

## Chapter 12

# Solubility of $\text{PbI}_2$ by use of $^{131}\text{I}$ tracer

### Assignment 12

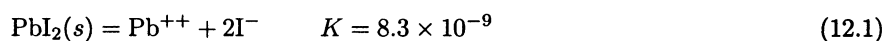
#### 12.1 References

- Friedlander, Kennedy, Macias, and Miller, pp. 410-411.
- Wahl and Bonner, p. 98.
- Latimer, pp. 151-153, 349-351.

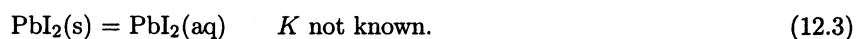
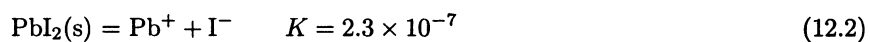
#### 12.2 Introduction and Prelab assignment

The nearly identical behavior of isotopes allows radioactive isotopes to be used as tracers for determination of small amounts of material. One application of the tracer method is the determination of solubilities of slightly soluble substances.

In this assignment you will determine the solubility of  $\text{PbI}_2$  in water and in aqueous  $\text{KNO}_3$  solutions. The main net reaction that occurs is:



Other minor reactions that may also occur are:



1. Calculate the solubility of  $\text{PbI}_2$  in water at  $25^\circ\text{C}$  assuming that only reaction 12.1 occurs and that the saturated solution is ideal (i.e., activity coefficients are unity).

2. Calculate the solubility of  $\text{PbI}_2$  in a solution with ionic strength  $\mu = 5 \times 10^{-3}$  (final value) assuming that only reaction 12.1 occurs and that the Debye-Hückel limiting law is applicable for calculating the mean activity coefficient  $y$ .

$$\log y = -0.509|Z_1 Z_2| \sqrt{\mu}, \quad (12.4)$$

$|Z_1 Z_2|$  being the absolute value of the product of the charges on the ion. The equilibrium-constant expression for reaction 12.1 is:

$$K = [\text{Pb}^{++}][\text{I}^-]^2 (y_{\text{Pb}^{++}})(y_{\text{I}^-})^2 = K' y^3 \quad (12.5)$$

$$K' = [\text{Pb}^{++}][\text{I}^-]^2 \quad (12.6)$$

$$y^3 = (y_{\text{Pb}^{++}})(y_{\text{I}^-})^2 \quad (12.7)$$

3. Calculate the percent of  $^{131}\text{I}$  (half-life 8.05 day) that will decay in 1, 3, and 5 hours.

### 12.2.1 Experimental Procedures

**General:** Count your standard and start a background measurement on your scintillation counter.

**Preparation of labeled  $\text{PbI}_2$ :** Place 15.00 ml of standardized KI carrier ( $\sim 10 \text{ mg I}^-/\text{ml}$ ) and 1.00 ml of ( $^{131}\text{I}$ ) $^-$  tracer solution in a centrifuge tube, stir, and place two 1.00-ml aliquots in counting tubes for reference standards. Note the  $\text{I}^-$  concentrations of the carrier and tracer solutions, and calculate the  $\text{I}^-$  concentration in the reference standards. Transfer one-half of the remaining solution to a second centrifuge tube, and add 10 ml of  $\text{Pb}(\text{NO}_3)_2$  solution (20 mg  $\text{Pb}^{++}/\text{ml}$ ) to each centrifuge tube. Stir, centrifuge, and discard the supernatant solution into the radioactive waste bottle. Wash each precipitate twice with  $\sim 10 \text{ ml}$  of the solution to be used for solubility measurements (water or 0.03 M  $\text{KNO}_3$ ). Discard the wash solutions into the radioactive waste bottle.

