Lab 7: 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 ; three 150 mL beakers; 250 mL Erlenmeyer flasks; magnetic stirrer; magnet bar; 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.

$$AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq) \qquad \text{(Equation 7.1)}$$

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:

$$K_{sp} = [Ag^+][Cl^-] \qquad \text{(Equation 7.2)}$$

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 Equation 7.2 works very well. However, as the **ionic strength** of the solution increases, the solubility of the salt starts to increase. Ionic strength of a solution is a measure of the concentration of all ions in that solution. The large concentration of ions in solution begins to interfere with the ability of the Ag^+ and Cl^- ions to combine and form

solid AgCl. In other words, the **activity** of Ag^+ and Cl^- ions decreases as the ionic strength of solution increases. Activity can be considered as "effective" concentration of an ion in a non-ideal (e.g., concentrated) solution. Under these conditions, a more appropriate form of the equilibrium constant expression would be:

$$K_{sp} = (A_{Ag})(A_{Cl}) \qquad \text{(Equation 7.3)}$$

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 7.4:

$$K_{sp} = (A_{Ag})(A_{Cl}) = (\gamma_{Ag}\,[Ag^+])(\gamma_{Cl}\,[Cl^-]) \qquad \text{(Equation 7.4)}$$

where γ_{Ag} and γ_{Cl} represent the **activity coefficients** of the Ag^+ and Cl^- ions. The activity coefficient is a correction factor to account for decreases in ionic activity at high ionic strengths (e.g., non-ideal solutions, concentrated solutions). 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 Equation 7.4 is identical to Equation 7.2. As the ionic strength of the solution increases, the activity coefficient decreases. The ion product in Equation 7.2, however, would increase. By including the activity coefficients in the K_{sp} expression, the value of K_{sp} remains constant.

The equilibrium point for Equation 7.1 can be approached from either direction. If we add solid AgCl to solution, for example, the salt will dissolve until the ion product in Equation 7.4 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}, 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 the Example below.

Example. 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 white AgCl precipitate first appears. 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 7.5 and 7.6.*

$$[Ag^+]_{eq} = \frac{(\text{moles of } Ag^+)}{(\text{total volume})} = \frac{(M_{Ag^+})(V_{Ag^+})}{(V_{Ag^+})+(V_{Cl^-})} = \frac{(0.0010\text{ M})(0.100\text{ L})}{(0.100\text{ L})+(0.00118\text{ L})} = 9.88 \times 10^{-4} \qquad \text{Equation 7.5}$$

$$[Cl^-]_{eq} = \frac{(\text{moles of } Cl^-)}{(\text{total volume})} = \frac{(M_{Cl^-})(V_{Cl^-})}{(V_{Ag^+})+(V_{Cl^-})} = \frac{(0.00025\text{ M})(0.00118\text{ L})}{(0.100\text{ L})+(0.00118\text{ L})} = 2.92 \times 10^{-6} \qquad \text{Equation 7.6}$$

We can now estimate the value of K_{sp} as the ion product using Equation 7.2.

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

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:

$$PbI_2(s) \leftrightarrows Pb^{2+}(aq) + 2I^-(aq) \qquad \text{(Equation 7.7)}$$

$$K_{sp} = (\gamma_{Pb}[Pb^{2+}])(\gamma_I[I^-])^2 \qquad \text{(Equation 7.8)}$$

We can perform a series of titrations using a 0.0500 M KI solution as titrant and varying the initial concentration of $Pb(NO_3)_2$ 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 7.9 and 7.10.

$$[Pb^{2+}]_{eq} = \frac{(\text{moles of } Pb^{2+})}{(\text{total volume})} = \frac{(M_{Pb^{2+}})_{initial}\,(V_{Pb^{2+}})_{initial}}{(V_{Pb^{2+}})_{initial} + (V_{I^-})_{added}} \qquad \text{(Equation 7.9)}$$

$$[I^-]_{eq} = \frac{(\text{moles of } I^-)}{(\text{total volume})} = \frac{(M_{KI})_{initial}\,(V_{KI})_{added}}{(V_{Pb^{2+}})_{initial} + (V_{I^-})_{added}} \qquad \text{(Equation 7.10)}$$

Since we don't know the values of the activity coefficients in Equation 7.8, we will calculate the ion product, $[Pb^{2+}][I^-]^2$. 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. $[Pb^{2+}]_{initial}$, one can extrapolate to the y-intercept (at which $[Pb_{2+}]_{initial} = 0$), allowing us to estimate the value of K_{sp} for PbI_2.

