

# Solubility Product Constant, $K_{sp}$ , for Calcium Hydroxide by Acid-Base Titration

## Goal and Overview

A saturated solution of  $\text{Ca}(\text{OH})_2$  will be made by reacting calcium metal with water. Following filtration to remove precipitate particles, aliquots of the saturated solution will be titrated with standardized dilute HCl. The  $K_{sp}$  for  $\text{Ca}(\text{OH})_2$  will be calculated from the experimentally-determined concentration of  $\text{OH}^-$  in the saturated solution.

## Objectives and Science Skills

Qualitatively and quantitatively describe the equilibrium of a slightly soluble salt,  $\text{Ca}(\text{OH})_2$ , in water.

Perform volumetric dilution and calculate resulting molarity.

Perform gravity filtration of a saturated aqueous solution of  $\text{Ca}(\text{OH})_2$  and titrate aliquots with hydrochloric acid.

Manipulate the  $K_{sp}$  equation for  $\text{Ca}(\text{OH})_2$  and calculate its value from the concentration of  $\text{OH}^-$  in solution determined from titration data.

Identify and discuss factors or effects that may contribute to deviations between the theoretical and experimental results and formulate optimization strategies.

Qualitatively describe the effect dissolved  $\text{CO}_2$  might have on the results.

## Suggested Review and External Reading

Reference materials and textbook sections on equilibrium, solubility, acids, bases, dilutions, and titrations

## Introduction

Calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , is used in many lab-scale and industrial applications, ranging from sewage treatment to ammonia production to paper production to pickling.  $\text{Ca}(\text{OH})_2$  is relatively insoluble in water, but its dissociation is sufficient to produce solutions that are appreciably basic.

A saturated solution of  $\text{Ca}(\text{OH})_2$  is commonly known as limewater. Aside from its reactions with acids, limewater attacks some metals, such as aluminum, but protects others like iron from corrosion by creating a passivation layer on the metal surface. It is also finds uses in a wide variety of applications, including food preparation, waste gas treatment, water processing, parchment making, and aquarium maintenance.

The solubility product constant,  $K_{sp}$ , quantifies the extent of dissociation at a given temperature.



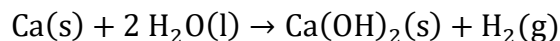
Assuming that the dissolution is perfect, the concentration of  $\text{Ca}^{2+}$  at equilibrium can be taken as half that of  $\text{OH}^{-}$ . The theoretical  $\text{OH}^{-}$  concentration can be calculated by rearranging the  $K_{sp}$  equation and solving for  $[\text{OH}^{-}]$ .

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^{-}]^2 = \frac{1}{2}[\text{OH}^{-}][\text{OH}^{-}]^2 = \frac{1}{2}[\text{OH}^{-}]^3$$

$$[\text{OH}^{-}] = \sqrt[3]{2 \cdot K_{sp}} = \sqrt[3]{2 \cdot 6.5 \times 10^{-6}} = 0.024 \text{ M}$$

The  $\text{OH}^{-}$  present in an aliquot of known volume of limewater can be titrated with dilute standardized HCl solution. The moles of acid added at the equivalence point equals the moles of  $\text{OH}^{-}$  in the aliquot of limewater analyzed, allowing  $[\text{OH}^{-}]$  and  $K_{sp}$  to be determined.

Limewater can be prepared by the reaction of calcium metal with water.



Filtration is a very important step that must be carried out prior to titration, particularly when the above preparation method is used. Microscopic  $\text{Ca(OH)}_2$  precipitate particles not removed will dissolve as a titration proceeds, leading to an artificially high experimental value of  $K_{sp}$ . It is also important to minimize exposure to  $\text{CO}_2$  to prevent the formation of calcium carbonate,  $\text{CaCO}_3$ .

## Equipment List

Labeled beakers, Erlenmeyer flasks (with stoppers), volumetric flask  
Volumetric pipets, disposable pipet  
Filter paper, funnel, glass rod  
Buret/titration equipment

## Procedure

## Caution

Saturated  $\text{Ca(OH)}_2$  solution is basic. HCl is a strong acid. Handle both with care.