**Solubility Measurements:** Add 10 ml of water or 0.03 M  $\text{KNO}_3$  solution to the appropriate  $\text{PbI}_2$  precipitate, and place the centrifuge tube in the constant-temperature water bath set at  $25^\circ\text{C}$ . Stir frequently for 10 minutes, allow the precipitate to settle for 5 minutes, take a 1.00 ml aliquot of the clear solution from each sample, and place the aliquot in a counting tube. *Take care not to have precipitate in the aliquot.*<sup>1</sup>

Repeat the above procedure until the radioactivity of successive aliquots is constant within the experimental uncertainty of  $\sim 2\%$ . Count each sample with your scintillation counter long enough to achieve a statistical accuracy of 1% or better. Also count your reference standards. Record the time of each count and correct for decay of  $^{131}\text{I}$ , if appreciable ( $> 0.5\%$ ).

Centrifuge  $\text{PbI}_2$  from the solution remaining, and wash each precipitate twice with  $\sim 10 \text{ ml}$  of 0.1 M or 0.2 M  $\text{KNO}_3$ , placing discarded solution in the radioactive waste bottle. Add 10 ml of 0.1 M or 0.2 M  $\text{KNO}_3$  to the  $\text{PbI}_2$  precipitate that has been washed with the solution, place in the constant temperature bath, and repeat the saturation procedure described above.

<sup>1</sup>You may experiment with a technique to minimize the amount of precipitate in an aliquot. In addition to allowing time for a precipitate to settle, you might try, for example, placing a piece of filter paper over the tip of your pipet or centrifuging  $> 1 \text{ ml}$  of solution before taking a 1.00-ml aliquot. Note, however, that the solubility of  $\text{PbI}_2$  changes with temperature, and that filter paper wet with radioactive  $\text{PbI}_2$  solution should be placed in the dry radioactive waste.

4. From the data on the label of the  $^{131}\text{I}$  tracer solution, calculate the  $^{131}\text{I}^-$  concentration in your reference standards. Also calculate the total  $\text{I}^-$  concentration in your reference standards.
5. From the  $\text{I}^-$  concentration in your reference standards and the relative counting rates of the standards and each solution saturated with  $\text{PbI}_2$ , calculate the  $\text{I}^-$  concentration (moles/liter) and the solubility of  $\text{PbI}_2$  in each saturated solution.
6. Calculate  $K'$  (equation 12.6) for each saturated solution assuming that only reaction 12.1 occurs.
7. Calculate the ionic strength  $\mu$  for each solution and plot of  $K'$  vs.  $\mu^{1/2}$ . Draw a curve through your points, and with the aid of the Debye-Hückel limiting law (equation 12.4) and of equation 12.5, extrapolate your curve to  $\mu^{1/2} = 0$  to obtain  $K$ .
8. Compare your value with the value given in Eq. 12.1, a value determined from electromotive force measurements of cells (Latimer pp. 151–153). Discuss possible reasons for any difference between the values.

## 12.3 Lecture No. 12.

### Solubility of $\text{PbI}_2$ using $^{131}\text{I}$ as a tracer

This is the first of two experiments using  $^{131}\text{I}$  as radioactive tracer in chemical problems.

1. This Assignment: Measure small amounts of Iodine in solution (very low  $[\text{I}^-]$ ), hence the solubility of  $\text{PbI}_2$ .
2. Assignment 14: Isotopic Exchange, where one measures the rate of a reaction by following the radioactive  $^{131}\text{I}$  species. We will not do it this year.

#### 12.3.1 The Idea

- The naturally occurring iodine isotope is  $^{127}\text{I}$ .
- We tag iodine compounds with the  $^{131}\text{I}$ , which has a convenient half life of 8.05 d and low energy  $\beta^-$  particles and  $\gamma$ -rays that make easy to count with a well-type NaI(Tl) detector.
- There is no significant difference in the chemistry of  $^{131}\text{I}$  and  $^{127}\text{I}$ . If isotopic exchange occurs rapidly, then we can follow the  $^{131}\text{I}$  as an indicator of the bulk iodine behavior.

