

Determining K_{sp} of Lead(II) Iodide

Objective: Determine the solubility product constant K_{sp} for lead(II) iodide (PbI_2) from titrimetric data

Materials: Solutions of lead(II) nitrate $Pb(NO_3)_2$, of 0.250 M, 0.100 M, 0.0500 M, and 0.0200 M; solution of 0.0500 M potassium iodide, KI

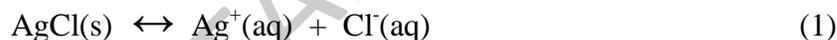
Equipment: 50-mL buret; three 150-mL beakers; 250-mL Erlenmeyer flask; pipet bulb and 50-mL (or 25-mL) pipet

Safety: Lead compounds are toxic; solutions of lead salts should be handled carefully. If contact is made with skin, wash affected areas with plenty of water. Safety goggles should be worn in the lab at all times.

Waste Disposal: All titration solutions and leftover reagents should be placed in the inorganic waste container.

INTRODUCTION

Most ionic compounds are soluble in aqueous solution. Some salts, however, are insoluble or sparingly soluble. In such cases, the extent to which the salt dissolves can be expressed using an equilibrium expression. Consider the dissolution of the sparingly soluble salt silver chloride, $AgCl$.



The double-headed arrow indicates a dynamic equilibrium between the solid salt on the left and the dissolved ions on the right. The equilibrium constant expression for this process would be

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

where K_{sp} is called the **solubility product constant**, since it is calculated as the product of the soluble ion concentrations. For sparingly soluble salts the concentration of dissolved ions at equilibrium is very small, so values of K_{sp} for these salts are significantly less than 1. For example, the K_{sp} for $AgCl$ is 1.8×10^{-10} .

For dilute ionic solutions, the expression for K_{sp} in Eq. (2) works very well. However, as the ionic strength of the solution increases the solubility of the salt starts to increase. The large concentration of ions in solution begins to interfere with the ability of the Ag^+ and Cl^- ions to

interact and form the solid. In other words, the **activity** of the ions decreases as the ionic strength of solution increases. Under these conditions, a more appropriate form of the equilibrium constant expression would be

$$K_{sp} = (A_{Ag^+})(A_{Cl^-}) \quad (3)$$

where A_{Ag^+} and A_{Cl^-} represent the activities of the Ag^+ and Cl^- ions, respectively. The ion activities are related to concentration by Equation (4).

$$K_{sp} = (A_{Ag^+})(A_{Cl^-}) = (\gamma_{Ag^+} [Ag^+])(\gamma_{Cl^-} [Cl^-]) \quad (4)$$

where γ_{Ag^+} and γ_{Cl^-} represent the **activity coefficients** of the Ag^+ and Cl^- ions. The activity coefficient acts as a correction factor to account for decreases in ionic activity at high ionic strengths. While a detailed study of activity coefficients is beyond the scope of this exercise, some general observations will be useful. For very dilute ionic solutions the value of the activity coefficient approaches unity, and Eq. (4) is identical to Eq. (2). As the ionic strength of the solution increases, the activity coefficient decreases. The ion product in Eq. (2), however, would increase. By including the activity coefficients in the K_{sp} expression the value of K_{sp} remains constant.

The equilibrium point for Eq. (1) can be approached from either direction. If we add solid AgCl to solution, for example, the salt will dissolve until the ion product in Eq. (4) is equal to K_{sp} . Alternatively, we can mix solutions containing Ag^+ and Cl^- ions; when the ion product exceeds the value of K_{sp} then solid AgCl will precipitate from solution. Using this second approach, we can estimate the value of K_{sp} for a sparingly soluble salt by performing a titration, as illustrated in Example 1.

Example 1: Consider a 100.0 mL solution of silver nitrate having an initial $[Ag^+] = 0.0010 M$. A 0.00025 M solution of KCl is added dropwise until the first appearance of the white AgCl precipitate. The total volume of KCl added was 1.18 mL. Estimate the value of K_{sp} using the titration data.

