E10

Chemical Equilibria: K_{sp} of Calcium Iodate

Objective

- Understand the relation between the molar solubility and the solubility product constant of a sparingly soluble salt.
- Measure the molar solubility of calcium iodate in pure water and determine the solubility product constant.
- Investigate the common ion effect by measuring the molar solubility of calcium iodate in a solution containing added potassium iodate.

Discussion

K_{sp} *and Molar Solubility*

Calcium iodate, a salt whose solubility you will study in this experiment, undergoes the following equilibria in aqueous solution:

$$Ca(IO_3)_2(s) \rightleftarrows Ca^{2+}(aq) + 2\ IO_3^-(aq) \qquad (1)$$

Reaction (1) shows the dissociation of solid[1] $Ca(IO_3)_2$ in a saturated aqueous solution. The equilibrium constant expression for this reaction (often called the *solubility product* expression) is written as shown in Equation (2), observing the convention that the activity (or effective concentration) of the pure solid is taken to be equal to 1.00 so that it does not appear in the equilibrium constant expression[2]

$$K_{sp} = [Ca^{2+}][IO_3^-]^2 \qquad (2)$$

For any salt that dissolves to give just the ions originally present in the salt, there is a simple relation between the molar solubility of the salt and the solubility product constant of the salt. The concentration of each ion will be equal to the molar solubility or to some multiple of it.

What do we mean by the molar solubility of the salt? This quantity is just the concentration of the dissolved salt, expressed in units of moles per liter. In the calcium iodate example, the calcium ion concentration is equal to the molar solubility; the iodate ion concentration is equal to two times the molar solubility. This is true because each mole of calcium iodate that dissolves gives one mole of calcium ions and two moles of iodate ions.

If we let the symbol ***s*** represent the molar solubility of calcium iodate (in units of moles per liter), the concentrations of Ca^{2+} and IO_3^- ions will be related to the molar solubility, ***s***, by the equations

$$[Ca^{2+}] = \boldsymbol{s} \qquad (3)$$

$$[IO_3^-] = 2\boldsymbol{s} \qquad (4)$$

If we substitute for the concentration of each ion by its equivalent in units of molar solubility, ***s***, as in Equations (3) and (4) and substitute these into Equation (2), we obtain an equation that shows a simple relation between the K_{sp} and the molar solubility of the salt:

---

[1] The actual form of the solid is the hexahydrate, $Ca(IO_3)_2 \cdot 6H_2O(s)$.

[2] As we have discussed in lecture, the effective concentration (or activity) of a pure solid is constant.

$$K_{sp} = [Ca^{2+}][IO_3^-]^2 = s(2s)^2 = 4\,s^3 \qquad (5)$$

A frequently asked question about this expression is, “Why are you doubling the concentration of IO_3^- and then squaring it?” The short answer is that we aren’t doubling the concentration of IO_3^-; its concentration is equal to 2s. {Consider the ICE table.}

The solubility of $Ca(IO_3)_2$ in KIO_3 solution: The common ion effect

From Le Châtelier’s principle we would predict that the molar solubility of calcium iodate would be smaller in a solution of potassium iodate, KIO_3, which is a strong electrolyte that completely dissociates in water. The hypothesis is that the addition of KIO_3 would shift the equilibrium shown in reaction (1) toward the left, decreasing the amount of calcium iodate that dissolves. Such a decrease in solubility, which occurs when a salt is dissolving in a solution that already contains one of the salt’s ions, is called the ***common ion effect***.

To test this hypothesis, you will measure the solubility of calcium iodate in 0.01 M KIO_3. Under these conditions, the concentrations of the ions will be related to the molar solubility of $Ca(IO_3)_2$ in the following way [compare Equations (6) and (7) with Equations (3) and (4)]:

$$[Ca^{2+}] = \boldsymbol{s} \qquad (6)$$

$$[IO_3^-] = 0.01 + 2\boldsymbol{s} \qquad (7)$$

Note that all of the calcium ion must come from dissolved calcium iodate. However, the iodate ion comes from both KIO_3 and dissolved $Ca(IO_3)_2$. As before, we get two moles of iodate ions and one mole of calcium ions for every mole of calcium iodate that goes into solution.

