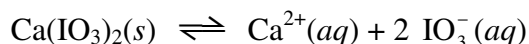CHM 106
The Solubility of Calcium Iodate

BACKGROUND

The purpose of this experiment is to measure the solubility product constant of calcium iodate at room temperature. A saturated solution of calcium iodate is governed by the following equilibrium:

$$Ca(IO_3)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ IO_3^-(aq)$$

From this equilibrium, we can write the equilibrium expression $K_{sp} = [Ca^{2+}][IO_3^-]^2$. In this experiment, you will determine the concentration of iodate in solution by titration with a solution of sodium thiosulfate ($Na_2S_2O_3$) using starch as an indicator. The concentration of the calcium ion is then determined by stoichiometry.

The iodate ions are reduced by iodide ions from KI added to each titration flask as shown by the following oxidation-reduction reaction:

$$IO_3^-(aq) + 5\ I^-(aq) + 6\ H^+(aq) \rightarrow 3\ I_2(aq) + 3\ H_2O(l)$$
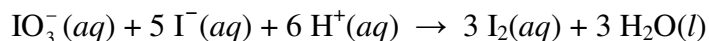
During the titration, this iodine reacts with thiosulfate to form tetrathionate and iodide:

$$2\ S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2\ I^-(aq)$$
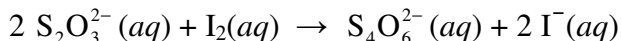
The net reaction for this titration can thus be obtained by adding the reactions together:

$$IO_3^-(aq) + 6\ S_2O_3^{2-}(aq) + 6\ H^+(aq) \rightarrow I^-(aq) + 3\ S_4O_6^{2-}(aq) + 3\ H_2O(l)$$
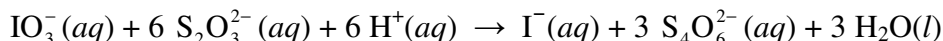
While the yellowish-brown color of the iodine can be used to follow the progress of the titration, it becomes difficult to see this color as concentration drops close to the end point. Also, colored species in solution may mask the iodine color. Because of these problems, we will use starch as an indicator, since it forms a highly colored complex with iodine.

Sodium thiosulfate solutions cannot be prepared accurately by weighing the solid because the sodium thiosulfate is slightly deliquescent[1] in air and it tends to decompose when heated to drive off water. Due to these properties, sodium thiosulfate solutions must be standardized against a primary standard.

Sodium thiosulfate solutions are also not stable over long periods of time. Sulfur-consuming bacteria tend to grow in solution, and their metabolic processes lead to the formation of sulfate, sulfite, and colloidal sulfur. The presence of the latter causes turbidity, which is a justification

---

[1] A deliquescent substance can absorb enough moisture from the air to dissolve the solid and form a concentrated solution.

for discarding the solution. In order to minimize this problem, the water used to prepare thiosulfate solutions can be boiled to render it sterile, and preservatives can be added to retard bacterial growth. Air oxidation of thiosulfate is slow, and the addition of a basic compound like sodium carbonate serves to inhibit both atmospheric and microbial oxidation.

Thiosulfate decomposes in acidic solutions to liberate sulfur as a milky precipitate. This reaction is kinetically slow and does not occur when thiosulfate is titrated into strongly acidic solutions of iodine, provided that the titration flask is well stirred. The reaction between iodine and thiosulfate is much more rapid that the reaction with hydrogen ions. Iodine oxidizes thiosulfate to tetrathionate; this reaction is rapid and goes to completion:

$$2 \ S_2O_3^{2-} \ (aq) + I_2(aq) \ \rightarrow \ S_4O_6^{2-} \ (aq) + 2 \ I^-(aq)$$
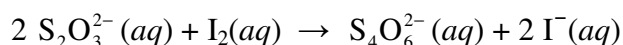
A number of primary standards are available to determine accurately the concentration of thiosulfate solutions. Pure iodine is the most obvious standard, but it is seldom used in practice due to difficulties associated with handling and weighing; iodine is volatile and sublimes under normal laboratory conditions. Commonly, a strong oxidizing agent is employed to liberate iodine from iodide. This type of process is called iodometry.

Potassium dichromate is a useful primary standard for redox reactions. It can be obtained in high purity, it has a high equivalent weight, it is nonhygroscopic, and the solid and its solutions are quite stable. The reaction with iodide is carried out in about 0.2 $\underline{M}$ to 0.4 $\underline{M}$ acid and is complete in five to ten minutes:

$$Cr_2O_7^{2-} \ (aq) + 6 \ I^-(aq) + 14 \ H^+(aq) \ \rightarrow \ 2 \ Cr^{3+}(aq) + 3 \ I_2(aq) + 7 \ H_2O(l)$$
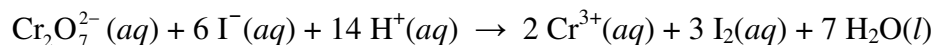
At acid concentrations greater than 0.4 $\underline{M}$, air oxidation of potassium iodide becomes appreciable. For best results, a small amount of a substance that reacts to form carbon dioxide is added to the titration flask. The carbon dioxide produced displaces air, after which the reaction mixture is allowed to stand until the reaction is complete. As in the case of iodate, we can add the above reaction to the oxidation of thiosulfate to obtain the overall reaction for the standardization:

$$Cr_2O_7^{2-} \ (aq) + 6 \ S_2O_3^{2-} \ (aq) + 14 \ H^+(aq) \ \rightarrow \ 2 \ Cr^{3+}(aq) + 3 \ S_4O_6^{2-} \ (aq) + 7 \ H_2O(l)$$
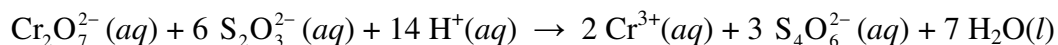
MATERIALS AND REAGENTS