Solution *Since the volume of the solution changes as titrant is added, we will need to calculate the actual concentrations of Ag^+ and Cl^- at the endpoint of the titration. We can calculate these concentrations using Equations (5) and (6).*

$$[Ag^+]_{eq} = \frac{(\text{moles of } Ag^+)}{(\text{total volume})} = \frac{(M_{Ag^+})(V_{Ag^+})}{(V_{Ag^+}) + (V_{Cl^-})} = \frac{(0.0010 M)(0.100 L)}{(0.100 L) + (0.00118 L)} = 9.88 \times 10^{-4} \quad (5)$$

$$[Cl^-]_{eq} = \frac{(\text{moles of } Cl^-)}{(\text{total volume})} = \frac{(M_{Cl^-})(V_{Cl^-})}{(V_{Ag^+}) + (V_{Cl^-})} = \frac{(0.00025 M)(0.00118 L)}{(0.100 L) + (0.00118 L)} = 2.92 \times 10^{-6} \quad (6)$$

We can now estimate the value of K_{sp} as the ion product using Eq. (2).

$$K_{sp} = [Ag^+][Cl^-] = (9.88 \times 10^{-4})(2.92 \times 10^{-6}) = 2.89 \times 10^{-9}$$

While we can obtain estimates of K_{sp} from the ion product, as shown in the Example, we need to be able to correct for the variations in ionic activity with ionic strength. One way to do this is to perform a series of titrations in which the initial concentration of one of the ions is varied. At higher initial concentrations, the ion product will be greater than the true K_{sp} . As the initial concentration is decreased, the value of the ion product will also decrease and approach the true value of K_{sp} . If we plot the ion product vs. the initial concentration of the ion in solution, we can extrapolate to an initial concentration of zero. The y-intercept of this plot should be equal to K_{sp} .

Titration of Lead(II) Iodide

In this lab exercise we will determine the K_{sp} of lead(II) iodide by titration. The solubility equilibrium and K_{sp} expression for this insoluble salt are:



$$K_{sp} = (\gamma_{\text{Pb}}[\text{Pb}^{2+}])(\gamma_{\text{I}}[\text{I}^{-}])^2 \quad (8)$$

We can perform a series of titrations using a 0.0500 M KI solution as titrant, and varying the initial concentration of $\text{Pb}(\text{NO}_3)_2$ in our sample. We will add titrant dropwise until the first appearance of pale-yellow lead(II) iodide (PbI_2) signals the end point. We can calculate the concentrations of Pb^{2+} and I^{-} ions at the end point using Equations (9) and (10).

$$[\text{Pb}^{2+}]_{eq} = \frac{(\text{moles of Pb}^{2+})}{(\text{total volume})} = \frac{(M_{\text{Pb}^{2+}})_{initial} (V_{\text{Pb}^{2+}})_{initial}}{(V_{\text{Pb}^{2+}})_{initial} + (V_{\text{I}^{-}})_{added}} \quad (9)$$

$$[\text{I}^{-}]_{eq} = \frac{(\text{moles of I}^{-})}{(\text{total volume})} = \frac{(M_{\text{KI}})_{initial} (V_{\text{KI}})_{added}}{(V_{\text{Pb}^{2+}})_{initial} + (V_{\text{I}^{-}})_{added}} \quad (10)$$

Since we don't know the values of the activity coefficients in Eq. (8), we will calculate the ion product, $[\text{Pb}^{2+}][\text{I}^{-}]^2$. At high initial concentrations of Pb^{2+} the ion product will be greater than K_{sp} . As the initial concentration of Pb^{2+} decreases, the ion product will approach a constant value of K_{sp} . Plotting the ion product vs $[\text{Pb}^{2+}]_{initial}$ yields a graph similar to Figure 1. Extrapolating to the y-intercept (at which $[\text{Pb}^{2+}]_{initial} = 0$) allow us to estimate the value of K_{sp} for PbI_2 .

The plot in Figure 1 is unsatisfactory for two reasons. First, due to curvature in the trend line as we approach the intercept there may be considerable error in our extrapolated value. Second, the value of K_{sp} on the graph is exceedingly small; the extrapolation approaches a value of zero. The extrapolated value of K_{sp} is too small to be shown accurately on the graph.

