

Experiment 10

The Thermodynamics of the Solubility of Borax

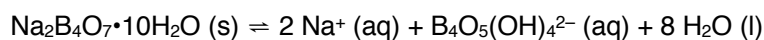
Pre-Lab Assignment

Before coming to lab:

- Read the lab thoroughly.
- Answer the pre-lab questions that appear at the end of this lab exercise. The questions should be answered on a separate (new) page of your lab notebook.
- Follow the guidelines in the "Lab Notebook Policy and Format for Lab Reports" section of the lab manual to complete in your lab notebook the following sections of the report for this lab exercise: Title, Lab Purpose, Procedure and Data tables for Parts B and D of the experiment.

Purpose

To determine the thermodynamic quantities ΔH° and ΔS° for the solvation reaction of borax in water by measuring the solubility product constant, K_{sp} , over the temperature range 50–15°C.



Background

As you have seen or will see in thermodynamics, (Chapter 19) the free energy change in a reaction, ΔG , is related to the equilibrium constant for the reaction by the equation:

$$\Delta G^\circ = -RT \ln(K) \quad \text{Equation 1}$$

In addition, the free energy (ΔG) is related to two thermodynamic quantities—the enthalpy, ΔH (the heat absorbed or released in a reaction), and the entropy, ΔS (the molecular disorder created during a reaction). Under isothermal conditions, this is expressed by the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{Equation 2}$$

Because the right sides of both of the above equations are equal ΔG° , we may set them equal to each other to come up with a new equation:

$$-RT \ln(K) = \Delta H^\circ - T\Delta S^\circ \quad \text{Equation 3}$$

Rearranging the equation to solve for $\ln(K)$ yields the equation below called the van't Hoff Equation

$$\ln K = - \frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad \text{Equation 4}$$

$$y = mx + b$$

This equation can be studied by constructing a graph where $y = \ln K$ and $x = (1/T)$. The equation will have the form of the linear relationship $y = mx + b$, where m is the slope of the line, $-(\Delta H^\circ/R)$, and b is the y-intercept $(\Delta S^\circ/R)$. Thus, if the quantities $\ln K$ and $1/T$ are plotted, the measured slope and intercept of a best-fit line through the data points can be used to determine ΔH° and ΔS° for this reaction.

The relationship between $\ln K$ and $1/T$ is valid only if ΔH° and ΔS° are not temperature-dependent quantities. Over the small temperature range that you are investigating, the assumption is reasonably valid for borax.

The Equilibrium Constant K_{sp}

In order to construct a graph of $\ln K$ versus $1/T$, we will need the values of T (temperature) and K (the equilibrium constant) for each trial of our experiment. Temperature will be easily obtained using a thermometer. To find the value of K will require more effort.

The equilibrium for the reaction to be studied is actually a solubility product constant, K_{sp} . For the chemical reaction under study:



The value of the equilibrium constant (K_{sp}) is given by

$$K_{sp} = [\text{Na}^+]^2 [\text{B}_4\text{O}_5(\text{OH})_4^{2-}]$$

Letting $x = [\text{B}_4\text{O}_5(\text{OH})_4^{2-}]$, $[\text{Na}^+]$ would equal $2x$ due to the stoichiometry of the reaction

Recall that solids and liquids do not appear in equilibrium expressions.

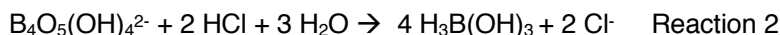
Substituting

$$K_{sp} = [\text{Na}^+]^2 [\text{B}_4\text{O}_5(\text{OH})_4^{2-}]$$

$$K_{sp} = [2x]^2 [x]$$

$$K_{sp} = 4x^3 \quad \text{where } x = [\text{B}_4\text{O}_5(\text{OH})_4^{2-}] \quad \text{Equation 5}$$

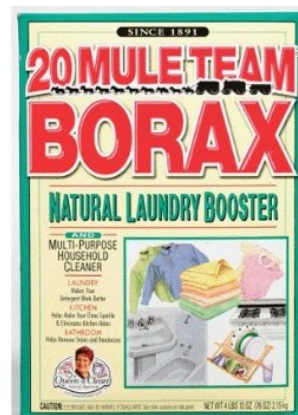
This equation means that we can determine the value of K_{sp} if we can find the concentration of $[\text{B}_4\text{O}_5(\text{OH})_4^{2-}]$ in our samples. This can be done by titrating our samples of $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ with HCl using bromocresol green as an indicator. The balanced equation for the titration is



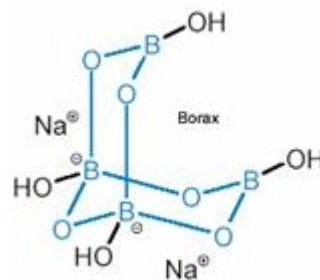
Borax

In today experiment, you will be working with borax. Borax occurs naturally in dry lake beds in the Southwest and California. These beds have long been important sources of this valuable mineral. An early use of Borax was in soap and other cleaning products. These products continue to be used today. Borax is also used as a flux for solder, in the manufacture of glass, and as a preservative. You may be most familiar with borax because of the laundry additive brand, "20 Mule Team Borax."

