

Determination of K_{sp} , ΔG° , ΔH° , and ΔS° for the Dissolution of Calcium Hydroxide in Water

A General Chemistry Experiment

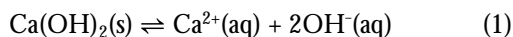
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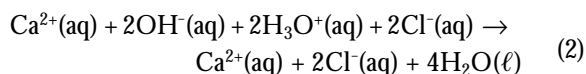
Most first-year college chemistry courses include the concepts of equilibrium, free energy, enthalpy, and entropy and the relationships between them. All are incorporated in one titrimetric experiment presented here. The chemicals used are sufficiently low in toxicity that waste disposal is simple. The chemical operations are straightforward. In this exercise, saturated solutions of calcium hydroxide at two (or more) temperatures are prepared and titrated with standardized hydrochloric acid solution. Using these titration data, the K_{sp} and ΔG° for the dissolution of calcium hydroxide are determined. ΔG° , ΔS° , and ΔH° for the reaction are determined from the temperature dependence.

Theory

When the sparingly soluble compound calcium hydroxide is added to water, an equilibrium is established between the solid and aqueous material that can be approximated by eq 1, ignoring ion-pair formation. The equilibrium concentration of OH^- is large enough to allow its accurate determination by titration with 0.01 M HCl.



Aliquots of the filtered solution are titrated with standardized hydrochloric acid. The molar solubility, s , of calcium hydroxide is then determined from the calculated $[\text{OH}^-]$.



$$\text{moles of hydroxide} = \text{moles of HCl} = \text{liters of HCl} \times [\text{HCl}] \quad (3)$$

$$\text{moles of Ca(OH)}_2 = \frac{1}{2} \text{ moles of hydroxide} \quad (4)$$

$$\text{Molar solubility of Ca(OH)}_2 (s) = \frac{\text{moles of Ca(OH)}_2 \text{ in aliquot}}{\text{volume of aliquot in liters}} \quad (5)$$

The apparent solubility product, K_{sp} , is then calculated from the molar solubility.

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2 = 4s^3 \quad (6)$$

The Gibbs free energy at temperature T , ΔG_T° , is related to the equilibrium constant, K_{sp} , by eq 7:

$$\Delta G_T^\circ = -RT \ln(K_{sp}) \quad (7)$$

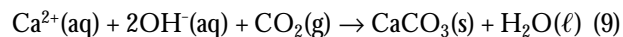
where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. Since ΔH° and ΔS° do not change significantly over small temperature ranges, these quantities can be calculated from eq 8 by generating simultaneous linear equations at two temperatures:

$$\Delta G_T^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

Discussion

Calcium hydroxide is unusual in that it is more soluble at low temperature than at high temperature, which gives an opening for thought-provoking student discussions. If the hot solution cools after filtration, calcium hydroxide will not precipitate out of solution, but rapid filtration should be performed, using a plastic funnel, to remove the precipitate from the cooling solution. Since calcium hydroxide would precipitate from a warming solution formed below room temperature, and since the establishment of the equilibrium would also be slowed, additional trials below room temperature are not recommended.

Reaction with atmospheric carbon dioxide (eq 9) should not be a significant interference.



The solubility of calcium carbonate is estimated to be only about 0.8% that of calcium hydroxide at 25 °C and 2% at 100 °C (1), so that any common-ion effect from dissolved calcium carbonate should be negligible. Calcium hydroxide removed from the solution by carbon dioxide while still in the presence of solid calcium hydroxide will be replaced. Any calcium carbonate formed between the time the solution is filtered and the time it is titrated would be expected to dissolve in and react with the acid and not change the results; that is, the net stoichiometry remains as described in eqs 1 and 2. Boiling the distilled water before adding the solid calcium hydroxide for the high-temperature measurement represents a simple operation to minimize the potential interference of dissolved carbon dioxide.

While variables such as the coarseness of particles or their age might influence the apparent solubility of calcium hydroxide (2), samples from a single bottle should give consistent results for a given class of students. Although concern has been raised about the suitability of simple solubility product calculations for general chemistry students (3–5) the solubility of calcium hydroxide was considered to give adequate agreement between experimental and computational results (5). Although a more accurate treatment could include consideration of the effect of ionic strength, activities, and the ion pair Ca(OH)^+ , which may be 20% to 40% of the concentration of Ca^{2+} (6), this simple treatment gives adequate results for pedagogical purposes. These factors might, nonetheless, make excellent points for discussion with students, particularly since the presence of Ca(OH)^+ would explain why a simple pH measurement would not be expected to give an accurate measurement of the solubility of calcium hydroxide.

Experimental Procedure

WARNING: Although sparingly soluble, calcium hydroxide is a strong base. Ingestion or contact with skin or eyes should be avoided.

