex which will be used in the ICE tables.

moles of $Ag(NH_3)_2^+$ = _____

Part B. Titration of the Free Silver Ions with Potassium Bromide

1. From the titration data, calculate the moles of bromide ion added to each solution. Show your work for Flask 1.

	Flask 1	Flask 2	Flask 3	Flask 4
moles of Br^- added				

2. Before carrying out further calculations, we must correct for the dilution of the original solutions caused by adding the KBr in the titration. The correct volume for each flask is the sum of the original 0.0500 L and the volume of KBr added (in Liters). Then, calculate the initial concentrations of the complex ion, ammonia, and bromide ion using these volumes and the number of moles for each, calculated above. Fill in the following table of volumes and molarities. Show your work for Flask 1.

	Flask 1	Flask 2	Flask 3	Flask 4
volume in flask after titration				
$[Ag(NH_3)_2^+]_{initial}$				
$[NH_3]_{initial}$				
$[Br^-]$				

3. From the concentration of bromide ions added, we can calculate the concentration of free silver ions present in each flask, using Equation 3 given on page E23B-2 of the discussion. These calculations will give us the value for $[Ag^+]_{equil}$. Calculate these values and place them in the table. Show your work for Flask 1.

$$[Ag^+]_{equil} = \frac{5.0 \text{ x } 10^{-13}}{[Br^-]}$$

	Flask 1	Flask 2	Flask 3	Flask 4
$[Ag^+]_{equil}$				

4. Using the ICE table shown on page E23B-2 and below as a template, create ICE tables for each of the four flasks. From these ICE tables, calculate K_2 for each flask.

Template

	$Ag(NH_3)_2^+$ (aq) $\rightleftharpoons$	Ag^+ (aq)	+ 2 NH_3 (aq)
Initial Concentration	0.00010 mol/V_{final}	0	y
Change	-x	+x	+2x
Equilibrium Concentration	(0.00010/V_{final} - x)	x	(y + 2x)

Flask 1

	$Ag(NH_3)_2^+$ (aq) $\rightleftharpoons$	Ag^+ (aq)	+ 2 NH_3 (aq)
Initial Concentration			
Change			
Equilibrium Concentration			

Flask 2

	$Ag(NH_3)_2^+$ (aq) $\rightleftharpoons$	Ag^+ (aq)	+ 2 NH_3 (aq)
Initial Concentration			
Change			
Equilibrium Concentration			

Flask 3

	$Ag(NH_3)_2^+$ (aq) $\rightleftharpoons$	Ag^+ (aq)	+ 2 NH_3 (aq)
Initial Concentration			
Change			
Equilibrium Concentration			

Flask 4

	$Ag(NH_3)_2^+$ (aq) $\rightleftharpoons$	Ag^+ (aq)	+ 2 NH_3 (aq)
Initial Concentration			
Change			
Equilibrium Concentration			

5. List the values of K_2 in the table. Calculate the average value for K_2 and the average percent deviation from the mean for your values.

	Flask 1	Flask 2	Flask 3	Flask 4	Average	Average Percent Deviation from Mean
K_2						

QUESTIONS
Experiment 23B

1. How precise are your results for K_2? Explain one specific way in which the precision could be improved.

2. There are several steps in the procedure which could cause the calculated results to be inaccurate, as well as imprecise. List one of these and explain how the experimental procedure could be improved.

3. As noted in the discussion, the dissociation of the complex is the inverse of the reaction wherein the complex ion is formed. Calculate the value for the equilibrium constant for the formation of the complex ion, K_1. Show your reasoning.