The empirical formula of the natural form of the mineral borax is



$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and its IUPAC name is sodium tetraborate decahydrate, but here we shall simply refer to it by its common name, “borax.” Its crystalline form and structure are shown in the pictures below.



Procedure

GENERAL SAFETY: Students must wear safety goggles at all times. Use caution when working with the hydrochloric acid solution; be sure to rinse any area of skin that comes into contact with this solution well.

WASTE DISPOSAL: All solutions used in this lab may be disposed of in the sink.

CLEAN-UP: Borax crystals are difficult to remove from glassware and the bench tops once dry. Be certain to rinse all glassware that comes into contact with the borax thoroughly using warm water at the end of the experiment. Also be certain to wipe down any spills of the borax solution that occur using several rinses of warm water. *You lab instructor may chose to deduct points from any group leaving a “white crust” behind on their bench top.*

Materials and Equipment:

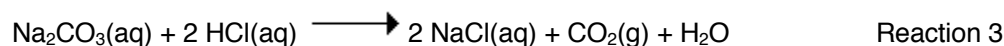
- Borax (make sure it is not “cut” with other cleaning ingredients)
- Concentrated hydrochloric acid solution
- Anhydrous sodium carbonate
- Bromocresol green indicator
- 125 mL Erlenmeyer flask
- 500 mL Erlenmeyer flask
- one clean 150-mL beaker
- one clean 100-mL beaker
- stirring hotplate
- thermometer
- 50 mL buret
- 5 mL pipette
- six small test tubes

Part A: Preparing a Saturated Borax Solution

1. In a 100-mL beaker, prepare a saturated solution of borax by adding roughly 20 g of borax to 80 mL of distilled water.
 2. Obtain a stirring hot plate and set the heat setting at about midpoint; place the borax solution on the hot plate and stir gently using a magnetic stir bar.
 3. Take temperature readings constantly of the beaker containing borax. Make sure the bulb of the thermometer is not touching the sides or bottom of the beaker or the magnetic stir bar. When the temperature of the solution reaches 52-55°C, turn down the hot plate and maintain the temperature in this range for 30 minutes.
- Caution:** Heating over 60°C will decompose (not dissolve) the borax. Keep monitoring the temperature of the solution. If it rises above 55 ° C, remove it from the hot plate temporary.
4. You should see some solid borax in the flask at all times. If all of the solid dissolves, add some more borax (around 5 grams). During this heating, the solid will come to equilibrium with the aqueous ions. If there is solid borax in the mixture, you can assume the water is as saturated with dissolved borax as it can get, and this is the condition you want.
 5. While the borax solution stirs, continue with part B of the lab. You will use the borax solution in Part D.

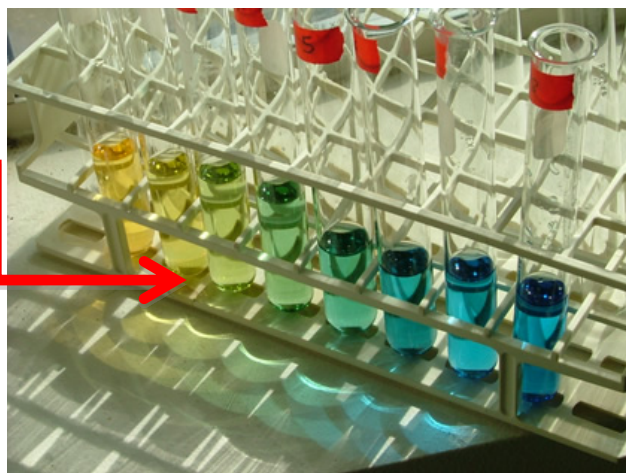
Part B: Preparation and Standardization of HCl

1. In a fume hood, add 8 mL of concentrated HCl to about 400 mL of distilled water in a 500 mL Florence flask. Stir well. This gives a solution of approximately 0.2 M HCl.
2. To determine the exact concentration of the HCl in the solution, we will titrate it against a base whose mass can be accurately measured; i.e., we will standardize it. The base we will be using is anhydrous sodium carbonate. The titration reaction is:



- a) Rinse the buret with a few milliliters of HCl to clean it. Be sure to drain some of the HCl through the tip of the buret to remove any air bubbles.
- b) Into a 125 mL Erlenmeyer flask, accurately weigh 0.15 g of anhydrous primary standard grade sodium carbonate that has been dried for at least 2 hours in a drying oven at 110 °C and cooled in a desiccator. Record the exact mass in your notebook.
- c) Add 50 mL of deionized water and swirl until all the solid dissolves.
- d) Add 5-10 drops of bromocresol green indicator.
- e) Titrate your sample of sodium carbonate until you reach the yellow-green endpoint. Record the initial volume of HCl, final volume of HCl and the volume of HCl used to the nearest 0.01 mL.

