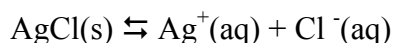


The Solubility Product Constant of Calcium Iodate

Background

Weak acids and bases are not the only aqueous ionic equilibrium systems commonly encountered. Ionic solids (some of which are the products of the reactions of acids and bases) have varying solubilities in water and quite a few are practically "insoluble". When these solids are added to water, agitated, and allowed to equilibrate, *saturated solutions* result.

The equilibrium in a saturated solution differs from the ionic equilibrium in aqueous acids and bases in an important way: it is heterogeneous. The solid material is in contact with a liquid aqueous phase containing separated ions of the solid. Ions move back and forth from the aqueous phase to the solid phase at the same rate. Using silver chloride as an example, the equilibrium reaction is represented:



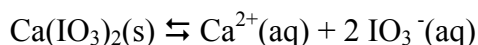
For an "insoluble" solid, the equilibrium lies far to the left and the ion concentrations in solution are very small. An equilibrium constant for this process would not include the solid reactant which is said to have "unit activity", i.e., its activity = 1. Remember that equilibrium constants are actually defined in terms of activities, not Molarities. We use molar concentrations as a convenient approximation.

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

Because of the established convention for writing these "solubility product constants", it is possible to restate these expressions in terms of the molar solubility of the salt. If we let "s" be the amount of AgCl that actually does dissolve (i.e., the solubility) the stoichiometry in the reaction above tells us that this same amount of silver ions and chloride ions will be present in the solution at equilibrium. We can substitute this variable for the molar concentrations in the K_{sp} :

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (s)(s) = s^2$$

A similar analysis can be used for salts which are not simple binary combinations of ions, following the stoichiometry of the dissolving process. For example, in this experiment the sparingly soluble salt calcium iodate, $\text{Ca}(\text{IO}_3)_2$, is used. In water this salt would dissolve to a very small extent according to the reaction:



The balanced equation shows that for each calcium ion in solution there should be two iodate ions. Thus if "s" amount of calcium iodate goes into solution, the concentrations of ions present should be "s" of calcium and "2s" of iodate:

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{IO}_3^-]^2 = (s)(2s)^2 = 4s^3$$

This kind of expression is frequently confusing to students because of the multiple appearance of the stoichiometric coefficient "2". The different occurrences have distinct meanings. The exponent of "2" on the iodate ion is part of the form of the equilibrium constant that results from the Law of Mass Action. This is standard procedure in writing any equilibrium constant: coefficients become exponents.

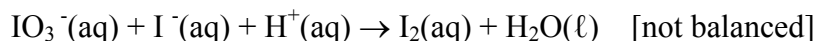
The appearance of the "2" as a coefficient before the "s" in the position of iodate ion is different. In the actual K_{sp} expression this "2" is not required since it is clear that two different ions are represented and presumably each has its own concentration. Those concentrations are stoichiometrically related in the case of the solid dissolving in water, but they need not be. If calcium nitrate and potassium iodate solutions of arbitrary concentrations are mixed together, the ions will probably not be in a 1:2 concentration ratio. Hence, no coefficient is inserted in the K_{sp} expression.

When the expression is rewritten in terms of molar solubility ("s"), however, a single variable must carry the necessary information: in this case, the fact that there are twice as many iodate ions as calcium ions in this mixture because that is the stoichiometry of the dissolving process. Therefore the "2" is needed for the "s" which takes the place of iodate ion.

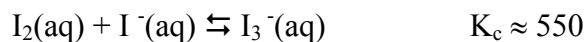
The fixed stoichiometric relationship between the ions in a sparingly soluble salt solution suggests an avenue for the determination of their concentrations and, eventually, the value of the K_{sp} . In fact, it is only necessary to find the concentration of one of the ions because the other must be related to it by the stoichiometric ratio. In the case of calcium iodate there is a fairly straightforward analytical method for determining the iodate ion in solution. Once the iodate concentration in a saturated solution is determined this is equivalent to "2s" in the earlier expression of the K_{sp} .

Although calcium iodate is relatively insoluble it is not practical to mix various concentrations of soluble calcium salts and iodate salts and determine when a precipitate forms since the kinetics of this process are slow and equilibration is also slow. The opposite approach has been taken for this investigation. Calcium iodate was synthesized from calcium nitrate and potassium iodate and then purified. The purified solid was used to prepare a saturated solution.

