Thermodynamics:

Entropy of Borax Dissolution

Purpose

Determine the enthalpy and entropy changes associated with dissolving the sparingly soluble substance commonly known as borax.

Learning Objectives

Determine the moles of borax dissolved at different temperatures using acid-base titration.

Calculate K_{sp} at different temperatures based on the moles of dissolved borax and the stoichiometry of the dissolution equation.

Construct a van't Hoff plot from multiple K_{sp} measurements of borax at different temperatures.

Determine the enthalpy and entropy changes associated with the dissolution of borax from the van't Hoff plot.

Laboratory Skills

Precisely use graduated glassware to dispense volume to 0.01 mL.

Precisely use a balance to measure mass to 1 g.

Precisely use a thermometer to measure to 0.1 °C.

Safely use a hot plate.

Carry out an acid-base titration.

Equipment

- 250 mL beaker
- 125 mL Erlenmeyer flask
- 50 mL buret
- 10 mL graduated pipette
- Thermometer
- Hot plate
- Stir bar

Chemicals

- Borax
- Bromocresol green indicator
- ~0.500 M HCl (standardized)

Background

Gibbs Free Energy and Solutions

Gibbs free energy, ΔG^{o}, is a numerical indication of the spontaneity of a system. You may recall that the superscript ^{o} indicates values measured under the thermodynamic standard conditions, which are 298 K, 1 atm of pressure and 1 M concentrations of all solutes. 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 other energetic data as well. ΔG^{o} is related to the change in enthalpy, ΔH^{o}, and entropy, ΔS^{o}, and is related to the equilibrium constant, K, for the system. These relationships are given in Equation BX.1, which includes the gas constant, R, in energy units (8.314 J/(mol K)).

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

Note that 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 $\Delta H^{o}$and positive ΔS^{o} is exothermic and increasing in entropy, which leads to a process that is spontaneous at any temperature. If ΔH^{o} is positive and ΔS^{o} is negative, the process is favored neither by enthalpy nor entropy considerations is not spontaneous at any temperature. For situations in which the signs of $\Delta H^{o}$and ΔS^{o} are both positive or both negative, the processes are temperature dependent.

The two equations for ΔG^{o} (Equation BX.1 provide a relationship between entropy, enthalpy and the equilibrium constant. The van't Hoff equation, defined in Equation BX.2, provides a particularly useful depiction of this relationship.

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

This version of the van't Hoff equation is in linear ($y = mx + b$) format, making it a powerful tool for determining the values of ΔH^{o} and ΔS^{o} for a process. When the equilibrium constant of a system is measured at various temperatures, the data can be plotted as $\ln(K)$ versus $1/T$, in Kelvin and the best-fit line determined. 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 sparingly soluble solid can be studied using the van't Hoff equation to determine the enthalpy and entropy of the process. From these values, the effect of temperature on the spontaneity of the process can be determined. That is, should the temperature be raised or lowered to increase the solubility of the solid? To study the system, the solubility product, K_{sp}, must be measured at various temperatures.

In this experiment, the solid being dissolved and studied is borax, $Na_2B_4O_5(OH)_4 \cdot 8\,H_2O$, which is a common component of detergents. Borax dissolves into sodium ions and borate ions, $B_4O_5(OH)_4{}^{2-}$, according to the equilibrium in Reaction BX.1.

$$Na_2B_4O_5(OH)_4 \cdot 8\,H_2O(s) \rightleftharpoons 2\,Na^+(aq) + B_4O_5(OH)_4{}^{2-}(aq) + 8\,H_2O(l) \qquad \text{(Reaction BX.1)}$$

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 BX.3. 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.

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

Borate ions are basic and can be measured by titration with an acid. To follow the titration, bromocresol green will be used as an indicator. In the presence of a base, bromocresol green is blue and will become yellow once sufficient acid has been added to neutralize the borate present. Each mole of borate requires 2 moles of acid for the neutralization reaction, according to the stoichiometry of Reaction BX.2).

$$B_4O_5(OH)_4{}^{2-}(aq) + 2\,HCl(aq) + 3\,H_2O(l) \longrightarrow 4\,B(OH)_3(aq) + 2\,Cl^-(aq) \qquad \text{(Reaction BX.2)}$$

The titration results give the concentration of borate at the various temperatures. These concentrations can then be used to determine the value of the solubility product for the dissolution of borax at those same temperatures. A plot of $\ln K_{sp}$ versus $1/T$ then gives the enthalpy and entropy change for dissolving, which provides insight into the spontaneity and temperature dependence of the system.

Procedure

Safety Precautions

Borax can be an eye or skin irritant.

Measurements of Borax Solubility Products

1. In a 250-mL beaker, stir about 30 g of borax into about 75 mL of RO water. All of borax may not dissolve.
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. Place a 250-beaker containing about 150 mL of RO 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 pipet. Do not pull any solid into the pipet. Record the *exact* volume of sample transferred and the *actual* temperature of the solution when the sample is taken.
7. Working quickly, transfer the solution from the graduated pipet to a clean 125-mL Erlenmeyer flask.
8. Rinse the pipet with several portions of the heating water and add the rinses to the flask. Make sure no solid remains in the pipet.
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 pipet and repeat steps 6-9 at the new temperature.
12. Continue cooling and obtaining samples at approximately these temperatures: 40 °C, 30 °C and 20 °C, recording the *actual* temperatures for each sample.
13. After collecting all your solution samples, wash the beaker and pipet quickly before the borax solidifies. Otherwise, it will be very hard to clean the glassware.
14. Fill a clean 50-mL buret with a standardized 0.500 M HCl solution. Record the exact concentration of the HCl solution.
15. If any solid has appeared in the borate ion solution collected at approximately 60 °C, add a small amount of distilled water before beginning the titration.
16. Record the initial color of the solution and the initial buret reading. Titrate the the borate ion solution collected at approximately 60 °C until you reach the endpoint of the indicator. Record the final buret reading and the color of the solution at the endpoint.
17. Repeat the titration with the solutions collected at approximately 50 °C, 40 °C, 30 °C and 20 °C.
18. Add baking soda to to neutralize the completed titrations with baking soda before disposal, using litmus paper or pH paper to determine when you have added sufficient baking soda.

Name: ______________________________

Section: __________ Date: ______________

Measurements of Borax Solubility Products

Report Table BX.1: Volume and Temperature Data

Approx. temp	**~60°C**	**~50°C**	**~40°C**	**~30°C**	**~20°C**
Actual temp (°C)					
Vol. of borate solution (mL)					

Exact HCl concentration, M ____________________

Color at start of titration ____________________

Color at endpoint of titration ____________________

Report Table BX.2: Titration Data

Approx. temp	**~60°C**	**~50°C**	**~40°C**	**~30°C**	**~20°C**
Initial buret reading (mL)					
Final buret reading (mL)					
Vol. of HCl used (mL)					

The report will ask that you include the following sample calculations.

K_{sp} for 60°C trial ____________________

Show calculations

ΔH^o ____________________________

Show calculations including all units and cancelling units

ΔS^o ____________________________

Show calculations including all units and cancelling units