Online Activity 4

Thermodynamics and Solubility

Introduction

The most common way to experimentally determine the value of the thermodynamic variables, such as $\Delta G°$, $\Delta H°$, or $\Delta S°$, 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, $\Delta G°$,** is related to the value of the equilibrium constant at a particular temperature by the following relationship:

$$\Delta G^0 = -RT\ln K$$

$\Delta G°$ is also related to **enthalpy, $\Delta H°$** and **entropy, $\Delta S°$** by the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

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

$$\ln K = -\frac{\Delta H^0}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^0}{R}$$

Luckily, $\Delta H°$ and $\Delta S°$ vary little with temperature. Therefore, for small temperature variations, $\Delta H°$ and $\Delta S°$ are considered to be constant. If both $\Delta H°$ and $\Delta S°$ 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 $\Delta H°/R$ and intercept equal to $\Delta S°/R$.

If you measure the value of K at two temperatures, K(T_1) and K(T_2), you now have 2 new equations that can be written as follows:

$$lnK(T_1) = -\frac{\Delta H^0}{R}\left(\frac{1}{T_1}\right) + \frac{\Delta S^0}{R}$$

$$lnK(T_2) = -\frac{\Delta H^0}{R}\left(\frac{1}{T_2}\right) + \frac{\Delta S^0}{R}$$

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

$$\ln K(T_2) - \ln K(T_1) = \ln\frac{K(T_2)}{K(T_1)} = -\frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{K(T_2)}{K(T_1)} = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Solving for $\Delta H°$:

$$\Delta H^0 = \frac{R \ln \frac{K(T_2)}{K(T_1)}}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

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 $\Delta S°$:

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

In Your Simulation…

In today's experiment, you will determine the solubility product, K_{sp}, of silver sulfate, Ag_2SO_4 by measuring the concentration of Ag_2SO_4 in a saturated solution. Silver sulfate is a sparingly soluble salt that dissolves according to the following reaction:

$$Ag_2SO_4(s) \leftrightarrows 2Ag^+(aq) + SO_4^{2-}(aq)$$

The solubility product expression for this reaction is:

$$K_{sp} = [Ag^+]^2[SO_4^{2-}]$$

You will determine the concentration of silver sulfate using a chemcollective.org simulation called Determining the Solubility Product. The link is http://chemcollective.org/vlab/88

The simulation will give you both the Ag^+ and SO_4^{2-} concentrations in the saturated solution. Plugging the ion concentrations into the solubility product expression will give you a value for the K_{sp} for Ag_2SO_4. 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.

Online Activity 4: Procedure and Data Sheet
Include as part of your Online Activity Report

Record all measurements with the correct number of significant figures and units.

1. Go to the ChemCollective simulation Determining the Solubility Product at http://chemcollective.org/vlab/88
2. In the "Stockroom: menu on the right, select solutions, then click on the 100mL flask of distilled water and the Ag_2SO_4 to add them to your workbench. The flask of 100mL distilled water is at the end of the list.
3. Select tools, and add the balance to your workbench.
4. Select glassware, then other, and add a plastic weigh boat to your work bench.
5. Drag the weigh boat over your balance until you see a green + sign telling you that the weigh boat is being placed on the balance.
6. Drag the silver sulfate over the weigh boat until you see the green + sign. Type in 1.000 to add 1.000g silver sulfate to the weigh boat.
7. Drag the weigh boat over the flask containing 100mL distilled water until you see the green + sign. Enter 1.000 to add the 1.000g silver sulfate to the distilled water. A box will open on the right to show you how much of the solid has dissolved. Wait until the number stops changing, and record the concentration of silver and sulfate ions in your solution.

Concentration of Ag^+ ions at 25°C: ________________

Concentration of SO_4^{2-} ions at 25°C: ________________

8. Click where it says Stockroom at the top left, and then add another flask of 100mL distilled water to your work bench. Repeat steps 5-7 to add 1.000g silver sulfate to the second flask of distilled water.
9. Go back to the Stockroom, click on tools, and add the Bunsen burner to your work bench.
10. Drag the second flask of silver sulfate solution over the Bunsen burner, and allow it to heat the water to 100°C. Record the concentration of silver and sulfate ions in the heated solution.