This plot 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 this graph 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:

$$\log([Pb^{2+}][I^-]^2) \text{ vs } \sqrt{[Pb^{2+}]}/\left(1 + \sqrt{[Pb^{2+}]}\right) \qquad \text{(Equation 7.11)}$$

Theory predicts that this plot will become linear as ion concentrations are more dilute. Linear plots are easier to extrapolate (Figure 7.1). 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 7.12:

$$K_{sp}=10^{\left([Pb^{2+}][I^-]^2\right)} \qquad \text{(Equation 7.12)}$$

(Note that the antilog function in Equation 7.11 would be used if the data were plotted using $\log_{10}$. If natural logs (ln) were used, then Equation 7.11 would be calculated using e^x as the antilog function.)

The percent error in your calculated K_{sp} can be determined using Equation 7.13:

$$\%\ \text{error} = \frac{(\text{accepted } K_{sp})-(\text{experimental } K_{sp})}{(\text{accepted } K_{sp})} \times 100 \quad \text{(Equation 7.13)}$$

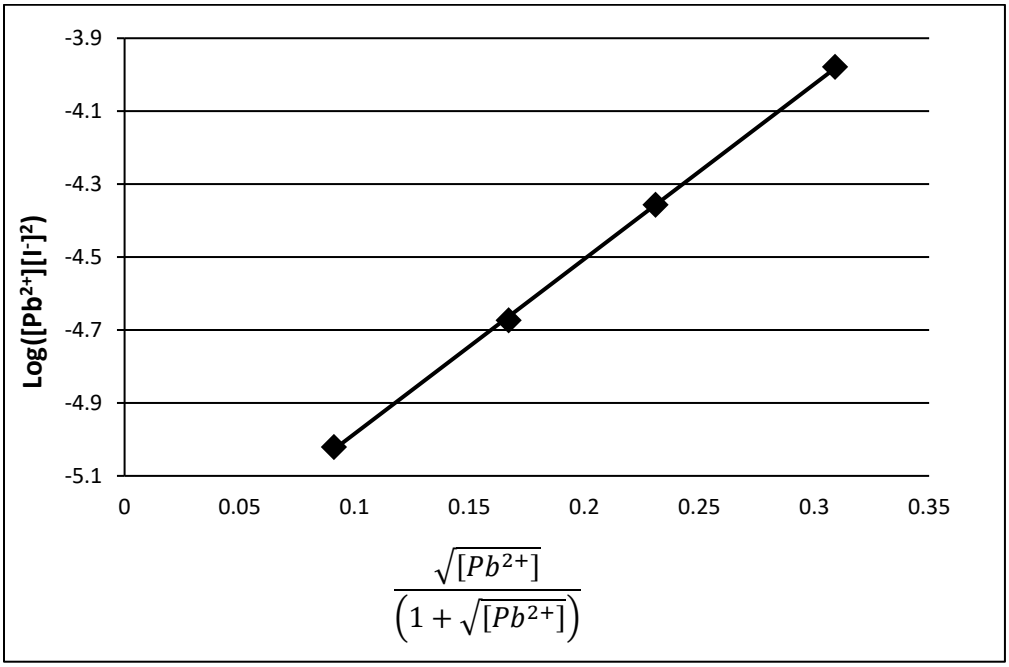

Figure7.1. Extrapolation of data to find Log(K_{sp}) of PbI_2.

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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. The following data were collected:

$[Zn(NO_3)_2]_{initial}$, M	0.226	0.101	0.0452	0.0118
$[KIO_3]_{initial}$, M	0.200	0.200	0.200	0.200
$V_{initial}$ of $Zn(NO_3)_2$, mL	100.0	100.0	100.0	100.0
V of KIO_3 added, mL	12.9	12.4	13.0	18.3
At endpoint:				
V_{total}, mL	_____	_____	_____	_____
$[Zn^{2+}]$, M	_____	_____	_____	_____
$[IO_3^-]$, M	_____	_____	_____	_____
$[Zn^{2+}][IO_3^-]^2$	_____	_____	_____	_____
$\text{Log}([Zn^{2+}][IO_3^-]^2)$	_____	_____	_____	_____
$\frac{\sqrt{[Zn^{2+}]}}{1+\sqrt{[Zn^{2+}]}}$	_____	_____	_____	_____

Graph using equation 7.11, equal to Y-intercept Log K_{sp} = _____

Equation 7.12 K_{sp} of $Zn(IO_3)_2$ = _____

2. Which of the ion products found in question 1 is closest to the K_{sp}? Why?

3. The titration volumes for the first three samples in question 1 do not vary greatly. The titration volume for the *last* sample, however, is considerably larger than that of the first samples. Why is this to be expected?