The color change for the indicator will be from blue to green. Yellow means you went too far.
endpoint



f) Repeat steps b-e two times for a total of three trials.

g) Calculate the HCl concentration for each sample and the average HCl concentration. Check with your instructor concerning the quality of the results.

3. Stopper your flask containing the standardized HCl into to preserve it. If you will be titrating your borax samples next period, save the remaining HCl in your drawer.

Part C: Preparing Test Tube for Sample Collections

1. With a volumetric pipette, measure precisely 5.00 mL of water into each of six small test tubes and mark the levels with a wax pencil. You will use these as a measure of your volume of solution later.

2. Label the test tubes $\sim 50^\circ$, $\sim 45^\circ$, $\sim 35^\circ$, $\sim 30^\circ$, $\sim 20^\circ$, and $\sim 15^\circ$ °C.

3. Empty the test tubes and dry them.

Part D: Collection of Saturated Borax Samples

General Note: Do not cool the sample in an ice bath to speed up sampling. Doing so risks introducing errors due to super-cooling and should be avoided. Experience has shown that a 10-degree temperature drop can occur in about 10 - 15 minutes, and your patience will be rewarded with excellent samples from which to obtain data.

1. After the borax solution from Part B has stirred for 30 minutes at 52-55°C, remove it from the hot plate. Let the beaker stand with the thermometer in it until the solid has settled out of solution (about 2 minutes).

2. When the solid has settled out, read and record the temperature to the nearest 0.1°C then immediately decant exactly 5.0 mL into one of the labeled test tube you prepared in Part C by filling it to the marked line. Be sure not to get any of the solid that is at the bottom of the beaker when decanting.

3. Stopper the test tube and save the sample until the next lab period when it will be titrated with HCl. The sample may precipitate as it cools. This is normal.
4. Now allow the borax solution to cool to about 45°C; make sure you are stirring the solution frequently. When the solution is about 45°C, let the solution stand for two minutes (as above) until the solid settles out.
5. Follow the sample collection process in step 2 for transferring 5.0 mL of the solution to another labeled test tube. Remember to record the temperature of the borax solution to the nearest 0.1°C.
6. Stopper and save the sample in your drawer until next lab period.
7. Repeat this procedure near 35°C, 30°C, 20°C and 15°C (the last temperatures may require an cool water bath—be careful not to let the beaker tip over in the bath), transferring 5.0 mL aliquots to separate labeled test tubes. You may find that it is difficult to obtain samples at the lower temperature, because of the large amount of solid that forms. If this happens, you can decant the liquid into a smaller flask or beaker and allow it to cool in this new container. This allows you to remove most of the solid so it is easier to pour samples of the solution which are uncontaminated by solid borax.
8. Once all six samples have been collected and stored in labeled test tubes, dispose of any remaining borax solution down the sink.

Part E: Titrating the Borax samples.

1. If you do not already have a buret set up, clean and fill a buret with your standardized HCl from Part B of the lab.
2. Before we can titrate our samples of borax, any precipitate the formed as the samples cooled to room temperature must be re-dissolved and the samples must be transferred to a 125 mL Erlenmeyer flask. This will be done by:
 - a) Using a hot plate, warm a 150 mL beaker of water to 45°C. Place the test tubes containing the borax samples in the warm water until the solid borax has mostly re-dissolved (approximately 5 minutes). **Do not over heat the test tubes!**
 - b) Using the same hot plate, warm another 100 mL beaker filled with distilled water to 45 ° C.
 - c) After five minutes of heating in the warm water, pour one of the test tubes containing the borax solution into your 125 mL Erlenmeyer flask. Rinse all of the solid borax out of the test tube with warm distilled water; pouring these rinsings into the same 125 mL Erlenmeyer flask.
3. Add enough distilled water to the 125 mL Erlenmeyer Flask so they each have a volume of about 50 mL total (the marking on the flask is sufficient precision). Stir each sample so that they are well-mixed. All of the borax should be fully dissolved into solution.
4. Add 5-10 drops of your bromocresol green indicator to the 125 mL Erlenmeyer flask.
5. Titrate the flask with the borax with hydrochloric acid from the buret until it reaches the same green-yellow endpoint. Dispose of the sample down the sink when done with the titration.
6. Repeat steps 2c- 5 for the other borax samples being sure to clean, but not necessarily dry, the 125 mL Erlenmeyer flask between each sample. It is also a good idea to refill the buret with HCl before starting each titration.

