Enthalpy and Entropy Changes of Dissolving Borax

Objectives

- Construct a van't Hoff plot from multiple K_{sp} measurements of Borax at different temperatures
- Use the van't Hoff plot to determine the enthalpy and entropy changes involved in dissolving Borax

Background

Gibbs Free Energy and Solutions

Gibbs free energy, ΔG^o, is a numerical indication of the spontaneity of a system. A spontaneous process occurs without the addition of external energy and has a negative ΔG^o value. The Gibbs free energy for a process captures a lot of other energetic data as it is related to both the change in enthalpy, ΔH^o, and entropy, ΔS^o, as well as the equilibrium constant, K, for the system, according to Equation 1.

$$\Delta G^o = \Delta H^o - T\Delta S^o = -RTln(K) \qquad \text{Equation 1}$$

The value of ΔG^o in both definitions relies on temperature, T, as well as the energetics of the system. The impact of temperature on spontaneity can be determined by looking at the favorability of the enthalpy and entropy. A system with a negative ΔH^o and positive ΔS^o is exothermic and increasing in entropy, which leads to a process that is always spontaneous. If ΔH^o is positive and ΔS^o is negative, the process is neither enthalpically nor entropically favorable and is not spontaneous at any temperature. Other enthalpy and entropy conditions depend on temperature.

Because ΔG^o relies on both the enthalpy and entropy values as well as the equilibrium constant, the definitions of ΔG^o create a relationship between those quantities, as defined in a version of the van't Hoff equation, Equation 2. In the equation, R is the gas constant, 8.314 J/mol-K.

$$ln(K) = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad \text{Equation 2}$$

The van't Hoff equation is a powerful tool as it fits the form for the equation of a line. If the equilibrium constant of a system is measured at multiple different temperatures, a plot of ln(K) versus 1/T, in Kelvin, yields the enthalpy and entropy change for the system. The slope is equal to $-\Delta H^o/R$ and the *y*-intercept is equal to $\Delta S^o/R$.

Energetics of Dissolving Borax

The process of dissolving a solid can be studied using the van't Hoff equation. The energetics of dissolving can indicate whether the spontaneity solubility should increase or decrease with an increase in temperature. To study the system, the solubility product, K_{sp}, needs to be measured at multiple different temperatures.

In this experiment, the solid being dissolved and studied is Borax, $Na_2B_4O_5(OH)_4{\cdot}8H_2O$, which is a common component of detergents. Borax dissolves according to the equilibrium in Equation 3, into sodium ions and borate ions, $B_4O_5(OH)_4^{2-}$.

$$Na_2B_4O_5(OH)_4{\cdot}8H_2O(s) \rightleftharpoons 2Na^+(aq) + B_4O_5(OH)_4^{2-}(aq) + 8H_2O(l) \qquad \text{Equation 3}$$

To measure the K_{sp} of a solution, it needs to be at equilibrium, which is when the solution is saturated or has dissolved as much solid as possible. The concentrations of the ions at saturation can be used to calculate the K_{sp}, according to Equation 4. The concentration of sodium ions is twice the concentration of borate ions, so the whole expression can be written in terms of the borate ion, which is easier to measure.

$$K_{sp} = [Na^+(aq)]^2\left[B_4O_5(OH)_4^{2-}(aq)\right] = 4[B_4O_5(OH)_4^{2-}(aq)]^3 \qquad \text{Equation 4}$$

Borate ions are basic and can be measured by titration with an acid, according to Equation 5. To follow the titration, bromocresol green will be used as an indicator. In the presence of a base, bromocresol green is blue but it will become yellow once sufficient acid has been added. Note that the ratio between borate and the acid is not 1:1.

$$B_4O_5(OH)_4^{2-}(aq) + 2HCl(aq) + 3H_2O(l) \rightarrow 4B(OH)_3(aq) \qquad \text{Equation 5}$$

By titrating saturated solutions of Borax at different temperatures, the concentration of borate and solubility product for the dissolving process can be determined. A subsequent plot of ln K_{sp} versus 1/T gives the enthalpy and entropy change for dissolving, which provides insight into the spontaneity and temperature dependence of the system.