#### 12.3.2 Why use radioactivity?

Consider the quantitative assay of iodine. Note that  $^{131}\text{I}$  has  $t_{1/2} = 8.05$  d and  $\lambda = 5.98 \cdot 10^{-5} \text{ m}^{-1}$ . Now compare the limits chemical measurement vs. tracer:

Weight mg	Chemistry	N	$\lambda N$ d/m	Tracer
1mmole=127 mg	Easy	$6.0 \cdot 10^{20}$	$3.6 \cdot 10^{16}$	Easy
127 $\mu\text{g}$	hard	$6.0 \cdot 10^{17}$	$3.6 \cdot 10^{13}$	easy
127 ng	very hard	$6.0 \cdot 10^{14}$	$3.6 \cdot 10^{10}$	easy
127 pg	impossible	$6.0 \cdot 10^{11}$	$3.6 \cdot 10^7$	easy
127 fg	"	$6.0 \cdot 10^8$	$3.6 \cdot 10^4$	easy
127 ag	"	$6.0 \cdot 10^5$	$3.6 \cdot 10^1$	hard

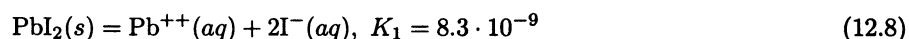
#### 12.3.3 Solubility of $\text{PbI}_2$

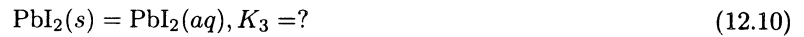
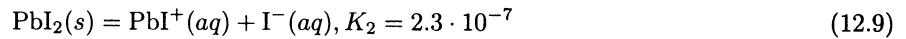
1. Some small fraction of I is converted into  $^{131}\text{I}$ .
2.  $^{131}\text{I}$  emits  $\beta^-$  and  $\gamma$ -rays so we can use either the  $\beta$ -counter or the well-type NaI  $\gamma$ -counter. We will use the latter
3. We need to know the number of  $\gamma$ -rays/decay.

#### 12.3.4 Chemical equilibrium for the solubility of $\text{PbI}_2$

##### Reactions

The main net reaction (MNR) is 12.8 below but there are other reactions present:





The thermodynamic equilibrium for the solubility based on the MNR of Eq. 12.8 is:

$$K_1 = a_{\text{Pb}} \cdot a_{\text{I}^-}^2 = \{[\text{Pb}^{++}][\text{I}^-]^2\} \{y_{\text{Pb}^{++}} \cdot y_{\text{I}^-}^2\} = K_1' \cdot y^3 \quad (12.11)$$

where the  $a$ 's are the activities for a real solution and  $y = y^\pm = (y_{\text{Pb}^{++}} \cdot y_{\text{I}^-}^2)^{1/3}$  is the mean activity coefficient.

If  $y = 1$  then:

$$K_1 = K_1' = [\text{Pb}^{++}][\text{I}^-]^2. \quad (12.12)$$

If  $y \neq 1$  then:

$$K_1 = [\text{Pb}^{++}][\text{I}^-]^2 \cdot y^3 \quad (12.13)$$

### Solubility

The expressions for the solubility are: Number of moles of  $\text{PbI}_2$  dissolved per liter = [sol].

$$\begin{aligned} [\text{sol}] &= [\text{Pb}^{++}] + [\text{PbI}^+] + [\text{PbI}_2] \\ &= [\text{I}^-]/2 + [\text{PbI}^+] + [\text{PbI}_2] \end{aligned}$$

Assuming that Eq. 12.8 is the main net reaction, then the  $\text{PbI}_2$  solubility is:

$$[\text{sol}] \simeq [\text{Pb}^{++}] = [\text{I}^-]/2.$$

If Eq. 12.12 applies (ideal or very dilute solution) then:

$$K_1 = K_1' = [\text{Pb}^{++}][\text{I}^-]^2 = [\text{sol}] \cdot (2[\text{sol}])^2 = 4 \cdot [\text{sol}]^3. \quad (12.14)$$

If Eq. 12.13 applies then:

$$K_1 = 4 \cdot [\text{sol}]^3 \cdot y^3$$

### 12.3.5 Debye-Hückel theory of dilute electrolytes at 25°C

In reality ideal solutions do not exist, and Eq. 12.14 can not be used. Even for very dilute solutions we need to estimate or measure  $y^3$ .

