

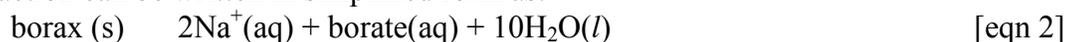
CHM130 – Free Energy Experiment

Experiment: Thermodynamic Study of a Reaction - Determination of K_{sp} , ΔH° , ΔG° , and ΔS° for $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 10\text{H}_2\text{O}$

Introduction: In this experiment you will determine the solubility product constant (K_{sp}) of borax, $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 10\text{H}_2\text{O}$, a slightly soluble sodium salt, in water at two different temperatures and evaluate the enthalpy, entropy and Gibbs free energy change for dissolving borax in water. The equilibrium expression for the process that gives two sodium ions, one borate ion, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, and ten water molecules is:



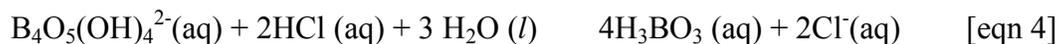
The reaction can be written in simplified form as:



Since liquid water and solid borax are not included in the K_{sp} expression, the solubility product expression associated with this reaction is:

$$K_{sp} = [\text{Na}^+]^2[\text{borate}] \quad [\text{eqn 3}]$$

The concentration of the borate ion in equilibrium with solid borax will be determined by titration with standardized HCl according to the equation:



According to equation 4, two moles of HCl are required for 1 mol of borate. The solubility product constant of borax can then be calculated from the values of $[\text{B}_4\text{O}_5(\text{OH})_4^{2-}]$ and $[\text{Na}^+]$ after $[\text{Na}^+]$ is determined from the stoichiometric relationship, 1 mol borate \equiv 2 mol Na^+ .

The K_{sp} for borax will be evaluated at room temperature and at about 5 °C . Knowing K_{sp} values at two temperatures allows the evaluation of the enthalpy change using Equation 5.

$$\ln \frac{K_{sp1}}{K_{sp2}} = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad [\text{eqn 5}]$$

Knowing the solubility product constant at two different temperatures also allows the evaluation of the Gibbs free energy change (ΔG°) at each of the two temperatures using Equation 6.

$$\Delta G^\circ = - RT \ln K_{sp} \quad [\text{eqn 6}]$$

Remember that ΔH and ΔS are not supposed to change with temperature. On the other hand, ΔG usually does change appreciably with temperature. Once ΔH° and ΔG° values are known for each temperature, the values (which should be the same or very close) of the entropy change, ΔS , at each temperature can be evaluated using the Gibbs free energy expression, shown in Equation 7.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad [\text{eqn 7}]$$

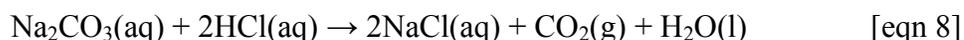
Experimental:

Preparation of the Borax-Borate Equilibrium Mixtures: These solutions will be prepared and shared by three to four lab groups. Each group will then take about 60 mL of each solution and work alone on the titrations.

To two separate 500mL Erlenmeyer flasks containing magnetic stirring bars add about 20g of borax and 400mL of distilled water. Designate one flask as the room temperature system and one as the ice-water system. Stir the room temperature mixture gently on a magnetic stirrer (with no heating) for at least **ten minutes**. Shut off the stirrer, place a thermometer in the flask and leave it undisturbed to allow the excess undissolved borax to settle to the bottom. The solution portion should become clear after a few minutes.

Place the second Erlenmeyer flask in an ice-water bath (be sure to use enough ice) on a magnetic stirrer and stir the mixture with no heating for at least **20 minutes**. Shut off the stirrer, place a thermometer in the flask and allow the undissolved borax to settle to the bottom. This mixture temperature should be close to 5°C and the solution portion should become clear. Keep the flask undisturbed in the ice bath until aliquots are removed for titration.

Preparation and Standardization of 0.1 M HCl Titrating Solution: While the borax mixtures are stirring, add, in a fume hood, about 3.5 mL of conc. (12M) HCl to about 400 mL of distilled water in a 500 mL Volumetric flask. This will give a solution of approximately 0.1 M HCl. Stir/Mix well. Use three 5-mL portions to rinse a clean 50 mL buret and then fill the buret with the solution. Accurately weigh three approximately 0.15 g portions of Na₂CO₃ to 0.001 g into separate clean but not necessarily dry Erlenmeyer flasks. To each flask add 3 drops of bromocresol green indicator and 50mL of distilled water. The solution will turn blue. Titrate each portion of sodium carbonate to the yellow-green endpoint. Do more than three titrations if your instructor says your results are not consistent. Use the titration data to calculate the actual concentration of your HCl solution (see calculation tab in Excel) according to equation 8:



K_{sp} of Borax at Room Temperature: Record the temperature of the room temperature borax mixture. Without disturbing the solid at the bottom, carefully decant about 60 mL of the borate solution into a *clean* and *dry* beaker and pipet three 10.00 mL aliquots into three separate clean but not necessarily dry Erlenmeyer flasks. Add 20 mL of distilled water and 3 drops of bromothymol blue indicator to each flask. The solutions should turn blue. Titrate each sample with your standardized HCl solution until the solution changes from blue to yellow-green. Use your best three titrations to evaluate the K_{sp} of borax at room temperature.

K_{sp} of Borax at Ice Temperature: Read the temperature of the iced borax mixture and carefully decant about 60 mL of the solution into a clean and dry beaker. Pipet three 10.00 mL aliquots into three separate Erlenmeyer flasks. To each flask, add 20 mL of distilled water and 3 drops of bromothymol blue indicator. Titrate each sample with HCl until the color changes to yellow-green. Use your best three titrations to evaluate the K_{sp} of borax at ice temperature.

Calculations:

- 1. Standardization of HCl Titrating Solution:** Using your best two or three standardization titrations, calculate the concentration of the HCl titrating solution for each trial using equation 8. What is the average concentration of your HCl solution?

- 2. Room Temperature K_{sp} Determination:** Calculate the room temperature K_{sp} for borax.
 - a. From the HCl volume used in each titration and equation (4), calculate the concentration of borate in each room temperature aliquot.
 - b. From the stoichiometric relationship between borate and sodium ion, calculate [Na⁺] in each aliquot.
 - c. Calculate the room temperature K_{sp} for each titration using equation (3) and calculate the average K_{sp} value.

- 3. Ice Bath Temperature K_{sp} Determination:** Calculate K_{sp} for borax as you did for the room temperature system.
 - a. Calculate the concentration of borate in each ice temperature aliquot.
 - b. Calculate [Na⁺] for each ice temperature aliquot.
 - c. Calculate each ice temperature K_{sp} and the average K_{sp} value.

- 4. ΔH° Determination:** Dissolving borax in water is an endothermic process shown by equation 8: $\text{heat} + \text{borax (s)} \leftrightarrow 2 \text{Na}^+(\text{aq}) + \text{borate (aq)} + 8 \text{H}_2\text{O (l)}$
 Evaluate ΔH° for the dissolving of borax using equation (5), where K_{sp2} is the borax solubility product at room temperature and T₂ is room temperature in Kelvins, K_{sp1} is the borax solubility product at ice temperature and T₁ is the temperature of the borate solution in the ice-water bath. R = 8.314 J/mol·K.

- 5. ΔG° Determination:** Calculate ΔG° for each of the two temperatures using equation (6);

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

- 6. ΔS° Determination** Calculate the entropy changes at the two temperatures using equation (7);

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