Thermodynamics of Borax

The purpose of this experiment is to determine the thermodynamic parameters $\Delta H°$ and $\Delta S°$ for a reaction at equilibrium. The reaction is the dissolution (K_{sp} reaction) of borax:

$$Na_2B_4O_7{\cdot}10H_2O \leftrightarrows 2\ Na^+ + B_4O_5(OH)_4^{2-} + 8\ H_2O$$

We will investigate this reaction at various temperatures between about 0°C and about 60°C. The decahydrate loses water at 61°C, so there are additional complications above this temperature. Data could be collected below 0°C (down to the freezing point of the saturated solution), though it is not convenient to do so in the time available. Over the temperature range to be studied, saturated solutions will be prepared at approximately ten-degree intervals. We will collect and analyze 5-mL portions at each interval. The quantity of borax dissolved in the saturated solution will be determined by titration with HCl, using methyl red as the indicator. The titration reaction is:

$$B_4O_5(OH)_4^{2-} + 2\ H^+ + 3\ H_2O \rightarrow 4\ B(OH)_3$$

The determination of $[B_4O_5(OH)_4^{2-}]$ allows the calculation of the value of K_{sp} (at each temperature).

We will use a **van't Hoff plot** to determine the thermodynamic parameters ($\Delta H°$ and $\Delta S°$) from the temperature variation in the equilibrium constant. It's based on rearrangement of the expression of the standard Gibbs free energy ($\Delta G°$) in terms of the thermodynamic parameters into a linear relationship between the equilibrium constant (K) and temperature (T):

$$\Delta G° = \Delta H° - T\Delta S°$$

$$\Delta G° = -RT\ \ln(K)$$

$$-RT\ \ln(K) = \Delta H° - T\Delta S°$$

$$\ln(K) = -\Delta H°/RT + \Delta S°/R$$

$$\ln(K) = (-\Delta H°/R)(1/T) + \Delta S°/R$$

Thus a plot of ln(K) (y axis) versus 1/T (x axis) is a straight line with a slope of $-\Delta H°/R$ and an intercept of $\Delta S°/R$.

Procedure:

Work in pairs. Obtain from the designated point in the lab: a thermometer.

I. Preparation of Samples

Carefully measure 5.0 mL of water into each of five separate test tubes. Mark the water level on each with a label. (Don't wrap the label all the way around the tube—just halfway, so you can use it as a fill line later.) Pour out the water and let the tubes drain while carrying out the next operation.

Using a 100 mL beaker and the thermometer as a stirring rod, prepare a saturated solution of borax by adding about 30 g of the decahydrate to 49 mL of water. Heat carefully with your Bunsen burner to above 55°C, but less than 60°C. (Be careful not to heat it too strongly!) Stir the mixture long

enough and thoroughly enough to make sure that the solution is really saturated. Excess solid must be present; more can be added if necessary. Allow the beaker to cool, stirring the mixture frequently. When it reaches about 56°C, stir it steadily for about 10 seconds and then let the beaker stand with the thermometer in it in order to allow the solid to settle out. Now set the marked test tubes in the rack and number them from 1 to 5. When the solid has settled out, read and record the temperature. Immediately decant (gently pour only liquid, leaving the solid sitting at the bottom) enough of the supernatant liquid into test tube #1 to fill it exactly to the 5.0 mL mark.

Allow the solution in the beaker with the thermometer to cool to about 46°C. Stir for about 10 seconds and let the system stand until the solid settles out. Read and record the temperature. Immediately decant exactly 5.0 mL of the supernatant liquid into test tube #2.

Immerse the beaker in cold water and stir with the thermometer until the solution cools to about 36°C and repeat the sample collection process, using test tube #3. Cool to about 26°C (some ice may be required), and collect a sample in test tube #4. Cool to 16°C, and collect a sample in test tube #5.

Put excess solid and mother liquor in the collection bottle for borax residues.

II. Analysis Of Samples

Obtain about 100 mL of the HCl solution in a clean, *dry* 150 mL beaker. Be sure to record the concentration of the HCl. Rinse and fill your buret with the acid.

Analyze the contents of each test tube one at a time, beginning with test tube #5, as follows: Warm the solution and solid in the test tube using a hot water bath. Transfer the contents to an Erlenmeyer flask, rinsing the test tube several times with de-ionized water. Make sure that all the borax is transferred to the beaker and dissolved. Add enough water to make a total volume about 100 mL and warm if necessary to dissolve all solid. Add about five drops of methyl red and titrate to the end point. The titration end point is indicated by the color change from yellow to salmon pink. It is safe to dispose of the contents of the flask by rinsing them down the drain. Determine the contents of test tube #4 in exactly the same way. Remember that the solubility of borax is greater at higher temperature and proportionately more acid will be required. Analyze the contents of test tubes #3 through #1 in exactly the same way.

After completing the procedure but before leaving lab, write in your notebook a brief statement (two to three sentences) on the quality and reasonableness of the data you collected. Note what you might do differently if you performed the lab again.

III. Calculations

Calculate the concentration of the dissolved $B_4O_5(OH)_4^{2-}$ and then the value of K_{sp} at each temperature. Plot ln K versus 1/T and fit a straight line to these points. Determine the value of the standard enthalpy of reaction ($\Delta H°$) from the slope, and determine the value of the standard entropy of reaction ($\Delta S°$) from the intercept.

Adapted from: Jolly, *Encounters in Experimental Chemistry*, 1985