Determination of the Thermodynamic Parameters for the Solvation of Borax

- To learn about Thermodynamics.
- To learn about Solubility.
- To learn about the chemistry of Borax.


In this laboratory exercise, we will measure the three chemically important thermodynamic parameters, $\Delta G^0$ (Std. Gibb’s Free Energy Change), $\Delta H^0$ (Std. Enthalpy Change) and $\Delta S^0$ (Std. Entropy Change), for the dissolution of Borax in Water:

$$\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4\cdot8\text{H}_2\text{O(s)} \iff 2\text{Na}^+(\text{aq}) + \text{B}_4\text{O}_5(\text{OH})_4^{2-}(\text{aq}) + 8\text{H}_2\text{O(l)}$$

(Borax) \hspace{2cm} \text{(Eq. 1)} \hspace{2cm} \text{(Borate)}

Although these thermodynamic parameters are macroscopic in nature, they do provide a peek at the microscopic processes occurring during the chemical reaction. $\Delta H$ is a measure of the degree
of change in the intermolecular forces and the bond energy for the molecules involved in the chemical reaction. \( \Delta S \) is a measure of the change in "randomness" in the system. And, \( \Delta G \) codifies within it the 2\textsuperscript{nd} Law of Thermodynamics as applied to chemical reactions.

Thermodynamics seeks to inform us about the spontaneity of processes and to predict the equilibrium position a system will settle into. Historically, thermodynamics comes to us from studies by physicists concerning the efficiency of Steam Engines. Bases on such analyses, physicists soon discovered a dissymmetry exists in nature; Work can be converted with 100\% efficiency into Heat, but the reverse is not true. This observation led to consideration of a property we call the Entropy (S) of systems and to a statement of the Second Law of Thermodynamics in terms of this property:

\[
\text{Natural processes are accompanied by an increase in the Entropy of the universe;}
\]
\[
\Delta S_{\text{Univ}} > 0.
\]

The application of the Laws of Thermodynamics to chemical reactions did not occur quickly. Lavoisier studied Heat output during respiration in the late eighteenth century, but it was not until 1852 before systematic studies of Heats of Reaction (\( \Delta H \)) were carried out by Julius Thomsen and Macellin Berthelot. They initially thought “chemical forces” were driven by the magnitude of the Heat output of the chemical reaction. However, it was soon realized this could not account for Endothermic reactions. Another driving force for these reactions had to be found and it was soon identified as the Entropy change (\( \Delta S \)) for a reaction. A fully consistent treatment of the thermodynamics of chemical equilibria was finally provided by the physicist Josiah Willard Gibbs in a paper entitled \textit{On the Equilibrium of Heterogeneous Systems} published in 1876-1878.

In short, a consideration of the Enthalpy change for a chemical reaction is not sufficient to predict its state of equilibrium. But neither again is a consideration of its Entropy change. Yes, \( \Delta S_{\text{Univ}} = 0 \) when the reaction comes to equilibrium; it is no longer spontaneously proceeding forward and:

\[
\Delta S_{\text{Univ}} \neq 0
\]

But, we are not interested in analyzing the entire Universe in order to make predictions concerning the spontaneity or equilibrium position of a given chemical reaction. We are only interested in our little piece of the Universe; namely our beaker and its contents.

Basically, Gibbs realized that a new function was needed to predict the equilibrium point for a chemical reaction and defined this new function, now called the Gibbs Free Energy (G), as:

\[
G \equiv H - TS
\]

(Eq. 2)

When a chemical reaction occurs at constant temperature and pressure, it is found the 2\textsuperscript{nd} Law of Thermodynamics requires that the Gibb’s Function (G) must be minimized.

\[
\Delta G < 0
\]

(Eq. 3)
Hence when a chemical reaction achieves equilibrium:

\[ \Delta G = 0 \]  
(Eq. 4)

In terms of concentrations of reactants and product, it can be shown that for a given chemical reaction:

\[ \Delta G = \Delta G^o + RT \ln Q \]  
(Eq. 5)

where Q is the Reaction Quotient for the reaction. Hence, we have that when a reaction achieves its equilibrium point:

\[ \Delta G^o = -RT \ln K_{eq} \]  
(Eq. 6)

where \( K_{eq} \) is its Equilibrium Constant.

