**Thermodynamics of the Solubility of Borax**

**Purpose:**

To determine the thermodynamic quantities $\Delta H^\circ$ and $\Delta S^\circ$ for the solvation reaction of borax in water, by measuring the solubility product constant, $K_{sp}$, over the temperature range 55–15°C.

\[
\text{Na}_2\text{B}_4\text{O}_7\cdot10\text{H}_2\text{O}(s) \rightleftharpoons 2 \text{Na}^+(aq) + \text{B}_4\text{O}_5(\text{OH})_2^2(aq) + 8 \text{H}_2\text{O}(l)
\]

**Introduction:**

The experimental results for this experiment are to be compared to another group’s results. **You are to identify a group partner—another group for your group to make comparisons.** Each group partner will be responsible for collecting five data points during the lab period. At the end of lab, exchange data sets with your partner.

As you have seen or will see in Thermochemistry (Chapter 18) the free energy change in a reaction, $\Delta G$, is related to the equilibrium constant for the reaction by the equation

\[
\Delta G^\circ = -RT \ln(K) \quad (\text{text eqn. 18.10})
\]

Looking at this equation we see that if the reaction is thermodynamically favored, $\Delta G^\circ < 0$, then we would expect $K$ to be large, $K \gg 1$. If $K$ is much greater than one, we will observe the reaction proceeding primarily to products.

The free energy expresses the net effect of two thermodynamic quantities the enthalpy, H, and the entropy, S. Under constant temperature conditions, this is expressed by the equation

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (\text{text eqn. 18.7})
\]

The two physical contributions to the free energy are the heat absorbed or released during a reaction, $\Delta H$, and the molecular disorder created during a reaction, $\Delta S$.

Because the above two equations are expressions of $\Delta G^\circ$, the right hand side of each equation must be equivalent.

\[-RT \ln(K) = \Delta H^\circ - T\Delta S^\circ\]

Rearranging this expression yields

\[
\ln(K) = \frac{-\Delta H^\circ}{R} \cdot \frac{1}{T} + \frac{\Delta S^\circ}{R}
\]

As long as we can determine the equilibrium constant at several temperatures, this equation is well suited for determining $\Delta H^\circ$ and $\Delta S^\circ$ by linear regression.

\[
\ln(K) = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}
\]

\[y = m \cdot x + b\]
The above expression is valid only if $\Delta H^\circ$ and $\Delta S^\circ$ are not temperature dependent quantities. Over the small temperature range that we shall investigate, this assumption is valid for borax.

The method of determining the equilibrium constant in this experiment is worth discussing. The equilibrium for the reaction to be studied is actually a solubility product constant, $K_{sp}$. For the chemical reaction given above the equilibrium constant is given by

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

Setting up an ICE table, we see that

$$K_{sp} = (2x)^2x = 4x^3$$

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

The amount of $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ in solution is determined by titration with HCl using methyl red as an indicator. The balanced equation for the titration is

$$\text{B}_4\text{O}_5(\text{OH})_4^{2-} + 2 \text{H}^+ + 3 \text{H}_2\text{O} \rightarrow 4 \text{B(OH)}_3$$

**Experimental Procedure:**

Obtain 5 clean 250 mL beakers and label them 1-5 (you may need to check out additional beakers). Using a 100 mL beaker and a thermometer for a stirring rod, prepare a saturated solution of borax by adding about 25 g of borax to approximately 80 mL of water. Turn a hot plate on to a heat setting of 5, and place the 100 mL beaker on the hot plate. Monitor the temperature of the solution by stirring it with your thermometer and checking the reading frequently. **It is important to stir the solution frequently and take temperature readings while the bulb of the thermometer is not resting on the bottom of the beaker.** When the temperature of the solution is 57-58°C (heating over 60°C will decompose Borax), remove the beaker from the hot plate.

