

What Should We Teach Beginners about Solubility and Solubility Products?

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The Dilemma

When solubilities of salts in pure water are calculated using the solubility product algorithms in introductory texts, 50% of the answers are in error (1) by a factor greater than 5. For similarly calculated solubilities in solutions that are 0.1 M in the salt's negative ion, more than 50% of the answers are in error by a factor greater than 50.

When we teach these calculations, our students believe them, pass them on to the next generation of students (as I did), include them in textbooks of disciplines requiring a little chemistry, and use them in real-world calculations where they are dangerously deceptive.

Solubility equilibria are important and must be taught. How do we do this without deceiving our students?

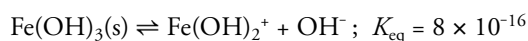
Examples

A few examples illustrate the problem. A statistical summary of such calculations showing the distribution of error factors is given in ref 1.

Example 1. This question was submitted to the ACS General Chemistry Examination Committee by an experienced chemistry professor. It required the solubility of $\text{Fe}(\text{OH})_3$ in pure water to be calculated from the solubility product, which was assumed to be

$$K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^-]^3 = 1.5 \times 10^{-39}$$

and the expected answer was $K_{\text{sp}}/(10^{-7})^3 = 1.5 \times 10^{-18}$. Actually, the important equilibrium is

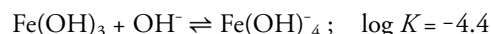


The logical answer is therefore $K_{\text{eq}}/10^{-7} = 8 \times 10^{-9}$. This differs from the expected answer by a factor of a billion. The simplistic textbook calculation is therefore not acceptable for any purpose for which this calculation might be used.

The values of K_{eq} were taken or calculated from Smith and Martell's data (2).

The logic that it is much easier to pull one OH^- off $\text{Fe}(\text{OH})_3$ than to remove a second is the same as the explanation why first acid dissociation constants K_{a1} are greater than K_{a2} .

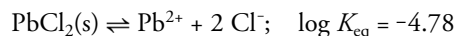
Example 2. A worse error occurs with iron(III) hydroxide in 0.1 M OH^- . The usual calculation gives solubility 10^{-36} M, but the equilibrium



increases this to 4×10^{-6} , an increase of 10^{30} !

Example 3. $\text{Hg}(\text{SCN})_2$ has $\log K_{\text{sp}} = -19.56$, so the simplistically calculated solubility is 1.9×10^{-7} M. However, the salt dissolves mostly as the undissociated $\text{Hg}(\text{SCN})_2$ and the true solubility is 0.017, an error factor of 9×10^4 .

Example 4. Consider the familiar textbook example "Calculate the solubility of lead chloride PbCl_2 from the solubility product K_{sp} at 25 °C." This occurs in many texts and the solubility is shown to be $(K_{\text{sp}}/4)^{1/3} = 0.016$. The calculation assumes that the only significant equilibrium in the system is



This ignores the equilibria

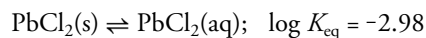
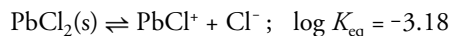


Table 1 shows the concentrations of these species, calculated from the above equilibrium constants. Pb^{2+} accounts for only half the solubility. The error in the calculated solubility caused by neglect of PbCl^+ and the activity coefficients is a factor of 2.4.

Many students must have calculated this solubility as 0.016, looked up the solubility in the *Handbook of Chemistry and Physics*, and found 0.99 g/dL (= 0.036 M) at 20 °C and wondered why the solubility was lower at 25 °C.

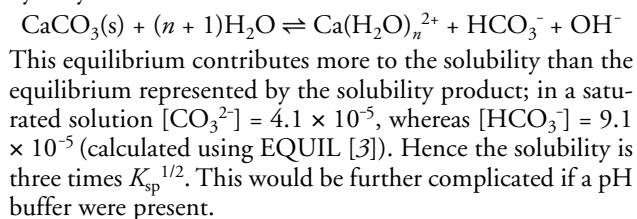
Table 1. Species Present in Saturated PbCl_2

Species	Concentration/(mol/L)	
	Allowing for activity coefficients	Not allowing for activity coefficients
Pb^{2+}	0.019	0.011
PbCl^+	0.019	0.017
PbCl_2	0.001	0.001
Total solubility	0.039	0.029

NOTE: In pure water at 25 °C.