The relation between the solubility product constant and the molar solubility will also be changed {compare Equation (8) with Equation (5)}.

$$K_{sp} = [Ca^{2+}][IO_3^-]^2 = s(0.01 + 2s)^2 \qquad (8)$$

If we know the concentration of potassium iodate, a single measurement of the total iodate concentration allows us to calculate the molar solubility of calcium iodate and the solubility product constant.

Determining the molar solubility of calcium iodate

When calcium iodate dissolves in solution, both the solid and the solution remain electrically neutral. This is called the electroneutrality principle, meaning that in the case of calcium iodate, two IO_3^- ions will go into solution for each Ca^{2+} ion that goes into solution. So molar solubility can be determined by measuring either the concentration of calcium ion or the concentration of iodate ion. We will use a procedure for measuring the IO_3^- concentration that makes use of the fact that IO_3^- oxidizes iodide ion:

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O \qquad (9)$$

The I_2 produced is in turn titrated with sodium thiosulfate:

$$2\,S_2O_3^{2-} + I_2 \rightarrow 2\,I^- + S_4O_6^{2-} \qquad (10)$$

From the overall stoichiometry (sum of the two reactions) we see that each mole of IO_3^- will produce enough I_2 to consume 6 mol of $S_2O_3^{2-}$. Therefore, the concentration of IO_3^- ion will be given by

$$[IO_3^-](\text{mol/L}) = M\cdot V(S_2O_3^{2-})/V(IO_3^-) \text{ x } 1 \text{ mol } IO_3^-/6 \text{ mol } S_2O_3^{2-} \tag{11}$$

Experimental Procedure

Supplies: 25- or 50-mL buret; two 10-mL pipets or graduated cylinders.

Chemicals: Standardized 0.05 M sodium thiosulfate ($Na_2S_2O_3$) solution. KI(s); 1 M HCl; 0.1% starch indicator solution; saturated solution of $Ca(IO_3)_2{\bullet}6\ H_2O$ in pure water; saturated solution of $Ca(IO_3)_2{\bullet}6\ H_2O$ in 0.0100 M KIO_3. The saturated solutions should be prepared a week in advance.

1. The Molar Solubility of $Ca(IO_3)_2$ in Pure Water

Record the exact concentration of the sodium thiosulfate ($Na_2S_2O_3$) titrant in your notebook. Also record the temperature of the saturated calcium iodate solutions.

Fill a 50-mL buret with 0.050 M sodium thiosulfate solution, taking care to rinse the buret and to expel all bubbles from the tip of the buret. Obtain about 30 mL of saturated calcium iodate solution in a clean, dry flask. (The sample must not show any visible solid particles of undissolved calcium iodate.) To insure that there are no solid particles of undissolved calcium iodate filter the 30mL solution through a short neck funnel into a beaker or Erlenmyer flask. Put 50 mL of deionized water and 2 g of KI into a 250-mL Erlenmeyer flask and swirl to dissolve the KI. Then, using a pipet-filling device fill a 10.00 mL Mohr or volumetric the pipet with filtered saturated calcium iodate solution and transfer into the 250-mL flask and add 10 mL of 1.0 M HCl. (10-mL graduated cylinders may be used to measure the 1.0 M HCl solution.) When the HCl is added, the solution should turn brown. Without delay, titrate the solution with the standardized 0.05 M sodium thiosulfate until the solution is yellow. Then add 5 mL of 0.1% starch indicator. The solution should turn blue-black, the color of the starch–iodine complex. Continue the titration until you get a sharp change from blue to a colorless solution. Record the final buret reading. Repeat the titration procedure with a second sample. The volumes should agree to within 5%. (A possible source of error is the air oxidation of I^- to give I_2. If the solution is allowed to stand for too long before it is titrated, the oxidation will produce values that are too high.)

