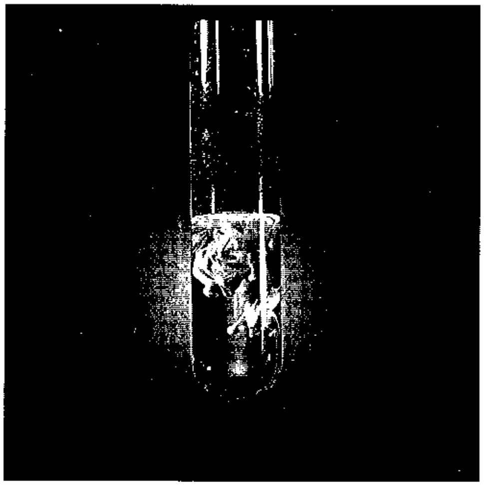


Experiment 22

Molar Solubility, Common-Ion Effect

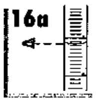
Silver oxide forms a brown mudlike precipitate from a mixture of silver nitrate and sodium hydroxide solutions.

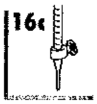
OBJECTIVES

- To determine the molar solubility and the solubility constant of calcium hydroxide
- To study the effect of a common ion on the molar solubility of calcium hydroxide

TECHNIQUES

The following techniques are used in the Experimental Procedure:





INTRODUCTION

Salts that have a very limited solubility in water are called **slightly soluble** (or "insoluble") **salts.** A saturated solution of a slightly soluble salt is a result of a dynamic equilibrium between the solid salt and its ions in solution; however, because the salt is only slightly soluble, the concentrations of the ions in solution are low. For example, in a saturated silver sulfate, Ag_2SO_4, solution, the **dynamic equilibrium** between solid Ag_2SO_4 and the Ag^+ and SO_4^{2-} ions in solution lies far to the *left* because of the low solubility of silver sulfate:

Slightly soluble salt: a qualitative term that reflects the very low solubility of a salt

Dynamic equilibrium: the rate of the forward reaction equals the rate of the reverse reaction

$$Ag_2SO_4(s) \rightleftharpoons 2\ Ag^+(aq) + SO_4^{2-}(aq) \qquad (22.1)$$

The mass action expression for this system is

$$[Ag^+]^2[SO_4^{2-}] \qquad (22.2)$$

As Ag_2SO_4 is a solid, its concentration is constant and therefore does not appear in the mass action expression. At equilibrium, the mass action expression equals K_{sp}, called the **solubility product** or, more simply, the equilibrium constant for this slightly soluble salt.

The **molar solubility** of Ag_2SO_4, determined experimentally, is 1.4×10^{-2} mol/L. This means that in 1.0 L of a saturated Ag_2SO_4 solution, only 1.4×10^{-2} mol of silver sulfate dissolves, forming 2.8×10^{-2} mol of Ag^+ and 1.4×10^{-2} mol of SO_4^{2-}. The solubility product of silver sulfate equals the product of the molar concentrations of the ions, each raised to the power of its coefficient in the balanced equation:

Molar solubility: the number of moles of salt that dissolve per liter of (aqueous) solution

$$K_{sp} = [Ag^+]^2[SO_4^{2-}] = [2.8 \times 10^{-2}]^2[1.4 \times 10^{-2}] = 1.1 \times 10^{-5} \qquad (22.3)$$

What happens to the molar solubility of a salt when an ion, common to the salt, is added to the saturated solution? According to LeChâtelier's principle (*Experiment 16*),

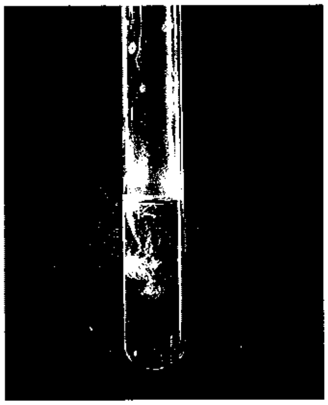


Figure 22.1 The addition of *conc* HCl to a saturated NaCl solution results in the formation of solid NaCl.