Data Tables and Calculations

For Parts B and D of the lab

You will need to prepare and organize your own data tables for this part of the lab. The tables need to be done **before** you come to lab as part of your pre-lab assignment.

Reminders and hints:

- Data should be organized into tables with either a line or a box for each number you will need to record.
- Tables should be clearly labeled with the quantity to be recorded along with the unit it will be recorded in.
- Besides measured quantities you should leave room and label areas for quantities that will be calculated. Sample calculations should be shown as well.

For Part E *Sample data tables for Part E only and its calculations are below:*

Sample	1	2	3	4	5	6
Temperature						
Final Buret Reading						
Initial Buret Reading						
Volume HCl						
[B ₄ O ₅ (OH) ₄ ²⁻] In the original 5.0 mL aliquot						
K _{sp}						
ln K _{sp}						
Temperature (K)						
1/T						

1. Prepare a graph of your results, plotting the two quantities x and y (as defined in the introduction). Using Excel, determine the equation of the best-fit line through your data points. Be sure to label your graph correctly and display the value of R².

2. From the parameters of the best-fit line equation, calculate ΔH° and ΔS° for this reaction. Make sure to keep track of units, especially for R, so that the units of ΔH° and ΔS° work out sensibly.

Slope: _____ $\Delta H^\circ =$ _____ Intercept: _____ $\Delta S^\circ =$ _____

3. **Obtain the rest of the class's** ΔH° and ΔS° values and calculate the mean and standard deviation of each for the class. Pay attention to the units and sig figs.

4. The literature values for enthalpy and entropy of the dissolution of **borax** in water are 110 kJ/mol and 380 J/mol K, respectively. Determine the percent error in your experimentally determined values and the class's mean values.

Post-Lab Questions

1a) Based on the values of ΔH and ΔS that you determined for the dissolution of borax, what would be the value of K_{sp} at 70.0°C?

1b) Based on the values of ΔH and ΔS that you determined for the dissolution of borax, what would be the solubility of borax in grams per liter at 85.0°C?

2. Does the solubility of borax increase or decrease with increasing temperature? Use both your physical observations and your K_{sp} measurements to justify your response.

3. A geologist removes a sample of water from a lake in Nevada where the water level has been slowly dropping over time. The sample is found to be 0.02 M in borax. The lake is circular in shape and is currently 500 meters in diameter and 50 meters deep. Use your experimental data to predict the level of the lake when borax will begin to precipitate on the shore if the mean temperature of the lake water is 15°C. Assume that the lake is equally deep at all points.

4. If the K_{sp} for PbI_2 is 8.1×10^{-9} , will a precipitate of PbI_2 form when 25 mL of 1.0×10^{-4} M $Pb(NO_3)_2$ is mixed with 25 mL of 1.0×10^{-3} M KI?

Pre-Lab Questions

1. A student who is performing this experiment pours an 8.50 mL sample of the saturated borax solution into a test tube after the borax solution. The student rinses the sample into a small beaker using distilled water, and then titrates the solution with a 0.550 M HCl solution. The student finds that 12.00 mL of the HCl solution is needed to reach the endpoint of the titration. Calculate the value of K_{sp} for borax.

Here is a suggested procedure for doing this calculation:

- Calculate the number of moles of HCl that were added during the titration.
- Use reaction 2 in the lab manual to relate the number of moles of HCl to the number of moles of $B_4O_5(OH)_4^{2-}$ in the 8.50 mL sample.
- Calculate the concentration of $B_4O_5(OH)_4^{2-}$ in the 8.50 mL sample.
- Use equation 5 in the lab manual to calculate the equilibrium constant (K_{sp}).

2. Do you expect ΔS° for the dissolution of borax to be a positive or negative number? Explain your reasoning.

3. Show how equation 3 can be rearranged to equation 4 from the first page of the lab.

4. A reaction is studied at various temperatures, and a graph of $\ln K$ (*equilibrium constants on y axis*) versus $1/T$ (*Temperature on x axis*) is prepared in Excel. The equation of the line is found to be

$$y = -9500x + 21.5$$

- What is the value of ΔH for this reaction? Be sure to include units in your answer.
- What is the value of ΔS for this reaction? Be sure to include units in your answer.

5. A 0.458 g sample of anhydrous sodium carbonate Na_2CO_3 is dissolved in deionized water and titrated HCl. If it required 21.34 mL of HCl to neutralize the Na_2CO_3 , what is the concentration of the HCl?

6. On a new sheet of paper, prepare your data tables for Parts B and D of the lab. You will fill in the tables during your lab time, but you need to know what to be recording by setting up the tables in advance.