EXPERIMENT 9

Thermodynamics and Solubility

Introduction

The most common way to experimentally determine the value of the thermodynamic variables, such as ΔG°, ΔH°, or ΔS°, is to measure the concentrations of reactants and products at equilibrium and calculate the value of the equilibrium constant. In order to obtain all three thermodynamic variables, the equilibrium constant must be determined for at least two temperatures. The standard free energy change, ΔG°, is related to the value of the equilibrium constant at a particular temperature by the following relationship:

$$\Delta G^\circ = -RT\ln K$$

ΔG° is also related to ΔH° and ΔS° by the following equation:

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

If you rearrange these two equations and solve for ln$K$, you obtain the following equation:

$$\ln K = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

Luckily, ΔH° and ΔS° vary little with temperature. Therefore, for small temperature variations, ΔH° and ΔS° are considered to be constant. If both ΔH° and ΔS° are constants, then equation above is the equation of a straight line with ln$K$ as the *y* variable and 1/T as the *x* variable. The straight line would have a slope equal to $\Delta H^\circ/R$ and intercept equal to $\Delta S^\circ/R$.

If you measure the value of K at two temperatures, T_1 and T_2, K *at* T_1 is equal to the value of K at T_1 and $K(T_2)$ be equal to the value of K at T_2. Thus you now have 2 new equations that can be

$$\ln K(T_1) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_1}\right) + \frac{\Delta S^\circ}{R}$$

$$\ln K(T_2) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2}\right) + \frac{\Delta S^\circ}{R}$$

If you subtract equations, and rearrange them back into the equation for a line, you now have

$$\ln K(T_2) - \ln K(T_1) = \ln\frac{K(T_2)}{K(T_1)} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{K(T_2)}{K(T_1)} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Solving for ΔH°:

$$\Delta H^\circ = \frac{R\ln\dfrac{K(T_2)}{K(T_1)}}{\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)}$$

Once you know the value of an equilibrium constant at two temperatures, you can calculate the value of $\Delta H°$ for that reaction. Once, the values for $\Delta G°$ and $\Delta H°$ have been determined for a reaction, then $\Delta S°$ for the reaction can be determined by solving for $\Delta S°$:

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T}$$

In Your Lab…

In today's experiment, you will determine the solubility product, K_{sp}, of calcium hydroxide, $Ca(OH)_2$ by measuring the concentration of $Ca(OH)_2$ in a saturated solution. Calcium hydroxide is a sparingly soluble salt that dissolves according to the following reaction:

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

The solubility product expression for this reaction is:

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

You will determine the concentration of $Ca(OH)_2$ in a saturated solution by titrating the saturated solution against a standardized hydrochloric acid solution. The neutralization reaction of $Ca(OH)_2$ with HCl is:

$$Ca(OH)_2(aq) + 2\,HCl(aq) \rightleftharpoons CaCl_2(aq) + 2\,H_2O(l)$$

From the concentration of $Ca(OH)_2$ in the saturated solution, you will be able to determine both the Ca^{2+} and OH^- concentrations in the saturated solution. Plugging the ion concentrations into the solubility product expression will give you a value for the K_{sp} for $Ca(OH)_2$. You will measure the K_{sp} at both room temperature and at the temperature of boiling water. This will give you two values of K_{sp} at two temperatures which will allow you to calculate $\Delta G°$, $\Delta H°$, and $\Delta S°$.

Calcium hydroxide is an unusual salt in that it is more soluble in cold water than in hot water. This property allows us to perform this particular experiment which could not be done with most salts which increase in solubility as the solution is heated. Do not feel that you have done something wrong when you find that the solubility, and thus the K_{sp}, is higher for the cold water than the hot water for this salt.

Lab Procedures

Your TA must sign your data before leaving lab or you will not receive credit for attending the lab.
You will work in pairs in this lab; 1 partner does Part 2, the other partner does Part 3

Part 1: Preparation of dilute hydrochloric acid (Repeat this prep if you need more HCl for your titrations)

1. Add exactly 2.00 mL of the stock 1.00M HCl solution to a 50 mL volumetric flask using your 10 mL graduated cylinder. Fill to the line with distilled water and mix well. This diluted solution is to be used in all titrations. Repeat as needed for the titrations.
2. Take a small portion (~5 mL) of the diluted HCl solution and rinse the insides of the buret with it. Fill the buret with the diluted HCl solution.

