INTRODUCTION

Electrolytes are compounds that are present in solution as ions. They are more likely to be soluble in water than in most other liquids that are commonly used as solvents. For example, NaCl (sodium chloride) is fairly water soluble; about 6.1 moles of NaCl will dissolve in a liter of water at 25°C. But some electrolytes are only slightly water soluble; only about $10^{-4}$ mole of CaCO$_3$ (calcium carbonate, the main component of limestone) will dissolve in a liter of water at 25°C.

In this experiment you will determine the solubility of the slightly soluble electrolyte Cu(IO$_3$)$_2$, copper(II) iodate, for which the dissolving equilibrium is

$$\text{Cu(IO}_3\text{)}_2(s) \rightleftharpoons \text{Cu}^{2+}(aq) + 2\text{IO}_3^-(aq) \quad (22-1)$$

This equilibrium can be described by a solubility product constant, $K_{sp}$, which is calculated from molar concentrations of ions in a saturated solution of Cu(IO$_3$)$_2$:

$$K_{sp} = [\text{Cu}^{2+}][\text{IO}_3^-]^2 \quad (22-2)$$

TECHNIQUE

A saturated solution of Cu(IO$_3$)$_2$ in distilled water is prepared. Carefully measured 20-mL portions of this solution are taken, and the amounts of Cu$^{2+}$ and IO$_3^-$ contained in 20 mL are determined by a titration. Using this information, the solubility of the salt in moles/liter and the solubility product can be calculated.

An indirect procedure is used to determine the amounts of Cu$^{2+}$ and IO$_3^-$ in the saturated solution. Solid KI is added to the solution causing the following reactions to occur:

$$2\text{Cu}^{2+} + 5\text{I}^- \rightarrow 2\text{CuI}(s) + \text{I}_3^- \quad (22-3)$$
$$\text{IO}_3^- + 8\text{I}^- + 6\text{H}_3\text{O}^+ \rightarrow 3\text{I}_3^- + 9\text{H}_2\text{O} \quad (22-4)$$

For each mole of Cu(IO$_3$)$_2$ that dissolves and reacts with I$, 6 \frac{1}{2}$ moles of I$_3^-$ are produced; $\frac{1}{2}$ mole from the reaction of one mole of Cu$^{2+}$ and six moles from the reaction of two moles of IO$_3^-$. By determining the amount of I$_3^-$ produced, the quantity of Cu(IO$_3$)$_2$ originally present in the solution is calculated.

The amount of I$_3^-$ produced in the reactions of EQUATIONS 22-3 and 22-4 can be determined by titration with a standardized Na$_2$S$_2$O$_3$ solution using a starch indicator. Iodine forms a deep-blue complex with starch; the color will disappear when all the brown I$_3^-$ has been reconverted to colorless I$^-$ by its reaction with S$_2$O$_3^{2-}$:

$$2\text{S}_2\text{O}_3^{2-} + \text{I}_3^- \rightarrow \text{S}_4\text{O}_6^{2-} + 3\text{I}^- \quad (22-5)$$

**EQUATION 22-5** states that for each mole of I$_3^-$ in the solution, two moles of S$_2$O$_3^{2-}$ will be needed for the titration. Since each mole of Cu(IO$_3$)$_2$ produces $6\frac{1}{2}$ moles of I$_3^-$, each mole of Cu(IO$_3$)$_2$ originally present in the solution will require 13 moles of S$_2$O$_3^{2-}$. Knowing the molarity and the volume of the Na$_2$S$_2$O$_3$ solution used in the titration
permits the calculation of the number of moles of \( S_2O_3^{2-} \) used and of the number of moles of Cu(IO\(_3\))\(_2\) originally present in the solution.