The shortcomings of the plot in Figure 1 can be overcome by plotting the data in a different fashion. The best choice of functions to be plotted may be based on theory, intuition, or trial-and-error. In this case, the Debye-Hückel theory of dilute ionic solutions has shown that the best plot is $\log([\text{Pb}^{2+}][\text{I}^{-}]^2)$ vs $\sqrt{[\text{Pb}^{2+}]} / (1 + \sqrt{[\text{Pb}^{2+}]})$. Theory predicts that this plot will become linear as ion concentrations are more dilute. Linear plots are easier to extrapolate. Also, the y-axis is

logarithmic, so that there is less error in the estimate of K_{sp} obtained by extrapolation. The value of K_{sp} can be calculated as the antilog of the intercept, as shown in Equation (11).

$$K_{sp} = 10([Pb^{2+}][I^-]^2) \quad (11)$$

(Note that the antilog function in Eq. (11) would be used if the data were plotted using \log_{10} . If natural logs (\ln) were used, then Eq. (11) would be calculated using e^x as the antilog function.)

The percent error in your calculated K_{sp} can be determined using Equation (12).

$$\% \text{ error} = \frac{(\text{accepted } K_{sp}) - (\text{experimental } K_{sp})}{(\text{accepted } K_{sp})} \times 100 \quad (12)$$

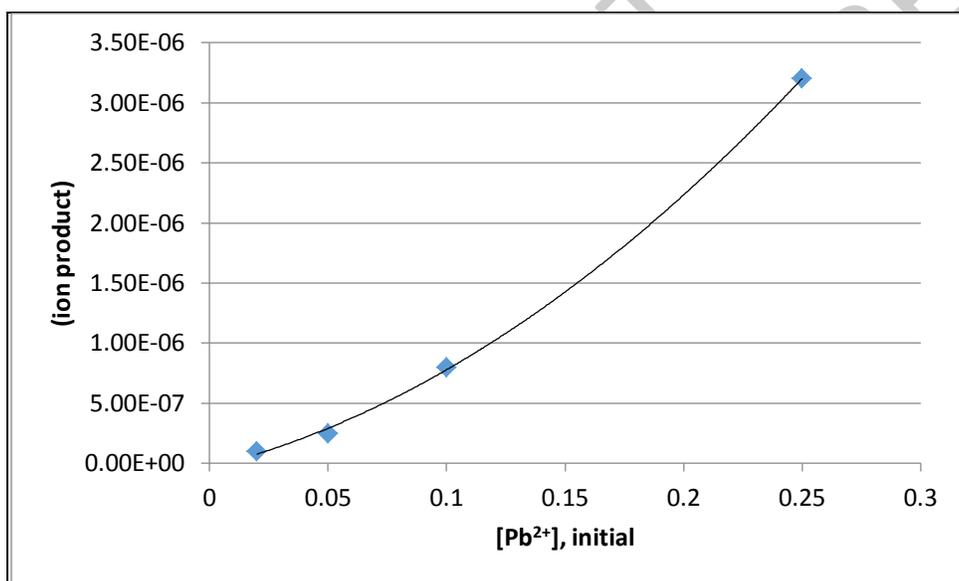


Figure 1. Possible extrapolation of data to find K_{sp} of PbI_2 .

Pre-Lab Questions

1. A student followed the procedure of this experiment to determine the K_{sp} of zinc(II) iodate, $Zn(IO_3)_2$. Solutions of $Zn(NO_3)_2$ of known concentrations were titrated with 0.200 M KIO_3 solutions to the first appearance of a white precipitate. For each of the zinc(II) nitrate solution concentrations below, calculate the expected concentration of iodate that would be required to initiate precipitation of zinc(II) iodate. Show all calculations. (Assume that $K_{sp} = 3.9 \times 10^{-6}$ at 25°C for zinc(II) iodate).
 - a) 0.100 M $Zn(NO_3)_2$:

 - b) 0.0100 M $Zn(NO_3)_2$:
2. Assuming that you performed the titrations described above using 100.00 mL samples of zinc nitrate, what volumes of 0.200 M potassium iodide would be required to initiate precipitation in each case? To simplify the calculations, neglect dilution effects from the added potassium iodate and assume a total final solution volume of 100.00 mL.
 - a)

 - b)
3. The actual volumes of 0.200 M potassium iodate required when the student performed the experiment were 7.54 mL and 17.82 mL, respectively. Explain.

PROCEDURE

Note: Students may perform individual titrations for each lead(II) nitrate solution concentration or may perform replicate titrations for one or more assigned lead(II) nitrate solution concentrations, depending on time constraints.