Calculations: Calculate the concentration of iodate ion in the sample of saturated solution {see Equation (11)}. The molar solubility of calcium iodate will be equal to one half the iodate concentration {see Equations (3) and (4)}. Calculate the solubility product constant for calcium iodate {see Equation (5)}.

2. The Molar Solubility of Calcium Iodate in 0.0100 M Potassium Iodate

Filter ~30mL of the saturated calcium iodate solution in 0.0100 M KIO_3 through a short neck funnel. Titrate two 10-mL samples of the saturated solution of $Ca(IO_3)_2$ in 0.0100 M KIO_3.

Calculations: Calculate the total iodate concentration as in part 1. Subtract 0.0100 M from the total concentration to obtain the concentration of iodate ion that comes from dissolved calcium iodate. Divide this result by 2 to obtain the molar solubility of calcium iodate. Is it smaller, as we predicted from Le Châtelier's principle? Calculate the solubility product constant for calcium iodate {see Equation (8)}. Does the calculated value of Ksp agree with the value for Ksp calculated in part 1? Note that a 10% error in measuring the molar solubility, ***s***, will lead to a larger error in the calculation of K_{sp}, because K_{sp} depends on $\mathbf{s}^3$ — cubing the number magnifies the error.

E10 Chemical Equilibria: K_{sp} of Calcium Iodate

Report Form

Name: ____________________ Partner's Name: __________________(if any)_Lab Section: MW/TTH/M-TH
(*circle*)

Advanced Study Assignment:

1. How is the molar solubility of a slightly soluble salt defined? Give an example.

2. What is the common ion effect?

3. How will we test the common ion effect in this experiment?

4. How will we measure the amount of IO_3^- ions that are dissolved in the solution when equilibrium is reached?

5. The amount of IO_3^- ions dissolved in solution will be determined by titration. What is the indicator for the end-point of the titration and what color change occurs?

E10 Chemical Equilibria: K_{sp} of Calcium Iodate
Report Form

Name: ____________________ Partner's Name: _________________(if any)_Lab Section: MW/TTH/M-TH
(*circle*)

Data and Calculations

☐ Standardization of the sodium thiosulfate solution (optional)

Volume of 0.0100 M KIO_3 samples ______________ mL

Data	Trial 1	Trial 2	Trial 3
Volume of $Na_2S_2O_3$ titrant Final buret reading	mL	mL	mL
Initial buret reading	mL	mL	mL
Net volume of $Na_2S_2O_3$	mL	mL	mL
Calculated concentration of $Na_2S_2O_3$	M	M	M

For each trial, calculate the concentration of $Na_2S_2O_3$; show a sample calculation in the space below.

Record Concentration from bottle here!
Average $Na_2S_2O_3$ concentration ______________ M

(If you did not perform the standardization procedure in part 1, record here the concentration of the sodium thiosulfate titrant, $Na_2S_2O_3$.)

1. The molar solubility of $Ca(IO_3)_2$ in pure water

Temperature of the saturated solution of calcium iodate: ______________ °C

Volume of saturated calcium iodate solution titrated: ______________ mL

Data	Trial 1	Trial 2	Trial 3
Volume of $Na_2S_2O_3$ titrant Final buret reading	mL	mL	mL
Initial buret reading	mL	mL	mL
Net volume of $Na_2S_2O_3$	mL	mL	mL
Calculated concentration of IO_3^-	M	M	M

For each trial, calculate the concentration of IO_3^-; show a sample calculation in the space below.

Average IO_3^- concentration ______________ M

Chemical Equilibria: K_{sp} of Calcium Iodate
Report Form

Calculate the molar solubility of $Ca(IO_3)_2$ in pure water from the average value of the IO_3^- concentration.

Molar solubility: ______________ mol/L

Calculate the solubility product constant, K_{sp}, for a saturated solution of $Ca(IO_3)_2$ in water .