The actual determination of the amount of calcium iodate in solution is based on the fact that iodate ion is a fairly good oxidizing agent and will oxidize *iodide* ion in acidic solution:

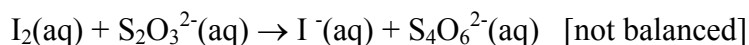


Because iodine in solution is somewhat volatile and subject to oxidation by the air it is generally stabilized in such circumstances by using an excess of iodide so that the following equilibrium lies far to the right



The presence of triiodide ion (I_3^-) imparts a dark orange to reddish color to the solution.

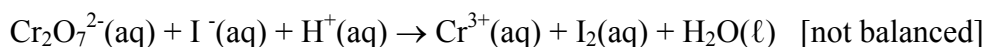
Once the iodate in solution has been converted to triiodide ion, the free iodine in solution can be titrated with standardized thiosulfate:



As the iodine is consumed the equilibrium with triiodide shifts, supplying more iodine until all of the iodine has been consumed. This is a fast process so there is no discernable lag time in the titration.

As you have seen in earlier experiments, thiosulfate (from sodium thiosulfate) is not a good primary standard for accurate work because the solid cannot be readily dried without decomposing. It must therefore be standardized before use. Among the many possible primary standards, potassium dichromate ($K_2Cr_2O_7$) is perhaps one of the more interesting. It has fallen out of favor because Cr(VI) species have been implicated as carcinogens. Handling of the solid by students preparing standard solutions is therefore problematic and disposal of dichromate (or chromate) solutions in the public sewer system is not allowed. Still, the reaction is a good one to see and so we will use it here, but the standardization will be carried out by the instructor as a demonstration, thereby minimizing both the hazard and the amount of material used.

In the standardization titration, a known amount of dichromate ion reacts with excess iodide ion in acidic solution, oxidizing it to iodine (triiodide):



The reduction of dichromate to Cr^{3+} is accompanied by a color change from orange to sky blue. However the presence of triiodide makes this transition difficult to discern. In order to further sharpen all thiosulfate endpoints in this experiment, starch indicator is also used. Recall that starch forms an intensely colored dark blue complex with iodine. Once all of the iodine has been consumed, this color disappears. In the standardization titrations the light blue color of the Cr^{3+} remains. *In the actual titrations of calcium iodate solution, the final mixture is colorless.*

The experiment, as described so far, is fairly straightforward. It might be expected that for a solution with as few ions present as a saturated solution of a sparingly soluble salt concerns about real solution behavior would be minimal. The assumption made in the experiment that $[Ca^{2+}] = [IO_3^-]/2$ is not, however, completely valid except at extremely low concentration since other combinations of ions such as $CaIO_3^+$ may exist in the saturated solution. It can be demonstrated that the K_{sp} value is sensitive to ionic strength and accurate work requires the determination of the K_{sp} at "zero" ionic strength. This is sometimes known as the thermodynamic equilibrium constant, K_{th} :

$$K_{th} = (a_{Ca^{2+}})(a_{IO_3^-})^2$$

In this expression the ion concentrations are expressed as their activities. Recall that as a solution approaches infinite dilution the activity approaches the Molarity (strictly, the molality). How can we dilute a saturated solution and still determine the concentration of the ions present?

The answer lies in the addition of *foreign ions*. If a series of saturated solutions of calcium iodate is prepared, each with a progressively lower concentration of foreign ions present (in this experiment, potassium nitrate), the effect of decreasing the ionic strength of the solution can be observed.

We have seen in earlier work that $a = \gamma m$ (or, for our purposes, γM). The K_{th} expression could thus be written as:

$$K_{th} = \gamma_{Ca^{2+}} [Ca^{2+}] \gamma_{IO_3^-}^2 [IO_3^-] = \gamma_{\pm}^3 K_{sp}$$

As the solution becomes more dilute (i.e., as the concentration of foreign ions decreases), the value of γ approaches 1 and the K_{sp} determined under those conditions approaches the K_{th} .

We have seen before that the activity coefficient, γ , is not easy to measure. It is related, however, to the ionic strength of the solution, I , which can be calculated from the molar concentrations of the ions present:

$$\log \gamma = -A z^2 \sqrt{I}$$

$$\text{where } I = \frac{1}{2} \sum c_i z_i^2$$

A is an empirical constant for the solvent at a given temperature (0.5091 for water at 298 K), z is the charge on the ion and c is the molar concentration of each ion [including the foreign ions].

