**Advanced Study Assignment:** Determination of the Solubility Product of PbI₂

1. State in your own words what the solubility product is and explain in terms of $K_{sp}$ for PbI₂

   $$K_{sp} = [\text{Pb}^{2+}][\Gamma]^2$$

2. When 5.00mL of 0.0120 M Pb(NO₃)₂ are mixed with 5.00 mL of 0.0300 M KI, a yellow precipitate of PbI₂(s) forms.

   a. How many moles of Pb²⁺ are initially present? (no. moles A = $M_A \times$ volume in liters).

      __________ moles

   b. How many moles of I⁻ are originally present?

      __________ moles

   c. In a colorimeter the equilibrium solution is analyzed for I⁻, and its concentration is found to be $8.0 \times 10^{-3}$ moles/L. How many moles of I⁻ are present in the solution (10 mL)?

      __________ moles

   d. How many moles of I⁻ precipitated? (You know how many you started with and how many remain in solution, so?)

      __________ moles

   e. How many moles of Pb²⁺ precipitated? (Note that PbI₂ is the precipitate, so the amounts of Pb²⁺ and I⁻ that precipitated must be related.)

      __________ moles

   f. How many moles of Pb²⁺ are left in solution?

      __________ moles

   g. What is the concentration of Pb²⁺ in the equilibrium solution? (still 10 mL)

      __________ moles/L
h. Find a value for $K_{sp}$ of PbI$_2$ from these data.

3. In another experiment a small sample of pure PbI$_2$ is shaken with water to produce a saturated solution, as in Test tube 5.

a. What must be the relationship between [Pb$^{2+}$] and [I$^-$] in that solution? (See Reaction 1).

b. The concentration of I$^-$ in the saturated solution is found to be 5.0 x 10$^{-3}$ M. What is the concentration of Pb$^{2+}$ ions?

$$\text{________ M}$$

c. Using the results of Part b, calculate a value for $K_{sp}$ for PbI$_2$. (Use Eq. 1.)

$$\text{________}$$
Solubility Product of Lead (II) Iodide

Introduction

The purpose of the experiment is to determine the solubility product of PbI$\text{}_2$. The equation for the solution reaction is:

$$\text{PbI}_2 (s) \leftrightarrow \text{Pb}^{2+} (aq) + 2 \Gamma^{-} (aq) \quad (1)$$

The equilibrium constant expression is:

$$K_{sp} = [\text{Pb}^{2+}][\Gamma]^2 \quad (2)$$

The equilibrium mixtures of solid PbI$\text{}_2$ and its ions will be prepared by mixing various solutions containing the ions. Mixture 5 will be prepared from pure solid PbI$\text{}_2$ in water. The equilibrium concentrations of the ions will be determined by measuring the concentration of I$_2$ produced from I$^{-}$ ions by oxidation due to the addition of KNO$_2$. Under slightly acidic conditions, the formation of I$_2$ from I$^{-}$ is quantitative and the brown color of the aqueous solution of iodine allows accurate analysis with spectrophotometer at a wavelength of 525 nm.

In all of the equilibrium mixtures used here, potassium nitrate, KNO$_3$, is present as a dissolved inert salt in order to keep the ionic strength of the mixtures essentially constant and to promote the formation of well-defined crystals of PbI$\text{}_2$.

Experimental procedure

Special equipment

- one 5-mL graduated pipet
- three 5-mL graduated pipet
- pipet bulb
- stoppers for regular, small, and large test tubes

Reagents

- Pour these solutions into the smallest possible clean dry beakers.
  - 40 mL of 0.0120 M Pb(NO$_3$)$_2$ prepared in 0.20 M KNO$_3$
  - 40 mL of 0.0300 M KI prepared in 0.20 M KNO$_3$
  - 15 mL of 0.20 M KNO$_3$

For use in later experiments:
25 mL of 0.02 M KNO$_3$; Note: do not confuse this solution with the KNO$_3$ which is used to prepare equilibrium mixtures.

**Preparation of equilibrium mixtures**

1. Label four regular (6”) test tubes 1 to 4 in pencil.

2. As precisely as possible as you can, measure solutions into test tubes 1 to 4 according to the following table:

<table>
<thead>
<tr>
<th>Volumes of reagent in mL</th>
<th>Test tube number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0.0120 M Pb(NO$_3$)$_2$</td>
<td>5.00</td>
</tr>
<tr>
<td>0.0300 M KI</td>
<td>2.00</td>
</tr>
<tr>
<td>0.20 M KNO$_3$</td>
<td>3.00</td>
</tr>
</tbody>
</table>

3. Stopper each test tube and shake thoroughly at intervals of several minutes while you are proceeding with the next part of the experiment.

