



Experiment

The Thermodynamics of the Dissolution of Borax

Borax is commonly added to (clothes) wash water to increase the pH for more effective cleansing.

- To determine the solubility product of borax as a function of temperature
- To determine the standard free energy, standard enthalpy, and standard entropy changes for the aqueous dissolution of borax

OBJECTIVES

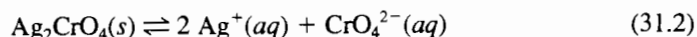
Large deposits of borax are found in the arid regions of the southwestern United States, most notably in the Mojave Desert (east central) region of California. Borax is obtained as tincal, $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$, and kernite, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, from an open pit mine near Boron, California, and as tincal from brines from Searles Lake near Trona, California. Borax, used as a washing powder for laundry formulations, is commonly sold as 20-Mule Team Borax®. Historically, borax was mined in Death Valley, California, in the late nineteenth century. To transport the borax from this harsh environment, teams of 20 mules were used to pull a heavy wagon loaded with borax (and a water wagon) across the desert and over the mountains to railroad depots for shipment to other parts of the world. Borax is used as a cleansing agent, in the manufacture of glazing paper and varnishes, and as a flux in soldering and brazing; however, its largest current use is in the manufacture of borosilicate glass.

The free energy change of a chemical process is proportional to its equilibrium constant according to the equation

$$\Delta G^\circ = -RT \ln K \quad (31.1)$$

where R , the gas constant, is $8.314 \times 10^{-3} \text{ kJ/mol}\cdot\text{K}$ and T is the temperature in kelvins. The equilibrium constant, K , is expressed for the equilibrium system when the reactants and products are in their **standard states**. For a slightly soluble salt in an aqueous system, the precipitate and the ions in solution correspond to the standard states of the reactants and products, respectively.

The “standard state” equilibrium for the slightly soluble silver chromate salt is



The solubility product, K_{sp} , is set equal to the product of the molar concentrations of the ions, each raised to the power of their respective coefficients in the balanced equation—this is the mass action expression for the system:

$$K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] \quad (31.3)$$

INTRODUCTION

Standard state: the state of a substance at one atmosphere (and generally 25°C)

and the free energy change for the equilibrium is

$$\Delta G^\circ = -RT \ln K_{sp} = -RT \ln [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] \quad (31.4)$$

Additionally, the free energy change of a chemical process is a function of the enthalpy change and the entropy change of the process:

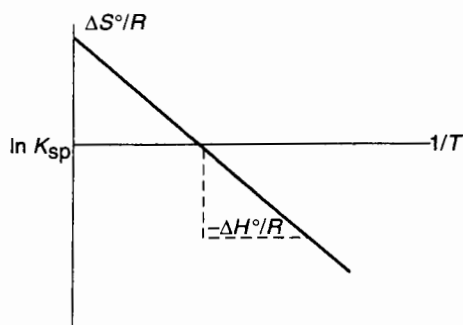
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (31.5)$$

When the two free energy expressions are set equal for a slightly soluble salt, such as silver chromate, then

$$-RT \ln K_{sp} = \Delta H^\circ - T\Delta S^\circ \quad (31.6)$$

Rearranging and solving for $\ln K_{sp}$,

$$\ln K_{sp} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad (\text{analogous to the equation } y = mx + b) \quad (31.7)$$



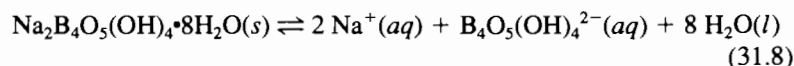
This equation can prove valuable in determining the thermodynamic properties of a chemical system, such as that of a slightly soluble salt. A linear relationship exists when the values of $\ln K_{sp}$ obtained at various temperatures are plotted as a function of the reciprocal temperature. The (negative) slope of the line equals $-\Delta H^\circ/R$, and the y-intercept (where $x = 0$) equals $\Delta S^\circ/R$. Since R is a constant, the ΔH° and the ΔS° for the equilibrium system can easily be calculated.

