Solubility Product for Calcium Hydroxide

GOAL AND OVERVIEW

A saturated solution of $Ca(OH)_2$ will be made by reacting calcium metal with water, then filtering off the solids.

$$Ca(s) + H_2O \to Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2 OH^{-}(aq)$$
(1)

The concentration of dissolved hydroxide will be determined by acid-base titration with standardized HCl solution. The $K_{\rm sp}$ for Ca(OH)₂ will be calculated from the experimentally-determined saturation concentration of hydroxide.

Objectives

- understand solubility equilibria, acid-base neutralization, and the chemistry of lime (Ca(OH)₂), limewater, and calcium carbonate (called limestone when occurring naturally as a mineral)
- manipulate equations for saturation equilibria, acid-base titrations, and volumetric dilutions

SUGGESTED REVIEW AND EXTERNAL READING

• reference information on equilibrium and solubility; relevant reference and textbook information on solubility, acids, and bases

BACKGROUND

Whenever solid calcium hydroxide, $Ca(OH)_2$ (commonly known as *lime*), is present in water, it dissolves according to Eq. 2 until the rate of the backward reaction equals the rate of the forward reaction and the solution is saturated.

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

The equilibrium constant for the reaction is the solubility product constant, $K_{\rm sp}$, given by the following.

$$K_{\rm sp} = [{\rm Ca}^{2+}][{\rm OH}^{-}]^2$$
 (3)

The concentration of $Ca(OH)_2(s)$ does not appear in the equilibrium constant expression because it is always present as the pure solid (activity is 1), no matter how much or how little of it is present. A saturated solution of $Ca(OH)_2$ can be prepared by the reaction of calcium metal with water. Calcium is oxidized by water, yielding calcium hydroxide and hydrogen gas.

$$Ca(s) + 2 H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$$
(4)

PROCEDURE

1 Check out any required equipment from the stockroom (or borrow necessary items from the reagent bench). Clean everything well before using it.

If your TA prepares the saturated $Ca(OH)_2$ solution, carefully dispense approximately 30 mL of the liquid above the precipitate into an Erlenmeyer flask and stopper it immediately. PLEASE be sure to replace the lid on the reagent container (the TA-prepared solution). Proceed to step 5.

- 2 To prepare the saturated $Ca(OH)_2$ solution, use your forceps to safely add a small piece of calcium metal to 150 mL of distilled water in a beaker.
 - If you add too much metal, a large excess of calcium hydroxide solid can form and be difficult to remove by filtration.
 - If you add too little metal, you will not form enough calcium hydroxide to saturate the solution, which is the goal of adding the metal to the water.
 - Calcium metal is a strong reducing agent and should not touch skin.
 - You may have to score the metal to rub off the tarnish and expose a clean surface to get the reaction to start.
- **3** You should see the *white precipitate* of solid $Ca(OH)_2$, indicating that the supernatant liquid is a *saturated solution* of limewater.
- 4 Stir the solution and allow the precipitate to settle.
- 5 Slowly pour the solution through a funnel lined with filter paper into an Erlenmeyer flask to collect the solid-free supernatant (saturated solution of $Ca(OH)_2$). To better separate the fine precipitate particles from the supernatant, you may use two pieces of filter paper or you may filter the solution twice. Filtration may take a long time, so make the dilutions for the rest of the experiment while you wait. Do not use vacuum filtration. Do not wash the precipitate.
- 6 Once the filtration is complete, immediately stopper the flask containing the supernatant. Limewater can react with carbon dioxide to yield the *very insoluble* calcium carbonate.

$$\operatorname{Ca}^{2+}(aq) + 2 \operatorname{OH}^{-}(aq) + \operatorname{CO}_{2}(g) \to \operatorname{CaCO}_{3}(s) + \operatorname{H}_{2}\operatorname{O}$$
(5)

Carbon dioxide from the air acts as an acid and will neutralize some of the OH⁻ you are measuring. Minimize your saturated solution's contact with air by **stoppering your flasks** once you have collected the filtrate.