Determination of Calcium Hydroxide Solubility at Room Temperature

Calcium hydroxide solution (approximately 40 mL) is drawn off from a carboy containing an excess of solid that has been stirred for at least 24 hours. The temperature of the sample is recorded. This sample is filtered using qualitative filter paper in a long-stem plastic funnel. A 10.00-mL aliquot is transferred to a 125-mL Erlenmeyer flask, to which 25 mL of distilled water and a drop of bromothymol blue indicator (approximately 0.0016 M in aqueous ethanol) are added. The sample is titrated with standardized hydrochloric acid (approximately 0.01 M). The titration is repeated twice.

Determination of the Calcium Hydroxide Solubility at Elevated Temperature

Distilled water (approximately 100 mL) is heated to boiling in a 250-mL beaker. After several minutes, calcium hydroxide (approximately 2 g) is added to the gently boiling water, which is kept at the boiling point with occasional stirring for two minutes. The temperature is recorded and about 45 mL of solution is decanted and immediately filtered. Three 10.00-mL aliquots of the cooled filtrate are titrated as above.

Results

Typical student results compare remarkably well to literature values. All the student data (75 data sets) for one semester were collected and examined. At room temperature (23 °C that semester), the average K_{sp} was found to be 2.15×10^{-6} with a standard deviation of 8.3×10^{-7} , based on 66 data points. Nine points were rejected because they were more than an order of magnitude larger or smaller than the average. Thus, 86% of our students got satisfactory results. At 100 °C, the average student K_{sp} was found to be 7.83×10^{-7} with a standard deviation of 4.56×10^{-7} , using 68 data points and the same rejection criterion as above. The larger standard deviation for 100 °C is probably a result of poor temperature control. These results agree well with a tabulated value of 4.7×10^{-6} at 25 °C (8) or 4.0×10^{-6} at 23 °C and 9.8×10^{-7} at 100 °C calculated using reported enthalpies and absolute entropies (7, 8).

The average K_{sp} values give ΔG° values of $+32.3 \text{ kJ mol}^{-1}$ at room temperature and $+43.60 \text{ kJ mol}^{-1}$ at 100 °C. The enthalpy of the reaction is $\Delta H^\circ = -12.60 \text{ kJ mol}^{-1}$ and the entropy of the reaction is $\Delta S^\circ = -150.7 \text{ J mol}^{-1} \text{ K}^{-1}$. Using tabulated values for standard enthalpies of formation and absolute entropies ($\text{OH}^-(\text{aq})$, $\text{Ca}(\text{OH})_2(\text{s})$, $\text{Ca}^{2+}(\text{aq})$) [7, 8]) predicts $\Delta H^\circ = -16.86 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -160.2 \text{ J mol}^{-1} \text{ K}^{-1}$. Thus, the enthalpy found from the student data is about 25% more exothermic and the entropy is only about 6% in error, compared to referenced values.

Disposal

The neutralized titration solutions may be washed down the drain, local regulations permitting (9). Bromothymol blue (which is sold in pet stores for monitoring fish tank pH) has no particular hazards or disposal methods listed in the Material Safety Data Sheets investigated. If the calcium hydroxide in solution exceeds the amount of hydrochloric acid, 2 M HCl may be used to carefully neutralize the remainder (9).

Supplemental Material

Materials for students, a sample laboratory lecture, and preparation instructions are available in this issue of *JCE Online*.

Literature Cited

1. *CRC Handbook of Chemistry and Physics*, 50th ed.; Weast, R. C., Ed.; Chemical Rubber Company: Cleveland, OH, 1969; p B-97.
2. Bassett, H.; *J. Chem. Soc.* **1934**, 1270–1275.
3. Meites, L.; Pode, J. S.; Thomas, H. C. *J. Chem. Educ.* **1966**, *43*, 667–672.
4. Hawkes, S. J. *J. Chem. Educ.* **1998**, *75*, 1179–1181.
5. Clark, R. W.; Bonicamp, J. M. *J. Chem. Educ.* **1998**, *75*, 1182–1185.
6. *Stability Constants of Metal-Ion Complexes*, Sillén, L. G.; Martell, A. S., Eds.; Special Publication 17; The Chemical Society: London, 1964; p 42.
7. McMurry, J.; Fay, R. C. *Chemistry*, 2nd ed.; Prentice Hall: Upper Saddle River, NJ, 1998; pp A-10–A-14.
8. Ebbing, D. D. *General Chemistry*, 5th ed.; Houghton-Mifflin: Boston, 1996; pp A-10–A-15.
9. Armour, M.-A. *Hazardous Laboratory Chemicals Disposal Guide*, 2nd ed.; Lewis: New York, 1996; pp 104–105.