Since the values of $\ln K_{sp}$ may be positive or negative for slightly soluble salts and T^{-1} values are always positive, the data plot of $\ln K_{sp}$ versus $1/T$ appears in the first and fourth quadrants of the Cartesian coordinate system.

The Borax System

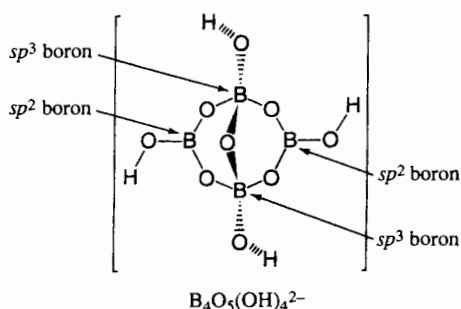
Borax is often given the name sodium tetraborate decahydrate and the formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. However, according to its chemical behavior, a more defining formula for borax is $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$, also called tincal.

In this experiment the thermodynamic properties, ΔG° , ΔH° , and ΔS° , are determined for the aqueous solubility of borax (tincal), $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$. Borax dissolves and dissociates in water according to the equation

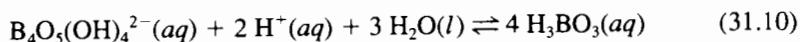


The mass action expression, set equal to the solubility product at equilibrium, for the solubility of borax is

$$K_{sp} = [\text{Na}^+]^2 [\text{B}_4\text{O}_5(\text{OH})_4^{2-}] \quad (31.9)$$



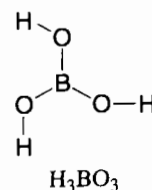
The $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ anion, because it is the conjugate base of the weak acid boric acid, is capable of accepting two protons from a strong acid in an aqueous solution:



Therefore, the molar concentration of the $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ anion in a saturated borax solution can be measured with a titrimetric analysis of the saturated borax solution using a standardized hydrochloric acid solution as the titrant.

$$\text{mol B}_4\text{O}_5(\text{OH})_4^{2-} = \text{volume (L) HCl} \times \frac{\text{mol HCl}}{\text{volume (L) HCl}} \times \frac{1 \text{ mol B}_4\text{O}_5(\text{OH})_4^{2-}}{2 \text{ mol HCl}} \quad (31.11)$$

$$[\text{B}_4\text{O}_5(\text{OH})_4^{2-}] = \frac{\text{mol B}_4\text{O}_5(\text{OH})_4^{2-}}{\text{volume (L) sample}} \quad (31.12)$$



This analysis is also a measure of the molar solubility of borax in water at a given temperature—according to the stoichiometry, one mole of the $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ anion forms for every mole of borax that dissolves.

$$[\text{B}_4\text{O}_5(\text{OH})_4^{2-}] = \text{molar solubility of borax} \quad (31.13)$$

Temperature changes do affect the molar solubility of most salts, and borax is no exception. For example, the solubility of borax is 2.01 g/100 mL at 0°C and is 170 g/100 mL at 100°C.¹

As a consequence of the titration and according to the stoichiometry of the dissolution of the borax, the molar concentration of the sodium ion in the saturated solution is twice that of the experimentally determined $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ anion concentration.

$$[\text{Na}^+] = 2 \times [\text{B}_4\text{O}_5(\text{OH})_4^{2-}] \quad (31.14)$$

The solubility product for borax at a measured temperature is, therefore,

$$\begin{aligned} K_{\text{sp}} &= [\text{Na}^+]^2 [\text{B}_4\text{O}_5(\text{OH})_4^{2-}] = [2 \times [\text{B}_4\text{O}_5(\text{OH})_4^{2-}]]^2 [\text{B}_4\text{O}_5(\text{OH})_4^{2-}] \\ &= 4 [\text{B}_4\text{O}_5(\text{OH})_4^{2-}]^3 = 4 [\text{molar solubility of borax}]^3 \end{aligned} \quad (31.15)$$

To obtain the thermodynamic properties for the dissolution of borax, values for the molar solubility and the solubility product for borax are determined over a range of temperatures.

