

# *CH 223 Spring 2024:*

## **“Determination of $K_{sp}$ , $\Delta G^\circ$ , $\Delta H^\circ$ and $\Delta S^\circ$ for $\text{Ca}(\text{OH})_2$ ”**

### *(online) Lab: Instructions*

**Note:** This is the lab for section W1 of CH 223 only.

- If you are taking section 01 or section H1 of CH 223, please use this link:

<http://mhchem.org/q/7a.htm>

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*Step One:*

**Watch the lab video** for the “Determination of  $K_{sp}$ ” lab, found here:

<http://mhchem.org/v/k.htm>

**Record** the data found at the *end* of the lab video on page Ib-7-5.

*Step Two:*

**Complete pages Ib-7-5 through Ib-7-12** using the “Determination of  $K_{sp}$ ” video and the actual lab instructions on pages Ib-7-2 through Ib-7-4. Include your name on page Ib-7-5!

*Step Three:*

**Submit your lab** (pages Ib-7-5 through Ib-7-12 *only* to avoid a point penalty) **as a single PDF file to the instructor via email ([mike.russell@mhcc.edu](mailto:mike.russell@mhcc.edu)) on Wednesday, May 22 by 11:59 PM.** I recommend a free program (ex: CamScanner, <https://camscanner.com>) or a website (ex: CombinePDF, <https://combinepdf.com>) to convert your work to a PDF file.

*If you have any questions regarding this assignment, please email ([mike.russell@mhcc.edu](mailto:mike.russell@mhcc.edu)) the instructor! Good luck on this assignment!*

## Determination of $K_{sp}$ , $\Delta G^\circ$ , $\Delta H^\circ$ and $\Delta S^\circ$ for $\text{Ca(OH)}_2$

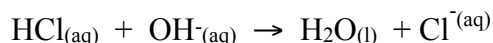
The solubility of hydroxides is easily determined through a titration with a suitable acid (such as HCl). From the molar solubility, the solubility equilibrium constant,  $K_{sp}$ , can be calculated and from this the  $\Delta G^\circ$  for the dissolution of the material can be determined. Using  $\Delta G^\circ$  values at two different temperatures and noting that the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are relatively invariant over small temperature ranges, the enthalpy and entropy changes can also be estimated. With knowledge of these constants,  $\Delta G^\circ$  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  $\text{Ca(OH)}_2$  is *half* of the  $\text{OH}^{-}$  concentration found by titration.

### Determination of $K_{sp}$ , $\Delta G^\circ$ , $\Delta H^\circ$ and $\Delta S^\circ$

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

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

where  $M_{\text{HCl}}$  and  $M_{\text{OH}^{-}}$  are the molarities and  $V_{\text{HCl}}$  and  $V_{\text{OH}^{-}}$  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  $\text{Ca(OH)}_2$  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**,  $\Delta G^\circ$ , is related to the equilibrium constant ( $K_{sp}$ ) by

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

where **R** is the **ideal gas constant** ( $R = 8.3145 \text{ J/mol-K}$ ) and **T** is the **absolute temperature** in Kelvin.

To find the **enthalpy** ( $\Delta H^\circ$ ) and **entropy** ( $\Delta S^\circ$ ) 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  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change significantly with temperature which is usually true for this small of a temperature change. Using the free energies ( $\Delta G^\circ$ ) found for two different temperatures,  $\Delta H^\circ$  and  $\Delta S^\circ$  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  $0.0674/2 = \mathbf{0.0337 \text{ M}}$ .  $K_{\text{sp}}$  at 0 °C can then be found:

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

$\Delta G^\circ$  can be determined at 0 °C (273 K):

$$\Delta G^\circ = -RT \ln K_{\text{sp}} = -(8.3145)(273) \ln(1.53 * 10^{-4}) = \mathbf{19.9 \text{ kJ/mol}}$$

Similarly, the molar solubility at 25 °C is found to be 0.0290 M;  $K_{\text{sp}}$  is 0.995; and  $\Delta G^\circ$  is 0.0124 kJ/mole.