First you must determine the molarity of the Na\(_2\)S\(_2\)O\(_3\) solution; this is called standardizing the solution. For a Na\(_2\)S\(_2\)O\(_3\) solution, this must be done shortly before the solution is used, for S\(_2\)O\(_3^{2-}\) is not stable in solution for extended periods of time. The solution that will be supplied is ~0.08 M, but its molarity must be determined to a greater number of significant figures. Weighed samples of KIO\(_3\) are dissolved in distilled water and then treated with excess I\(^{-}\) to produce I\(_3^{-}\) via the reaction of \textbf{Equation 22-4}. The I\(_3^{-}\) is then titrated with Na\(_2\)S\(_2\)O\(_3\) solution. Since the number of moles of IO\(_3^{-}\) is known from weighing, the number of moles of S\(_2\)O\(_3^{2-}\) required for the titration can be calculated from \textbf{Equations 22-4} and \textbf{22-5}. Because this number of moles must be contained in whatever volume of Na\(_2\)S\(_2\)O\(_3\) solution was used in the titration, the molarity can then be calculated.

\textbf{Equipment Needed}

<table>
<thead>
<tr>
<th>balance</th>
<th>buret clamp</th>
</tr>
</thead>
<tbody>
<tr>
<td>graduated cylinder</td>
<td>pipet pump or bulb</td>
</tr>
<tr>
<td>beaker</td>
<td>Erlenmeyer flasks</td>
</tr>
<tr>
<td>buret</td>
<td>funnel</td>
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<tr>
<td>10-mL volumetric pipet</td>
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</tbody>
</table>

\textbf{Chemicals Needed}

<table>
<thead>
<tr>
<th>Cu(IO(_3))(_2); copper(II) iodate (or a saturated solution)</th>
<th>KIO(_3); potassium iodate</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC(_2)H(_3)O(_2); glacial acetic acid</td>
<td>0.08M Na(_2)S(_2)O(_3); sodium thiosulfate</td>
</tr>
<tr>
<td>KI; potassium iodide</td>
<td>0.2% starch solution</td>
</tr>
</tbody>
</table>

\textbf{Procedure}

\textbf{A. Preparation of Saturated Cu(IO\(_3\))\(_2\) Solution}

Omit this part of the experiment if a saturated solution is supplied.

\textbf{B. Standardization of Na\(_2\)S\(_2\)O\(_3\) Solution}

Obtain about 150 mL of ~0.08 M Na\(_2\)S\(_2\)O\(_3\) in a beaker. The beaker must be clean, but it need not be dry; if it is wet, swirl the solution over the entire inside wall to wash all the water into the solution homogeneously. This is all of the Na\(_2\)S\(_2\)O\(_3\) solution that you will use for the entire experiment and is more than you should need. After the standardization, save the remaining Na\(_2\)S\(_2\)O\(_3\) solution. Clean a buret and rinse it with three 3- mL portions of the Na\(_2\)S\(_2\)O\(_3\) solution; then fill the buret with this solution.

Place a 125 mL Erlenmeyer flask on an analytical balance and tare the balance. Weigh 0.10–0.11 g of KIO\(_3\) into the flask and record the exact mass. Dissolve the KIO\(_3\) in 25–30 mL of distilled water.

Weigh ~0.8g of KI into a beaker, add it to the KIO\(_3\) solution, and swirl the flask until all of it dissolves. Add 2 mL of glacial acetic acid to this mixture and swirl the flask to mix it in homogeneously. The mixture should be brown in color because I\(_3^{-}\) is formed in the reaction of IO\(_3^{-}\) and I\(^{-}\).
CAUTION!: Glacial acetic acid is corrosive. If you get it on your skin, wash it off immediately under lots of cold, running water; if you spill any on the outside of the bottle or on the table top, sponge it off and wash out the sponge.

Immediately begin to titrate this mixture with the Na$_2$S$_2$O$_3$ solution. The brown color will gradually become lighter as S$_2$O$_5^{2-}$ converts I$_3^-$ to colorless I$^-$. When the solution is pale yellow, add 2 mL of starch solution to the mixture. (The cylinder that you used to measure acid does not have to be rinsed out before you measure starch, but it does have to be rinsed out before you measure acid again after measuring starch.) The remaining I$_3^-$ will form a deep-blue complex with the starch; if the color is brownish instead of blue, you can continue with the titration, but for the next titration you should let the solution become a lighter yellow before you add the starch. Titrate until the blue color just disappears showing that all of the I$_3^-$ has reacted.