D. Data Analysis

Appendix C



1. Calculate the molar solubility of borax at each of the measured temperatures.
2. Calculate the solubility product of borax at each of the measured temperatures.
3. Plot the natural logarithm of the solubility product versus the reciprocal temperature (K^{-1}) for each sample and draw the “best straight line” through the data points.
4. Determine the slope of the linear plot and calculate the standard enthalpy of solution for borax.
5. Determine the y-intercept (at $x = 0$) of the linear plot and calculate the standard entropy of solution for borax.

PROCEDURE

Procedure notes

Lab Session 1:

- Prepare the mixture (described in Section 3) and begin stirring the mixture so that it will be saturated when you are ready to begin collecting samples.
- Prepare the standardized HCl solution (Section 1).
- Prepare the test tubes (Section 2).
- Collect the saturated solutions at $\sim 20^{\circ}\text{C}$, $\sim 10^{\circ}\text{C}$, $\sim 0^{\circ}\text{C}$ (Section 3).
- If time permits, titrate the three samples (Section 5).

Lab Session 2:

- Prepare the mixture (described in Section 4) and begin stirring and heating the mixture.
 - If you did not complete the titrations of the 3 samples from Section 3 in the previous lab session, titrate them now (Section 5). Be sure to watch the solution you are heating to prevent it from exceeding 70°C .
 - Collect the saturated solutions at $\sim 50^{\circ}\text{C}$, $\sim 40^{\circ}\text{C}$, $\sim 30^{\circ}\text{C}$ (Section 4).
 - Titrate the three samples (Section 5).
-

Section 1: Standardized HCl solution

1. Carry out the procedure on the addendum.

Section 2: Preparing the test tubes

2. With pipette, measure precisely 5.00 mL of water into each of six test tubes and mark the levels with a wax pencil. You will use these as a measure of your volume of solution later.
3. Label the test tubes $\sim 50^{\circ}$, $\sim 40^{\circ}$, $\sim 30^{\circ}$, $\sim 20^{\circ}$, $\sim 10^{\circ}$, and $\sim 0^{\circ}\text{C}$.
4. Empty the test tubes and dry them.

Section 3: Obtaining the saturated solutions for 0° - 20 °C

5. In beaker, mix 15 g of borax and 65 mL of water and allow to stir on a magnetic stirrer for at least one hour (60 minutes).
6. *Record the measured temperature of the solution*, and transfer 5.00 mL to the test tube labeled ~ 20°C.
7. Then, put the beaker into an ice bath and carefully monitor the temperature, as you stir the solution carefully with the thermometer, until the solution is at ~10°C. Transfer 5.00 mL to the 10°C test tube. *Record the precise temperature.*
8. Allow the solution to cool as low as it will go (may not get to 0°C), *record the precise temperature* and transfer 5.00 mL to the ~ 0°C test tube.
- 9.

Section 4: Obtaining the saturated solutions for 30° - 60 °C

10. On a hot plate, heat a mixture of about 30 g of borax and 65 mL of water in a 150 mL beaker to about 65°C. Try not to allow the solution to exceed 70°C, as thermal decomposition may occur.
11. Keep the solution at ~ 65°C for 45-60 minutes.
12. Remove from the hot plate.
13. While carefully stirring the solution occasionally with a thermometer (be gentle – your thermometer is fragile), allow the solution to cool to ~ 50°.
14. Allow the borax to settle out and decant precisely 5.00 mL of the solution into the test tube labeled ~ 50°. Record the precise temperature in your notebook and use it in your calculations. It will likely not be exactly 50°.
15. Allow the mixture to cool to ~ 40°C and decant a second sample. Repeat for ~ 30°C.

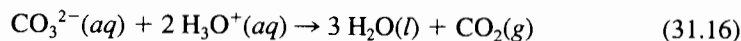
Section 5: Analyzing samples for Borate ion

16. If borax has precipitated from the solution (usually only a problem for the 40° or 50°C samples), carefully warm the test tube to redissolve the crystallized borax.
17. Transfer the contents of this test tube to a 250 mL Erlenmeyer flask. Rinse the test tube with several portions of water to assure that you have transferred all the borax to the flask.
(You should see no white film on the inside of the tube – the white film would be precipitated borax.)
18. Add enough deionized water to the flask to keep the borax dissolved.
19. Add two or three drops of bromocresol green indicator and titrate the solution with the standardized 0.5 M HCl. The end point is signified by a color change from blue to green to yellow.
20. Repeat this procedure for each of the remaining samples.

