

Name \_\_\_\_\_ Section \_\_\_\_\_

Partner(s) \_\_\_\_\_

Chemistry 118 Laboratory  
University of Massachusetts Boston

## AN EQUILIBRIUM CONSTANT DETERMINATION

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### PRELAB ASSIGNMENTS

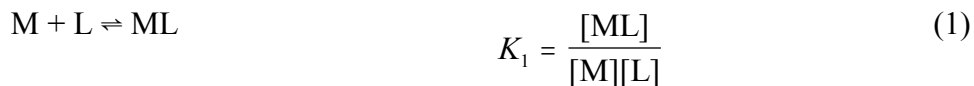
1. At the beginning of the laboratory session your instructor will prepare a standard solution containing a known concentration of the  $ML_x$  complex ( $x = 1$  or  $2$ ) by pipetting 5.00 mL of 2.04 mM  $M(NO_3)_m$ , the nitrate salt of the metal cation, M, into a 250.0-mL volumetric flask and filling the flask to the line with a concentrated solution of  $K_mL$ , the potassium salt of the anion ligand, L. The high concentration of L ensures that virtually all the M is converted to  $ML_x$ . What is the concentration of  $ML_x$  in the flask?  
Answer \_\_\_\_\_ mM
2. Fill in the blanks in Table 2 (page 6) for total concentration of M and total concentration of L. Use millimolar (mM) concentrations. Table 1 at the bottom of page 2 shows the composition of the reaction mixtures.

### INTRODUCTION

If we mix the nitrate salt of a certain metal cation, M, with the potassium salt of certain anion, L, a reaction occurs forming a complex species of M and L, which we will denote as  $ML_x$ . In complexes of this type, L is called a *ligand* and is bonded directly to the metal ion. Although the aqueous solutions of the two salts are virtually colorless, the  $ML_x$  complex is red. This happy circumstance allows us to use absorption spectroscopy to measure the concentration of  $ML_x$  in equilibrium with its two ions. We can use this information to determine the composition of the complex and its formation equilibrium constant.

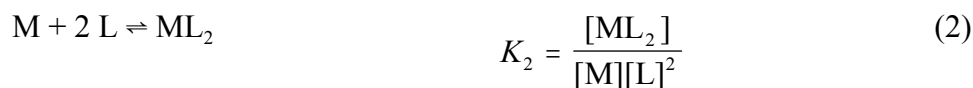
Most complex species of this type consist of a single cation bonded to one or more ligands. We will assume that our complex either has the formula ML or the formula  $ML_2$ , and we will try to determine which of these it is. Thus, we have two hypotheses for the formation reaction.

Hypothesis 1: The complex is ML, for which the equilibrium and its constant are



## An Equilibrium Constant Determination

Hypothesis 2: The complex is  $ML_2$ , for which the equilibrium and its constant are



In order to choose between these, you will prepare four solutions containing different proportions of M and L. You will then measure the absorbance of each solution, and from this calculate the concentrations of reactants and product. From these concentrations, you will calculate a value for  $K_1$  and a value for  $K_2$  for each solution. In principle, with the correct hypothesis all four solutions will yield the same value of  $K$  (a constant) within the variation expected from experimental error. On the other hand, with the wrong hypothesis, the calculated values of  $K$  for the four solutions will be vastly different.

### IN THE LABORATORY

- Clean and thoroughly dry seven 50-mL beakers. Label these M, L, std, 2, 3, 4, and 5.
- Using the marking on the beakers, add the following to the first three as follows:
  - Beaker M – 40 mL of M nitrate solution,  $M(NO_3)_n(aq)$ ;
  - Beaker L – 30 mL of potassium L solution,  $K_mL(aq)$ ;
  - Beaker std – about 10 mL of  $ML_x$  standard solution from the volumetric flask.
- Rinse a 5-mL serological pipet with your  $M(NO_3)_n(aq)$  solution (Beaker M), and then pipet 5.00 mL of  $M(NO_3)_n(aq)$  solution into each of the four numbered beakers. Remember that you must empty liquid from the tip of a serological pipet.
- Rinse the serological pipet with deionized water and then with your  $K_mL(aq)$  solution (Beaker L). Then pipet the volumes of  $K_mL(aq)$  solution indicated in Table 1 (below) into the designated beakers.