Weigh out and titrate two more portions of KIO$_3$. If you have time, calculate the molarity of the Na$_2$S$_2$O$_3$ solution for each trial (see the Calculations and Results section below). If you do not have two consecutive titrations that agree within 1% for the molarity of the Na$_2$S$_2$O$_3$ solution, repeat the titration with new portions of KIO$_3$ until you do have this agreement. Note: you will record your three best trials onto the Chem21 report sheet.

To discard a solution after you finish a titration, wash it down the drain with lots of water.

C. Determination Of Cu(IO$_3$)$_2$ Solubility

Obtain ~40 mL (no more!) of the saturated Cu(IO$_3$)$_2$ solution. If the solution is cloudy, begin by removing any undissolved solid from the solution by filtration. Be sure the funnel and all glassware that you use in this filtration are clean and dry; do not wet the filter paper with water before you begin the filtration. Because you want to know the concentration of the solute in a saturated solution, it is essential that you do not dilute the solution. If the filtrate is cloudy, repeat the filtration. Filter all of the solution before you begin the titrations.

Pipet 10.00 mL of the clear filtrate, the saturated Cu(IO$_3$)$_2$ solution, into an Erlenmeyer flask (which must be clean, but not necessarily dry). Add about 10 mL of distilled water, 0.2 g of KI, and 1.0 mL of glacial acetic acid. Immediately titrate this solution with your standardized Na$_2$S$_2$O$_3$ solution following the same procedure you used in the standardization. Repeat the titration with two more 10.00-mL portions of the saturated Cu(IO$_3$)$_2$ solution. If you have time, calculate the molarity of the Cu(IO$_3$)$_2$ solution for each trial (see the Calculations and Results section below). If you do not have two consecutive titrations that agree within 1% for the molarity of the Cu(IO$_3$)$_2$ solution, repeat the titration with new portions of Cu(IO$_3$)$_2$ until you do have this agreement. Note: you will record your three best trials onto the Chem21 report sheet.

To discard a solution after you finish a titration, wash it down the drain with lots of water. Any unused Na$_2$S$_2$O$_3$ solution and Cu(IO$_3$)$_2$ solution may also be washed down the drain.
CALCULATIONS AND RESULTS

B. Standardization of Na₂S₂O₃ Solution

Calculate the number of moles of KIO₃ in each sample that you weighed. EQUATION 22-5 shows that two moles of S₂O₃²⁻ are required to titrate each mole of I⁻, and EQUATION 22-4 shows that each mole of IO₃⁻ in your sample KIO₃ produces three moles of I⁻. Thus, the number of moles of S₂O₃²⁻ used in a titration is six times the number of moles of KIO₃. This is the number of moles of S₂O₃²⁻ contained in the volume of Na₂S₂O₃ solution used in the titration. The molarity of the Na₂S₂O₃ solution can be calculated from the definition

\[ M = \frac{\text{moles S}_2\text{O}_3^{2-}}{\text{liters of solution}} = \frac{6 \text{(moles KIO}_3\text{)}}{\text{liters of Na}_2\text{S}_2\text{O}_3 \text{ solution}} \]  

(22-6)

Average your trials that agree within 1% and use this value as the molarity of the Na₂S₂O₃ solution in the remaining calculations.