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Example 5. A popular text on environmental engineering calculates the solubility of CaCO_3 as $K_{\text{sp}}^{1/2}$, neglecting the hydrolysis of the carbonate:

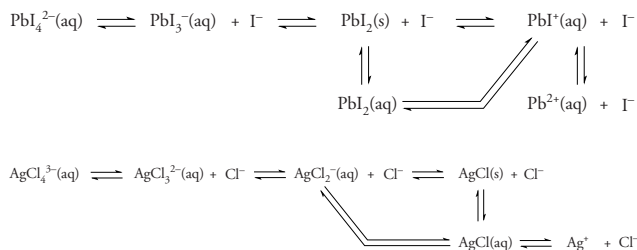


Qualitative Discussion

We can teach solubility equilibria without these calculations. In fact, it has been shown (4) that the concept of equilibrium is not understood even by students who can plug numbers successfully into equilibrium algorithms.

Students can readily understand the following. When a little chloride is added to a solution of Pb^{2+} it forms mostly PbCl^+ , but a very little of the PbCl^+ collects a second chloride ion and forms the undissociated PbCl_2 . Because this dissociates rapidly in equilibrium with PbCl^+ , the concentration of undissociated PbCl_2 is low. When the concentration of chloride is increased, the probability of Pb^{2+} accumulating two chloride ions is greater, so the concentration of PbCl_2 increases, eventually to the point that groups of PbCl_2 molecules stay together long enough to form crystals.

Reality can be most easily recognized if each solubility equilibrium is seen as one step in a series of dissociations. For example, the lead iodide and silver chloride systems can be represented thus:



Presenting the complexity of the equilibria will show students that calculations have to be more complex than can be taught in an introductory course.

Concentrations in Equilibrium with Solids

Not everything is wrong. If we ask what is the concentration of the uncomplexed ions Ag^+ or Fe^{3+} or Pb^{2+} in equilibrium with an insoluble salt and an excess anion, then plugging into the definition of K_{sp} will give an approximation to the correct answer.

Even so, there are problems. Activity coefficients or conditional K_{sp} values are needed for solutions more concentrated than about 10^{-3} M. The meaning of very low concentrations such as 10^{-23} M needs some philosophy. $\text{Fe}(\text{OH})_3$ in 0.001 M OH^- gives $[\text{Fe}^{3+}] = 1.5 \times 10^{-30}$, or about one ion per million liters. In any real situation, the slightest impurity or crystal fault would create errors of many orders of magnitude, even if equilibrium could be established in so large a volume.

Rigorous Computation

Software exists that will solve these problems rigorously without requiring students to understand the mathematical

complexities. The available programs are not sufficiently user-friendly for introductory chemistry, but they could be modified appropriately. A reviewer pointed out “that many of these complex problems can be treated easily using something like Excel, and that use of a spreadsheet allows the student to see just how much of an effect complexation has on solubility.”

Whether such calculations are valuable enough to students taking one year of chemistry to justify teaching them is open to question. My own searches in the literature of other disciplines has not revealed their usefulness.

Effect of Pressure, Temperature, and Ionic Strength

Seashells dissolve as they fall to the ocean floor because, among other things, the solubility of CaCO_3 increases with pressure. Values of K_{sp} for the calcite form of CaCO_3 change by a factor of 11 over the range 1 to 950 atm, as shown in Table 2. Pressures at the ocean floor would not usually exceed 10^3 atm, but pressures in special geological situations may be higher. The gible for most situations th

Table 2. Variation of $\log K_{sp}$ for CaCO_3 with Pressure

Pressure/atm	$\log K_{sp}$
1	-8.48
25	-8.39
250	-8.17
410	-8.00
518	-7.87
690	-7.68
950	-7.45

NOTE: In pure water at 25 °C.

tions may be higher. The effects of pressure will be negligible for most situations that students meet.

The effect of temperature is more important. Smith and Martell (2) give ΔH and ΔS for the solubility equilibria at 25 °C; these seem from the IUPAC collection (5) to be reasonably constant with temperature from about 15 °C to 40 °C, which covers the range of temperature of greatest interest for aqueous equilibria. Beyond this range, the temperature dependence of the thermodynamic constants is, in general, too great to be reliable. Furthermore, some salts have a temperature at which solubility is a minimum.

Moreover, ions must meet in order for there to be solid in equilibrium with the solution. This is hindered by the electric fields of other ions, so solubility is greater in ionic solutions. The greater the charge on the ions and the concentration of the ions, other things being equal, the greater is the solubility. The students need not be able to calculate the ionic strength or the activity coefficients.

The Meaning of K_{sp}

Solubility products present a rich opportunity to discuss solubility qualitatively, but the opportunity is seldom used. K_{sp} represents the balance between solution forces and crystal forces, complicated by the usually positive entropy of solution. This becomes obvious when two forms of the crystal exist, because the different crystal forces produce different solubility products, but introductory texts show only one value for any salt, with no obvious basis for the choice or even an indication that the value is valid for only one crystal form. This avoids confusion in the often worthless calculations, but at the price of meaningful qualitative understanding.