PROCEDURE

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. Obtain a ring stand, hotplate/ stirrer, a magnet bar, buret clamp. Prepare the titration assembly as illustrated in Figure 7.2

7. Start the stirrer at a medium speed, you do not need to turn on the hot plate.

8. 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.

9. 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.

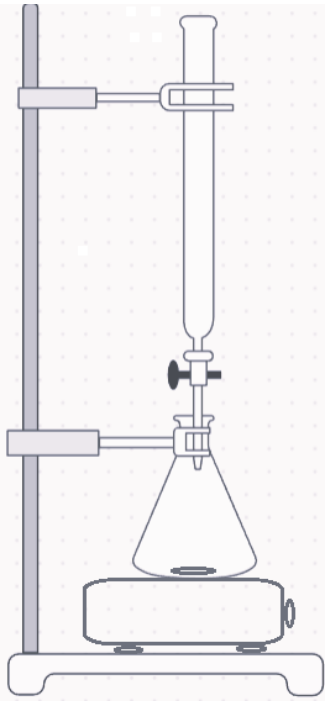

Figure 7.2. Titration setup.

10. Dispose of all titration mixtures and excess reagent solutions in the inorganic waste container provided.

11. 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.

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

CALCULATIONS

Record the results of all calculations in the appropriate spaces on data sheet 1 for your five 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 $[Pb^{2+}][I^-]^2$ 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 in Excel by plotting the ion product (y-axis) vs. $[Pb^{2+}]$ (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.

9. Using the average class data, calculate values of $\sqrt{[Pb^{2+}]}/\left(1+\sqrt{[Pb^{2+}]}\right)$ and log (ion product) using the average class data from data sheet 2. Construct another graph in Excel by plotting the log of the ion product vs. $\sqrt{[Pb^{2+}]}/\left(1+\sqrt{[Pb^{2+}]}\right)$. 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_{sp}. Calculate K_{sp} as the antilog of the intercept and record this result on data sheet 2.

10. Repeat the calculations in step 9 using your own titration results, and plot your data as small triangles on Graph 2. Both your data and the average class data should be plotted together on this graph. 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, K_{sp} @20 °C = 4.41×10^{-9} and K_{sp} @25 °C = 9.80×10^{-9}. Calculate % error using Equation 7.13.

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Data Sheet 1

Individual Data

$[Pb(NO_3)_2]_{initial}$, M	0.250	0.100	0.0500	0.0200	0.0100
$[KI]_{initial}$, M	0.0500	0.0500	0.0500	0.0500	0.0500
V of $Pb(NO_3)_2$, 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	_____	_____	_____	_____	_____
At Endpoint:					
V_{total} at endpoint, mL	_____	_____	_____	_____	_____
$[Pb^{2+}]$, M	_____	_____	_____	_____	_____
$[I^-]$, M	_____	_____	_____	_____	_____
$[Pb^{2+}][I^-]^2$	_____	_____	_____	_____	_____
$\log([Pb^{2+}][I^-]^2)$	_____	_____	_____	_____	_____
$\frac{\sqrt{[Pb^{2+}]}}{1+\sqrt{[Pb^{2+}]}}$	_____	_____	_____	_____	_____

Sample Calculations:

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Data Sheet 2

Average Class Data

$[Pb(NO_3)_2]_{initial}$, M	0.250	0.100	0.0500	0.0200	0.0100
$[KI]_{initial}$, M	0.0500	0.0500	0.0500	0.0500	0.0500
V of $Pb(NO_3)_2$, mL	100.00	100.00	100.00	100.00	100.00
V of KI added, mL	_____	_____	_____	_____	_____
At Endpoint:					
V_{total} at endpoint, mL	_____	_____	_____	_____	_____
$[Pb^{2+}]$, M	_____	_____	_____	_____	_____
$[I^-]$, M	_____	_____	_____	_____	_____
$[Pb^{2+}][I^-]^2$	_____	_____	_____	_____	_____
$\log([Pb^{2+}][I^-]^2)$	_____	_____	_____	_____	_____
$\frac{\sqrt{[Pb^{2+}]}}{1+\sqrt{[Pb^{2+}]}}$	_____	_____	_____	_____	_____

