Solubility Product Constants

PURPOSE

To measure the solubility product constant (K_{sp}) of copper (II) iodate, $Cu(IO_3)_2$.

GOALS

1 To measure the molar solubility of a sparingly soluble salt in water.

2 To prepare a calibration curve based on complex ion formation for absorbance enhancement.

3 To calculate the solubility product constant (K_{sp}) of a sparingly soluble salt from its molar solubility.

4 To confirm the common ion effect on the molar solubility of a sparingly soluble salt.

INTRODUCTION

In previous introductory chemistry courses, you learned some basic solubility rules that are useful in determining if an ionic solid will dissolve in water. Solids that dissolve completely, such as NaCl and NH_4NO_3, were referred to as "soluble" and others that did not dissolve completely, such as AgCl and $BaSO_4$, were referred to as "insoluble". In fact, very few ionic solids are completely insoluble, meaning that they will not form any ions when placed in aqueous solution. Most solids that are commonly referred to as "insoluble" are actually slightly soluble and will produce an equilibrium between undissolved solid and ions in solution. For example, when copper (II) iodate $(Cu(IO_3)_2)$ is placed in water, the following equilibrium is established.

$$Cu(IO_3)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2IO_3^-(aq) \tag{1}$$

The equilibrium constant associated with this reaction is called the **solubility product constant** and is given the symbol $\mathbf{K}_{sp}$.

$$K_{sp} = [Cu^{2+}][IO_3^-]^2 \tag{2}$$

It is important to emphasize that the equilibrium in equation 1 is only true if some solid is present. If the solid completely dissolves in solution, then the product of the ions as shown in equation 2 is not equal to the K_{sp}. However, as long as some solid is in contact with solution, the solution will become saturated[1] with the ions according to equation 1.

The molar solubility[2] of a solid is the maximum number of moles of the solid that will dissolve in one liter of solution. Molar solubility is measured in moles/liter and has units of molarity (M). Molar solubility can be determined by measuring the concentration of the ions formed in a solution

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[1] http://en.wikipedia.org/wiki/Saturation_%28chemistry%29
[2] http://en.wikipedia.org/wiki/Molar_solubility

saturated with the solid. For example, if the molarity of Cu^{2+} in a solution saturated with $Cu(IO_3)_2$ can be determined, the stoichiometry in equation 1 indicates that this is also equal to the molarity of $Cu(IO_3)_2$ that dissolved in solution or its molar solubility. Alternatively, if the molarity of IO_3^- in a solution saturated with $Cu(IO_3)_2$ can be determined, the stoichiometry in equation 1 indicates that the molar solubility of $Cu(IO_3)_2$ in water is one half the $[IO_3^-]$ in solution.

In a saturated solution, if all the ions came from the solid, then the ratio of cations to anions is known. In the case of $Cu(IO_3)_2$, it is known that $2[Cu^{2+}] = [IO_3^-]$. Thus, if the Cu^{2+} concentration can be measured, the IO_3^- concentration can be calculated and vice versa. These concentrations can then be entered into the K_{sp} expression (equation 2) to solve for the solubility product constant of $Cu(IO_3)_2$.

The preceding discussion referred to dissolving the sparingly soluble salt in pure water. However, if some of the ions that are to be produced by the solid are present in solution from another source, Le Châtelier's Principle predicts that the equilibrium in equation 1 will shift to the left and less solid will dissolve. This would result in a lower molar solubility. This is referred to as the common ion effect[3]. In the example of $Cu(IO_3)_2$, the presence of either Cu^{2+} or IO_3^- in solution should result in a lower molar solubility than in pure water.

Earlier this semester in **Lab 2—Solutions and Spectroscopy**, you prepared a calibration curve for Cu^{2+} over the range of approximately 0.1 M to 0.4 M. As you may recall, Cu^{2+} in solution has a pale blue color and you were able to measure its absorbance around 630 nm. For this experiment, it is necessary to prepare a calibration curve for Cu^{2+} over the range of 5 x 10^{-4} M to 0.01 M. At these concentrations, the absorbance of Cu^{2+} is too low to detect directly by spectroscopy. To improve the absorbance of the Cu^{2+} solutions, aqueous ammonia (NH_3) will be added to each solution to produce the complex ion $Cu(NH_3)_4^{2+}$ according to the following reaction.