Materials

- Borax
- Bromocresol green indicator
- 0.500 M HCl (standardized)
- 250-mL beaker
- 125-mL Erlenmeyer flask
- 50-mL buret
- 10-mL graduated pipette
- Thermometer
- Hot plate
- Stir bar

Safety goggles are required!

Borax can be an eye or skin irritant.

Procedure

Measurements of Borax Solubility Products

1. In a 250-mL beaker, dissolve about 30 g of borax in about 75 mL of deionized water.
2. Heat the solution on a hot plate with a stir bar stirring to almost reach 65°C. Do not heat beyond that temperature.
3. Add a beaker of deionized water next to the hot plate to heat along with the solution.
4. Make sure that the solution is saturated by looking for solid on the bottom of the beaker. If no solid is visible, add a small amount (about the end of a scoopula) more borax to the solution until a small amount of solid is visible at the bottom.
5. Turn down the heat and allow the solution to reach approximately 60°C and then stay at that temperature for about ten minutes. More solid may appear at the bottom of the beaker.
6. At the end of ten minutes at the temperature, draw up 5.00 mL of the solution into a 10-mL graduated pipette. Do not pull any solid into the pipette. Note the exact temperature of the solution when the sample is taken.
7. Working quickly, transfer the solution from the graduated pipette to a clean 125-mL Erlenmeyer flask.
8. Rinse the pipette with several portions of the heating water and add the rinses to the flask. Make sure no solid remains in the pipette.
9. Add 2–3 drops of the bromocresol green indicator to the flask.
10. Turn down the heat on the hot plate to cool the Borax solution to about 50°C.
11. Clean the graduated pipette and repeat steps 6-9 at the new temperature.
12. Continue cooling and obtaining samples around the temperatures of 40°C, 30°C and 20°C.
13. After collecting all your solution samples, wash the beaker and pipette to make sure the Borax does not solidify, which can be hard to clean.
14. Fill a clean 50-mL buret with a standardized 0.500 M HCl solution.

15. If any solid has appeared in the approximately 60ºC borate ion solution, add a small amount of H_2O before titration.
16. Titrate the approximately 60ºC borate ion solution until you reach the yellow endpoint of the indicator.
17. Repeat the titration with the solutions collected at approximately 50°C, 40°C, 30°C and 20°C.
18. Neutralize the completed titrations with baking soda before disposal.

Pre-Lab Questions

Prepare for lab by completing and understanding the answers to these questions. Refer to the Background or another resource, such as your textbook, if necessary.

1. Write a couple sentences explaining the relationship between the enthalpy, entropy, and spontaneity of a system.

2. When dissolving a solid, do you expect the entropy change to be positive or negative? Explain.

3. If dissolving a solid is spontaneous, do you expect the enthalpy change to be positive or negative? Explain.

4. Show how Equation 2 can be derived from the definition of Gibbs free energy, $\Delta G^o = \Delta H^o - T\Delta S^o$.

Enthalpy and Entropy Changes of Dissolving Borax Report Sheet

Name ____________________ Section ____________________

Date ____________________ Instructor ____________________

Enthalpy and Entropy Changes of Dissolving Borax

Approx. Temp	**60°C**	**50°C**	**40°C**	**30°C**	**20°C**
			Data Collection		
Actual Temp (°C)					
Vol. of borate solution (mL)					
[HCl] (M)					
Initial buret reading (mL)					
Final buret reading (mL)					
			Calculations		
Vol. of HCl used (mL)					
Moles of HCl used					
Moles of borate present					
[Borate] (M)					
K_{sp}					
ln (K_{sp})					
1/T (1/K)					

Plot your values of $\ln(K_{sp})$ vs. $1/T$ and find the slope and *y*-intercept of the best fit line. Use the equation for line and Equation 2 to calculate ΔH^o and ΔS^o for dissolving Borax

Slope ______________ ΔH^o ______________

y-intercept ______________ ΔS^o ______________

Post-Lab Questions

1. Do you expect the solubility of Borax to increase or decrease as temperature increases? Use the signs of your calculated ΔH^o and ΔS^o to explain.

2. Why was it necessary to make sure that some solid was present in the main solution before taking the samples to measure K_{sp}?