With the beaker sitting on the countertop, stir the solution with your thermometer until the temperature is around 55°C. Let the beaker stand with the thermometer in it until the solid has settled out of the solution. While the solution is settling, rinse your 10 mL graduated cylinder in hot water from a tap to warm the cylinder. **If you pour the hot borax solution into a cold graduated cylinder, the borax will precipitate in the cold cylinder.** When the solid has settled out, read and record the temperature to the nearest 0.1°C, then immediately decant exactly 5.0 mL of the solution into the warmed 10 mL graduated cylinder. Now transfer the contents of the 10 mL graduated cylinder into beaker #1. Rinse the cylinder several times with water and pour these rinses into the beaker as well.

Now allow the solution to cool to a temperature near 45°C (make sure you are stirring the solution frequently). When the solution temperature reaches 45°C, let the solution stand until the solid settles out and follow the above sample collection process for transferring 5.0 mL of the
solution to beaker #2. Again record the solution temperature to the nearest 0.1°C at the moment you remove the 5.0 ml portion. Repeat this procedure near the following temperatures 35°C, 25°C, and 15°C, transferring the 5.0 mL aliquots to beaker #3, beaker #4, and beaker #5, respectively. You may need to use a cold water bath to cool the solution from 45°C to 35°C, and you will need to use an ice bath to cool the solution to 25°C and 15°C.

Analysis of Samples:

Obtain about 100 mL of 0.2 M HCl in a clean, dry 150 mL beaker. **Be sure to record the exact molarity of the HCl.** Rinse and fill your buret with the acid.

Add enough water to beakers 1-5 to dissolve all the solid borax (not more than 100 mL) then add 5-6 drops of methyl red indicator to each beaker. Stir the solutions in the beakers to make sure that all of the borax is dissolved. You may need to warm beakers 1 and 2 if the borax is not completely dissolved in these samples.

Now titrate each sample with the 0.2 M HCl that is in your buret. Make sure you start with a full buret on the more concentrated samples. The titration endpoint occurs when the methyl red **indicator changes from a yellow to a salmon pink color.** The amount of HCl needed to titrate each sample should decrease significantly for each sample 1-5.

Calculations:

• Exchange data sets with your partner group.

• Determine the concentration, mol/L of the dissolved $B_4O_5(OH)_4^{2-}$ (s in $K_{sp}$ expression) in each sample titrated.

• Calculate the $K_{sp}$ of each Borax solution.

• To determine $\Delta H^\circ$ and $\Delta S^\circ$, make a plot of the experimental data on Excel using the equation developed in the introduction. Determine the slope, $m$, of the best-fit line through the experimental data.

• From the parameters of the best-fit line, determine $\Delta H^\circ$ and $\Delta S^\circ$. Be sure to report the correct units for these quantities ($m = -\Delta H^\circ/R; \ b = \Delta S^\circ/R$)
# Thermodynamics of the Solubility of Borax

**Report Sheet (1/group)**

**Names:** ____________________________

**Concentration of HCl:** ________________

**Your saturated solution data:**

<table>
<thead>
<tr>
<th>Beaker</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature</strong></td>
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<td></td>
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</tr>
<tr>
<td><strong>Volume HCl</strong></td>
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<td></td>
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<tr>
<td>([\text{B}_4\text{O}_5(\text{OH})_4^{2-}]) (in the original 5.0 mL aliquot)</td>
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<tr>
<td><strong>K\text{sp}</strong></td>
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</tbody>
</table>

**Partners’ saturated solution data:**

| Partners: | ____________________________ |

<table>
<thead>
<tr>
<th>Beaker</th>
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Attach the graph that includes your data and your partner’s including the theoretical fit. Make sure that each axis is properly labeled. If the two sets of data do not match up well, graph them as two separate lines on the same graph—labeling one line as your data and the other line as your group partner’s data.

Slope: _______________  \(\Delta H^\circ = \) _______________

Intercept: _______________  \(\Delta S^\circ = \) _______________