- 7 Your filtrate *must be clear*. Any solid Ca(OH)₂ interferes with the determination of the saturation concentration of OH⁻ ions. As the OH⁻ ions are removed from the sample during titration with acid, remaining solid dissociates, putting extra OH⁻ into solution to satisfy equilibrium. This extra OH⁻ would skew determination of the *saturated* OH⁻ concentration.
- 8 The approximate value of the $K_{\rm sp}$ for calcium hydroxide is 6.5×10^{-6} , so calculate a rough value of the concentration of OH⁻ ion, [OH⁻], in the saturated solution (see prelab question on WebAssign; to two significant figures).
- 9 Prepare a solution of HCl to use as your titrant.
 - **a** Record the exact concentration of the stock HCl solution (approximately 2 M; to 0.001 M).
 - **b** Make a volumetric dilution of the stock HCl solution.
 - **c** Plan the size of aliquot and the amount by which you will dilute the acid so that your titrations will require about 10 mL HCl (see prelab question on WebAssign). Hint a 1:100 dilution is a good start.
 - **d** Record the volume of stock solution used to 0.01 mL and the final volume of the solution after dilution with deionized water to 0.01 mL.
 - **e** Calculate the molarity of the dilute HCl solution using $M_1V_1 = M_2V_2$ to three significant figures.
- 10 Titrate the saturated $Ca(OH)_2$ solution with HCl. You should get four good sets of titration data.
 - **a** Pipet an aliquot of saturated supernatant into a flask containing 100 mL of distilled water and 3 or 4 drops of bromcresol purple indicator. It is okay to add extra deionized water after you record how much $Ca(OH)_2(aq)$ you use.
 - **b** Record the volume of the $Ca(OH)_2(aq)$ aliquot you use to 0.01 mL. Use either 5.00 mL or 10.00 mL for your trials. You should aim to use about 10 mL of the dilute HCl for each titration. Adjust your aliquot size up or down as necessary. If there is scum on top of your supernatant liquid, do not pick any of it up in your pipet.
 - **c** Prepare these flasks only when you are ready to titrate them, and keep all solutions stoppered whenever you are not working with them.
 - **d** Titrate each solution to the equivalence point with HCl (record the HCl volume required to 0.05 mL).

Waste disposal:When you are finished, follow your TA's instructions regarding waste disposal.
There will be liquid and solid waste containers in the back hood.
Nothing goes down the sink or in the trash can.

From the stoichiometry of Eq. 2 you get the following.

$$[OH^{-}] = 2[Ca^{2+}] \text{ (after dissociation)}$$
(6)

This can be substituted into Eq. 3.

$$K_{\rm sp} = 1/2 [{\rm OH}^-]^3$$
 (7)

- 11 Calculate the $[OH^-]$ in the saturated $Ca(OH)_2$ solution for each of your four trials.
- 12 Find an average concentration and its standard deviation.
- 13 Use the average $[OH^-]$ to determine an average for K_{sp} (including error propagation using the standard deviation of the average $[OH^-]$).

A scaling factor of $x10^{-6}$ might be used (in the online version). If your average $K_{\rm sp}$ is not raised to the -6, but rather to the -5, you will have two digits before the decimal place in your $K_{\rm sp}$ value. For example, if your experimental $K_{\rm sp}$ is $6.46x10^{-5}$, the scaled value would be $64.6x10^{-6}$. Please ask for help if you are uncertain about this.

14 Compare your value to the literature value by calculating the percent error in your value relative to the literature value. Include a discussion of why your value may be larger or smaller than the literature value.

RESULTS

Complete your lab summary or write a report (as instructed).

Abstract

Results

 nOH^- (each titration), nOH^- (titration)_{average}, $[OH^-]_{ave}$ (filtrate), K_{sp} (average) with error

Sample Calculations

titrated moles of hydroxide

average hydroxide concentration in aliquot

solubility product

error analysis

Discussion/Conclusions

Discuss what you found out and how, for each part.

Compare the solubility product with the literature value including possible reasons for differences.

How good are..

- the method you used to determine your solubility product?
- your results?

Review Questions