1. Obtain a 50-mL buret. Clean with soap solution, rinse thoroughly, and place it in a buret clamp to drain.
2. Obtain about 100 mL of 0.050 M potassium iodide solution in a clean, dry, labeled 150-mL beaker. Rinse the 50-mL buret with about 10 mL of the potassium iodide solution, tilting and turning the buret so that the inside walls of the buret are contacted by the solution. Drain the KI solution from the buret through the buret tip. Repeat this process with two more 10-mL portions of KI solution.
3. Fill the buret with the KI solution so that the level of solution is above the zero mark on the buret. Gently tap the sides of the buret to remove any air bubbles that may be present in the solution. Carefully open the stopcock of the buret and allow the KI solution to fill the buret tip. Continue draining the KI solution until the level of the meniscus in the buret is at or below the zero mark. Record this volume reading to the nearest 0.05 mL on Data Sheet 1.
4. Obtain about 130 mL of the 0.250 M lead(II) nitrate solution in a clean, dry, labeled 150-mL beaker. Using a pipet bulb, draw about 10 mL of this solution up into the 25-mL or 50-mL pipet. Tilt the pipet while turning so that the solution comes into contact with the entire inside surface of the pipet. Drain this solution into a 150-mL waste beaker. Repeat this rinse with two more 10-mL portions of lead(II) nitrate solution.
5. Using the rinsed pipet, carefully transfer 100.0 mL of the 0.250 M lead(II) nitrate solution into a 250-mL Erlenmeyer flask.
6. Add KI solution dropwise from the buret to the lead(II) nitrate solution in the Erlenmeyer flask while stirring thoroughly. Continue adding KI solution until the first appearance of yellow PbI_2 that remains after thorough mixing. Record the volume reading of the KI solution in the buret (to the nearest 0.05 mL) on Data Sheet 1.
7. Repeat Steps 4–6 for the 0.100 M, 0.0500 M, 0.0200 M, and 0.0100 M lead(II) nitrate solutions. You do not need to refill the buret before each titration, but should note the initial and final buret volume readings for each titration. If the volume reading in the buret approaches the 50.00 mL mark you should add more KI to ensure that you have enough titrant to complete the titration before you begin.
8. Dispose of all titration mixtures and excess reagent solutions in the inorganic waste container provided.
9. Submit your titration data to your TA. The TA will obtain class data and calculate the average volume of titrant used for each of the five titrations. Record the average class data for the five titrations on Data Sheet 2 before you leave lab.

CALCULATIONS

Record the results of all calculations in the appropriate spaces on Data Sheet 1 for your assigned titrations, and on Data Sheet 2 for the average class data.

1. Calculate the volume of titrant (KI) added to each titration solution as the difference between the initial and final buret volume readings.
2. Calculate the total volume of the titration solution at the end point as the sum of the added titrant and the initial volume of lead(II) nitrate solution.
3. Using the initial volume and molarity of the lead nitrate solutions, and the total volume of the solution at the endpoint, calculate the actual concentration of Pb^{2+} ion at the endpoint.
4. Using the molarity and volume of KI added, and the total volume of solution at the endpoint, calculate the actual concentration of I^- ion at the endpoint.
5. Calculate the ion product of $[\text{Pb}^{2+}][\text{I}^-]^2$ at the endpoint for each titration.
6. Calculate the log of each ion product. You may calculate either \ln or \log (base 10), as long as you are consistent for all calculations.
7. Repeat the calculations in Steps 3–6 for the average class data and record your results on Data Sheet 2.
8. Construct a graph by plotting the ion product (y-axis) vs. $[\text{Pb}^{2+}]$ (x-axis) using the average class data. Label this as Graph 1. Attempt to extrapolate the curve to zero concentration to find K_{sp} . Record this value of K_{sp} on Data Sheet 2. (Note: Extrapolated results can be improved by plotting the data using a spreadsheet, such as Excel, and adding a trend line (polynomial fit), and reporting the intercept of the trend line equation.)
9. Using the average class data, calculate values of $\sqrt{[\text{Pb}^{2+}]/(1 + \sqrt{[\text{Pb}^{2+}]})}$ and \log (ion product) using the average class data from Data Sheet 2. Construct another graph by plotting the \log of the ion product vs $\sqrt{[\text{Pb}^{2+}]/(1 + \sqrt{[\text{Pb}^{2+}]})}$. Plot the points as small circles on the graph. Label this plot as Graph 2. Extrapolate the curve to zero concentration to find $\log K_{\text{sp}}$. Calculate K_{sp} as the antilog of the intercept, and record this result on Data Sheet 2. As noted above, accuracy of K_{sp} estimations from extrapolation can be improved by plotting data using spreadsheet software, and using the trend line equation to find the intercept.
10. Repeat the calculations in Step 9 using your own titration results, and plot your data as small triangles on Graph 2. Compare your individual data with the average class data.
11. Compare the calculated value of K_{sp} from Graph 2 with an accepted literature value of K_{sp} for PbI_2 . Calculate % error using Eq. (12).

