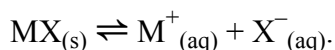


Experiment # 10: Solubility Product Determination

When a chemical species is classified as “insoluble”, this does not mean that none of the compound dissolves in the given solvent or solution system. In reality, a measurable level of material does go into solution, but it is sometimes considered negligible relative to the total amount of the chemical. Perhaps a better name for such salts is “sparingly soluble.” The dissolving of a solid monovalent-monovalent salt, represented as MX, in an appropriate solvent is represented by the general equation:



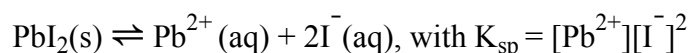
where the subscripts “(s)” and “(aq)” represent the solid and aqueous solution physical states, respectively. For a set of given conditions, the precipitate has a definite solubility (or maximum amount that will dissolve) expressed in units of grams/liter or moles/liter.

An equilibrium constant expression can be written for the above reaction, as: $K_{\text{eq}} = \frac{[\text{M}^+][\text{X}^-]}{[\text{MX}]}$. The “concentration” of any solid material, such as MX, is proportional to its density and is constant. Thus, the term [MX] is usually combined into the K_{eq} value, giving: $K_{\text{eq}} [\text{MX}] = [\text{M}^+][\text{X}^-] = K_{\text{sp}}$, where “ K_{sp} ” is called the “solubility product” constant. Note: Square brackets indicate saturation or equilibrium molarities.

The ideal or thermodynamic solubility product expression is written in terms of the “activities” or “effective concentrations” of all species, rather than in actual mass/volume or mole/volume concentrations. In solutions of low concentrations, the activity coefficients are near unity, and the simplification of terms is appropriate for equilibrium systems for most reactions.

For a given chemical species and solvent system, the main factor which affects the value of K_{sp} is the temperature. Most often, an increase in the temperature causes an increase in the solubility and value. However, there are some exceptions, as in the case of a salt which dissolves with a loss of energy (i.e., an exothermic dissolution). For a given temperature and set of experimental conditions, there are often kinetic limitations as to how fast crystalline solids form. Thus, sufficient time should be allowed for the system to come to a true state of equilibrium.

The amount of a slightly soluble salt that dissolves does not depend on the amount of the solid in equilibrium with the solution, so long as there is enough to saturate the solution. A non-symmetric salt, such as lead iodide or PbI_2 , would have a reaction as:



As with any equilibrium constant, the K_{sp} value holds under all conditions at the specified temperature. If there is an excess of one ion over the other, the concentration of the second is suppressed (due to the common-ion effect), and the solubility of the precipitate is decreased. Because the solubility product value always holds constant, precipitation will not occur unless the product of $[\text{M}^+]$ and $[\text{X}^-]$ exceeds the value of K_{sp} . If the product of the ion concentrations is just equal to K_{sp} , all the M^+ and X^- would remain in the solution (i.e., no precipitate or solid forms).

In this experiment, the relative solubility (and an approximate value of the K_{sp}) of lead iodide will be determined by direct observation. The procedure calls for the mixing of two standard solutions (one of a soluble lead salt, and a second of a soluble iodide salt) in different proportions and allowing time for the resulting mixture to come to equilibrium. In some of the mixtures, the solubility product constant for lead iodide will be exceeded, and precipitation of PbI_2 crystals will occur. In other mixtures, the final concentrations of lead and iodide ions will be such that precipitation does not occur.

A simple product function “Q,” called the Ion Product will be defined so that:

$$Q = \{\text{lead ion}\} \times \{\text{iodide ion}\}^2 = \{Pb^{2+}\} \{I^{-}\}^2,$$

where curly brackets indicate prepared molarities before precipitation occurs (if it does occur). An experimental value of “Q” will be calculated for each mixture, based on the total amount of lead ion and iodide ion added in each solution. Clearly, the formation of solid crystals of PbI_2 will occur when the value of “Q” exceeds the solubility product value of lead iodide (i.e., when $Q > K_{sp}$). Similarly, precipitation will not occur when the value of $K_{sp} > Q$.

Thus, in this experimental procedure, if some sample mixtures form PbI_2 crystals and other solutions do not, the value of the solubility product constant lies between Q values with precipitates and Q values without precipitates. The most precise value for K_{sp} is given as:

$$Q_{\text{minimum with } PbI_2} > K_{sp} > Q_{\text{maximum without } PbI_2}$$

The value for K_{sp} is determined with an uncertainty level equal to the difference of the two Q values. In order for a more precise determination of K_{sp} , the solution mixtures are designed such that the various Q values are rather close together.

Caution: lead salts are toxic, so be careful handling the solutions, and make sure to wash your hands after you complete the experimental work.

Preparation of lead iodide mixtures

Equimolar standard solutions of lead and iodide compounds are provided on the reagent shelf. A 1.00×10^{-2} M Pb^{2+} solution is prepared by dissolving 3.312 grams of $Pb(NO_3)_2$ in 1.00 liter of deionized water, while a solution of 1.00×10^{-2} M I^{-} is prepared by dissolving 1.660 grams of KI in 1.00 liter of deionized water.

Each student or group of students should assemble a set of nine clean, dry test-tubes (15 x 125 mm). A number (to be determined by the lab instructor) of buret stations will be set up in the laboratory. Each station will consist three delivery burets, one buret for each of the stock solutions and a third for deionized water. Following the specifications listed in Table I, prepare a mixture series of the lead and iodide stock solutions. To avoid local, temporary supersaturation, always mix the water first. Note that the total volume of each mixture solution is 10.0 mL. Be sure that the solutions are mixed thoroughly, and do not get the test tubes out of order. An easy check is to observe that the Q values progressively decrease from #1 to #9 samples.

After preparing the solutions, allow each mixture to set for at least 30 minutes before checking for precipitation. During this equilibration period, calculate the theoretical or maximum concentration of each ion in the mixture, using the equation:

$$[\text{Ion}]_{\text{mixture}} = [\text{Ion}]_{\text{standard}} \times \frac{\text{mL's ion in solution}}{\text{mL's total mixture}}$$

Use these concentration values to calculate the “Q” value for each mixture, and record the data in Table I. Colorless clarity (clearness) of solution indicates no precipitate. Golden cloudiness (lack of clarity) indicates formation of a precipitate.

After the equilibration period is completed record under the “PbI₂?” column whether or not a precipitate has formed in each test tube. If all goes well, the mixtures of higher Q values will contain shiny, golden crystals of lead iodide, while the tubes of lower Q values will have no solid.

Table I

#	mL Pb ²⁺	mL I ⁻	mL H ₂ O	[Pb ²⁺]	[I ⁻]	Q	PbI ₂ ?
1	4.00	5.00	1.00				
2	3.00	5.00	2.00				
3	2.00	5.00	3.00				
4	1.00	5.00	4.00				
5	2.50	2.00	5.50				
6	1.20	2.50	6.30				
7	1.25	2.00	6.75				
8	2.50	1.00	6.50				
9	1.00	1.00	8.00				

Data treatment and report

A single-page report will be submitted for this experiment. Under a full heading, recreate the completed data entries of Table I. Be sure to indicate which test tubes contain precipitates of lead iodide. Identify the smallest value mixture containing a precipitate and the largest Q value test tube which has no solid crystals. The K_{sp} for lead iodide should lie within these two Q values, so report the experimental value of K_{sp} within this range, as:

$$Q_{\text{minimum with PbI}_2} > K_{\text{sp}} > Q_{\text{maximum without PbI}_2}$$

Look up the actual K_{sp} for lead iodide in a textbook or other reference book, list this value as “literature K_{sp}” in the report, and cite your source.