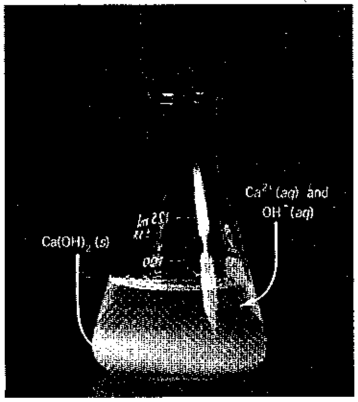


Figure 22.2 The solid $Ca(OH)_2$ in a saturated $Ca(OH)_2$ solution is slow to settle.

the equilibrium for the salt shifts to compensate for the added ions; that is, it shifts *left* to favor the formation of more of the solid salt. This effect, caused by the addition of an ion common to an existing equilibrium, is called the **common-ion effect.** As a result of the common-ion addition and the corresponding shift in the equilibrium, fewer moles of the salt dissolve in solution, lowering the molar solubility of the salt.

The equilibrium in equation 22.1 shows that both Ag^+ and SO_4^{2-} ions are present. Addition of Ag^+ and/or SO_4^{2-}(ions common to the equilibrium) will shift the equilibrium to the *left* (LeChâtelier's principle), resulting in the formation of additional $Ag_2SO_4(s)$, thereby decreasing the solubility of Ag_2SO_4.

While molar solubility is often associated with slightly soluble salts, soluble salts are also affected by the addition of a common-ion to the equilibrium. For example, consider the equilibrium for a saturated solution of sodium chloride:

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq) \qquad (22.4)$$

The addition of chloride ion, a common ion in the equilibrium, shifts the equilibrium left to cause the formation of solid sodium chloride (Figure 22.1).

Molar Solubility and Solubility Product

In Part A of this experiment, you will determine the molar solubility and the solubility product for calcium hydroxide, $Ca(OH)_2$. A saturated $Ca(OH)_2$ solution[1] (Figure 22.2) is prepared; after an equilibrium is established between the solid $Ca(OH)_2$ and the Ca^{2+} and OH^- ions in solution, the supernatant solution is analyzed. The hydroxide ion, OH^-, in the supernatant solution is titrated with a standardized HCl solution to determine its molar concentration.

According to the equation

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,OH^-(aq) \qquad (22.5)$$

for each mole of $Ca(OH)_2$ that dissolves, 1 mol of Ca^{2+} and 2 mol of OH^- are present in solution. Thus, by determining the molar concentration of hydroxide ion, the $[Ca^{2+}]$, the K_{sp}, and the molar solubility of $Ca(OH)_2$ can be calculated.

$$\begin{gathered}[Ca^{2+}] = \tfrac{1}{2}[OH^-] \\ K_{sp} = [Ca^{2+}][OH^-]^2 = \tfrac{1}{2}[OH^-]^3 \\ \text{molar solubility of } Ca(OH)_2 = [Ca^{2+}] = \tfrac{1}{2}[OH^-]\end{gathered} \qquad (22.6)$$

---

[1] A saturated solution of calcium hydroxide is called **limewater.**

Likewise, the same procedure is used in Part B to determine the molar solubility of $Ca(OH)_2$ in the presence of added calcium ion, an ion common to the slightly soluble salt equilibrium.

EXPERIMENTAL PROCEDURE

Procedure Overview: The supernatant from a saturated calcium hydroxide solution is titrated with a standardized hydrochloric acid solution to the methyl orange endpoint. An analysis of the data results in the determination of the molar solubility and solubility product of calcium hydroxide. The procedure is repeated on the supernatant from a saturated calcium hydroxide solution containing added calcium ion.