Use labels on glassware, wash everything very thoroughly, and wash your hands frequently.

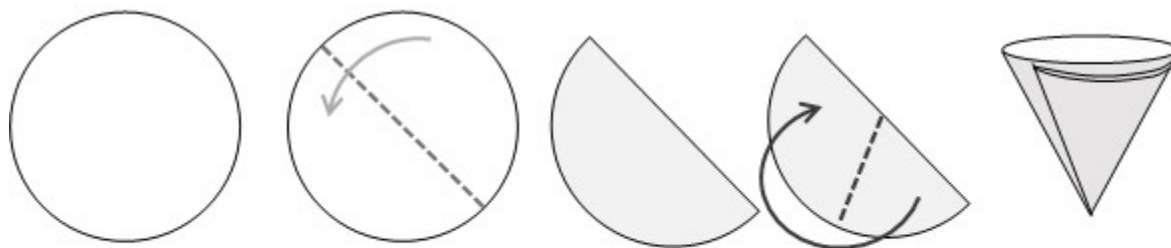
## Limewater preparation

1. Your TA may prepare the limewater (saturated  $\text{Ca}(\text{OH})_2$  solution) for the class. If this is the case, please take a small, labeled beaker to the reagent counter so that your TA can dispense ~50-60 mL of the unfiltered limewater for you.

If the limewater is not prepared for you, add a very small amount of Ca metal to ~100 mL deionized water. Once the reaction is complete, the unfiltered solution should be faintly cloudy but not thick with precipitate.

## Gravity filtration (please NO vacuum filtration)

2. Obtain a piece of filter paper. Fold it as shown.



Fold the filter paper in half. Fold it again *almost* in half.

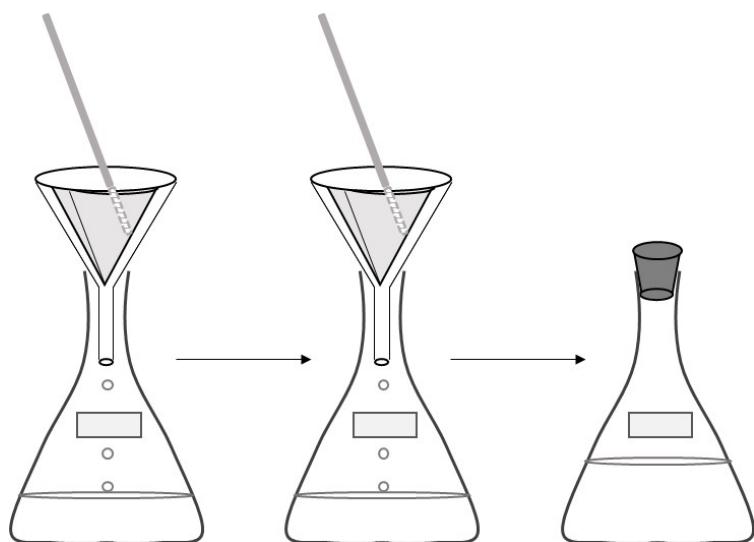
Pull the larger side open to form the “cone” through which the filtration will occur.

3. Place your short stemmed funnel into a labeled 125-mL Erlenmeyer flask. Insert the folded filter paper cone into the funnel and hold it in place with a glass rod. Do not wet the filter paper with water.

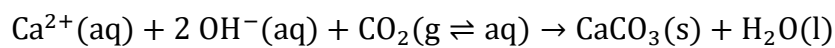
4. Carefully pour a small amount of your limewater down the glass rod so that the filter paper becomes moist and sticks to the funnel.

5. Slowly pour the limewater into the funnel in small volumes, being careful **not** to let the solution go over the top of the filter paper. Filtration can be a slow process, but it is important to be patient.

6. Although after one filtration the filtered solution in the flask (the “supernatant”) should appear clear and free of precipitate, repeat the filtration a second time using a new piece of filter paper. Dispose of the used filter papers in the solid waste container, **not the trash**.