[A combined activity coefficient such as the γ_{\pm}^3 in the earlier expression maintains its proportionality to \sqrt{I} . The various ion charges are simply multiplied together and become part of the numerical constant, Az^2]

Extrapolation of the titration data to zero ionic strength may be done graphically once the apparent K_{sp} value for each titration has been determined in the simple approximation. Taking the log of both sides of the K_{th} expression we obtain:

$$\log K_{th} = 3 \log \gamma_{\pm} + \log K_{sp}$$

Rearranging:

$$\log K_{sp} = -3 \log \gamma_{\pm} + \log K_{th}$$

$$\log K_{sp} = 3 Az_{\pm}^2 \sqrt{I} + \log K_{th}$$

$$y = m x + b$$

A plot of $\log K_{sp}$ vs. \sqrt{I} should therefore yield a straight line where the y-intercept can be used to evaluate the K_{sp} at infinite dilution (or K_{th}).

The Experiment

There are two parts to this experiment:

- standardization of the thiosulfate solution
- titration of the saturated calcium iodate solutions

The following non-locker materials will be provided:

- 5 saturated solutions of $\text{Ca}(\text{IO}_3)_2$ in various concentrations of KNO_3
- six 125 mL flasks w/stoppers
- solid KI
- 1 M H_2SO_4
- starch indicator
- approx. 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$

The Chemicals

Calcium iodate exists as nonhygroscopic crystals with limited solubility in water (0.10 g/100 mL at 0°C). It is used as a nutritional source of iodine in foods and feedstuffs (pet food also) and is more stable in table salt than iodides. The anhydrous salt was formerly used as a topical antiseptic.

Potassium nitrate is commonly known as "saltpeter". It is a colorless, odorless solid with a saline, pungent taste. It is used in fireworks, pickling brines, the manufacture of glass, matches, gunpowder, freezing mixtures and candle wicks.

Sodium thiosulfate (photographer's "hypo") is most commonly obtained as a pentahydrate in colorless, odorless crystals or granules. It melts at 48°C and has a tendency to form supersaturated solutions. The compound dissolves silver halides and many other salts of silver. It is used as a fixer in photography, for extraction of silver from ores, as a mordant in dyeing and printing textiles and in the manufacture of leather. The compound has relatively low toxicity. Large doses orally cause purging.

Potassium dichromate consists of bright orange-red crystals which are soluble in water. It is used in tanning leather, in dyeing, painting, decorating porcelain and in pyrotechnics. Taken internally the compound is a corrosive poison (30 g is fatal within 35 minutes). Industrial contact may result in ulceration of the skin. Chromates have been reported as causing cancer of the lungs. Chromates and dichromates contain chromium in oxidation state VI and constitute an environmental as well as medical hazard.

Sulfuric acid is a clear, colorless, oily liquid in concentrated form (98%). It is highly corrosive and has a high affinity for water, abstracting it from wood, paper, sugar, etc., leaving a carbon residue behind. Dilution of concentrated sulfuric acid generates a tremendous amount of heat. Here in the lab your instructor prepares the dilute sulfuric acid you use by pouring the concentrated acid slowly over ICE while stirring! Even so, the resulting solution is very warm. As with all acid dilutions, acid is added to water, not the reverse, since the heat generated can boil the water at the point of contact and cause spattering.

Sulfuric acid is used to make fertilizers, explosives, dyes, parchment paper, and glue. It is used, in concentrated form, in automobile batteries as the electrolyte. It is corrosive to all body tissues and contact with eyes may result in total blindness. Ingestion may cause death. Frequent skin contact with dilute solutions may cause dermatitis.

Potassium iodide is a white solid, slightly deliquescent, and prone to oxidation in air. It is used in the manufacture of photographic emulsions, and in table salt and some drinking water to help prevent iodine deficiency disease.

Starch (soluble starch, *amyloextrin*) is a white, odorless, tasteless powder which is soluble in water when heated. It is frequently used in the lab as an indicator for iodometric analysis since it forms an intense blue-to-black complex with I_2 but not with I^- .