Part 2: Determination of K_{sp} for $Ca(OH)_2$ at Room Temperature

3. Create a saturated solution of calcium hydroxide by adding 0.10-0.30g of $Ca(OH)_2$ to 30 mL of distilled water in a 50 mL beaker. You should see some undissolved calcium hydroxide at the bottom of the beaker. If not, add a little more calcium hydroxide.
4. Record the temperature of the solution in your laboratory notebook.
5. Filter the saturated $Ca(OH)_2$ solution through a piece of filter paper in a funnel into a 100 mL beaker.
6. Using a 10 mL graduated cylinder, measure out 5.00 mL of the filtered solution with a plastic pipet. Pour the 5.0 mL of solution into a clean 125 mL Erlenmeyer. Add 10 mL of distilled water to the solution and about 5 drops of bromothymol blue.
7. Record the initial volume of HCl in the buret to the nearest 0.01mL in your laboratory notebook.
8. Titrate with the diluted HCl until the color of the solution changes from blue to greenish yellow.
9. Record the final volume of HCl solution added to the nearest 0.01 mL in your laboratory notebook.
10. Repeat for a total of 3 titrations.
11. Rinse out the Erlenmeyer flasks after use.

Part 3: Determination of K_{sp} for $Ca(OH)_2$ in Boiling Water

1. Using a 50 mL beaker, heat approximately 30mL of distilled water to boiling on your hot plate. Add about 0.10-0.30g of $Ca(OH)_2$ gently to the boiling water and stir for 2 minutes. You should still see some undissolved calcium hydroxide. If not, add a little more calcium hydroxide.
2. Record the temperature of the solution to the nearest degree.
3. Set up your filtration apparatus while the solution is heating.
4. Quickly filter this solution. While the filtrate is still very hot, quickly measure out three 5.00 mL portions of the filtered solution (using a plastic pipet and a 10 mL graduated cylinder) into three 125 mL Erlenmeyer flasks. (You may need to borrow one of your partners flasks)
5. Add 10 mL of distilled water to the solution and about 5 drops of bromothymol blue to each Erlenmeyer flask.
6. Record the initial volume of HCl in the buret to the nearest 0.01mL in your laboratory notebook.
7. Titrate with the diluted HCl until the color of the solution changes from blue to greenish yellow.
8. Record the final volume of HCl solution added to the nearest 0.01 mL in your laboratory notebook.
9. Repeat the titration using the remaining two samples of $Ca(OH)_2$.
10. Rinse out the Erlenmeyer flasks well with distilled water after use.

Laboratory Data

Include the correct number of significant figures and units for each value

Concentration of Stock HCl Solution __________
Temperature of saturated $Ca(OH)_2$ Solution __________

Tables 1 and 2: Titration of $Ca(OH)_2$ Solution at both temperatures

You need initial and final buret readings for each trial at each temperature.
Be sure to record your partner's data.

Calculations

Remember to show 1 example of each calculation either handwritten or typed on a separate sheet.
Include correct significant figures and units

Concentration of Diluted HCl

The following formula can be used to determine the concentration of the dilute HCl used in the titrations. Set up the equation to solve for M_2, the concentration of the diluted HCl.

$$M_1V_1=M_2V_2$$

M_1 = concentration of stock solution
V_1= volume of stock solution used
M_2 = concentration of diluted solution
V_2 = total volume of diluted solution

Moles HCl Used in the Titration

Multiply the volume of diluted HCl solution added (in liters) during the titration by the concentration of diluted HCl solution. Repeat for all 6 titrations.

Moles $Ca(OH)_2$ in the Saturated Solutions

For every mole of $Ca(OH)_2$ used, you needed 2 moles of HCl, so divide the moles of HCl used in the titration by 2 to find the moles of $Ca(OH)_2$ in the titrated solutions.

$$2\ HCl(aq) + Ca(OH)_2 \longrightarrow 2\ H_2O(l) + CaCl_2(aq)$$

Concentration of $Ca(OH)_2$ in the Saturated Solutions

Calculate the concentration of $Ca(OH)_2$ in the saturated solution by dividing the number of moles of $Ca(OH)_2$ by the volume of saturated solution used in liters.