A. Molar Solubility and Solubility Product of Calcium Hydroxide

Three analyses are to be completed. To hasten the analyses, prepare three *clean*, labeled 125- or 250-mL Erlenmeyer flasks. Obtain no more than 50 mL of standardized 0.05 *M* HCl for use in Part A.5.

Ask your laboratory instructor about the status of the saturated $Ca(OH)_2$ solution. If you are to prepare the solution, then omit Part A.3; if the stockroom personnel has prepared the solution, then omit Parts A.1 and A.2.

1. **Prepare the stock calcium hydroxide solution.** Prepare a saturated $Ca(OH)_2$ solution 1 week before the experiment by adding approximately 3 g of $Ca(OH)_2$ to 120 mL of boiled, deionized water in a 125-mL Erlenmeyer flask. Stir the solution and stopper the flask.
2. **Transfer the saturated calcium hydroxide solution.** Allow the solid $Ca(OH)_2$ to remain settled (from Part A.1). *Carefully* [do not disturb the finely divided $Ca(OH)_2$ solid] decant about 90 mL of the saturated $Ca(OH)_2$ solution into a second 125-mL flask. Proceed to Part A.4.
3. **Obtain a saturated calcium hydroxide solution (alternate).** Submit a clean, dry 150-mL beaker to your laboratory instructor (or stockroom) for the purpose of obtaining ~90 mL of supernatant from a saturated $Ca(OH)_2$ solution for analysis.
4. **Prepare a sample for analysis.** Rinse a 25-mL pipet at least twice with 1- to 2-mL portions of the saturated $Ca(OH)_2$ solution and discard. Pipet 25 mL of the saturated $Ca(OH)_2$ solution into a clean 125-mL flask and add 2 drops of methyl orange indicator.[2]
5. **Set up the titration apparatus.**
   a. Prepare a clean, 50-mL buret for titration. Rinse the clean buret and tip with three 5-mL portions of the standardized 0.05 *M* HCl solution and discard. Fill the buret with standardized 0.05 *M* HCl, remove the air bubbles in the buret tip, and, after 10–15 seconds, read and record the initial volume in the buret to the correct number of significant figures.
   b. Record the *actual* concentration of the 0.05 *M* HCl on the ***Report Sheet***.
   c. Place a sheet of white paper beneath the receiving flask.
6. **Titrate.** Titrate the $Ca(OH)_2$ solution with the standardized HCl solution to the methyl orange endpoint, where the color changes from yellow to a faint red-orange. Remember the addition of HCl should stop within *one-half drop* of the endpoint. After 10–15 seconds of the persistent endpoint, read and record the final volume of standard HCl in the buret.
7. **Repeat.** Titrate two additional samples of the saturated $Ca(OH)_2$ solution until 1% reproducibility is achieved.
8. **Do the calculations.** Complete your calculations as outlined on the ***Report Sheet***. The reported values for the K_{sp} of $Ca(OH)_2$ will vary from chemist to chemist.

---

[2] Methyl orange changes from red-orange to yellow in the pH range of from 3.2 to 4.4.

B. Molar Solubility of Calcium Hydroxide in the Presence of a Common Ion

Three analyses are to be completed. Clean and label three 125- or 250-mL Erlenmeyer flasks.

Again, as in Part A, ask your instructor about the procedure by which you are to obtain the saturated $Ca(OH)_2$ solution with the added $CaCl_2$ for analysis. If you are to prepare the solution, then complete Parts B.1 and A.2; if the stockroom personnel prepared the "spiked" saturated $Ca(OH)_2$ solution, then repeat Part A.3.

In either case, complete Part B.2 in its entirety for the analysis of the saturated $Ca(OH)_2$ solution with the added $CaCl_2$.

1. **Prepare the stock solution.** Mix ~3 g of $Ca(OH)_2$ and ~1 g of $CaCl_2{\bullet}2H_2O$ with 120 mL of boiled, deionized water in a 125-mL flask 1 week before the experiment. Stir and stopper the flask.
2. **Prepare a buret for analysis, prepare the sample, and titrate.** Repeat Parts A.4–A.8.