7. Immediately stopper (#5) the 125-mL Erlenmeyer flask containing the limewater filtrate to reduce exposure to  $\text{CO}_2$  in air. Aqueous  $\text{CO}_2$  can act as an acid in water, neutralizing some of the  $\text{OH}^-$  before you perform your titrations. Highly **insoluble**  $\text{CaCO}_3$  is also generated.



After two filtrations, the resulting solution (the “filtrate”) must be clear. If any  $\text{Ca}(\text{OH})_2$  particles remain in the filtrate, they will dissolve as the titration with acid progresses. This “extra”  $\text{OH}^-$  skews the value of  $[\text{OH}^-]$  that is used to calculate your experimental  $K_{sp}$ .

### HCl titrant (1:100 volumetric dilution)

8. Borrow one of the small beakers of stock HCl from the reagent counter. The approximate molarity of the stock solution is roughly 2 M, but record the more exact value written on the bottle (to four significant figures, 3 decimal places).
9. Fill a labeled 100.00-mL volumetric flask approximately 1/4-full with deionized water.
10. Volumetrically pipet 1.00 mL of the  $\sim 2 \text{ M}$  HCl into the flask. Be very careful (see Caution). Return the beaker of stock HCl to the reagent counter immediately.

### Caution

Incorrect use of the pipet and pipetter can result in **serious injury**. Please **do NOT force or jam the pipet** into the pipetter.

If you push too hard, the pipet can break and **cut your hand**.

Use **just enough force** to create a seal. The pipet does not “click” into place.

**Hold both** the pipet and pipetter at all times.

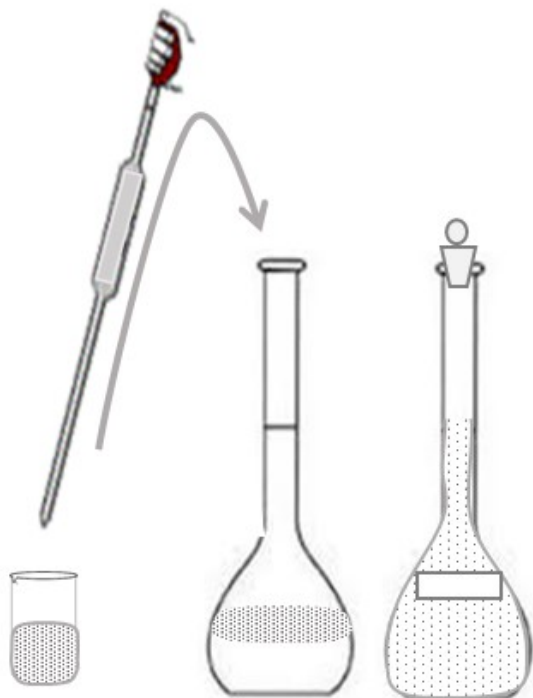
If you pull any solution into the pipetter, please give it to your TA so that it can be cleaned.

If you have trouble, **ask your TA for help**.

11. Fill the flask almost to the line on the neck of the volumetric flask with deionized water. Use a disposable pipet to adjust the level of the liquid so that the bottom of the meniscus is exactly on the line.

12. Insert the stopper into the flask, hold the stopper in firmly, and invert the flask to mix the solution thoroughly. The dilute HCl **must** be well mixed.

This method of preparing a solution via dilution is sometimes called the “sandwich” method – the more concentrated solution is “sandwiched” between two volumes of solvent.



