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## Thermodynamics of Borax Solubility

### Introduction

In this experiment, you will determine the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the reaction which occurs when borax (sodium tetraborate octahydrate) dissolves in water.

In previous experiments, you have determined  $\Delta H^\circ$  values directly, by measuring temperature changes when the reaction occurred. However, in many cases, this technique is not practicable. For example, the reaction may not go to completion, or it may give off such a small amount of heat that the temperature change is too small to measure. In addition, there is no direct method for measuring  $\Delta S^\circ$  for a reaction. It is therefore useful to be able to determine  $\Delta H^\circ$  and  $\Delta S^\circ$  indirectly, by using their relationship to the equilibrium constant of a reaction.

The equilibrium constant of any reaction can be related to the free energy change of the reaction:

$$\Delta G^\circ = -RT \ln K$$

The free energy change is also related to the enthalpy and entropy changes during the reaction:

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

Combining these two equations gives the general relationship between  $K$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ :

$$-RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

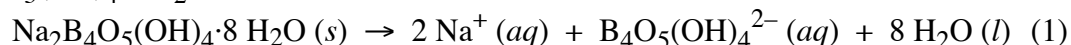
Dividing both sides by  $-RT$  gives a particularly useful form of this relationship:

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

This represents a linear equation of the form  $y = mx + b$ . In this case,  $y = \ln K$  and  $x = 1/T$ ; a plot of  $\ln K$  against  $1/T$  will therefore be linear. In addition, the slope of this line ( $m$ ) will equal  $-(\Delta H^\circ/R)$ , and its  $y$ -intercept ( $b$ ) will equal  $(\Delta S^\circ/R)$ . It is therefore possible to determine  $\Delta H^\circ$  and  $\Delta S^\circ$  by simply measuring the equilibrium constant at two different temperatures, graphing  $\ln K$  against  $1/T$ , and measuring the slope and intercept

of the resulting line. In practice,  $K$  is measured at several temperatures, so that the effect of any experimental errors in one measurement will be minimized.

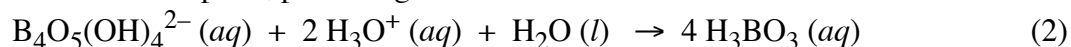
The reaction you will study is the dissolution of borax (sodium tetraborate octahydrate) in water. "Borax" is a naturally occurring compound; it is in fact the most important source of the element boron, and it has been used for many years as a water softening agent. Borax is a rather complicated ionic salt which has the chemical formula  $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8 \text{H}_2\text{O}$ . When it dissolves, it dissociates as follows:



Notice that the products of this reaction are two sodium ions and one other ion (this ion is called "tetraborate"), along with the eight molecules of water. Since water does not appear in equilibrium constant expressions, the  $K$  expression for this reaction is:

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

You will measure  $K$  by analyzing a saturated solution of borax (i.e. a solution in which Reaction (1) has come to equilibrium!) for the tetraborate ion. Tetraborate is a weak base, so it can be titrated with a strong acid. It may surprise you that tetraborate can react with only two hydrogen ions -- not four! -- and that in this reaction, the tetraborate ion "falls apart", producing four molecules of boric acid:



Once you know the number of moles of tetraborate in the solution, you can calculate the number of moles of sodium ion by using the stoichiometry of Reaction (1). Then, you can calculate the molar concentrations of the two ions and, finally, the value of  $K$ .

## Experimental Procedure

**SAFETY PRECAUTIONS:** Wear your SAFETY GOGGLES. If you spill any acid on your skin or clothing, wash it off immediately with copious amounts of running water.

**WASTE DISPOSAL:** All solutions should be poured down the drain, followed by plenty of running water. Solid borax should be dissolved in an excess of warm water, and then poured down the drain.

### A. Preparing a Saturated Borax Solution

Obtain a sample of solid borax. You will need enough borax to reach the 40 mL line in a small beaker. Pour the borax into a 250-mL Erlenmeyer flask and add around 80 mL of distilled water. Then place this flask into a large beaker of water (which will serve as a heating bath) and heat the bath VERY GENTLY until the bath temperature is around 55 °C. Stir the mixture gently during this heating.

