Experiment 15 – Thermodynamics of the Solution Process

Objectives

- To learn about the relationship between K and ΔG°.
- To learn how the van’t Hoff equation can be used to determine thermodynamic values.
- To gain a better understanding of ΔG°, ΔH°, and ΔS° and their relationship.

Introduction

Thermodynamic Properties

The following equation describes the relationship among three primary thermodynamic properties.

\[ ΔG° = ΔH° - TΔS° \]  

(1)

ΔG° is the change in the standard Gibbs free energy for a process. For a given chemical reaction, \( ΔG° = G°(\text{products}) - G°(\text{reactants}) \); common units for ΔG° are J/mol or kJ/mol. As we will see later in this experiment, ΔG° is related to the equilibrium constant, K, which tells us whether a process is product or reactant favored. Thus, from the ΔG° value for a reaction, we can determine whether the reaction is reactant or product favored at equilibrium. If ΔG° is positive, the reactants are favored, and if ΔG° is negative, the products are favored.

ΔH° is the change in enthalpy. When ΔH° is positive, we say the process is endothermic, and when ΔH° is negative the process is exothermic. Typical units for ΔH° are J/mol or kJ/mol.

ΔS° is the change in entropy. For a process in which the number of degrees of freedom or configurations increases, the ΔS° is positive, and for a process in which the number of degrees of freedom or configurations decreases ΔS° is negative; common units for ΔS° are J/mol K. T is the absolute temperature in Kelvin.

Before we continue, it is very important to make clear that ΔG° and ΔG have different meanings. (Even many textbooks in general chemistry confuse their meanings.) ΔG° is related to the equilibrium constant: a positive value of ΔG° means that there are more reactants present at equilibrium, and a negative value of ΔG° means that the more products are present at equilibrium. In contrast, ΔG expresses spontaneity: a negative value of ΔG means that the reaction is spontaneous in the forward direction, a positive value of ΔG means that the reaction is spontaneous in the reverse direction. At equilibrium, ΔG = 0.

In this experiment, we will determine the values of ΔG°, ΔH°, and ΔS° for the simple process of dissolving potassium nitrate in water:

\[ \text{KNO}_3(\text{s}) \rightleftharpoons K^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \]  

(2)

\[ K_{sp} = [K^+][\text{NO}_3^-] \]  

(3)

We will measure \([K^+]\) and \([\text{NO}_3^-]\) for saturated solutions of potassium nitrate and use these values to calculate \( K_{sp} \). We will then calculate ΔG° from the following relationship.

\[ ΔG° = -RT\ln K_{sp} \]  

(4)

where R is the gas constant, 8.314 J/mol K.

The following equation, known as the van’t Hoff equation, describes the relationship between \( K_{sp}, ΔH°, ΔS°, \) and T. (The equation is named for its discoverer, the Dutch physical chemist Jacobus Hendricus van’t Hoff, 1852-1911, who received the first Nobel Prize in Chemistry in 1901).

\[ \ln K = -\frac{ΔH°}{RT} + \frac{ΔS°}{R} \]  

(5)

We will thus determine ΔH° and ΔS° by finding \( K_{sp} \) values at several different temperatures.

The van’t Hoff equation can be related to the familiar equation for a line,

\[ y = mx + b \]  

(6)

Thus, a plot of \( \ln K_{sp} \) as a function of \( 1/T \) provides a straight line from which we can easily calculate the values of ΔH° and ΔS°.
When we have determined numerical values for $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$, we will use them to understand, from a thermodynamic point of view, the process by which potassium nitrate dissolves in water.

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**Safety**

Wear goggles. Wear gloves and use caution with the potassium nitrate, as it is a strong oxidizing agent and skin irritant. Do not let it contact your skin. Keep computers out of the way of reagents. Clean-up any spilled reagents immediately. Ask the instructor for assistance with spilled reagents. Be careful with the hot plates. Make sure you turn off the hot plates when not in use.

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**Procedure**

1. Obtain a 50 mL graduated cylinder, and a 1000 mL beaker from the stock room.

2. Put about 600 mL of water in a 1000 mL beaker, and set the beaker on the hot plate. Heat the water to boiling then reduce temperature on the hot plate to maintain the water at near boiling. From time to time throughout the rest of the experiment, add small amounts of water to the beaker to maintain the water level at about 600 mL.

3. Using a toploader balance, weigh about 12 g of potassium nitrate, and record the weight with five significant digits. **CAUTION:** Potassium nitrate is a strong oxidizing agent and a skin irritant – do not let it contact your skin.

4. Transfer your sample of potassium nitrate into the 50 mL graduated cylinder, add 9 mL of deionized water, and place the graduated cylinder in the hot water. Clamp it into place on the ring stand.

5. As the solution heats up, Open Logger Pro if it is not already open. Click on the **Data Collection** button. You will see a Dialog Box. Change Mode from “Time Based” to “Events with Entry”. Type “Solution” for column name and “Sol” for short name then click “Done.” Change the temperature to the x-axis by clicking on the x-axis label and select “Temperature”. Change the y-axis to solution by clicking on the y-axis label and select “Solution.” Next, select “Graph Options” from the Options menu to call up the Graph Options dialog box. Uncheck the “connect points” option. Click **Collect**.