Concentration of Ag^+ ions at 100°C: ________________

Concentration of SO_4^{2-} ions at 100°C: ________________

Grading

Points

Neatness and Clarity of Data	5pts	___________pts
Significant figures and units	5pts	___________pts
All data is present	10pts	___________pts

Deductions (sliding based on TA discretion)

Lab area left unclean	20pts	___________pts
Improper waste disposal	20pts	___________pts
Disruptive behavior	20pts	___________pts
Other: ____		___________pts

Grade for Experimental Procedures and Data **________pts**

Online Activity 4: Results Table
Submit as part of the Online Activity Report

Record all results with the correct number of significant figures and units

Table 1: K_{sp} Calculations the Thermodynamic Constants for $AgSO_4$

Results	**Room Temperature (25.00°C)**	**Elevated Temperature (100.00°C)**
Concentration of Ag^+		
Concentration of SO_4^{2-}		
Concentration of $AgSO_4$		
Solubility of $AgSO_4$		
K_{sp}		
ΔG		
ΔH		
ΔS		

Grading

Points

Significant figures and units	5pts	___________pts
Table is neat and legible	5pts	___________pts
All results are present	10pts	___________pts

Deductions (sliding based on TA discretion)

Results do not make sense	20pts	___________pts
Results do not match data	20pts	___________pts
Other: ____		___________pts

Plagiarism!!! Results are identical to another student 100pts __________pts

Grade on results table __________pts

Calculations Section: Submit as part of your Online Activity Report

Concentration of Ag_2SO_4

Based on the concentration values obtained from the simulation, what is the concentration of $AgSO_4$ in the room temperature and 100°C solutions?

Concentration in 25.00°C water: _______________

Concentration in 100.00°C water: _______________

Solubility of Ag_2SO_4

Calculate the solubility of silver sulfate in g/100mL water at room temperature and at 100°C.

Solubility in water at 25.00°C: _______________

Solubility in water at 100.00°C: _______________

Values of K_{sp} for Ag_2SO_4

Enter the concentrations for Ag^+ and So_4^{2-} into the K_{sp} expression for silver sulfate and calculate a value for K_{sp} at room temperature. Repeat the calculations for the titrations using the saturated silver sulfate solution in boiling water.

K_{sp} at 25.00°C: __________________

K_{sp} at 100.00°C: __________________

Value of ΔG°

Using your values for the K_{sp}, calculate the values of ΔG° for the solubility of silver sulfate at the two temperatures using the following equation:

$$\Delta G^0 = -RT \ln K_{sp}$$

Remember to convert your temperatures to Kelvin and include the sign either positive (+) or negative (-) with your value. Repeat for the K_{sp} at elevated temperature.

ΔG° at 25.00°C: __________________

ΔG° at 100.00°C: __________________

Value of ΔH°

Using the room temperature and the elevated temperature values for K_{sp} and the two temperatures calculate the value of Δ*H*° for the following reaction using the following equation:

$$\Delta H^0 = \frac{R \ln \dfrac{K_{sp}(\ at\ T_{boiling})}{K_{sp}(\ at\ T_{room\ temperature})}}{\left(\dfrac{1}{T_{room\ temperature}} - \dfrac{1}{T_{boiling}}\right)}$$

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

ΔH°: ___________________

Value of ΔS°

Calculate Δ*S*° at room temperature and at elevated temperature for the reaction by using the following equation:

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

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

ΔS° at 25.00°C: ___________________

ΔS° at 100.00°C: ___________________

Online Activity 4 Additional Questions
Submit as part of your Online Activity Report

Record all values with the correct number of significant figures and units.
Place all answers on the line next to the question.
Show calculations for any numerical answers.

Show all work:

> A saturated solution of the $Ca(OH)_2$ is prepared and allowed to equilibrate at 25˚C. A 32.40mL sample of the solution is titrated with 0.050M HCL solution. 14.90mL of the HCl solution are required to fully react with the sample.

1. Write the balanced chemical equation for the reaction of the salt with the HCl.

2. Write the K_{sp} expression for the salt.

3. Calculate the molarity of the $Ca(OH)_2$ solution from the titration data.

4. Calculate the concentrations of the cation and the anion in the salt solution.

5. Show the calculation for the K_{sp} of the salt from the concentrations of the cation and anion in the salt solution.

6. Calculate ΔG for the salt using the K_{sp} you calculated for the question above.

7. Is the reaction spontaneous or nonspontaneous? Why did you answer that way?

8. If you calculate a positive ΔH^o for this reaction, what does that tell you about your reaction?

9. What is an unusual thermodynamic property of calcium hydroxide?

10. How would this property make the results of your simulation different if you had used $Ca(OH)_2$ rather than Ag_2SO_4?