K_{sp} of PbI_2 from Graph 1: _____

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

K_{sp} from Graph 2: _____

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

Show % error Calculations:

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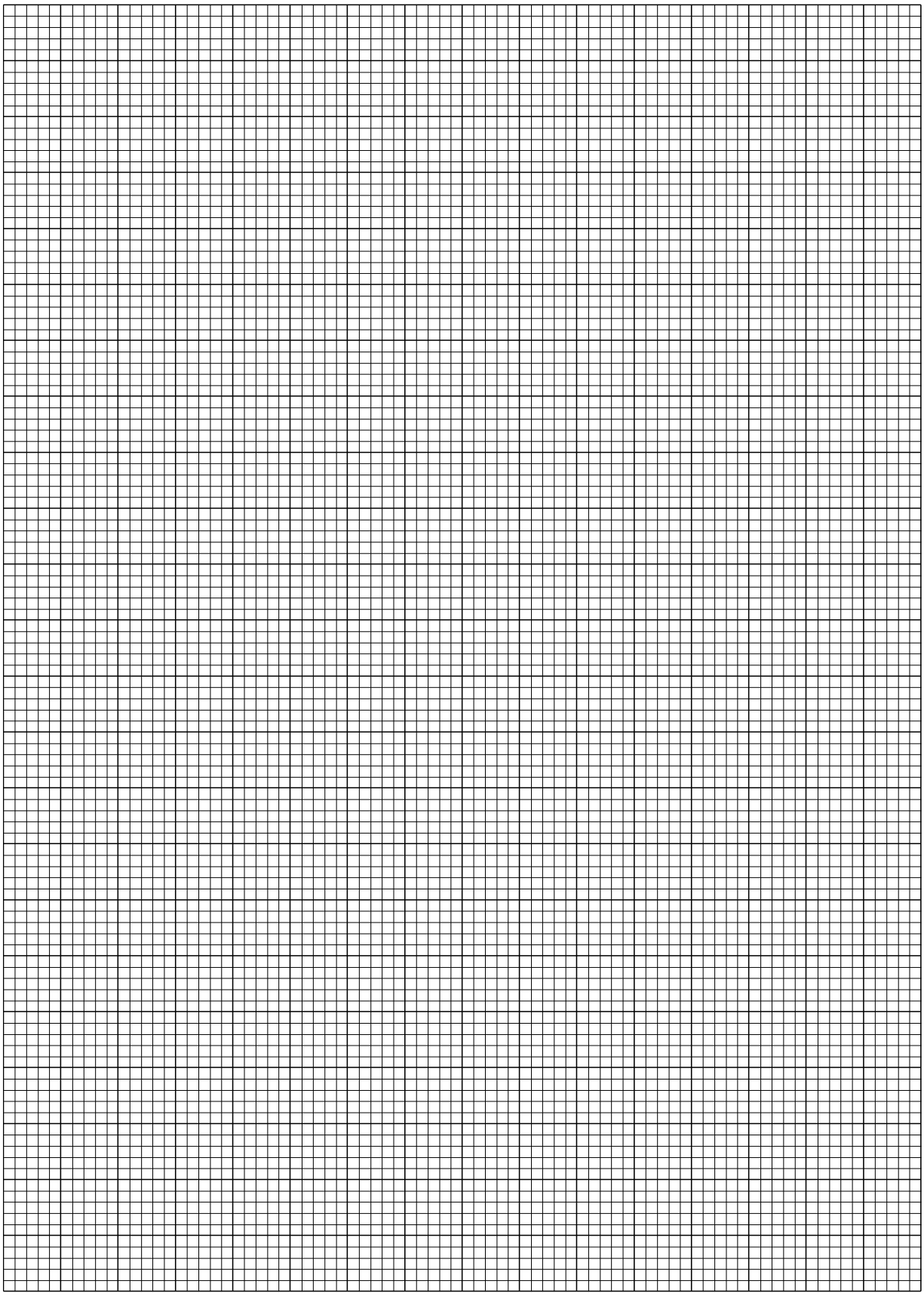