6. Use glass stir rod to stir the mixture in the graduated cylinder until all of the potassium nitrate dissolves; we will refer to this solution as Solution 1. Record the volume, in mL, of Solution 1 after all the solid has dissolved (it will NOT be 9 mL, as that much solid will account for some of the volume). Make sure your reading has the proper number of significant figures.

7. Remove the graduated cylinder containing Solution 1 from the hot water. You can cool it gently in some cold water, but don’t cool it too fast because you can miss the crystallization temperature. As the solution cools, have one person gently stir it with the temperature probe. Watch carefully for the appearance of crystals in the solution; when they appear, have the other person hit **Keep** in Logger Pro and enter 1 (for Solution 1). This is the crystallization temperature. Write your data down in your notebook. **NOTE that you do NOT need to see the entire solution crystallize, you just need to observe the start of crystallization.**

8. Add 3 mL of deionized water to the potassium nitrate solution, return the graduated cylinder to the hot water, and stir the solution until all of the potassium nitrate dissolves; we will refer to this solution as Solution 2. Record the volume. Repeat step 7 for Solution 2 (except enter “2” for the solution number).

9. Repeat step 8 six more times; we will refer to the corresponding solutions as Solutions 3 through 8. Once you are done with all the 8 solutions click **Stop**.

10. For each solution calculate the concentration of potassium ions and nitrate ions, and then calculate the $K_{sp}$ and $\ln K_{sp}$.

11. You will now prepare your data in Logger pro...
Pro in order to make a van't Hoff plot:

a. Go to "data" and select “calculated column.” You will be creating a column with 1/T with the temperature in Kelvin. Type 1/T in the name box and short name box. In the equation box, type: 1/("Temperature" + 273.15). Click done.

b. Go to “data” and select “manual column.” This will be for your ln Ksp values. So, enter “ln Ksp” in the name and short name boxes. Click done. Now you can enter the ln Ksp values that you calculated for each solution.

c. Graph the correct variables for the x and y axis by clicking on the axis label and selecting the correct variable.

d. Fit the data with a line of best fit by clicking the linear fit button, on the toolbar. Then click on to autoscale the graph. Write down the equation for the line in your notebook. Save this data on a flash drive (you may check one out from Bruce if you don't have one). Take your flash drive to the computer lab and print a copy of your graphs and data table from Logger Pro and attach them to your lab report.

12. Dispose of the solution as directed by your instructor, rinse the graduated cylinder and return it, and thoroughly rinse off your temperature probes.
1. The reaction investigated in this lab involves the dissolution of an ionically bound solid, held together by strong ionic bonds, into a solution where the resulting ions are stabilized by relatively weak water-ion interactions. Do you expect this process to endothermic or exothermic?

2. Do you expect this dissolution of the solid to have a $\Delta S$ or a $-\Delta S$. Explain.

3. Do you expect the potassium nitrate to become more or less soluble in water as the temperature is lowered? Explain in terms of Le Chatlier’s Principle. (Refer to your answer in question 1).

4. You dissolve 12.050 g of KNO$_3$ in water and the final volume of the solution is 10.5 mL.
   a. How many moles of KNO$_3$ is this?

   ______________________

   b. What are the molarities of the K$^+$ and NO$_3^-$ ions in solution?

   $[\text{K}^+] = \underline{\underline{}} \quad [\text{NO}_3^-] = \underline{\underline{}}$

   c. What is the $K_{sp}$ for this reaction?

   ______________________

   d. What is the $\Delta G^{\circ}$ for this reaction in kJ/mol at 25°C?
Calculate the number of moles of potassium nitrate in your sample; show your calculation below.
Calculate the following quantities and then fill in the table below.

<table>
<thead>
<tr>
<th>Solution</th>
<th>[K⁺]</th>
<th>[NO₃⁻]</th>
<th>KSP</th>
<th>In KSP</th>
<th>Crystallization Temperature (K)</th>
<th>( \frac{1}{T} ) (K⁻¹)</th>
<th>( \Delta G^\circ ) (kJ mol⁻¹)</th>
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2. Show a sample calculation for [K⁺] and [NO₃⁻] in Solution 3 below.

3. Show a sample calculation for KSP for Solution 3 below.

4. Show a sample calculation of \( \Delta G^\circ \) for Solution 3 below.

5. Write the equation for your line of best fit here: ____________________________
6. Determine $\Delta H^\circ$ and $\Delta S^\circ$ from your fit data and show your work below.

\[
\Delta H^\circ = \underline{\quad} \quad \Delta S^\circ = \underline{\quad}
\]

7. Discuss the meanings of the signs of your values for $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$. What do they tell you about the process in which potassium nitrate dissolves in water? (I'm looking for use of appropriate thermodynamic terms here...)

8. Discuss the relative importance of temperature in determining the sign of $\Delta G^\circ$ (i.e. what parameter dominates) for the forming an aqueous solution of potassium nitrate.