Disposal: Discard all of the reaction mixtures as advised by your instructor.

CLEANUP: Discard the HCl solution in the buret as advised by your instructor. Rinse the buret twice with tap water and twice with deionized water.

The Next Step

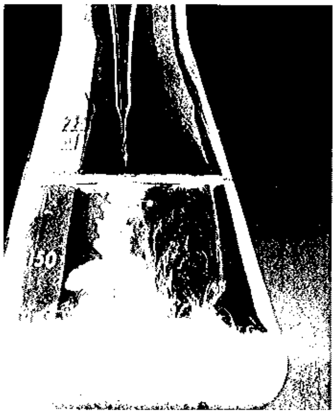
(1) Design an experiment to determine the molar solubility of a salt without using a titration procedure. (2) How does the molar solubility of the hydroxide salts vary within a group and/or within a period of the periodic table? (3) Does the amount of $CaCl_2$ added to saturated $Ca(OH)_2$ solution produce a linear correlation to its molar solubility? Try additional sample preparations.

NOTES AND CALCULATIONS

Experiment 22 *Prelaboratory Assignment*

Molar Solubility, Common-Ion Effect

Date __________ Lab Sec. ______ Name ____ Desk No. __________



Lead iodide precipitate.

1. A saturated solution of lead(II) iodide, PbI_2 has an iodide concentration of 3.0×10^{-3} mol/L (see photo).

a. What is the molar solubility of PbI_2.?

b. Determine the solubility constant, K_{sp}, for lead(II) iodide.

c. Does the molar solubility of lead(II) iodide increase, decrease, or remain unchanged with the addition of potassium iodide to the solution? Explain.

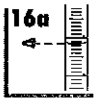
2. Experimental Procedure, Part A.4. What is the purpose of rinsing the pipet twice with aliquots of the saturated $Ca(OH)_2$ solution?

3. Experimental Procedure, Part A.4

a. What is the indicator used to detect the endpoint in the titration for this experiment?

b. What is the expected color change at the endpoint in this experiment?

4. Experimental Procedure, Part A.5. The directions are to read and record the initial volume of the buret to the correct number of significant figures. Explain what this means.



5. Experimental Procedure, Part A.6 versus Part B.2. Would you expect more or less standard 0.05 *M* HCl to be used to reach the methyl orange endpoint in Part B.2? Explain.

6. A saturated solution of magnesium hydroxide (commonly called *milk of magnesium*) is prepared and the excess solid magnesium hydroxide is allowed to settle. A 25.0-mL aliquot of the saturated solution is withdrawn and transferred to an Erlenmeyer flask, and two drops of methyl orange indicator are added. A 0.00053 *M* HCl solution (titrant) is dispensed from a buret into the solution (analyte). The solution turns from yellow to a very faint red-orange after the addition of 13.2 mL.

a. How many moles of hydroxide ion are neutralized in the analysis?

b. What is the molar concentration of the hydroxide ion in the saturated solution?

c. What is the molar solubility of magnesium hydroxide? See equation 22.6.

d. What is the solubility product, K_{sp}, for magnesium hydroxide? Express the K_{sp} with the correct number of significant figures.

***7.** Phenolphthalein has a color change over the pH range of 8.2 to 10.0; methyl orange has a color change over the pH range of 3.2 to 4.4. Although the phenolphthalein indicator is commonly used for neutralization reactions, why instead is the methyl orange indicator recommended for this experiment?

