CHM 115 Lab 13

Thermodynamics Of The Solubility Of Borax

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

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

which will be investigated at various temperatures. The decahydrate loses water at 61 °C, so there are additional complications above this temperature. Data even below zero (to the freezing point of the saturated solution) could be collected, 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. Five-milliliter portions of each will be collected and analyzed. The quantity of borax dissolved in the saturated solution is 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).

From $\Delta G° = \Delta H° - T\Delta S° = -RT \ln K$, and $\Delta G° = -RT \ln K$, we get $\Delta H° - T\Delta S° = -RT \ln K$. This can be rearranged to $\ln K = -\Delta H°/RT + \Delta S°/R$ or $\ln K = (-\Delta H°/R)(1/T) + \Delta S°/R$. 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 $\Delta S°/R$. (Note that we are assuming that ΔH and ΔS are temperature independent.)

Procedure

Work in pairs. Obtain from the stockroom: thermometer and test tube rack.

Preparation of Samples

Carefully measure 5.0 mL of water into each of five separate test tubes. Mark the level on each with a label. Pour out the water and let the tubes drain while carrying out the next operation.

Using a 100 mL beaker, and a thermometer for a stirring rod, prepare a saturated solution of borax by adding about 30g of 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 55 °C, stir it steadily for about 10 seconds and let the beaker stand with the thermometer in it 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, and immediately decant 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 25 °C (some ice may be required) and collect a sample in test tube #4. Cool to 15 °C and collect a sample in test tube #5.

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

Analysis Of Samples

Obtain about 100 mL of the HCl 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 as follows, beginning with test tube #5. 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 where the methyl red changes from a yellow to a 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.

Calculations

Calculate the concentration of the dissolved $B_4O_5(OH)_4^{2-}$ and then the value of K_{sp} at each temperature. On good graph paper plot ln K versus 1/T. Draw what you judge to be the best straight line through these points. From the slope determine the value of $\Delta H°$. Since 1/T = 0 will not be on the graph, use a point on the best straight line and calculate the value of the intercept from the equation for a straight line. Then determine $\Delta S°$.

Adapted from Jolly, Encounters in Experimental Chemistry,1985.