At constant temperature and pressure, it is true that:

\[ \Delta G = \Delta H - T \Delta S \]  
(Eq. 7)

Thus, a reaction will be driven forward if it is exothermic (\( \Delta H < 0 \)) and its products exhibit a greater degree of randomness (\( \Delta S > 0 \)). However, a reaction can be enthalpically unfavorable, endothermic (\( \Delta H > 0 \)), if it sufficiently entropically favorable; \( \Delta S \gg 0 \), such that \( \Delta G < 0 \) on net. Conversely, it is also true that a reaction can be spontaneous even if it is entropically unfavorable (\( \Delta S < 0 \)), if it release sufficient heat (\( \Delta H < 0 \)) that once again \( \Delta G < 0 \).

In our experiment, we will measure the Equilibrium Constant for our solvation reaction:

\[ K_{sp} = [Na^{+}]^2 [borate] \]  
(Eq. 8)

and this will allow us to determine the Standard Gibb’s Free Energy change for the reaction via (Eq. 6):

\[ \Delta G^o = -RT \ln(K_{sp}) \]  
(Eq. 9)

This is then related to the Standard change in the Enthalpy and Entropy for our chemical reaction via Equation 3:

\[ \Delta G^o = \Delta H^o - T \Delta S^o \]  
(Eq. 10)

If the Equilibrium Constant (\( K_{sp} \)) is determined at two different temperatures, \( T_1 \) and \( T_2 \), we can apply van't Hoff's formulation for the dependence of the equilibrium constant \( K_{eq} \) on temperature and determine the Standard Enthalpy change for this reaction as well:

\[ \ln \left( \frac{K_{sp,2}}{K_{sp,1}} \right) = - \left( \frac{\Delta H^o}{R} \right) \times \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]  
(Eq. 11)
This formulation assumes $\Delta H^0$ is temperature independent; a pretty good assumption provided the temperature difference is not too great in our experiment.

Thus, by measuring the $K_{sp}$ for this reaction at two different temperatures, we can determine $\Delta H^0$ from (Eq. 11), $\Delta G^0$ at each temperature from (Eq. 9) and then $\Delta S^0$ at each temperature from (Eq. 10).

All we need now is a method of measuring the amount of Borate Ion ($B_4O_5(OH)_4^{2-}$) and Sodium Ion ($Na^{+}$) concentrations in the equilibrium solution. There are several methods for doing this. In the present case, we will take advantage of the Basic nature of the Borate Ion and titrate it with a Standard HCl solution:

$$B_4O_5(OH)_4^{2-}(aq) + 2\text{HCl}(aq) + 3H_2O \rightarrow 4\text{H}_3\text{BO}_3(aq) + 2\text{Cl}^-(aq)$$

(Eq. 8)

By taking an aliquot of the saturated Borax solution and titrating it with standardized HCl, we can determine the concentration of the Borate Ion, $[\text{borate}]$, needed to calculate $K_{sp}$. The concentration of the Sodium Ion is then determined via the reaction stoichiometry:

$$[Na^+] = 2[\text{borate}]$$

(Eq. 9)

Borax, or Sodium Tetraborate Decahydrate, is an example of a class of compounds named Borates, which contain polyanions composed of trigonal $\text{BO}_3$ and/or $\text{BO}_4$ units linked by bridging oxygen atoms to form chain or ring structures. The tetraborate anion illustrates these features:

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 in use today. Borax is also used as a flux for solder, in the manufacture of glass, and as a preservative.
Pre-Lab Safety Questions

1. Suppose you are wearing a T-shirt and spill acid down the front of yourself. What should you do?

2. What is the purpose of the Fire Blanket in the lab? (Two purposes.)

3. Why do we require you to wear long pants or a long lab coat in the laboratory?
Procedure

Preparation of Sat’d Sodium Borate Solutions

1. To two separate 500mL Erlenmeyer Flasks add about 22g of Borax and 400mL of distilled Water. Add a magnetic stir bar to each flask.