C. Determination of Cu(IO₃)₂ Concentration

From the volume of Na₂S₂O₃ solution required to titrate the 10-mL portions of saturated Cu(IO₃)₂ and from the molarity of the Na₂S₂O₃ solution, calculate the number of moles of S₂O₃²⁻ used:

\[ \text{moles S}_2\text{O}_3^{2-} = M \text{(liters of S}_2\text{O}_3^{2-} \text{ used)} } \]  

(22-7)

From the information given in the INTRODUCTION

\[ \text{moles Cu(IO}_3\text{)}_2 = \frac{\text{moles S}_2\text{O}_3^{2-}}{13} \]  

(22-8)

This is the number of moles of Cu(IO₃)₂ contained in 10.00 mL of solution; use this to calculate the number of moles of Cu(IO₃)₂ in 1.000 L of solution, that is, the molarity of Cu(IO₃)₂ in a saturated solution. Because the solution is saturated, this concentration represents the molar solubility of Cu(IO₃)₂.

Write the concentration expression for \( K_{sp} \) of Cu(IO₃)₂, first in terms of molar concentrations of Cu²⁺ and IO₃⁻, and then in terms of molar solubility, \( s \).

For each of the titrations you carried out with the saturated Cu(IO₃)₂ solution, calculate \( K_{sp} \) using the value of \( s \) that you determined. For your reported value of \( K_{sp} \) take the average of the values you obtained for your best three trials.
**B. STANDARDIZATION OF Na$_2$S$_2$O$_3$ SOLUTION**

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<thead>
<tr>
<th></th>
<th>TRIAL 1</th>
<th>TRIAL 2</th>
<th>TRIAL 3</th>
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<tbody>
<tr>
<td>Mass of KIO$_3$</td>
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<tr>
<td>Moles of KIO$_3$</td>
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<tr>
<td>Moles of S$_2$O$_3^{2−}$ needed</td>
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<td>Volume of Na$_2$S$_2$O$_3$ used (mL)</td>
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<tr>
<td>Molarity of Na$_2$S$_2$O$_3$</td>
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<tr>
<td>Average molarity</td>
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For **TRIAL 1**, show the calculation of the molarity of the Na$_2$S$_2$O$_3$ solution.
C. Determination of Cu(IO₃)₂ Solubility

Average molarity of Na₂S₂O₃

<table>
<thead>
<tr>
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<th>TRIAL 1</th>
<th>TRIAL 2</th>
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<tbody>
<tr>
<td>Volume of Na₂S₂O₃ used (mL)</td>
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<tr>
<td>Moles of S₂O₃⁻² used</td>
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<tr>
<td>Moles of Cu(IO₃)₂ present</td>
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<td>_______</td>
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<tr>
<td>Volume of Cu(IO₃)₂ (mL)</td>
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<tr>
<td>Molarity of Cu(IO₃)₂</td>
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<tr>
<td>Molar solubility of Cu(IO₃)₂</td>
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<tr>
<td>$K_{sp}$</td>
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</table>

Average $K_{sp}$

For TRIAL 1, show the calculation of moles of Cu(IO₃)₂ present.

For TRIAL 1, show the calculation of molar solubility of Cu(IO₃)₂.

For TRIAL 1, show the calculation of $K_{sp}$. 
Notes
Experiment 22

Changes in Procedure:

- Omit Part A. The Cu(IO$_3$)$_2$ solution has already been prepared.
- Obtain ~40 mL of the Cu(IO$_3$)$_2$ solution—you shouldn’t any more than that, and it’s an expensive material!
- You should filter the Cu(IO$_3$)$_2$ solution prior to titration only if it is cloudy.

- **You will work in pairs on this experiment.**

Helpful Hints:

Use a disposable pipet to deliver the glacial acetic acid to the titration mixture.

Bureting tips:

- Make sure the buret is clean. Rinse the buret with water and then a small amount of thiosulfate solution before filling the buret.
- Remember to open the stopcock so that the buret tip is filled with solution before recording your initial volume reading. Record the initial volume at the bottom of the meniscus to **two decimal places**. Your initial volume does **not** have to be 0.00 mL.
- Swirl the flask continuously as you titrate.
- Rinse out the buret with water before returning!

- Titrate carefully! **Part of your grade will be determined by how close your calculate $K_{sp}$ is to the actual value.**