Concentration of Ca^{2+} and OH^- in the Saturated Solutions

Calculate the concentrations of Ca^{2+} and OH^- in the saturated solution by using the following relationships:

$$[Ca^{2+}] = [Ca(OH)_2]$$

$$[OH^-] = 2 \times [Ca(OH)_2]$$

Values of K_{sp} for $Ca(OH)_2$

Enter the concentrations for Ca^{2+} and OH^- into the K_{sp} expression for $Ca(OH)_2$ and calculate a value for K_{sp} at room temperature. Average your three values. Repeat the calculations for the three titrations using the saturated $Ca(OH)_2$ solution in boiling water. Find the average K_{sp} for this solution as well.

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

Value of $\Delta G°$

Using the room temperature average value for K_{sp}, calculate the value of $\Delta G°$ for the solubility of $Ca(OH)_2$ using the following equation:

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

Remember to convert your temperatures to Kelvin and include the sign (+/-) with your value.

Value of ΔH°

Using the room temperature and the boiling temperature values for K_{sp} and the two temperatures calculate the value of ΔH° for the following reaction using the following equation:

$$\Delta H^\circ = R\left(\frac{\ln \dfrac{K_{sp}(boiling)}{K_{sp}(low)}}{\dfrac{1}{T_{low}} - \dfrac{1}{T_{boiling}}}\right)$$

Remember to convert your temperatures to Kelvin and include the sign (+/-) with your value.

Value of ΔS°

Calculate ΔS° at room temperature for the reaction by using the following reaction:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

Remember to convert your temperatures to Kelvin and include the sign (+/-) with your value.

Results

Include the following results in your lab report.
Include the correct number of significant figures for each measurement.

Table 3: K_{sp} Calculations for $Ca(OH)_2$ Solution at Room Temperature

Well Number	Trial 1	Trial 2	Trial 3
Concentration of Diluted HCl (M)			
Moles HCl			
Moles of $CaOH_2$			
Concentration of $CaOH_2$ (M)			
Concentration of Ca^{2+} (M)			
Concentration of OH^- (M)			
K_{sp}			

Average K_{sp} __________

Table 4: K_{sp} Calculations for $Ca(OH)_2$ Solution at Increased Temperature

Well Number	Trial 1	Trial 2	Trial 3
Concentration of Diluted HCl (M)			
Moles HCl			
Moles of $CaOH_2$			
Concentration of $CaOH_2$ (M)			
Concentration of Ca^{2+} (M)			
Concentration of OH^- (M)			
K_{sp}			

Average K_{sp} __________

Table 5: Thermodynamic Calculations for $Ca(OH)_2$ Solutions

Well Number	Room T	Hot
$\Delta G°$		
$\Delta H°$		
$\Delta S°$		

Discussion Questions

You must use your data to answer these questions. If the answer you give does not reflect YOUR data and results, you will receive no credit for the question.

1. Calculate pK_{sp} values from both of your experimental K_{sp} values and the actual K_{sp}. Then, using your average pK_{sp} at room temperature as your experimental value, calculate your percent error based on the actual pK_{sp} of $Ca(OH)_2$. The tabulated K_{sp} for $Ca(OH)_2$ is 6.5 x10^{-6} at 25°C.

$$pK_{sp} = -\log K_{sp}$$

$$\%Error = \frac{\left| Experimental\ \mathrm{p}K_{sp} - Actual\ \mathrm{p}K_{sp} \right|}{Actual\ \mathrm{p}K_{sp}} x100$$

2. In general, the solubility of most salts increases as the temperature increases. Based on your results and the comparison to the pK_{sp} values given above, how does temperature affect solubility of $Ca(OH)_2$? Is this the result you expected to see?

3. Calcium carbonate, $CaCO_3$, is 100 times less soluble in cold water than $Ca(OH)_2$. Carbon dioxide is a component of air that readily dissolves in water. Write the chemical reaction that describes the reaction of aqueous $Ca(OH)_2$ with aqueous CO_2. How does this equation help explain why you should boil the water for several minutes before adding the solid $Ca(OH)_2$.

4. Explain how the negative and positive signs of $\Delta G°$, $\Delta H°$, and $\Delta S°$ on the values tell you about the process of $Ca(OH)_2$ dissolving in water.

5. Compare the tabulated K_{sp} values (found in your textbook or online) for $Ca(OH)_2$ with $Mg(OH)_2$ and $Sr(OH)_2$. What trend do you see in the K_{sp} values when related to the location of these cations in the periodic chart? Briefly explain why this trend exists.