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq) \qquad (3)$$
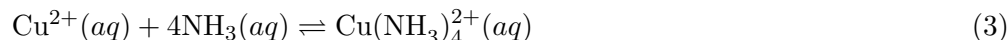
$Cu(NH_3)_4^{2+}$ in solution has a dark blue color and its absorbance at 600 nm can be measured over the range necessary for this experiment. The equilibrium constant associated with equation 3 is called the **formation constant** and is given the symbol K_f. The K_f for $Cu(NH_3)_4^{2+}$ is 4.8 x 10^{12}. which indicates that the forward direction of this reaction is greatly favored over the reverse. The result is that with a large excess of NH_3 present, essentially all of the Cu^{2+} ions are present as the complex ion, $Cu(NH_3)_4^{2+}$. Thus, we will make the assumption that the $[Cu(NH_3)_4^{2+}]$ that forms after NH_3 is added to a Cu^{2+} solution is equal to the $[Cu^{2+}]$ in the solution before the addition of NH_3.

In this experiment, you will prepare a calibration curve for $Cu(NH_3)_4^{2+}$ from four standard $Cu(NO_3)_2$ solutions. Then you will calculate the solubility product constant for $Cu(IO_3)_2$ from measurements of the $[Cu^{2+}]$ in five solutions saturated with $Cu(IO_3)_2$. You will also calculate the molar solubility of copper (II) iodate in pure water and in solutions containing Cu^{2+} and IO_3^- and compare your results to predictions of the common ion effect.

EQUIPMENT

15 13 x 100 mm test tubes

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[3]http://en.wikipedia.org/wiki/Common-ion_effect

5 stoppers

1 test tube rack

1 spatula

1 glass stir rod

1 MicroLab Spectrophotometer

1 MicroLab Spectrophotometer Instruction Sheet

6 vials

1 250 mL waste beaker

1 deionized water squirt bottle

1 box of Kimwipes

REAGENTS

~0.25 g solid $Cu(IO_3)_2$

~5 mL 5.0 x 10^{-4} M $Cu(NO_3)_2$

~10 mL 1.0 x 10^{-3} M $Cu(NO_3)_2$

~10 mL 5.0 x 10^{-3} M $Cu(NO_3)_2$

~5 mL 1.0 x 10^{-2} M $Cu(NO_3)_2$

~5 mL 5.0 x 10^{-3} M KIO_3

~5 mL 1.0 x 10^{-2} M KIO_3

~5 mL 3 M NH_3

deionized water

SAFETY

$Cu(NO_3)_2$ is listed as an oxidizer and corrosive. KIO_3 and $Cu(IO_3)_2$ are listed as strong oxidizing agents. NH_3 is corrosive. These chemicals can attack the skin and cause permanent damage to the eyes. If one of these solutions splashes into your eyes, use the eyewash immediately. Hold your eyes open and flush with water for at least 15 minutes. If contact with skin or clothing occurs, rinse the affected area with water for at least 15 minutes. Have your lab partner notify your teaching assistant about the spill and your exposure. The NH_3 solution also has irritating vapors. It should be used in a fume hood to avoid inhaling the vapors.

As with all chemicals in the lab, if you come in contact with a solid, you should gently brush off the affected area with a paper towel and then rinse the area with water. If you come in contact with a solution, you should rinse the affected area with water.

Students will have access to gloves due to the use of the concentrated ammonia solution during the lab period.

WASTE DISPOSAL

All solutions generated this week must be placed in the waste bottle in the lab. Designate a "waste" beaker and set it aside for use during your lab. You can put the small samples of solution you will make into this beaker and empty it into the waste bottle at the end of class, instead of going back and forth to the waste bottle. Always remember not to overfill the waste bottle. If your lab section's waste bottle is full, please alert your teaching assistant.