Experiment 22 *Report Sheet*

Molar Solubility, Common-Ion Effect

Date ________ Lab Sec. ______ Name ______________________________ Desk No. ________

A. Molar Solubility and Solubility Product of Calcium Hydroxide

	Trial 1	*Trial 2*	*Trial 3*	
1. Volume of saturated $Ca(OH)_2$ solution (*mL*)	25.0	25.0	25.0	
2. Concentration of standardized HCl solution (*mol/L*)				
3. Buret reading, *initial* (*mL*)				
4. Buret reading, *final* (*mL*)				
5. Volume of HCl added (*mL*)				
6. Moles of HCl added (*mol*)				
7. Moles of OH^- in saturated solution (*mol*)				
8. $[OH^-]$, equilibrium (*mol/L*)				
9. $[Ca^{2+}]$, equilibrium (*mol/L*)				
10. Molar solubility of $Ca(OH)_2$ (*mol/L*)	*			
11. Average molar solubility of $Ca(OH)_2$ (*mol/L*)				
12. K_{sp} of $Ca(OH)_2$	*			
13. Average K_{sp}				
14. Standard deviation of K_{sp}				***Appendix B***
15. Relative standard deviation of K_{sp} (*%RSD*)				***Appendix B***

*Calculations for Trial 1.

B. Molar Solubility of Calcium Hydroxide in the Presence of a Common Ion

	Trial 1	*Trial 2*	*Trial 3*
1. Volume of saturated $Ca(OH)_2$ with added $CaCl_2$ solution (*mL*)	25.0	25.0	25.0
2. Concentration of standardized HCl solution (*mol/L*)			
3. Buret reading, *initial* (*mL*)			
4. Buret reading, *final* (*mL*)			
5. Volume of HCl added (*mL*)			
6. Moles of HCl added (*mol*)			
7. Moles of OH^- in saturated solution (*mol*)			
8. $[OH^-]$, equilibrium (*mol/L*)			
9. Molar solubility of $Ca(OH)_2$ with added $CaCl_2$ (*mol/L*)			
10. Average molar solubility of $Ca(OH)_2$ with added $CaCl_2$ (*mol/L*)			

Account for the different molar solubilities in Part A.11 and Part B.10 (***Report Sheet***).

Laboratory Questions

Circle the questions that are to be answered.

1. Part A.2. Suppose some of the solid calcium hydroxide is inadvertently transferred along with the supernatant liquid for analysis.
   - **a.** Will more, less, or the same amount of hydrochloric acid titrant be used for the analysis in Part A.6? Explain.
   - **b.** Will this inadvertent transfer increase, decrease, or have no effect on the calculated solubility product for calcium hydroxide? Explain.
   - **c.** Will this inadvertent transfer increase, decrease, or have no effect on the calculated molar solubility of calcium hydroxide? Explain.
2. Part A.6. Does adding boiled, deionized water to the titrating flask to wash the wall of the Erlenmeyer flask and the buret tip increase, decrease, or have no effect on the K_{sp} value of the $Ca(OH)_2$? Explain.
3. Part A.6. While titrating the saturated $Ca(OH)_2$ solution, Isabella was distracted, and the endpoint was surpassed—a dark red-orange. As a result of this technique error, will the reported molar solubility of $Ca(OH)_2$- be too high or too low? Explain.

***4.** Part B.1. How will using tap water instead of boiled, deionized water affect the K_{sp} value of $Ca(OH)_2$—increase, decrease, or have no effect? Explain. *Hint:* How will the minerals in the water affect the solubility of $Ca(OH)_2$?

5. Part A.8. Jerry forgot to record the actual molar concentration of the standard HCl solution (which was actually 0.044 *M*). However, to complete the calculations quickly, the ~0.05 *M* concentration was used. Will the reported molar solubility of $Ca(OH)_2$ be too high or too low? Explain.

***6.** The ethylenediaminetetraacetate ion, H_2Y^{2-}, forms a strong complex with the calcium ion. How does the addition of H_2Y^{2-} affect the molar solubility of $Ca(OH)_2$? Explain. See *Experiment 21* for the reaction of Ca^{2+} with H_2Y^{2-}.