Part A: $Na_2S_2O_3 \cdot 5H_2O$, Na_2CO_3, oven dried $K_2Cr_2O_7$ primary standard, concentrated H_2SO_4, KI, 1% starch solution, 1L bottle, 100 mL volumetric flask, 10 mL pipet, buret

Part B: 0.2 $\underline{M}$ KIO_3, 1 $\underline{M}$ $Ca(NO_3)_2$

Part C: KI, 2 $\underline{M}$ HCl, 1% starch solution, 10 mL pipet, buret

PROCEDURE

Part A will be performed during the first lab period. Parts B and C will be performed during the second lab period.

Part A: Standardization of Sodium Thiosulfate
Working in pairs, prepare the following solutions:

$Na_2S_2O_3$: Dissolve about 6.5 g of sodium thiosulfate pentahydrate and about 0.2 g sodium carbonate in 1 liter of water that has recently been boiled and cooled. Transfer this solution to a 1 L bottle and label the bottle as appropriate.

$K_2Cr_2O_7$: Using an analytical balance, weigh accurately about 0.5 g of oven dried primary standard potassium dichromate[2] and place it in a 100 mL volumetric flask. Add 5 mL of concentrated sulfuric acid, and dilute to volume. *Caution: concentrated sulfuric acid is very corrosive and will cause material damage to person and property!*

Working individually, pipet 10.00 mL of the dichromate solution into a 250 mL Erlenmeyer flask. Carefully add about 0.5 g of sodium carbonate[3] with gentle swirling to liberate carbon dioxide to the flask. Then add about 1 g of potassium iodide dissolved in about 5 mL of water[4], swirl, cover the flask with a watch glass, and allow the solution to stand for 3 minutes[5]. Dilute the solution to about 100 mL and titrate with the thiosulfate solution to be standardized until the yellowish color of iodine has nearly disappeared[6]. Then add several drops of starch solution and continue the titration until one drop of titrant removes the blue color of the starch-iodine complex. The final solution will be a clear emerald green, the color imparted by the chromium (III) ion. Repeat the titration as necessary to obtain a good average value for the concentration of thiosulfate.

Excess dichromate solutions must not be poured down the drain because chromium (VI) species are toxic and corrosive. This waste will be collected in a designated container in the hood.

Part B: Preparation of Calcium Iodate
Working in pairs, prepare pure solid calcium iodate by mixing 50 mL of 0.2 $\underline{M}$ KIO_3 and 20 mL of 1 $\underline{M}$ $Ca(NO_3)_2$. The mixture should stand about 5 minutes to ensure that the precipitation is complete. Separate and wash the solid $Ca(IO_3)_2$ with distilled water. Prepare about 100 mL of saturated calcium iodate solution by using about one-half of the solid compound. Allow 30 minutes for the solution to reach saturation, stirring continuously.

---

[2] Potassium dichromate is toxic and corrosive. It will damage the analytical balance if accidental spills are not cleaned up promptly.
[3] The purpose of the sodium carbonate is to remove air from the flask and decrease the danger of air oxidation of iodide. Adding too much carbonate will consume too much acid, and will interfere with the proper reaction of dichromate with iodide.
[4] Do not allow this solution to stand as the iodide may be oxidized by air.
[5] This reaction is somewhat slow but should be complete within this time.
[6] Starch should not be added to a solution containing a high concentration of iodine. The starch may be coagulated and the complex with iodine may not easily break up. This will result in a recurring endpoint in the titration.

Part C: Iodometric Determination of Iodate in Saturated Calcium Iodate
Working individually, pipet 10.00 mL of saturated calcium iodate solution into an Erlenmeyer flask. *Be careful not to disturb the solid calcium iodate on the bottom of the flask in which the solution was prepared! Exhaust your pipet bulb off the pipet and outside the solution.* Add 0.5 g solid potassium iodide, 1 mL of 2 $\underline{M}$ HCl, and dilute to a convenient volume. Titrate with standard thiosulfate solution until the yellowish color of iodine has nearly disappeared. Add several drops of the starch indicator, and titrate until one drop of titrant causes the blue color of the starch-iodine complex to disappear. The final solution in the titration flask should be colorless. Repeat the titration as necessary to obtain a good average value for the concentration of iodate.

REPORT

In part A, calculate the concentration of the primary standard dichromate solution you prepared. Using this value, calculate the concentration of the thiosulfate solution for each titration in part A. Average together all good trials, and report an average value for the thiosulfate concentration. Using this average thiosulfate concentration, determine the concentration of iodate in each titration of part C. Once again, average together all good trials in part C and report an average concentration of iodate in saturated calcium iodate solution. From this value, calculate the molar solubility of calcium iodate and K_{sp}. Given that the reference value for $Ca(IO_3)_2$ is $K_{sp} = 6.47 \times 10^{-6}$, calculate the percentage error in your determination.

QUESTION

Suppose that tap water, which contains significant amounts of Ca^{2+} ions, was accidentally used while preparing the saturated calcium iodate solution in part B. What effect would this have on the molar solubility and calculated value of K_{sp} for calcium iodate? Explain.