Now we can determine  $\Delta H^\circ$  and  $\Delta S^\circ$  using the values of  $\Delta G^\circ$  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

$$\begin{aligned}19.9 \text{ kJ/mol} - 0.0124 \text{ kJ/mol} &= \Delta H^\circ - \Delta H^\circ - (273 * \Delta S^\circ) + (298 * \Delta S^\circ) \\ 19.9 \text{ kJ/mole} &= 25 \Delta S^\circ\end{aligned}$$

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

## PROCEDURE:

1. Record the concentration of the standardized HCl provided in the laboratory. Obtain about 40 mL of this HCl solution and place it in a 25 mL buret.
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 until you have at least 30 mL of filtrate (if the filtering is slow, consider starting step 3 below.) Place 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 to 0.01 mL. **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  $\text{Ca(OH)}_2$  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. Place 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 to 0.01 mL. **Repeat** two more times.
6. Dispose of all used and excess chemicals in a waste container. Rinse your buret and all glassware with water before returning to its original location.

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**CALCULATIONS:** *Be sure to look at the example on the previous page for hints on how to get started!*

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  $\text{Ca(OH)}_2$ . 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 using the average solubility value. Find  $\Delta G^\circ$  at each temperature using the two values of  $K_{sp}$ .
3. Find  $\Delta H^\circ$  and  $\Delta S^\circ$  using the values of  $K_{sp}$  and  $\Delta G^\circ$  at the two temperatures.

## Determination of $K_{sp}$ , $\Delta G^\circ$ , $\Delta H^\circ$ and $\Delta S^\circ$ for $\text{Ca(OH)}_2$ Lab

**Your name:**

**Purpose:** The goal of this lab is to find  $K_{sp}$ ,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  for  $\text{Ca(OH)}_2$ .

**Goal #1:** Watch the following video related to this lab: <http://mhchem.org/v/k.htm>

**Write down the following data *from the video* which relates to this lab:**

**Concentration of HCl (M):** \_\_\_\_\_

Temperature for first set of data = \_\_\_\_\_ °C *Lower temperature*

Temperature for second set of data = \_\_\_\_\_ °C *Higher Temperature*

\_\_\_\_\_ mL HCl at lower Temperature      \_\_\_\_\_ mL HCl at higher Temperature

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

*Notes: (optional)*

**Goal #2: Determine the solubility of  $\text{Ca(OH)}_2$  at two different temperatures.** We will do two simultaneous calculations in order to find the solubility of  $\text{Ca(OH)}_2$  at each temperature. We can use the mL of HCl titrated and the molarity to find moles of HCl, and this equals moles of hydroxide (1:1 ratio). There are two hydroxides per one  $\text{Ca(OH)}_2$ , so we will apply this stoichiometry to find the moles of  $\text{Ca(OH)}_2$  in the original mixture. Dividing by the liters of  $\text{Ca(OH)}_2$  used (0.0100 L in this lab) will give us the solubility. This calculation scheme will be applied to both temperature sets in order to find the solubility at each temperature.

**Convert mL of HCl into moles of  $[\text{OH}^-]$  at each temperature:**

*Convert mL to L of HCl*

*Multiply L of HCl by (HCl molarity) \* (1 mol  $\text{OH}^-$  / 1 mol HCl) = this equals moles  $\text{OH}^-$   
moles  $\text{OH}^-$  \* (1 mol  $\text{Ca(OH)}_2$  / 2 moles  $\text{OH}^-$ ) / 0.0100 L = solubility of  $\text{Ca(OH)}_2$  (in M)*

**Concentration HCl (M):** \_\_\_\_\_ from Goal #1

At **lower** temperature:

Temperature = \_\_\_\_\_ °C from Goal #1

\_\_\_\_\_ mL HCl equates to a solubility of \_\_\_\_\_ M

\_\_\_\_\_ mL HCl equates to a solubility of \_\_\_\_\_ M

\_\_\_\_\_ mL HCl equates to a solubility of \_\_\_\_\_ M

**Average of three lower temperature solubilities =** \_\_\_\_\_

**Parts per thousand =** \_\_\_\_\_

*Info on parts per thousand: <https://mhchem.org/ppt>*

*Show examples of how this work was accomplished*

**Goal #2:** (continued)

At **higher** temperature:

