

Determination of K_{sp} , ΔG° , ΔH° and ΔS° for $\text{Ca}(\text{OH})_2$

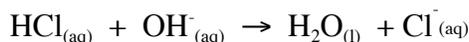
The solubility of hydroxides is easily determined through a titration with a suitable acid (such as HCl). From the molar solubility, the solubility equilibrium constant, K_{sp} , can be calculated and from this the ΔG° for the dissolution of the material can be determined. Using ΔG° values at two different temperatures and noting that the values of ΔH° and ΔS° are relatively invariant over small temperature ranges, the enthalpy and entropy changes can also be estimated. With knowledge of these constants, ΔG° and K_{sp} can be calculated at any temperature between 0 °C and 100 °C.

THE REACTION:

The solubility of an ionic substance in a solvent can be thought of as a reaction where the solid dissociates into ions in solution. In this experiment, the solubility of calcium hydroxide will be determined, as suggested in the reaction shown below.



Once equilibrium has been established and the solid removed, the concentration of hydroxide can be easily determined via an acid/base titration. Hydrochloric acid will be used to find the concentration of $\text{OH}^{-}_{(aq)}$.



Note that the molar solubility of $\text{Ca}(\text{OH})_2$ is *half* of the OH^{-} concentration found by titration.

Determination of K_{sp} , ΔG° , ΔH° and ΔS°

The concentration of hydroxide ion in a saturated solution of $\text{Ca}(\text{OH})_2$ is found by titration with standardized hydrochloric acid. Since HCl is a strong acid and H^+ and OH^{-} react with 1:1 stoichiometry, we can use:

$$M_{\text{HCl}} V_{\text{HCl}} = M_{\text{OH}^-} V_{\text{OH}^-}$$

where M_{HCl} and M_{OH^-} are the molarities and V_{HCl} and V_{OH^-} are the volumes of the acid and hydroxide solutions, respectively. The *molar solubility* of the salt is equal to half of the hydroxide ion concentration

The **equilibrium constant**, K_{sp} , for $\text{Ca}(\text{OH})_2$ is:

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

Remember that the calcium ion concentration is half the hydroxide ion concentration determined by the titration.

The **Gibbs Free Energy**, ΔG° , is related to the equilibrium constant (K_{sp}) by

$$\Delta G^\circ = -RT \ln K_{sp}$$

where **R** is the **ideal gas constant** ($R = 8.314 \text{ J/mol-K}$) and **T** is the **absolute temperature** in Kelvin.

To find the **enthalpy** (ΔH°) and **entropy** (ΔS°) changes, the following equation is used

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where **T** is the absolute temperature. We assume that ΔH° and ΔS° do not change significantly with temperature which is usually true for this small of a temperature change. Using the free energies (ΔG°) found for two different temperatures, ΔH° and ΔS° values are found by solving for two unknowns in two equations.

Example:

Consider the solubility of $\text{Sr}(\text{OH})_2$. Two solutions of $\text{Sr}(\text{OH})_2$ are allowed to equilibrate, one at 0°C and the other at 25°C . A 10.00 mL aliquot of each solution is titrated with 0.2000 M HCl. 3.37 mL of the acid are required for the 0°C solution, and 62.90 mL are required for the 25°C solution.

At 0°C , the $[\text{OH}^-]$ is found using:

$$[\text{OH}^-] = ([\text{HCl}] * V_{\text{HCl}})/V_{\text{OH}^-} = (0.2000 \text{ M} * 3.37 \text{ mL})/10.00 \text{ mL} = \mathbf{0.0674 \text{ M}}$$

Thus, the **molar solubility** of $\text{Sr}(\text{OH})_2$ at 0°C is $0.0674/2 = \mathbf{0.0337 \text{ M}}$. K_{sp} at 0°C can then be found:

$$K_{\text{sp}} = [\text{Sr}^{2+}][\text{OH}^-]^2 = [0.0337][0.0674]^2 = \mathbf{1.53*10^{-4}}$$

ΔG° can be determined at 0°C (273 K):

$$\Delta G^\circ = -RT \ln K_{\text{sp}} = -(8.314)(273) \ln(1.53*10^{-4}) = \mathbf{19.9 \text{ kJ/mol}}$$

Similarly, the molar solubility at 25°C is found to be 0.6290 M; K_{sp} is 0.995; and ΔG° is 0.0124 kJ/mole.

