

CHEM 1112: The Solubility of Ba(NO₃)₂

Introduction

For the salt Ba(NO₃)₂ the solubility product constant is given by $K_{sp} = (\text{Ba}^{2+})(\text{NO}_3^-)^2$. If S is the molar solubility of barium nitrate in pure water, then $(\text{NO}_3^-) = 2S$. For every one barium nitrate complex there are 2 nitrate ions. The K_{sp} expression can be rewritten as equation 1.

$$K_{sp} = (S)(2S)^2 = 4S^3 \quad (1)$$

On the other hand, if the salt is dissolved in a solution which contains an additional source of nitrate ion, such as nitric acid, then the concentration of nitrate ion arises from two sources: from the dissolution of the Ba(NO₃)₂ and from the nitric acid. For example, in 0.5 M HNO₃ solution $(\text{NO}_3^-) = S + 0.5$, where S is the solubility of barium nitrate in 0.5 M HNO₃(aq). The concentration of Ba²⁺ will be S and K_{sp} is given by equation 2, this is an illustration of the common ion effect.

$$K_{sp} = (S)(2S + 0.5)^2 \quad (2)$$

In Part 1 of this experiment you will measure the solubility of barium nitrate at room temperature in pure water and in 0.5 M HNO₃, and use your results to calculate K_{sp} . The values of K_{sp} obtained from the two solutions should be equal since K_{sp} depends only on temperature.

Temperature Dependence of K_{sp}

The solubility product constant is an equilibrium constant and is related to the Gibb's free energy change, ΔG , for the solution process by

$$\ln K_{sp} = - \frac{\Delta G}{RT} \quad (3)$$

This equation is exact only for very dilute solutions. Since $\Delta G = \Delta H - T\Delta S$, (where ΔH and ΔS are the enthalpy and entropy changes), equation 3 can be rewritten as equation 4. Equation 4 is only valid for dilute solutions.

$$\ln K_{sp} = - \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (4)$$

Equation 5 is a more general equation which is valid for concentrated solutions.

$$\ln K_{sp} = - \frac{\Delta H}{RT} + C \quad (5)$$

The value for C is a constant that depends upon ΔS , but is not equal to it. Equation (5) shows that if K_{sp} is measured as a function of temperature then a graph of $\ln K_{sp}$ versus $1/T$ should be a

straight line with slope given by

$$\text{slope} = - \Delta H/R \quad (6)$$

In Part 2 of the experiment you will measure K_{sp} as a function of temperature and use your results to obtain a value of ΔH . The values of K_{sp} will be calculated in terms of molal rather than molar concentration.

The molal concentration m is given by

$$\text{molal concentration of solute} = m = \frac{\text{moles solute}}{1000 \text{ g solvent}}$$

Then

$$K_{sp} = (m_{\text{Ba}^{+2}})(m_{\text{NO}_3^-})^2 = 4(S')^3 \quad (7)$$

where S' is the molal solubility of $\text{Ba}(\text{NO}_3)_2$.

Procedure

Part 1a

Weigh a clean, dry 250 mL beaker to ± 0.01 g. Place about 5 g of solid $\text{Ba}(\text{NO}_3)_2$ in the beaker and weigh to ± 0.01 g. Add 50.0 mL of distilled water, measured with a graduated cylinder. Stir for 10 min. Measure the temperature of the solution, and then decant as much as possible of the saturated solution of $\text{Ba}(\text{NO}_3)_2$ into a waste container. Heat the beaker and contents carefully over a low burner flame. The flame should be 6-8 inches from the bottom of the beaker. Evaporate to dryness (about 5 min.) being careful to avoid splattering. Let cool to room temperature, and then weigh the beaker and contents to ± 0.01 g. Save the dry solid for use in Part 2.

Part 1b

Repeat the procedure in Part 1a, except substitute 50.0 mL of 0.50 M HNO_3 for distilled water, and evaporate the contents in the hood.