When the mixture has reached the correct temperature, continue to heat it (even more gently!) so that you maintain the bath temperature in the range 53 °C - 57 °C for about 15 minutes. Stir the borax mixture gently throughout this heating, and swirl it vigorously from time to time. 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.

### ***B. Collecting Samples of Saturated Borax Solution at Different Temperatures***

Clean and label five 125 mL Erlenmeyer flasks.

Turn off the Bunsen burner and place the thermometer into the flask; from now on, you will measure the temperature of the reaction mixture, not the temperature of the bath. Leave the flask in the bath, and allow the temperature to drop slowly to 52 °C, stirring constantly. Once the temperature has reached 52 °C, stop stirring and allow the solid to settle to the bottom of the flask. The temperature will continue to drop: when it reaches 50 °C, quickly pour between 7 and 9 mL of the solution into a 10 mL graduated cylinder. Try to avoid pouring any solid. Swirl the flask, measure the temperature in the flask to  $\pm 0.1$  °C, and record this temperature. Now remove the flask from the bath and let it cool gradually; swirl it frequently, and monitor its temperature.

Read and record the volume of solution you poured into the graduated cylinder to  $\pm 0.01$  mL. Then pour the solution (which should contain some solid by now) into the first of your labeled 125 mL flasks. Rinse all of the solid borax out of the cylinder with warm distilled water; pour these rinsings into the same flask.

When the temperature of the reaction mixture (in the large flask) reaches 42 °C, stop swirling it and allow it to settle. When it reaches 40 °C, pour off a second 7-9 mL sample, using the procedure described in the previous two paragraphs. Allow the mixture to cool further, and take samples at 30 °C, 20 °C, and 10 °C. Use a separate 125 mL flask for each sample. Once the mixture has reached 30 °C, you may cool it VERY GRADUALLY using a cool water bath: do NOT use an ice bath!! It is critical that the mixture be allowed to come to equilibrium gradually. You should try to allow at least 10 minutes for each 10 °C decrease in temperature.

You may find that it is difficult to obtain samples at the lower temperatures, 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.

### ***C. Titrating the Borax Samples***

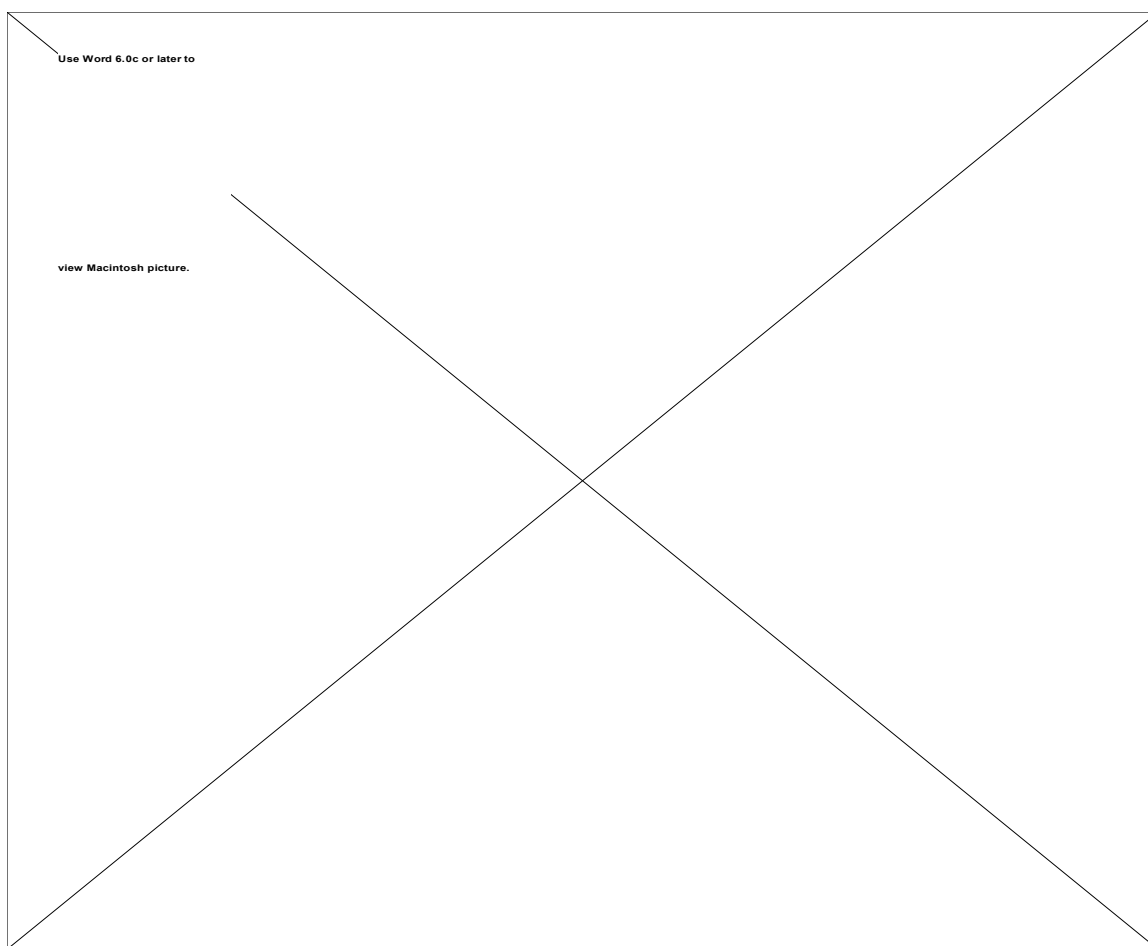
Rinse a buret three times with small portions of the standardized HCl solution provided. Record the concentration of the HCl solution. Put 5 drops of bromocresol green indicator into each of your flasks. Titrate the samples with the standardized HCl solution. Record the initial and final buret reading to  $\pm 0.01$  mL. This indicator is blue in basic solutions and yellow in acidic solutions, so the color of the endpoint should be green.