Now we can determine ΔH° and ΔS° using the values of ΔG° at two temperatures:

$$\begin{aligned}\Delta G^\circ &= 19.9 \text{ kJ/mole} = \Delta H^\circ - (273 * \Delta S^\circ) \\ \Delta G^\circ &= 0.0124 \text{ kJ/mole} = \Delta H^\circ - (298 * \Delta S^\circ)\end{aligned}$$

Subtracting the second equation from the first provides

$$19.9 \text{ kJ/mole} = 25 \Delta S^\circ$$

so $\Delta S^\circ = 0.80 \text{ kJ/mole-K}$. Using this value of ΔS° at either temperature gives $\Delta H^\circ = 240 \text{ kJ/mole}$.

PROCEDURE:

1. Record the concentration of the standardized HCl provided in the laboratory.
2. A solution of calcium hydroxide will be stirring at room temperature in the laboratory. Draw off approximately 40 mL of this solution and **record the temperature**. Filter the solution using a long stem funnel. Pipet 10.0 mL of the filtrate into a clean 125 mL Erlenmeyer flask and add 25 mL of distilled water and a few drops of bromothymol blue indicator. Titrate with the standard HCl solution until the **yellow** endpoint appears (probably no more than 5 mL of HCl will be required to reach the endpoint). Record the volume of HCl used. Repeat this procedure two more times.
3. Prepare a 100 °C saturated calcium hydroxide solution by bringing 100 mL of distilled water to a boil in a 250 mL beaker. After the water has been boiling for several minutes, add about 2 g of Ca(OH)₂ to the water and keep it near boiling with occasional stirring until needed.
4. Bring your hot solution to a gentle boil for about two minutes, turn off the burner, **measure the temperature** and quickly draw off about 40 - 50 mL of solution. Quickly filter the solution using a clean, dry long stem funnel.
5. Pipet 10.0 mL of the cooled filtrate into each of three clean 125 mL Erlenmeyer flasks and add 25 mL of distilled water and a few drops of bromothymol blue indicator. When the solution is cool, titrate with the standard HCl solution until the **yellow** endpoint appears (probably no more than 5 mL of HCl will be required to reach the endpoint). Record the volume of HCl used. Repeat two more times.

CALCULATIONS:

1. Find the **average solubility** (and **parts per thousand**) of calcium hydroxide at each temperature by finding the hydroxide ion concentration and then converting this value to the molar solubility of Ca(OH)₂. If one of the three equivalence point volumes differs from the other two, it is acceptable to omit the differing value and use the two values with close precision.
2. Find **K_{sp}** at each temperature. Find **ΔG°** at each temperature using the values of K_{sp}.
3. Find **ΔH°** and **ΔS°** using the values of K_{sp} and ΔG° at the two temperatures.

POST-LAB QUESTIONS:

1. Look up the 25 °C K_{sp} for calcium hydroxide in your text or in the *Handbook of Chemistry and Physics*. How does your room temperature value compare to the reference? What are the sources of error? Cite your reference for the K_{sp} value.
2. Calculate the molar solubility of $\text{Ca}(\text{OH})_2$ at 50 °C using your experimental values of ΔH° and ΔS° . Is this solubility the average of the 0 °C and 100 °C solubilities? Why or why not?
3. Why is it necessary to filter the solution before titrating? How would having a small amount of $\text{Ca}(\text{OH})_{2(s)}$ in the titration flask affect your results?
4. A 10.00 mL sample of $\text{Ba}(\text{OH})_2$ at 0 °C is titrated with 0.2500 M HCl, and 4.80 mL of the acid are used to reach the yellow endpoint.
 - a. Calculate the concentration of hydroxide in the $\text{Ba}(\text{OH})_2$ solution.
 - b. Determine the molar solubility and K_{sp} of $\text{Ba}(\text{OH})_2$.
 - c. Calculate ΔG° for this reaction using the value of K_{sp} .
5. A second 10.00 mL sample of $\text{Ba}(\text{OH})_2$ is obtained at a temperature of 50 °C. This solution is titrated with 44.15 mL of 0.2500 M HCl to reach the yellow endpoint.
 - a. Calculate the concentration of hydroxide in this $\text{Ba}(\text{OH})_2$ solution.
 - b. Determine the molar solubility and K_{sp} .
 - c. Calculate ΔG° for this reaction using the value of K_{sp} .
6. Using the values of ΔG° at 0 °C and 50 °C, calculate ΔH° and ΔS° for this reaction.