Technique Discussion

Standardization of the thiosulfate solution will be demonstrated by the instructor. A solution of potassium dichromate is prepared using about 0.2 g of the solid (analytical balance) and dissolving it in 50 mL of water in a volumetric flask. The exact mass of dichromate will be given during the demonstration titration. **BE SURE TO RECORD THIS VALUE!**

A solution of potassium iodide is needed to react with the oxidizing agent (either dichromate or iodate). Iodide solutions are slowly oxidized in air and therefore should be prepared fresh. 20 mL of distilled water is added to 8 g of KI in a clean 50 mL beaker. The beaker is covered with a watch glass to minimize air oxidation.

8 mL of 1 M sulfuric acid is added to three clean Erlenmeyer flasks and 2 mL of the standard dichromate solution is pipetted into each. 2 mL of the prepared iodide solution is then added to each and swirled to mix. The flasks are stoppered and allowed to stand for about 10 minutes. A "blank" is prepared in the same way, substituting distilled water for the dichromate solution and also adding 2 mL of starch indicator. The blank is needed to account for any oxidation of the KI solution during handling.

After 10 minutes each solution is titrated with thiosulfate, adding just enough until the orange color begins to fade. 2 mL of starch indicator is then added and the titration continues until the color of the starch/iodine complex disappears and the solution is light blue (Cr^{3+}).

If no blue color has developed in the "blank" during the standing period, it is discarded. If air oxidation has occurred, there will be blue and this is discharged with thiosulfate, drop-by-drop. This blank volume should be subtracted from the mean volume needed for the standardization titrations.

A solution of potassium iodide should be prepared as for the standardization titrations. The flasks provided for the titrations may be labeled appropriately and then 2 mL of the saturated solutions pipetted into each. The blank consists of 2 mL of distilled water. **BE CAREFUL NOT TO DISTURB THE SOLID CALCIUM IODATE ON THE BOTTOM OF THE FLASKS!!! EXHAUST YOUR PIPET BULB OUTSIDE THE SOLUTION.**

15 mL of distilled water and about 8 mL of 1 M H_2SO_4 is then added to each flask along with 2 mL of the iodide solution. 2 mL of starch indicator is added to the "blank" ONLY at this time. The flasks should then be stoppered, swirled and allowed to sit for 10 minutes. Meanwhile, the buret may be prepared with thiosulfate solution.

Each sample is titrated as demonstrated for the standardization of the thiosulfate solution, beginning with thiosulfate addition until the orange color starts to fade and then adding the starch. At the endpoint the mixture is colorless. If a blue color has developed in the "blank" it should be titrated also. Otherwise it is discarded. Unused potassium iodide solution should be turned in for recovery as the solid is rather expensive.

The Report

Your initial calculations should include:

1. The Molarity of the potassium dichromate solution
2. The moles of dichromate ion per 2 mL
3. The Molarity of the thiosulfate solution (average based on demonstration)
[best value/standard deviation, 95% confidence]
4. $[\text{IO}_3^-]$ in each of the saturated solutions
5. Value of K_{sp} in each mixture based on Molarities of IO_3^-
6. The ionic strength in each saturated solution used
7. A plot of $\log K_{\text{sp}}$ vs. \sqrt{I} and the regression equation
8. The best value of the K_{sp} at infinite dilution or zero ionic strength (K_{th})

Your conclusion to this experiment should include the balanced equations needed to complete the calculations. You should check a few sources to get values for the K_{sp} . Compare these with yours. What would happen to your results if you accidentally transferred some of the solid calcium iodate to your titration flask in the initial pipetting? Explain.

Your data should indicate that the presence of foreign ions has an effect on the solubility of calcium iodate. The compound becomes *more* soluble when foreign ions are present at higher concentrations. This contradicts a simple solution model in which solubility is based on the number of "spaces" available in the solvent for solute particles. Propose a model which would account for the observed behavior.

Finally, your value for the K_{sp} is, of course, for whatever the measured temperature of the solutions was at the time of the experiment. What you will find in a handbook is typically (but not always) for 25°C. Consider the thermodynamic data below for the equilibrium dissolution of calcium iodate hexahydrate:



$$\Delta H_{298}^{\circ} = +80 \text{ kJ/mol}$$

$$\Delta S_{298}^{\circ} = 152 \text{ J/mol}\cdot\text{K}$$

These values can be used to calculate a standard free energy change for the process at the actual temperature of the experiment since the enthalpy and entropy changes are not very much affected by small temperature variations. The free energy change can, in turn, be used to calculate a new reference value for the K_{sp} since $\Delta G^{\circ} = -RT \ln K_{\text{sp}}$. Does this improve your result?