Data Sheet 1

Individual Data

$[\text{Pb}(\text{NO}_3)_2]_{\text{initial}}$, M	0.250	0.100	0.0500	0.0200	0.0100
$[\text{KI}]_{\text{initial}}$, M	0.0500	0.0500	0.0500	0.0500	0.0500
V of $\text{Pb}(\text{NO}_3)_2$, mL	100.00	100.00	100.00	100.00	100.00
V of KI (initial), ml	_____	_____	_____	_____	_____
V of KI at endpoint, mL	_____	_____	_____	_____	_____
V of KI added, mL	_____	_____	_____	_____	_____
V_{total} at endpoint, mL	_____	_____	_____	_____	_____
$[\text{Pb}^{2+}]$, M	_____	_____	_____	_____	_____
$[\text{I}^-]$, M	_____	_____	_____	_____	_____
$[\text{Pb}^{2+}][\text{I}^-]^2$	_____	_____	_____	_____	_____
$\log([\text{Pb}^{2+}][\text{I}^-]^2)$	_____	_____	_____	_____	_____
$\frac{\sqrt{[\text{Pb}^{2+}]}}{1 + \sqrt{[\text{Pb}^{2+}]}}$	_____	_____	_____	_____	_____

Sample Calculations:

Data Sheet 2

Average Class Data

$[\text{Pb}(\text{NO}_3)_2]_{\text{initial}}$, M	0.250	0.100	0.0500	0.0200	0.0100
$[\text{KI}]_{\text{initial}}$, M	0.0500	0.0500	0.0500	0.0500	0.0500
V of $\text{Pb}(\text{NO}_3)_2$, mL	100.00	100.00	100.00	100.00	100.00
V of KI added, mL	_____	_____	_____	_____	_____

At Endpoint:

V_{total} at endpoint, mL	_____	_____	_____	_____	_____
$[\text{Pb}^{2+}]$, M	_____	_____	_____	_____	_____
$[\text{I}^-]$, M	_____	_____	_____	_____	_____
$[\text{Pb}^{2+}][\text{I}^-]^2$	_____	_____	_____	_____	_____
$\log([\text{Pb}^{2+}][\text{I}^-]^2)$	_____	_____	_____	_____	_____
$\frac{\sqrt{[\text{Pb}^{2+}]}}{1 + \sqrt{[\text{Pb}^{2+}]}}$	_____	_____	_____	_____	_____

K_{sp} of PbI_2 from Graph 1: _____

$\text{Log}(K_{\text{sp}})$ from Graph 2: _____

K_{sp} from Graph 2: _____

% error in K_{sp} from Graph 2: _____

Sample Calculations:

Post-Lab Questions

1. The % error in the extrapolated results is highly dependent on the error associated with the volume of the lead(II) nitrate solution used in each titration and the volume of potassium iodide solutions need to initiate precipitation in each trial. Given the data below, calculate the maximum % error associated with each of the typical measurements below.
 - a) 100.00 mL of lead(II) nitrate solution measured using a 50.00 mL pipette with a tolerance of ± 0.05 mL
 - b) 100.00 mL of lead(II) nitrate solution measured using a 100.00 mL volumetric flask with a tolerance of ± 0.02 mL
 - c) 7.42 mL of potassium iodide solution titrated from a 50.00 mL buret with a tolerance of ± 0.02 mL
2. Based on the calculations in question 1, which measurement introduces the greatest error? Can you suggest at least one possible modification to the procedure to improve the precision associated with individual titration points? (Note: “Reducing human error” or “using better technique” are not acceptable responses.)
3. Discuss how each of the following conditions might affect the volume of 0.200 M potassium iodide needed to reach the precipitation end point in a typical titration.
 - a) The lead(II) nitrate solution was prepared in 0.05 M NaCl instead of deionized water.
 - b) The temperature in the lab increased by 3°C.