Temperature = \_\_\_\_\_ °C *from Goal #1*

\_\_\_\_\_ mL HCl equates to a solubility of \_\_\_\_\_ M

\_\_\_\_\_ mL HCl equates to a solubility of \_\_\_\_\_ M

\_\_\_\_\_ mL HCl equates to a solubility of \_\_\_\_\_ M

**Average of three higher temperature solubilities =** \_\_\_\_\_

**Parts per thousand =** \_\_\_\_\_

*Info on parts per thousand:* **<https://mhchem.org/ppt>**

*Show examples of how this work was accomplished*

**Goal #3: Find the value of  $K_{sp}$  and  $\Delta G^\circ$  at each temperature.** We can use  $K_{sp} = 4(\text{solubility})^3$  to convert each average solubility into a  $K_{sp}$  value. Using  $K_{sp}$ , we can convert each value into a  $\Delta G^\circ$  using the relation  $\Delta G^\circ = -RT \ln K_{sp}$  where  $R = 8.3145 \text{ J/mol}\cdot\text{K}$  and  $T = \text{Kelvin temperature}$

At **lower** temperature:

Lower temperature ( $^\circ\text{C}$ ) = \_\_\_\_\_ from Goal #1

Lower temperature (K) = \_\_\_\_\_

Average of three lower temperature solubilities = \_\_\_\_\_ from Goal #2

$K_{sp} = 4(\text{solubility})^3 = \text{_____}$  where solubility = average lower temp. solubility

$\Delta G^\circ = -RT \ln K_{sp} = \text{_____}$  (kJ/mol)

Use  $R = 8.3145 \text{ J/mol}\cdot\text{K}$ ,  $T = \text{Kelvin temp.}$ ,  $K_{sp} = \text{answer on previous line}$

Convert J to kJ to get the final answer

*Show examples of how this work was accomplished*



**Goal #3: Continued**

At **higher** temperature:

Higher temperature ( $^{\circ}\text{C}$ ) = \_\_\_\_\_ *from Goal #1*

Higher temperature (K) = \_\_\_\_\_

Average of three higher temperature solubilities = \_\_\_\_\_ *from Goal #2*

$K_{\text{sp}} = 4(\text{solubility})^3 = \text{_____}$  *where solubility = average high temp. solubility*

$\Delta G^{\circ} = -RT \ln K_{\text{sp}} = \text{_____}$  (kJ/mol)

*Use  $R = 8.3145 \text{ J/mol}\cdot\text{K}$ ,  $T = \text{Kelvin temp.}$ ,  $K_{\text{sp}} = \text{answer on previous line}$*

*Convert J to kJ to get the final answer*

*Show examples of how this work was accomplished*

**Goal #4: Use the values of  $\Delta G^\circ$  and T to find  $\Delta H^\circ$  and  $\Delta S^\circ$ .** We will use the  $\Delta G^\circ$  and Kelvin temperatures to find  $\Delta H^\circ$  and  $\Delta S^\circ$  using the Gibbs Equation,  $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$

From Goal #3:

Lower temperature (K) = \_\_\_\_\_  $\Delta G^\circ$  = \_\_\_\_\_ (kJ/mol)

Higher temperature (K) = \_\_\_\_\_  $\Delta G^\circ$  = \_\_\_\_\_ (kJ/mol)

**Find  $\Delta H^\circ$  and  $\Delta S^\circ$  in the space below.** Follow the video for an example of how this can be done. Clearly show your work for full credit.

$\Delta H^\circ$  = \_\_\_\_\_ (kJ/mol)

$\Delta S^\circ$  = \_\_\_\_\_ (kJ/mol)

### **Postlab Questions:**

1. 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  $K_{\text{sp}}$  of  $\text{Ba}(\text{OH})_2$ .
  - c. Calculate  $\Delta G^\circ$  for this reaction using the value of  $K_{\text{sp}}$ .
  
2. 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  $K_{\text{sp}}$ .
  - c. Calculate  $\Delta G^\circ$  for this reaction using the value of  $K_{\text{sp}}$ .
  
3. Using the values of  $\Delta G^\circ$  at 0. °C and 50. °C, calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  for this reaction.

### **Postlab Questions:** *Continued*

- Look up and report the value of  $K_{sp}$  for calcium hydroxide at 25 °C in your textbook or on the internet. How does your room temperature (“lower temperature”) value compare to the reference? What are the sources of error? Cite your reference for the  $K_{sp}$  value.
- Calculate the molar solubility of  $\text{Ca}(\text{OH})_2$  at 50 °C using your experimental values of  $\Delta H^\circ$  and  $\Delta S^\circ$ . (*Hint:* First find  $\Delta G^\circ$  at the new temperature, then determine  $K_{sp}$  and finally solubility.) Is this solubility the average of the 0 °C and 100 °C solubilities? Why or why not? (*Hint:* are the equations used to determine solubility linear?)