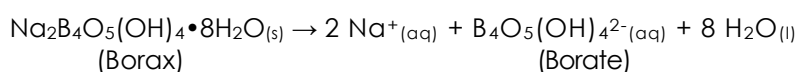


## Determination of Thermodynamic Parameters of Borax

**Objective:** The relationship between  $K_{sp}$ , Gibb's Free Energy, Enthalpy and Entropy will be explored by using titration to quantify the solubility of Borax at two different temperatures.



In this laboratory exercise, we will measure the three chemically important thermodynamic parameters,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  for the dissolution of Borax into Borate ion in water:



Historically, thermodynamics comes to us from studies by physicists concerning the efficiency of steam engines. These 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 the definition of the **Entropy** and a **Second Law of Thermodynamics**:

*Natural processes are accompanied by an increase in the Entropy of the universe.*

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 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 *On the Equilibrium of Heterogeneous Systems* published in 1876-1878.

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

$$K_{sp} = [\text{Na}^+]^2 [\text{borate}] \quad (\text{Eq. 1})$$

which will allow us to determine the Std. Gibb's Free Energy change for the reaction:

$$\Delta G^\circ = -RT \ln(K_{sp}) \quad (\text{Eq. 2})$$

It is the Gibb's Free Energy change which, besides telling us the maximum Work which can be obtained from the process, tells us how the driving forces of Entropy and Enthalpy are balanced for the reaction.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (\text{Eq. 3})$$

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  $K$  on temperature and determine the Std. Enthalpy change for this reaction as well:

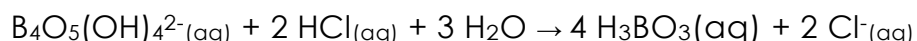
$$\ln (K_{sp2} / K_{sp1}) = - (\Delta H^\circ / R) \times (1/T_2 - 1/T_1) \quad (\text{Eq. 4})$$

This formulation assumes  $\Delta H^\circ$  is temperature independent; a 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  $\Delta H^\circ$  from (Eq. 4),  $\Delta G^\circ$  at each temperature from (Eq. 2) and  $\Delta S^\circ$  at each temperature from (Eq. 3).

All we need now is a method of measuring the amount of borate ion ( $B_4O_5(OH)_4^{2-}$ ) and sodium ion ( $Na^{2+}$ ) concentrations in the equilibrium solution.

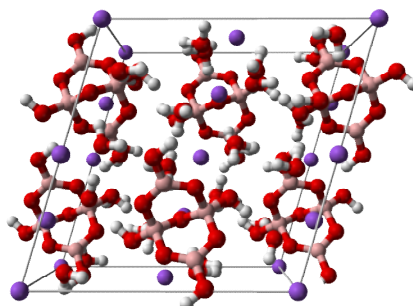
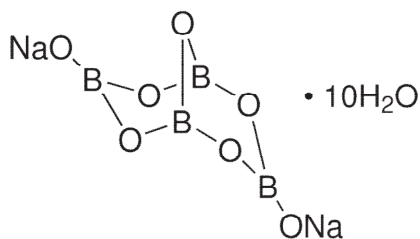
We will take advantage of the basic nature of the borate ion and titrate it with a standard hydrochloric acid solution:



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

$$[Na^+] = 2 [\text{borate}] \quad (\text{Eq. 5})$$

Borax, or **Sodium Tetraborate Decahydrate**, is an example of a class of compounds named Borates, which contain polyanions composed of trigonal  $BO_3$  and/or  $BO_4$  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 used today. Borax is also used as a flux for solder, in the manufacture of glass, and as a preservative.

## Procedure

**Very important:** Begin the preparation of the solutions at the beginning of class, before lecture or problem solving because the solutions have to stir for about an hour.

### Preparation of Sat'd Sodium Borate Solutions

To two separate 500mL Erlenmeyer Flasks add about 20g of Borax and 400mL of distilled Water. Add a magnetic stir bar to each flask. Allow one to stir at Room Temperature for at least 30 minutes. Place the other in an Ice-Water bath and allow to stir for at least 30 minutes.



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.

## 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. Filter this solution to remove any fine particles of undissolved borax.



3. Pipet a 10mL aliquot of the filtered solution into a 125mL Erlenmeyer flask using a 10mL volumetric pipet. Add about 20mL of deionized water. Add a few drops of Bromthymol Blue indicator.
4. Titrate the aliquot to the Yellow-Green endpoint.
5. Repeat the titration on two additional aliquots.
6. Repeat this procedure for the other saturated borax solution. Keep the solution on ice during the filtration.

## 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. Record your data and results in tables in your laboratory notebook.

## Questions to Answer in Your Reflections / Conclusions

1. Is the solvation reaction endothermic or exothermic? Is this reaction spontaneous? Does this agree with your expectations? Explain any discrepancies.
2. Identify the boron atoms in the borate ion pictured in this model. What is the geometry about each Boron atom?
3. What are sources of error in this experiment?
4. Can these thermodynamic quantities be calculated from a standard thermodynamic table? If so then compare your results to literature values.