Table 1. Composition of the Reaction Mixtures

| Reaction Beaker | 2.04 mM $M(NO_3)_n$<br>(mL) | 2.10 mM $K_mL$<br>(mL) | Deionized water<br>(mL) |
|-----------------|-----------------------------|------------------------|-------------------------|
| 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                       |

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- ❑ Rinse the serological pipet with deionized water. Then pipet the volumes of deionized water indicated in Table 1 (above) into the designated beakers.
- ❑ Take the four reaction beakers, the std beaker, and a wash bottle of deionized water to a spectrophotometer. Check that the wavelength is set to 460 nm. Notice that the cuvet supplied with the spectrophotometer is marked with two lines: a vertical line near the top for alignment in the sample compartment, and a horizontal line for the minimum volume level.
- ❑ Rinse the cuvet thoroughly with deionized water, and then fill it to the horizontal line with deionized water. Properly align the cuvet in the sample compartment, close the cover, and adjust the zeroing knob until the absorbance is set at 0.000.
- ❑ Measure the absorbance of the  $ML_x$  standard solution (std beaker) and each of the four solutions in the reaction beakers as follows:
  - Rinse the cuvet at least twice with the solution to be measured.
  - Fill the cuvet to the leveling line with the solution.
  - Wipe off any liquid or fingerprints from the outside of the cuvet below the leveling line.
  - Place the cuvet in the sample compartment and read the absorbance to 3 decimal places. (Alternately, read the transmittance,  $T$ , to three significant figures, and convert to absorbance,  $A$ , using the relationship,  $A = -\log T$ .) Record the data for the  $ML_x$  standard on the appropriate lines at the top of page 6. Record the data for the four reaction mixtures in Table 2 (page 6).

### CALCULATIONS

The concentration of  $ML_x$  is directly proportional to the absorbance,  $A$ . Thus, the four concentrations,  $[ML_x]_i$ , can be calculated from the four measured absorbances,  $A_i$  recorded in Table 2, using the formula

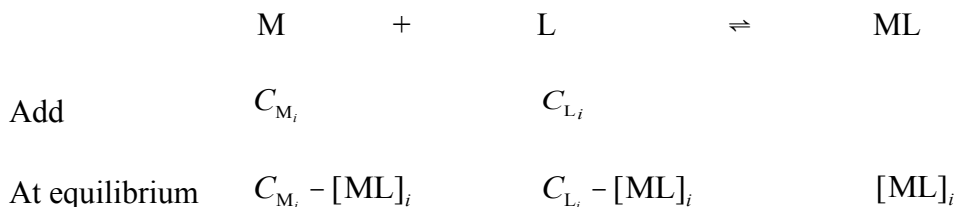
$$[ML_x]_i = A_i \left( \frac{C_{\text{std}}}{A_{\text{std}}} \right) \quad (3)$$

where  $A_{\text{std}}$  is the absorbance of the standard solution,  $C_{\text{std}}$  is the analytical concentration of the standard solution, and  $i = 2, 3, 4, 5$  is the label for each of the four reaction mixtures. The term *analytical concentration*, given the symbol  $C$ , refers to the number of moles of a species *added* per liter of solution, as distinct from its equilibrium concentration in solution, symbolized by the species' formula in square brackets. For example  $C_M$  and  $C_L$  are the analytical concentrations of M and L, respectively; but  $[M]$ ,  $[L]$  and  $[ML_x]$  are the equilibrium concentrations of the species M, L, and  $ML_x$ , respectively. Record the four values of  $[ML_x]_i$  calculated by equation (3) in Table 2.

In Table 3, you will calculate the presumed equilibrium concentrations  $[M]_i$  and  $[L]_i$ , using Hypothesis 1 and the values you calculated for  $[ML_x]_i$ . Here, we assume that  $ML_x$  is ML.

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Assuming Hypothesis 1, the relationships between the analytical concentrations  $C_{M_i}$  and  $C_{L_i}$ , and the equilibrium values  $[M]_i$ ,  $[L]_i$ , and  $[ML]_i$  can be determined from the equilibrium reaction stoichiometry as follows:



Thus, if Hypothesis 1 is correct, for each solution

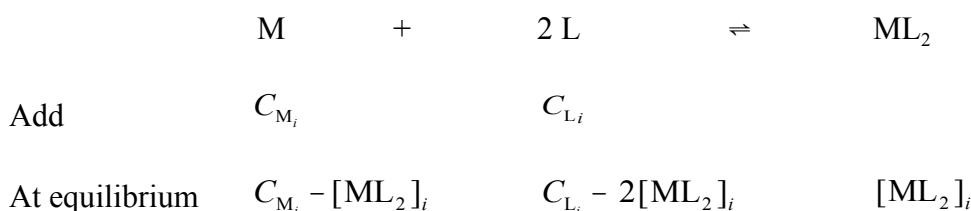
$$[M]_i = C_{M_i} - [ML]_i \quad (4)$$

and

$$[L]_i = C_{L_i} - [ML]_i \quad (5)$$

Use equations (4) and (5) to calculate the equilibrium concentrations of M and L, and enter your results in Table 3. Using these values, calculate  $K_1$  for each solution.