### **Calculations**

Calculate the concentration of the tetraborate ion in each sample, using Reaction (2), your titration data, and the volume of the sample. Then calculate the concentration of sodium ion in each sample, using Reaction (1). Finally calculate K at each temperature.

Prepare a graph of  $\ln K$  against  $1/T$  (what are the correct units of  $T$ ?), using the x-axis for the  $1/T$  values. You should make a table of these values before you draw your graph. Draw the best possible straight line through your points. A sample graph is shown below.

Calculate the slope of your line. Use this slope to calculate  $\Delta H^\circ$  for Reaction (1). Then use the  $\Delta H^\circ$  and the coordinates of any point that is on your line to calculate  $\Delta S^\circ$ . (NOTE: the intercept will not be on your graph if you have drawn the graph correctly, so you cannot use the intercept to calculate  $\Delta S^\circ$  directly.)



Reminder: For a line with the equation  $y = mx + b$ :

$$\text{slope} = m = \frac{y_2 - y_1}{x_2 - x_1}$$

$$\text{intercept} = b = y_1 - mx_1$$

## Pre-lab Questions

1. A student who is performing this experiment pours an 8.50 mL sample of the saturated borax solution into a 10 mL graduated cylinder after the borax solution had cooled to a certain temperature T. The student rinses the sample into a small beaker using distilled water, and then titrates the solution with a 0.500 M HCl solution. 12.00 mL of the HCl solution is needed to reach the endpoint of the titration.

Calculate the value of  $K_{sp}$  for borax at temperature T. (Answer: 0.176 Show your work.)

Here is a suggested procedure for doing this calculation:

- (a) Calculate the number of moles of HCl that were added during the titration.
  - (b) Use reaction (2) in the lab manual to relate the number of moles of HCl to the number of moles of tetraborate ion in the 8.50 mL sample.
  - (c) Calculate the concentration of tetraborate ions in the 8.50 mL sample.
  - (d) Use reaction (1) in the lab manual to relate the concentration of tetraborate ions to the concentration of sodium ions.
  - (e) Use the concentrations of tetraborate ions and sodium ions to calculate the equilibrium constant ( $K_{sp}$ ) at temperature T for reaction (1) in the lab manual.
2. Do you expect  $\Delta S^\circ$  for the dissolution of borax to be a positive or negative number? Explain your reasoning.

## Additional Questions (for the finished laboratory report)

1. Calculate K for Reaction (1) at 65 °C and at 25 °C, using your values of  $\Delta H^\circ$  and  $\Delta S^\circ$ .
2. Calculate the solubility of borax in grams per liter at 65 °C and at 25 °C, using your values of K at that temperature.