13. Calculate the molarity of the dilute HCl to four significant figures.

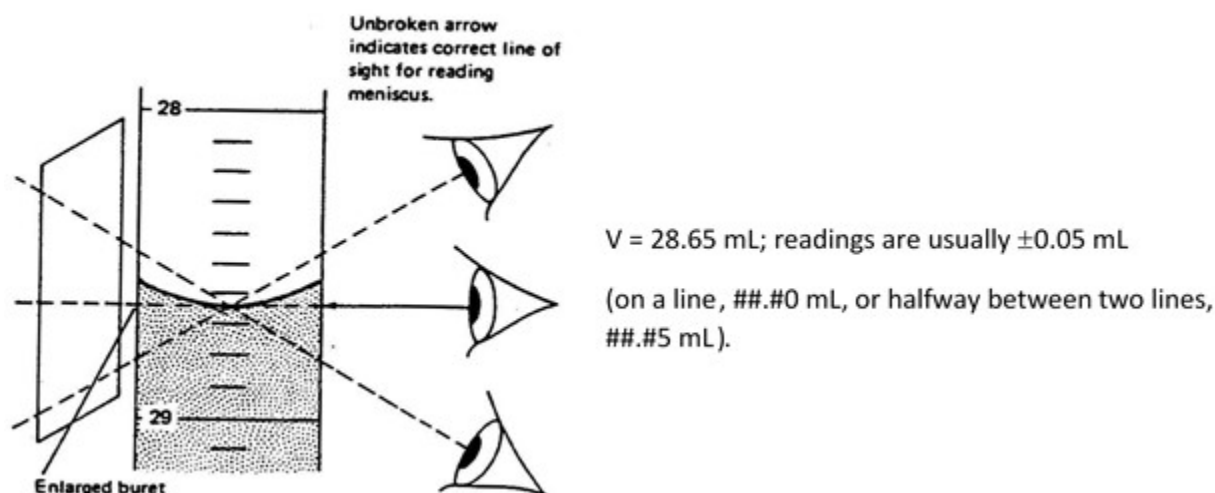
14. Carefully fill your buret with the dilute HCl you prepared (see Caution below). Record the initial volume reading,  $V_{in}$ , at the bottom of the meniscus to 2 decimal places.  $V_{in}$  does NOT need to be 0.00 mL. Do not dispose of the remaining dilute HCl until you have completed all of your titrations.

## Caution

Make sure that the buret is secure and straight in the buret clamp that is fastened to the stand. There should always be a labeled container under the buret large enough to capture the liquid contents.

Do not pour chemicals above eye level. You can carefully set the stand on the floor long enough to fill the buret. Use a funnel; have a labeled waste beaker beneath the buret; and, make sure that the stopcock is closed.

Carefully set the buret stand back on your lab bench. Allow a small amount of HCl to pass through the tip into the waste beaker. Record the initial volume,  $V_{in}$ , to two decimal places.



## Titration of the twice-filtered limewater

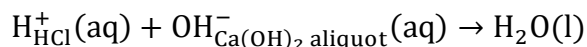
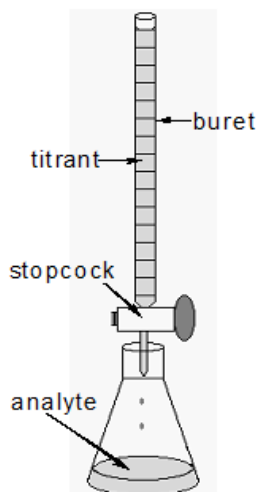
You must perform a minimum of four titrations. Make sure you have data for four consistent trials before leaving.

For each trial:

15. Fill a labeled 250-mL Erlenmeyer flask with about 80 to 100 mL deionized water.

16. Volumetrically pipet a 10.00-mL aliquot of the twice-filtered limewater into the flask. **Be very careful** (see **Caution** in the HCl titrant section regarding volumetric pipet use).

17. Add 2-3 drops of bromothymol blue (BTB) indicator to the analyte solution. In solutions with  $\text{pH} < 6.0$ , BTB appears yellow;  $\text{pH} > 7.6$ , blue. Place a light-colored sheet of paper or paper towel under your flask.



18. Make sure that you have recorded  $V_{in}$  from the buret to two decimal places.

19. Add HCl from the buret to the flask in  $\sim 1 \text{ mL}$  portions while swirling the analyte solution. When you see temporary yellow that disappears readily with swirling, decrease the volume of HCl per addition to  $\sim 0.5 \text{ mL}$ . When the yellow persists slightly longer, go to **dropwise** additions. At the endpoint, the color should be **pale lime green**. One drop of HCl can cause this. If the color goes from **blue to yellow, stop**. You have passed green. Do not add any more HCl.

11. Record  $V_f$  to two decimal places.

12. Once you know approximately how much HCl is required to reach the endpoint, you can titrate your second, third, and fourth solutions more quickly by adding a larger volume of HCl before switching to  $\sim 0.5 \text{ mL}$  and dropwise additions close to the endpoint.