4. In a large, 8, test tube, mix about 10 mL of Pb(NO$_3$)$_2$ solution and about 10 mL of KI solution. Stopper and shake vigorously for about a minute. Let the solid settle for a few minutes and then decant (= pour off) most (about ¾) of the supernatant solution into a waste beaker. Transfer the solid PbI$_2$ and the rest of the solution to a small (4”) test tube and centrifuge. Decant the supernatant solution into the waste beaker, leaving the solid PbI$_2$. Add about 3 mL of 0.20 M KNO$_3$ to the solid PbI$_2$, stir well and centrifuge. Discard the supernatant solution into the waste beaker. You have now a small sample of essentially pure solid PbI$_2$ in a small amount of KNO$_3$ solution.

5. Add about 5 mL of 0.20 M KNO$_3$ to the solid PbI$_2$ prepared in Step 4, stir well and transfer the solution and precipitate to a clean regular (6”) test tube. Add about 5 mL more of 0.20 M KNO$_3$, stopper the test tube and shake well. This is your test tube 5 where the mixture has been prepared starting from essentially pure PbI$_2$. Keep shaking the mixture while you work with the solutions in test tubes 1 to 4 so that it also attains equilibrium.

**Analysis of equilibrium mixtures to determine I$^{-}$ ion concentration**

- Each mixture must have been shaken for at least 15 minutes to be at equilibrium.
When equilibrium has been attained, the remaining solid PbI$_2$ must be removed from each equilibrium mixture because the solid would interfere with the beam of light in the spectrophotometer measurements.

1. After the last shaking, allow test tube 1 to stand for about 5 minutes to allow most of the solid to settle.

2. Pour the supernatant liquid from test tube 1 into a small (4") dry test tube until it is about $\frac{3}{4}$ full. Centrifuge it. Pour the supernatant liquid into another small dry test tube. This should now be a clear solution without any solid yellow particles. If this is not the case, centrifuge again and pour the supernatant liquid into another small dry test tube.

3. Pipet 3.00 mL of 0.020 M KNO$_2$ (not KNO$_3$!) into a clean dry spectrophotometer cuvette, add two drops of 6 M HCl. Then add 3.00 mL of the clear supernatant liquid originally from test tube 1 and prepared in Step 2 above. Mix well. The KNO$_2$ oxidizes the I$^-$ to I$_2$ which has a brown color in water.

4. **Immediately** (because I$_2$ evaporates quickly) measure and record the %T (transmittance) using the spectrophotometer at 525 nm wavelength and water as the blank.

5. Discard the solution in a waste beaker. Rinse the spectrophotometer cuvette with DW, then rinse with a small amount of acetone and dry by using a gentle stream of air from the air trap.

6. Repeat Steps 1 to 5 for the mixtures in the other test tubes. Complete each measurements before starting work on the next mixture.

**Clean-up:**

1. Pour all solutions containing lead ions or solid PbI$_2$ into your waste beaker. Empty your waste beaker into the class waste beaker.

2. Rinse the used pipets with DW and place them in the “Wet glassware” container.

3. Return the pipet bulb and the stoppers.
Solubility Product of PbI$_2$

**Results and Calculations**

1. Calculate the absorbance from each measured %T:
   \[
   \text{absorbance } A = \log(1/T) \text{ where } T = \%T/100.
   \]

2. Calculate $\Gamma^-$ concentration at equilibrium for each trial:
   \[
   [\Gamma^-] = \frac{\text{absorbance}}{\text{slope of calibration curve}}.
   \]
   The value of the slope of the calibration curve will be provided by the instructor or determined separately.

3. In the table on the next page, mixture 5 is different from the others because it is a saturated solution of pure PbI$_2$. Therefore according to equation (1), the concentration of Pb$^{2+}$ is half of the concentration of the $\Gamma^-$. Thus some of the calculations are not necessary for mixture 5. The other mixtures, 1 to 4, contain various proportions of lead and iodide ions, depending on how they were prepared. For them all values of the table must be calculated.

4. The solubility product, $K_{sp}$, is calculated according to equation (2).

5. Complete the table on the next page.
<table>
<thead>
<tr>
<th>Test tube number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume 0.0120 M Pb(NO₃)₂ mL</td>
<td>xxxxx</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume 0.0300 M KI mL</td>
<td>xxxxx</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume 0.20 M KNO₃ mL</td>
<td>xxxxx</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total volume mL</td>
<td>xxxxx</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Absorbance

[\text{I}^-] \text{at equilibrium} \quad \text{mol/L}

Initial no. moles Pb²⁺ x 10⁻⁵ | xxxxx |   |   |   |   |

Initial no. moles I⁻ x 10⁻⁵ | xxxxx |   |   |   |   |

No. moles I⁻ at equilibrium x 10⁻⁵ | xxxxx |   |   |   |   |

No. moles I⁻ precipitated x 10⁻⁵ | xxxxx |   |   |   |   |

No. moles Pb²⁺ precipitated x 10⁻⁵ | xxxxx |   |   |   |   |

No. of moles Pb²⁺ at equilibrium x 10⁻⁵ | xxxxx |   |   |   |   |

[\text{Pb}^{2+}] \text{at equilibrium} \quad \text{mol/L}

\( K_{\text{sp}} \) of PbI₂

\[ Average \ K_{\text{sp}} \ = \ \text{____________________} \]