In Table 4, you will calculate the presumed equilibrium concentrations  $[M]_i$  and  $[L]_i$ , using Hypothesis 2 and the values you calculated for  $[ML_x]_i$ . Here, we assume that  $ML_x$  is  $ML_2$ . Assuming Hypothesis 2, the relationships between the analytical concentrations  $C_{M_i}$  and  $C_{L_i}$ , and the equilibrium values  $[M]_i$ ,  $[L]_i$ , and  $[ML_2]_i$  can be determined from the equilibrium reaction stoichiometry as follows:



Thus, if Hypothesis 2 is correct, for each solution

$$[M]_i = C_{M_i} - [ML_2]_i \quad (6)$$

and

$$[L]_i = C_{L_i} - 2[ML_2]_i \quad (7)$$

Use equations (6) and (7) to calculate the equilibrium concentrations of M and L, and enter your results in Table 4. Using these values, calculate  $K_2$  for each solution.

## An Equilibrium Constant Determination

Equilibrium constants are more conventionally defined in terms of molar concentrations. Convert your values of  $K_1$  and  $K_2$  to values based on molar concentrations. Write these conventional  $K$  values in Table 3 and Table 4.

Finish Table 3 and Table 4 by calculating

- the mean of your conventional  $K_1$  and  $K_2$  values,  $\overline{K}$ , based on molar concentrations;
- the range of variation,  $\Delta K$ , i.e., the difference between the smallest and largest  $K$  value in each set;
- the percent variation for each set, calculated as

$$\% \text{ variation} = \left( \frac{\Delta K}{\overline{K}} \right) \times 100\% \quad (8)$$

On the basis of the variation in the calculated  $K_1$  and  $K_2$  values, decide which is the more plausible formula for the complex,  $ML$  or  $ML_2$ , and give your reasons.

## An Equilibrium Constant Determination

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Measured absorbance of  $ML_x$  standard,  $A_{std} =$  \_\_\_\_\_, for which  $C_{std} =$  \_\_\_\_\_ mM

Table 2. Absorbance and Concentration Data for Reaction Mixtures

| Reaction Beaker                            | 2     | 3     | 4     | 5     |
|--|-------|-------|-------|-------|
| Total volume (mL)                          | 10.00 | 10.00 | 10.00 | 10.00 |
| Volume of 2.04 mM $M(NO_3)_n(aq)$ (mL)     | 5.00  | 5.00  | 5.00  | 5.00  |
| Total concentration of M, $C_M$ (mM)       |       |       |       |       |
| Volume of 2.10 mM $K_mL(aq)$ (mL)          | 2.00  | 3.00  | 4.00  | 5.00  |
| Total concentration of L, $C_L$ (mM)       |       |       |       |       |
| Absorbance, $A_i$ ( $i = 2, 3, 4, 5$ )     |       |       |       |       |
| Concentrations of $ML_x$ , $[ML_x]_i$ (mM) |       |       |       |       |

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Table 3. Hypothesis 1:  $M + L \rightleftharpoons ML$

| Reaction Beaker                       | 2 | 3 | 4 | 5 |
|---------------------------------------|---|---|---|---|
| $[ML_x] = [ML]_i$ (mM) (From Table 2) |   |   |   |   |
| $[M]_i$ (mM)                          |   |   |   |   |
| $[L]_i$ (mM)                          |   |   |   |   |
| $K_1$ , using mM concentrations       |   |   |   |   |
| $K_1$ , using M concentrations        |   |   |   |   |

Mean  $K_1$ ,  $\bar{K}_1 =$  \_\_\_\_\_      Range of  $K_1$ ,  $\Delta K_1 =$  \_\_\_\_\_      % variation \_\_\_\_\_

Table 4. Hypothesis 2:  $M + 2L \rightleftharpoons ML_2$

| Reaction Beaker                         | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| $[ML_x] = [ML_2]_i$ (mM) (From Table 2) |   |   |   |   |
| $[M]_i$ (mM)                            |   |   |   |   |
| $[L]_i$ (mM)                            |   |   |   |   |
| $K_2$ , using mM concentrations         |   |   |   |   |
| $K_2$ , using M concentrations          |   |   |   |   |

Mean  $K_1$ ,  $\bar{K}_2 =$  \_\_\_\_\_      Range of  $K_2$ ,  $\Delta K_2 =$  \_\_\_\_\_      % variation \_\_\_\_\_

Which is the more plausible formula for the complex, ML or  $ML_2$ ? Explain.