A.P. CHEMISTRY
DETERMINATION OF SOLUBILITY PRODUCT OF PbI_2

INTRODUCTION:

In this experiment you will determine the solubility product of lead iodide, PbI_2. Lead iodide is relatively insoluble, having a solubility of less than 0.002 mole per liter at 20°C. The equation for the solution reaction of PbI_2 is:

$$PbI_2(s) \leftrightarrow Pb^{2+}(aq) + 2\ I^-(aq) \qquad (1)$$

The solubility product expression associated with this reaction is:

$$Ksp = [Pb^{2+}][I^-]^2 \qquad (2)$$

Equation 2 implies that in any system containing solid PbI_2 in equilibrium with its ions, the product of $[Pb^{2+}]$ times $[I^-]^2$ will at a given temperature have a fixed magnitude, independent of how the equilibrium system was initially made up.

In the first part of the experiment, known volumes of standard solutions of $Pb(NO_3)_2$ and KI will be mixed in several different proportions. The yellow precipitate of PbI_2 formed will be allowed to come to equilibrium with the solution. The value of $[I^-]$ in the solution will be measured experimentally. The $[Pb^{2+}]$ will be calculated from the initial composition of the system, the measured value of $[I^-]$, and the stoichiometric relation between Pb^{2+} and I^- in Equation 1.

By mixing the solutions as we have described, we approach equilibrium by precipitating PbI_2 and measuring the concentrations of I^- and Pb^{2+} remaining in the solution. We will also carry out the reaction in the other direction, by first precipitating PbI_2, washing it free of excess ions, and then dissolving the solid in the inert salt solution. Under such conditions the concentrations of Pb^{2+} and I^- in the saturated solution will be related by Equation 1, since both ions come from pure PbI_2. From the measured value of $[I^-]$ in the saturated solution, we can calculate $[Pb^{2+}]$ immediately.

The concentration of I^- ion will be found spectrophotometrically. Although the iodide ion is not colored, it is relatively easily oxidized to I_2, which is brown in water solution. Our procedure will be to separate the solid PbI_2 from the solution and then to oxidize the I^- in solution with potassium nitrite, KNO_2, under slightly acidic conditions, where the conversion to I_2 is quantitative. Although the concentration of I_2 will be rather low in the solutions you will prepare, the absorption of light by I_2 in the vicinity of 525 nm is sufficiently intense to make accurate analyses possible.

In all of the solutions prepared, potassium nitrate KNO_3 (note this distinction between KNO_2 and KNO_3!) will be present as an inert salt. This salt serves to keep the ionic strength of the solution essentially constant at 0.2 M and promotes the formation of well-defined crystalline precipitates of PbI_2.

EXPERIMENTAL PROCEDURE

<u>DAY 1</u> – Mixing solutions and obtaining a saturated solution of PbI_2 in 5 test tubes:

1. Label five regular test tubes 1 to 5, either with labels or by noting their positions in your test tube rack.
2. Into the 5 test tubes, transfer the correct volumes of 0.0120 M $Pb(N0_3)_2$ in KNO_3, 0.0300 M KI in KNO_3, and 0.200 M KNO_3 as summarized in the table below.

Note the total volume in each test tube will be 10.00 mL.

IN THIS EXPERIMENT IT IS ESSENTIAL THAT THE VOLUMES OF REAGENTS USED TO MAKE UP THE MIXTURES IN TEST TUBES 1 TO 4 BE MEASURED ACCURATELY.

Volumes of Reactants Used in Precipitating PbI_2 (mL)

Test Tube	0.0120 M $Pb(NO_3)_2$ (in 0.20 M KNO_3)	0.0300 M KI (in 0.20 M KNO_3)	0.200 M KNO_3
1	5.00	2.00	3.00
2	5.00	3.00	2.00
3	5.00	4.00	1.00
4	5.00	5.00	0.00
5	10.00	10.00	0.00

3. Once each tube contains the correct volumes of each solution, shake them **vigorously** for approximately 15 minutes.
4. Let the tubes stand for three to four minutes to let the solid settle.
5. Do the additional steps below for test tube five. The rest of the test tubes can go on to part 2.

IT IS ESSENTIAL THAT ALL FIVE MIXTURES BE SHAKEN THOROUGHLY SO THAT EQUILIBRIUM CAN BE ESTABLISHED. INSUFFICIENT SHAKING OF THE FIRST FOUR TEST TUBES WILL RESULT IN NOT ENOUGH PbI_2 WILL DISSOLVE TO ATTAIN EQUILIBRIUM.

<u>TEST TUBE 5 -:</u> ONE PARTNER SHOULD COMPLETE THESE STEPS WHILE THE SECOND PARTNER STARTS ON THE NEXT PAGE.