K_{sp} = ______________

2. **The molar solubility of calcium iodate in 0.0100 M potassium iodate**

Temperature of the saturated solution of calcium iodate: ______________ °C

Volume of saturated calcium iodate solution titrated: ______________ mL

Data	**Trial 1**	**Trial 2**	**Trial 3**
Volume of $Na_2S_2O_3$ titrant Final buret reading	mL	mL	mL
Initial buret reading	mL	mL	mL
Net volume of $Na_2S_2O_3$	mL	mL	mL
Calculated concentration of IO_3^-	M	M	M

For each trial, calculate the concentration of IO_3^-; show a sample calculation in the space below.

Average IO_3^- concentration ______________ M

Subtract the concentration of IO_3^- ion that came from the KIO_3 from the average value of the total IO_3^- concentration to get the iodate ion concentration that came from dissolved $Ca(IO_3)_2$.

Total IO_3^- concentration ______________ M

IO_3^- concentration from KIO_3 ______________ M

IO_3^- concentration from dissolved $Ca(IO_3)_2$ ______________ M

Calculate the molar solubility of $Ca(IO_3)_2$ in 0.0100 M KIO_3 solution.

Molar solubility ______________ mol/L

Chemical Equilibria: K_{sp} of Calcium Iodate
Report Form

Compare the molar solubility of $Ca(IO_3)_2$ in 0.0100 M KIO_3 solution with the molar solubility in pure water, determined in part 2. Is the change consistent with Le Châtelier's principle?

Calculate the solubility product constant, K_{sp}, for a saturated solution of $Ca(IO_3)_2$ in 0.0100 M KIO_3 [see Equation (13)].

Considering the magnitude of possible errors in the determination of molar solubility (of the order of 10% maximum error in careful work), is there reasonable agreement between the K_{sp}'s calculated in parts 1 and 2?

Chemical Equilibria: K_{sp} of Calcium Iodate
Report Form

Calculate the molar solubility, s, of calcium iodate in 0.020 M $Ca(NO_3)_2$, a completely dissociated strong electrolyte. (NO_3^- ion does not chemically interact with either Ca^{2+} or IO_3^-.) Assume that K_{sp} for $Ca(IO_3)_2 = 2.0 \times 10^{-6}$.

To set up the problem, we can write the following equations:

Material balance for calcium: $[Ca^{2+}] = s + 0.020$

Material balance for iodate: $[IO_3^-] = 2s$

$$K_{sp} = 2.0 \times 10^{-6} = [Ca^{2+}][IO_3^-]^2 = (s + 0.020)(2s)^2$$

The last equation contains only one unknown, the value of s, which we would like to calculate; but s is not negligible compared to 0.020, which leaves us with a nasty equation that is cubic in s. An approach that often works in a situation like this is to rearrange the equation into a more useful form and obtain s by iteration. Thus, we can write

$$4s^2 = \frac{K_{sp}}{s + 0.020} \qquad \text{or} \qquad s = \frac{1}{2}\left(\frac{K_{sp}}{s + 0.020}\right)^{1/2}$$

We must find the value of s that makes both sides of the equation equal. Start first by inserting a trial value of s (say, 0.006 M) in the right-hand side of the latter equation and calculating a value of s. You will get $s = 0.00438$. For your next trial value, take something about halfway between 0.00438 and 0.006. Continue the iteration process until you calculate a value of s that is nearly the same (within 5%) as the value you inserted on the right-hand side of the equation.

If your data for solubility were obtained at a temperature different from 25 °C, estimate the solubility at 25 °C from your data. Around 25 °C, the molar solubility of calcium iodate in water increases with temperature about 4.5% per degree. Calculate the molar solubility at 25 °C, s_{25}, by correcting your value determined at t °C, which we will call s_t, using the equation

$$s_{25} = s_t\left[\frac{2 - 0.045(t - 25)}{2 + 0.045(t - 25)}\right]$$

where t is the temperature (°C) of the saturated solution that you analyzed. Ramette (see the Bibliography) quotes the molar solubility of $Ca(IO_3)_2$ in pure water at 25 °C as 0.00798 mol/L. Compare your result with the literature value by calculating the percentage relative difference:

$$\text{percentage relative difference} = \frac{s_{25} - 0.00798}{0.00798} \times 100\%$$