PRIOR TO CLASS

Please read the following sections of the Introductory Material:

Plotting a Calibration Curve[4]

Centrifuges[5]

Please complete your WebAssign prelab assignment. Check your WebAssign account for due dates. Students who do not complete the WebAssign prelab assignment are required to print and hand in the prelab worksheet.

LAB PROCEDURE

Please print the worksheet for this lab. You will need this sheet to record your data.

1 A spectrophotometer will be set up in your work area. Make sure it is plugged in and allow it to warm up.

2 While the spectrophotometer is warming up, label five clean, dry test tubes A - E and set up a beaker for waste.

3 Fill each of the five test tubes to 3/4 full with the following solutions.

$Cu(IO_3)_2$ Saturated Solutions	
A	1.0×10^{-2} M KIO_3
B	5.0×10^{-3} M KIO_3
C	deionized water
D	1.0×10^{-3} M $Cu(NO_3)_2$
E	5.0×10^{-3} M $Cu(NO_3)_2$

4 Using the spatula provided, add a small amount of solid $Cu(IO_3)_2$ to each of the five test tubes. A "small amount" means just a little bit on the smaller end of the spatula. If the solid dissolves entirely, you can always add some more solid to the test tube.

5 Stopper each of the test tubes. While holding the stopper in place, invert the tubes and agitate the contents for several minutes.

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[4]../graphs/manual.html
[5]../equipment/manual.html#centrifuge

6   Allow the test tubes to equilibrate for a minimum of 10 minutes. Agitate the solutions periodically while you work on your standard solutions.

7   Label four additional clean, dry test tubes 1 - 4. These will be the standards for the calibration curve.

8   Fill each of the four test tubes to 2/3 full with the following solutions. Try to fill each test tube to the same level.

Standard Cu^{2+} Solutions	
1	5.0×10^{-4} M $Cu(NO_3)_2$
2	1.0×10^{-3} M $Cu(NO_3)_2$
3	5.0×10^{-3} M $Cu(NO_3)_2$
4	1.0×10^{-2} M $Cu(NO_3)_2$

9   Add 12 drops of 3 M NH_3 to each of the four test tubes (1 - 4).

10   With the glass stir rod provided, gently mix each solution so the dark blue color is uniform throughout the test tube. Be sure to rinse and dry the stir rod between solutions to avoid cross-contamination and errors from dilution.

11   Following the detailed instructions for the spectrophotometer provided in lab, take a background spectrum.

12   Take a blank spectrum with deionized water. To condition your vial, carefully pour some deionized water into a vial and pour it out to waste then refill with deionized water.

13   Condition a vial using standard solution 1 and take an absorbance spectrum. **Identify the wavelength of maximum absorbance near 600 nm**. Record the wavelength and absorbance at this wavelength in Data Table A. Absorbance values are reported to the 0.0001. For all remaining absorbance measurements in this experiment, be sure to use the same wavelength you have identified as the maximum. Retain this sample in the vial until you have completed your calibration plot. Students often choose to label a sheet of paper with positions 1, 2, 3, and 4, placing each vial on the appropriate position.

14   Repeat step 13 for each of the remaining standard solutions and record their absorbances in Data Table A.

Table A: Absorbances of Standard Cu^{2+} Solutions

15   The MicroLab software will plot the absorbance of the Cu^{2+} solutions that you made as a function of their concentrations. The trendline and R^2 value are displayed. If your plot is linear with an R^2 value of 0.9 or greater, continue the experiment. If your R^2 value is low, consult with your teaching assistant. Record these in Data Table A. Do not close the MicroLab file, as this calibration curve will be used to determine Cu^{2+} equilibrium concentrations.

16   Once you are satisfied with your calibration curve, empty the four standard solution vials into your waste beaker and rinse each one with deionized water.