However, we may question whether solubility products are the most convenient concept for teaching about solution forces. The free energy of solution would illustrate it better, as would the simple solubility in moles per liter.

The following questions test the qualitative relations. There is an asterisk by the correct answer.

- Two minerals have different solubility products even though both are calcium carbonate. K_{sp} for calcite is 4.5×10^{-9} , while K_{sp} for aragonite is 6.0×10^{-9} . Which is the most probable explanation for this?
 - The aragonite is partially covalent.
 - Aragonite is more porous than calcite.
 - The Ca^{2+} in calcite is partially hydrated.
 - The carbonate ions in calcite are more basic than those in aragonite.
 - * In calcite the Ca^{2+} and CO_3^{2-} ions are arranged so the attraction between them is stronger than in aragonite.
- When saturated sodium chloride solution is added to concentrated hydrochloric acid, sodium chloride is precipitated. Which is the best explanation for this?
 - There is an acid-base reaction between the sodium chloride and the hydrochloric acid.
 - The hydrogen chloride molecules attract the water of hydration away from the sodium and chloride ions so they can attract each other.
 - The heat released by diluting the hydrochloric acid causes water to evaporate so there is no longer sufficient to dissolve the sodium chloride.
 - * Mixing the two solutions increases the concentration of chloride in the solution, making it more likely that sodium and chloride ions will meet.
 - The hydrogen ions in the hydrochloric acid remove chloride ions from the sodium chloride solution, freeing sodium ions to form crystals.
- Which increases the solubility?
 - Both d and e but not c.
 - All of the following.
 - * Enthalpy of hydration.
 - Attraction between ions in the crystal.
 - Overlap of orbitals of adjacent ions in the crystal.
- Which will tend to increase the solubility of a salt M_2X ?
 - * Both c and e but not d.
 - All of the following.
 - Solvation of M^+ .
 - A strong MX bond.
 - An open crystal structure in which fewer ions are in contact with each other.
- CdS has a higher solubility product than HgS . Which would be a reasonable explanation for this?
 - * Both c and e but not d.
 - All of the following.
 - Cd^{2+} is more strongly attracted to water molecules than Hg^{2+} .
 - The orbitals of Cd and S overlap more than those of Hg and S.
 - The attraction between Hg and S is stronger than that between Cd and S.
- In which will lead sulfate PbSO_4 be most soluble?
 - pure water
 - * 0.05M NaNO_3
 - 0.05M Na_2SO_4
 - 0.05M NaHSO_4
 - 0.05M $\text{Pb}(\text{NO}_3)_2$

Cutting the Gordian Knot

We should consider whether teaching solubility product calculations is useful at all. They have been taught for most of this century, and yet experienced teachers seriously misunderstand and misuse them. Neither the teachers nor their students seem to have been sufficiently inconvenienced by this that they complain and revise the teaching. This surely means that they never found a use for the calculations in any real situation. Was it more useful to teach this than other aspects of chemistry that had to be omitted for lack of time?

Solubility product calculations are best omitted from introductory chemistry courses and reserved for later courses where they can be presented correctly to the limited population that has use for them, using computer programs to handle the complexities.

The Pedagogical Dilemma

The subject of this paper was addressed at length in this *Journal* thirty years ago (6). That paper included a description of a specific case in which the simplification introduced error and confusion in introductory chemistry. Little has changed as a result. Conscientious teachers face the dilemma that a rigorous treatment is beyond the scope of an introductory course while the simplistic treatment gives unacceptable error in most cases. While the dilemma can be solved either by omitting quantitative treatment altogether or by equipping students with computer programs to deal with complexity, there remains the hazard that national standardized exams may require the calculation of solubility from the simplistic algorithm. Examining bodies should avoid putting teachers in this invidious position. Textbooks could help by showing how unreliable the simplistic algorithm is, as do Umland and Bellama (7). Even so, students will trust us enough to believe that a calculation we have taught must be generally useful. Even though we tell them that the answer is affected by extraneous variables, the fact that we taught the method will be seen to imply that it usually gives an acceptable approximation (I believed it long after I became a professor). We can offer no algorithm that will enable them to decide when it can be expected to give an approximation to the correct answer.

No matter what the typical textbook says, we should strive to alert students to the reality of speciation and ancillary effects such as pH, particle size, ionic strength, incomplete dissociation, and complexation, rather than settle for unrealistic calculation exercises on inadequate models.

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