2. Allow one to stir at Room Temperature for at least 30 minutes.

3. Place the other in an Ice-Water bath and allow to stir for at least 30 minutes.

4. Once the stirring is complete, and the solution has been saturated, turn off the magnetic stirrer and allow the excess Borax to settle. (If there is no excess Borax solid present, the solution may not be saturated. Add an additional gram of Borax and stir for another 30 minutes.) Add a thermometer. The solution should become clear in a few minutes. Keep the flasks undisturbed until you are ready to perform the titrations.

Preparation and Standardization of the HCl Solution

1. In a fume hood, add ~3.5mL of Conc. HCl to about 400mL of distilled Water in a 500mL Erlenmeyer Flask. Stir well. This gives a solution of approximately 0.1M 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. This will be anhydrous Sodium Carbonate. The titration reaction is:

   \[
   \text{Na}_2\text{CO}_3(\text{aq}) + 2 \text{HCl}(\text{aq}) \rightarrow 2 \text{NaCl}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}
   \]

   a) Accurately weigh three 0.15g portions of Anhydrous Primary Std. Grade Sodium Carbonate that has been dried for at least 2hrs. in a Drying Oven at 110°C and cooled in a Desicator into 250mL Erlenmeyer Flasks.

   b) Add 50mL of water and swirl until all the solid dissolves.

   c) Add a few drops of Bromocresol Green indicator.

   d) Titrate until you reach the Yellow-Green endpoint.

   e) Repeat for each of the three solutions.

   f) Calculate the HCl concentration and check with your instructor concerning the quality of the results.
Determination of the Borate Concentration

1. Record the temperature of the saturated Borax solution.

2. Without disturbing the solid at the bottom, carefully decant about 60mL of the solution into a clean and dry beaker. Pipet a 10mL aliquot into a 125mL Erlenmeyer Flask using a 10mL volumetric pipet. Add 20mL of distilled Water. Add a few drops of Bromthymol Blue indicator.

3. Titrate the aliquot to the Yellow-Green endpoint.

4. Repeat the titration on 2 additional aliquots.

5. Repeat this procedure for the other saturated Borax solution.
Data Analysis

1. Determine the Molarity of the Borate Ion at $T_1$ (Ice-Water) and at $T_2$ (Room Temperature).

2. Calculate the $K_{sp}$ at $T_1$ (Ice-Water) and at $T_2$ (Room Temperature).

3. Calculate $\Delta G^\circ$ at $T_1$ (Ice-Water) and at $T_2$ (Room Temperature).

4. Calculate $\Delta H^\circ$.

5. Calculate $\Delta S^\circ$ at $T_1$ (Ice-Water) and at $T_2$ (Room Temperature).

6. Tabulate Your Results -

<table>
<thead>
<tr>
<th>$K_{sp}$</th>
<th>$\Delta G^\circ$</th>
<th>$\Delta S^\circ$</th>
<th>$\Delta H^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_2$</td>
<td>=</td>
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<tr>
<td>$T_1$</td>
<td>=</td>
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</table>
Post Lab Questions

1. Is this Reaction Endothermic or Exothermic? Is it Enthapically favorable? Is this in accord with your expectations. Explain. [Some points to consider. This reaction involves the dissolution of an Ionically Bound solid, held together by strong Ionic Bonds, into a solution where the resulting Ions are stabilized by relatively weak Ion-Dipole Interactions.]

2. Is this reaction Entropically favorable? Is this in accord with your expectations? Explain. [Some points to consider. Do you expect the dissolution of the solid itself to be Entropically favorable or unfavorable. Do you expect the Entropy change of the Water to be favorable or unfavorable? (Be careful. When the Ions dissolve into the water, the water molecules become oriented around them in hydrations layers.)]

3. Identify the Boron atoms in the Borate Ion pictured below. What is the geometry about each Boron atom?

![Borate Ion Diagram]

4. The combustion of Peoxyacetone is a heatless explosive in that ΔH ~ 0 for the reaction:

\[
2 \text{C}_9\text{H}_{18}\text{O}_6(s) + 21 \text{O}_2(g) \rightarrow 18 \text{H}_2\text{O}(g) + 18 \text{CO}_2(g)
\]

The reaction is instead driven Entropically. Rationalize this in terms of the chemical reaction.

5. What is the definition of the Standard State for ions in solution? For a chemical reaction, what is the difference between ΔG and ΔG°?