13. Dispose of liquid waste in the waste container in the back hood. Wash all glassware well (tap water and soap, thorough tap water flush, and final deionized water rinse); please be very careful. Clean your work area. Return any equipment that you borrowed clean.

14. Calculate the equivalence volume to two decimal places. Write your  $V_{eq}$  value(s) on the board.

$V_{eq} = V_f - V_{in}$ ; value should end in a 0 or 5 ( \_ . \_ 0 mL or \_ . \_ 5 mL).

15. Calculate the molarity of the  $\text{OH}^-$  in the 10.00-mL aliquot of limewater you used to prepare each analyte solution.

$$[\text{OH}^-] = \frac{n_{\text{OH}^-} \text{ in mol}}{\text{aliquot V in L}} = \frac{n_{\text{H}^+ \text{ at } V_{eq}} \text{ in mol}}{\text{aliquot V in L}} = \frac{(V_{eq} \text{ in L} \times M_{\text{HCl}} \text{ in mol/L})}{\text{aliquot V in L}}$$

$V_{eq} \geq 10.00$  mL (four significant figures)  $\rightarrow$  report  $[\text{OH}^-]_{\text{trial \#}}$  to four significant figures

$V_{eq} < 10.00$  mL (three significant figures)  $\rightarrow$  report  $[\text{OH}^-]_{\text{trial \#}}$  to three significant figures

16. Calculate the unrounded average  $[\text{OH}^-]$  and the standard deviation; then, round  $[\text{OH}^-]_{\text{average}} \pm \sigma_{[\text{OH}^-]}$  to the correct number of significant figures.

17. Calculate  $K_{sp}$  for each trial.

$$K_{sp} = \frac{1}{2} [\text{OH}^-]^3$$

18. Determine the average and standard deviation (unrounded then rounded  $K_{sp} \pm \sigma_{K_{sp}}$ ).  
A  $\times 10^{-6}$  factor may already be included in the online assignment.

Suppose your unrounded experimental  $K_{sp} \pm \sigma_{K_{sp}} = 6.465 \times 10^{-5} \pm 7.248 \times 10^{-7}$ .

Taking the  $\times 10^{-6}$  factor into account gives  $K_{sp} \pm \sigma_{K_{sp}} = 64.65 \times 10^{-5} \pm 0.7248 \times 10^{-6}$ .

Rounding gives the final reported value as  $K_{sp} \pm \sigma_{K_{sp}} = 64.7 \times 10^{-5} \pm 0.7 \times 10^{-6}$ .

19. Calculate the percent error in  $K_{sp}$  relative to the literature value of  $6.5 \times 10^{-6}$  to two significant figures. What are possible sources of error to explain the difference between the theoretical and experimental values?

## Results / Sample Calculations

Complete the online inlab or write a lab report as directed by your TA.

mol  $\text{OH}^-$  (each titration and average)

$[\text{OH}^-]_{\text{average}} \pm \sigma_{[\text{OH}^-]}$

$K_{sp} \pm \sigma_{K_{sp}}$  and %error

## Discussion Questions and Review Topics



What did you do and why?

How large was the standard deviation in your average  $[\text{OH}^-]$  and  $K_{sp}$ ? How could you reduce  $\sigma_{[\text{OH}^-]}$  and  $\sigma_{K_{sp}}$ ?

How large was the percent error in  $K_{sp}$ ? What are possible reasons to explain why the experimental  $K_{sp}$  might not match the literature value? What are possible modifications to the procedure that might reduce the discrepancy?

What would the effect of ion pairs like  $\text{CaOH}^+(\text{aq})$  be on  $[\text{OH}^-]$  and  $K_{sp}$ ? Would filtration be effective in removing species like  $\text{CaOH}^+(\text{aq})$ ?

Discuss the role of dissolved  $\text{CO}_2$ . There are many factors to consider, including its solubility in water at room temperature, its mole fraction in air, exposure time/area, pre-filtration vs. post-filtration, etc. Do you think it had a large impact on your results relative to other sources of error?