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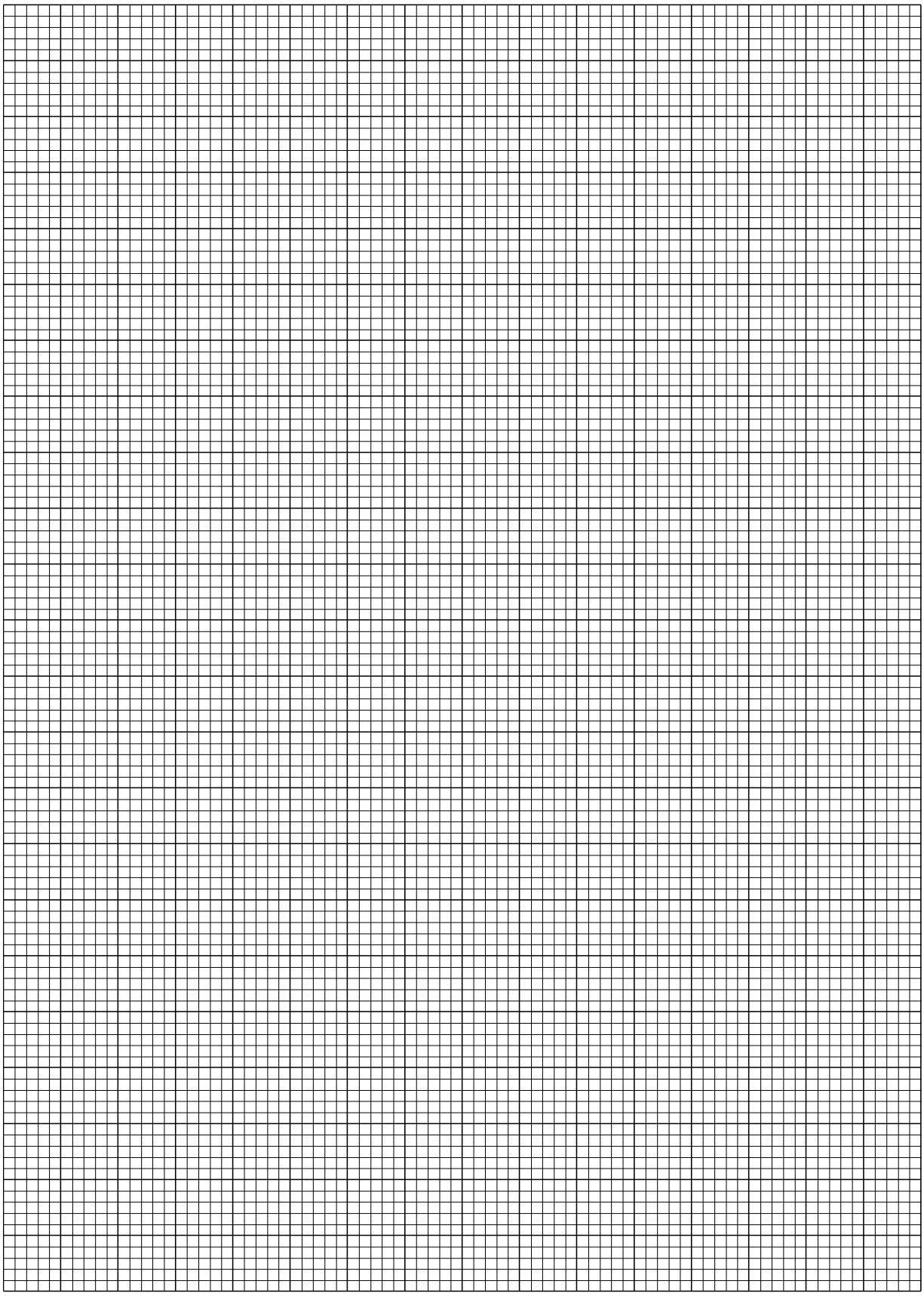

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Post-Lab Questions

1. Which method of plotting data from this experiment allows the best extrapolation to obtain K_{sp}? Explain why this is so.

2. Explain the difference between the "ion product" and K_{sp}. What conditions are necessary for the ion product to approach the value of K_{sp}?

3. Use Graph 1 of the experimental data to estimate a value for the ion product ($[Pb^{2+}][I^-]^2$) for an initial $[Pb^{2+}] = 0.175$ M. Compare this value to the extrapolated K_{sp}.

4. Both class average data and your individual data were plotted on Graph 2. Examine Graph 2 and determine the maximum and minimum values for K_{sp} that could be read from the extrapolated data. The experimental error can now be estimated as:

$$\text{Error} = \frac{K_{sp}(\text{max}) - K_{sp}(\text{min})}{2}$$

   a) What is the estimated experimental error based on your data?

   b) How does the experimental error compare with the % error calculated on data sheet 2?