1. After letting the solid settle for a few minutes, decant and discard three-fourths of the supernatant solution. (Keep a beaker at your table for waste solution. At the end of the lab period pour all your waste solution into your instructor's waste container.)
4. Transfer the solid PbI_2 and the rest of the solution to a small test tube and centrifuge for three minutes.
5. Discard the liquid in your waste container, retaining the solid precipitate in the small test tube.
6. Add 3 mL 0.20 M KNO_3 and shake to wash the solid free of excess Pb^{2+} or I^-.
7. Centrifuge again, and discard the liquid. By this procedure you should now have prepared a small sample of essentially pure PbI_2 in a little KNO_3 solution.
8. Add 0.20 M KNO_3 to the solid until the tube is about three-fourths full. Shake well at **<u>several</u>** one minute intervals (~ 15 minutes) to saturate the solution with PbI_2.
4. Let the tube stand for three to four minutes to let the solid settle.

ONCE YOU COMPLETE THESE STEPS FOR TEST TUBE 5 YOU NEED TO CONTINUE ON THE NEXT PAGE.

PART 2: Analyzing the saturated PbI_2 solution to obtain $[I^-]$.

ALL Tests Tubes (1-5):

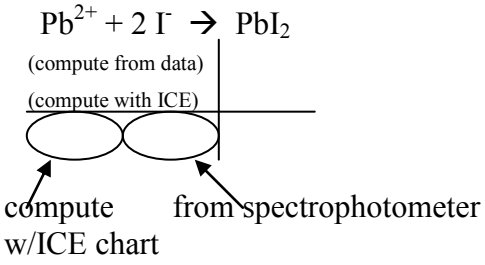
1. Pour the supernatant liquid in each test tube into a small dry test tube until it is three-fourths full and centrifuge for about three minutes to settle the solid PbI_2.
2. Pour the liquid into another small dry test tube; if there are any solid particles or yellow color remaining in the liquid, centrifuge again.
3. When you have a clear liquid, dip a small piece of clean, dry paper towel into the liquid to remove floating PbI_2 particles from the surface.

(Note: If you are "done" for the day, cover each of your small test tubes with parafilm or a rubber stopper. Place on a counter or in your drawer AWAY FROM the windows.)

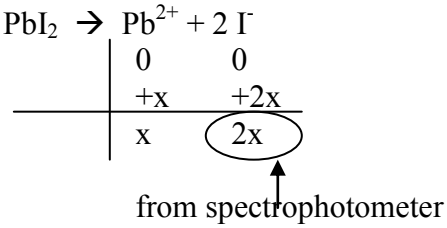
******Do not go on, if there is little time let in the block.**********

4. Obtain a set of six cuvettes from your instructor.
5. Transfer 3.0 mL of 0.020 M KNO_2, potassium NITRITE (NOT KNO_3, potassium nitrate), into a clean, dry spectrophotometer tube and add 2 drops of 6 M HCl.
6. Then, using a disposable pipet, add enough of the clear centrifuged solution (about 3 mL) to fill the spectrophotometer test tube just to the level indicated on the tube.
7. Shake gently to mix the reagents and then measure the percent transmittance of the solution as directed by your instructor.
8. The calibration curve will allow you to determine directly the concentration of I- ion that was in equilibrium with PbI_2. Be sure that the cuvette is clean and clear of bubbles prior to measuring the % transmittance.
9. Rinse the cuvettes with distilled water, then alcohol, and finally with acetone. The cuvette should dry in about two minutes. Return cuvettes to your teacher when finished.

Tests Tubes 1 → 4



Test Tube 5



AP Chemistry Name: _____
Pre-lab: Determination of Ksp for PbI_2 Hour: _____ Date: _____

TO BE COMPLETED AND HANDED IN PRIOR TO STARTING THE LAB.
SHOW WORK FOR CREDIT.

1. $Ksp = [Pb^{2+}] [I^-]^2$ is the equilibrium expression for the dissolving of lead (II) iodide. Explain what $[Pb^{2+}]$ means. _____

   _____

   _____

2. In order to use the above equation, what two conditions must be true? _____

   _____

   _____

3. When 4.0 mL of 0.012 M $Pb(NO_3)_2$ are mixed with 4.0 mL of 0.030 M KI, a yellow precipitate of PbI_2 forms. Solve all parts of Question 3 to two significant figures.

   _____ A. How many moles of Pb^{2+} are initially present? (See section 1, suggestions regarding calculations.)

   _____ B. How many moles of I^- are originally present (Section 2)?

   _____ C. In a colorimeter the equilibrium solution is analyzed for I^-, and its concentration is found to be 7.5×10^{-3} mol/L. How many moles of I^- are present in the solution (8.0 mL) (Section 3)?

   _____ D. How many moles of I^- precipitated (Section 4)?

   _____ E. How many moles of Pb^{2+} precipitated (Section 5)?

   _____ F. How many moles of Pb^{2+} are left in solution (Section 6)?

   _____ G. What is the concentration of Pb^{2+} in the equilibrium solution (Section 7)?

   _____ H. Find a value for Ksp of PbI_2 from these data (Section 8). Include the units for Ksp.