17 **Remove the stoppers** from the five test tubes labeled A - E that you prepared in steps 3 - 6. Place them in a centrifuge along with one additional tube filled 3/4 full with deionized water as a counter balance. Centrifuge the tubes for 2 full minutes. Allow the centrifuge to stop on its own so as not to agitate the solid present.

18 Label five additional clean, dry test tubes A - E.

19 Decant each of the five solutions from the centrifuge into the new test tube of the same label. Fill each to 2/3 full as you did for the standard solutions in step 8. Again, try to fill them to approximately the same level. When doing this, **be careful not to transfer any solid!** Do not start to pour and stop because this will stir up the solid and cause you to have to re-centrifuge the solution. If you over-decant, you may pour some back into the tube containing solid.

20 Add 12 drops of 3 M NH_3 to each of the five test tubes (A - E).

21 With the glass stir rod provided, gently mix each solution so the dark blue color is uniform throughout the test tube. Be sure to rinse and dry the stir rod between solutions to avoid cross-contamination and errors from dilution.

22 Condition a vial using solution A, refill the vial, and measure its absorbance. Remember that these next samples are not part of your calibration curve and should be read as unknown concentrations. Record this value in Data Table B. Be sure to use the same wavelength used in the calibration curve. Do not discard the solution until you have completed your measurements of solutions A - E.

23 Repeat step 22 for each of the remaining solutions and record their absorbances in Data Table B.

Table B: Absorbances of Solutions Saturated with $Cu(IO_3)_2$

24 Once you are satisfied with your results, empty the five vials into your waste beaker and rinse each one with deionized water.

25 When you are finished taking measurements, close the MicroLab software and unplug your spectrophotometer.

26 Collect all your copper solution waste and place it in the waste bottle in the lab, making sure not to overfill it. Rinse and dry all your glassware with water and return it to the set-up area where you found it.

Question 1: Using the trendline from your calibration curve, calculate the $[Cu^{2+}]$ in each of the solutions A - E. Show one representative calculation neatly. Enter these results in Data Table B.

Question 2: Calculate the $[IO_3^-]$ in each of the solutions A - E. Remember that for solutions A and B where IO_3^- was originally present, you must account for the initial amount plus any ions that were formed due to the solubility of the solid. Show one representative calculation neatly. Enter these results in Data Table B.

Question 3: Calculate the K_{sp} for each of the solutions A - E. Show one representative calculation neatly. Enter these results in Data Table C.

Table C: Calculated K_{sp} and Solubilities of $Cu(IO_3)_2$

Question 4a: Calculate the average of your five K_{sp} values. Enter the result in Data Table C.

Question 4b: The literature value for the K_{sp} of $Cu(IO_3)_2$ is 6.85×10^{-8}. How does this compare to your average experimental values? What is the percent error compared to your average?

$$\% \text{ error} = \frac{\text{experimental - theoretical}}{\text{theoretical}} \times 100$$

Question 5: Calculate the solubility of $Cu(IO_3)_2$ in each of the five solutions. Remember that for solutions D and E where Cu^{2+} was originally present, you must subtract the initial amount from the equilibrium amount to get the amount formed due to the solubility of the solid. Show one representative calculation neatly. Enter these results in Data Table C.

Question 6: Looking at your solubility results for solutions A and B as compared to C, did the solubility increase, decrease or stay about the same in the solutions that originally contained IO_3^- ions? Does this confirm the common ion effect? If not, can you explain why it does not?

Question 7: Looking at your solubility results for solutions D and E as compared to C, did the solubility increase, decrease or stay about the same in the solutions that originally contained Cu^{2+} ions? Does this confirm the common ion effect? If not, can you explain why it does not?

28 Remember to show your TA your calibration curve and calculated K_{sp} values. Your TA will manually grade the results and enter your score into WebAssign.

29 Before leaving, enter your results in the InLab assignment. If all results are scored as correct, log out. If not all results are correct, try to find the error or consult with your teaching assistant. When all results are correct, note them and log out of WebAssign. The InLab assignment must be completed by the end of the lab period. If additional time is required, please consult with your teaching assistant.