The Debye-Hückel theory provides a "limiting law" that allows us to do this for dilute solutions and provides a mechanism for measuring the true  $K_1$  thermodynamic constant.

We need the following:

1. The limiting law applies for very low ionic strengths (below  $10^{-6}$  or somewhat larger in special cases) and gives:

$$\log_{10} y = A \cdot |Z_+ Z_-| \cdot \sqrt{\mu}, \quad (12.15)$$

- $Z_i$  = ionic charge,

- $A = \text{function of temperature} = -0.509$  at  $25^\circ\text{C}$ .
- $\mu = \frac{1}{2} \sum_i c_i \cdot Z_i^2$ ,  $c_i$  are the concentrations of *all species present in the solution*, not only those originating from  $\text{PbI}_2$ . For example if  $\text{Pb}^{++}$ ,  $\text{I}^-$ ,  $\text{K}^+$ , and  $\text{NO}_3^-$  are the ions in solution then

$$\mu = \frac{4[\text{Pb}^{++}] + [\text{I}^-] + [\text{K}^+] + [\text{NO}_3^-]}{2}$$

Note that  $\log y \rightarrow 1$  as  $\mu \rightarrow 0$ , but the  $\lim y$  as  $\mu \rightarrow \infty$  has no meaning.

2. A better expression is

$$\log_{10} y = \frac{-0.509 \cdot |Z_+ Z_-| \cdot \sqrt{\mu}}{1 + B\sqrt{\mu}},$$

where  $B \sim 1.25$  at  $25^\circ\text{C}$  when  $\mu$  is in moles/liter. This is useful when  $B\sqrt{\mu} \sim 1$ .

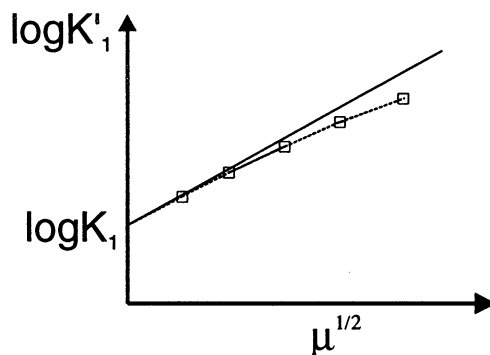


Figure 12.1: Plot of the  $\log K'_1$  as a function of the  $\sqrt{\mu}$ .

3. Now  $K_1 = ?$  Start with Eq. 12.11 and use Eq. 12.15,

$$K_1 = K'_1 y^3 \tag{12.16}$$

$$\log K_1 = \log K'_1 + 3 \log y = \log K'_1 - 3 \cdot 0.509 \cdot |Z_+ Z_-| \cdot \sqrt{\mu} \tag{12.17}$$

$$\log K'_1 = \log K_1 + 3 \cdot 0.509 \cdot |Z_+ Z_-| \cdot \sqrt{\mu} \tag{12.18}$$

Note that  $K'_1$  and  $\mu$  are experimental observables. They can be obtained from solutions where at constant temperature we measure the solubility at various ionic strengths. This is obtained from Eq. 12.18 where the intercept is  $\log K_1$  and the slope  $3 \cdot 0.509 \cdot |Z_+ Z_-|$ . Of course if the limiting law does not apply then deviation from a straight line will be seen as shown in Fig. 12.1