Part 2

Label and weigh four dry, clean 100 mL beakers to ± 0.01 g. Add additional $\text{Ba}(\text{NO}_3)_2$ to the solid $\text{Ba}(\text{NO}_3)_2$ saved from Part 1a to bring the total mass to 20 g. Add 100 mL of deionized water. Using a bunsen burner, heat the solution with stirring, until the temperature of the solution is about 70°C . Stop heating. As soon as the solution cools to 35°C , quickly decant about 10 mL of solution into one of the pre-weighed 100 mL beakers, and record the temperature. It is not necessary to know the exact volume of solution decanted (concentration in molality not molarity.) Be careful not to transfer any undissolved solid. Continue monitoring the temperature of the solution. When the temperature cools to 30°C , decant another 10 ml into a second pre-weighed 100 ml beaker. Repeat this when solution cools to 25°C and then to 0°C . The last temperature is attained by placing the solution in an ice bath. Allow each of the solutions in 100 ml beakers to come to room temperature and then weigh each to ± 0.01 g.

Heat each of the decanted solutions on a hot plate to evaporate to dryness. To avoid splattering, reduce the heat as evaporation nears completion. Allow the beaker to cool to room temperature, and weigh each beaker and remaining residue to 0.01 g.

Calculations

Part 1a:

The molar solubility of $\text{Ba}(\text{NO}_3)_2$ is equal to the moles of $\text{Ba}(\text{NO}_3)_2$ dissolved in the saturated solution divided by the volume of solution, 0.050 L.

$$S = \frac{\text{initial mass Ba}(\text{NO}_3)_2 - \text{mass Ba}(\text{NO}_3)_2 \text{ remaining in beaker}}{(0.050 \text{ L})(\text{Molar mass of Ba}(\text{NO}_3)_2)}$$

Once you have calculated S, use Equation 1 to calculate the value for Ksp.

Part 1b:

Calculate the molar solubility of $\text{Ba}(\text{NO}_3)_2$ using the same method as in Part 1a, and calculate Ksp using Equation 2.

Part 2:

A sample calculation for this part is shown below. Example: In the determination of the solubility of $\text{Ba}(\text{NO}_3)_2$ at 69°C a sample of saturated solution was decanted into a pre-weighed beaker, and the following data were obtained. Calculate the molal solubility and molal solubility product of $\text{Ba}(\text{NO}_3)_2$ at 69°C .

mass of beaker + sat. soln. =	111.08 g
mass of beaker + dry $\text{Ba}(\text{NO}_3)_2$ =	102.12 g
mass of water in sat. soln. =	8.96 g

mass of beaker + dry $\text{Ba}(\text{NO}_3)_2$ =	102.12 g
mass of empty beaker	99.62 g
mass of $\text{Ba}(\text{NO}_3)_2$ in sat. soln.	2.50 g

The molal solubility S' is

$$S' = \frac{(2.50 \text{ g Ba}(\text{NO}_3)_2)(1000 \text{ g/kg})}{(261.3 \text{ g/mole Ba}(\text{NO}_3)_2)(8.96 \text{ g H}_2\text{O})} = 1.07 \text{ mole/kg}$$

and Ksp is given by Eq. (7)

$$K_{sp} = 4(1.07)^3 = 4.90$$

Use your results to calculate the molal solubility and Ksp at four different temperatures. Using Excel, calculate $\ln K_{sp}$ and $1/T$ and make a plot of $\ln K_{sp}$ versus $1/T$. Use linear regression to determine the slope of your line. From the slope of the line and Eq. (6), calculate ΔH , the

enthalpy change for the solution process. Be sure to include your data table, and your graph with the data as points and the linear regression line (with no markers on the linear regression line.) Also indicate the slope of the line on the plot.

Example: In an experiment the slope of the $\ln K_{sp}$ versus $1/T$ plot was found to be given by:

$$\text{slope} = -7.00 \times 10^3 \text{ K}$$

What is ΔH for the solution process?

$$\begin{aligned} \Delta H &= -R(\text{slope}) = \frac{-8.314 \text{ J}}{\text{K mole}} (-7.00 \times 10^3 \text{ K}) \\ &= 58.2 \times 10^3 \text{ J/mole} \end{aligned}$$

Conclusions

In your well organized conclusion, be sure to address these points. Do not simply put the question number and the answer. Write your conclusion in paragraph form.

- 1) Report and compare the values of K_{sp} obtained in Parts 1a and 1b. Are the two values the same? Explain why.
- 2) Report the solubilities and the values of K_{sp} obtained at the different temperatures in Part 2. How does the solubility vary with temperature?
- 3) What is the enthalpy change for the solution process? Is this an endothermic or exothermic process? Does your value, combined with your answer to question 2, agree with LeChatelier's Principle?