Addendum – Preparing a standardized solution of HCl

A standardized HCl solution is prepared using anhydrous sodium carbonate as the primary standard. Sodium carbonate samples of known mass are transferred to Erlenmeyer flasks, dissolved in deionized water, and titrated to a methyl orange endpoint (pH range 3.1 to 4.4) with the prepared hydrochloric acid solution.

Standardized HCl Solution



The flask is heated to near boiling close to the stoichiometric point of the analysis to remove the carbon dioxide gas produced in the reaction.

The objectives of this experiment are fourfold: (1) determine the molar concentration of the $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ anion and the molar solubility of borax at five different temperatures using the titration technique with a standardized hydrochloric acid solution; (2) calculate the solubility product of borax at each temperature; (3) plot the natural logarithm of the solubility product versus the reciprocal temperature of the measurements; (4) extract from the plotted data the thermodynamic properties of ΔH° and ΔS° for the dissolution of borax, from which its ΔG° can be calculated.

A. Standardized HCl Solution

- Dry the Primary Standard.** Dry 2–3 g of anhydrous sodium carbonate, Na_2CO_3 , for several hours in a drying oven set at about 110°C . Cool the sample in a desiccator.
- Prepare the HCl Solution.** Prepare 200 mL of $\sim 0.5 \text{ M}$ HCl starting with concentrated (12 M) HCl. (**Caution:** *Concentrated HCl causes severe skin burns.*)
- Prepare the Primary Standard.** Calculate the mass of sodium carbonate that neutralizes 15–20 mL of 0.5 M HCl at the stoichiometric point. Measure this mass ($\pm 0.001 \text{ g}$) on a tared weighing paper or dish and transfer to a 125-mL Erlenmeyer flask. Prepare *at least* three samples of sodium carbonate for the analysis of the HCl solution.
- Prepare the Buret.** Clean a buret and rinse with several 3- to 5-mL portions of the $\sim 0.5 \text{ M}$ HCl solution. Use a clean funnel to fill the buret with the $\sim 0.5 \text{ M}$ HCl solution. After 10–15 seconds use the proper technique to read and record the volume of HCl solution in the buret, “using all certain digits (from the labeled calibration marks on the buret) *plus* one uncertain digit (the last digit which is the best estimate between the calibration marks).”
- Titrate the Primary Standard.** To each solid sodium carbonate sample add $\sim 50 \text{ mL}$ of deionized water and several drops of methyl orange indicator.² Dispense the HCl solution from the buret, swirling the Erlenmeyer flask during the addition.
Very near or at the apparent endpoint of the indicator, heat the flask over a direct flame to near boiling to drive off the carbon dioxide gas. Carefully (dropwise) add additional HCl titrant until the endpoint is reached and the color persists for 30 seconds (a color change caused by the addition of one “additional” drop of the HCl solution from the buret). Stop the addition of the HCl titrant. After 10–15 seconds read and record the volume of HCl in the buret.
- Repeat the Analysis.** Refill the buret and complete the standardization procedure with the remaining sodium carbonate samples.
- Do the Calculations.** Calculate the experimental molar concentration of the prepared HCl solution from the sodium carbonate samples. The molar concentrations of the HCl solution from the trials should agree within $\pm 1\%$; if not, complete additional trials as necessary.

²Methyl orange indicator changes color over the pH range of 3.1–4.4; its color appears yellow at a pH greater than 4.4, but orange at a pH less than 3.1.

3. Describe the preparation of 1.0 L of 0.5 M HCl, starting with conc HCl (12 M).

4. A 0.338-g sample of anhydrous sodium carbonate, Na_2CO_3 , is dissolved in water and titrated to a methyl orange end-point with 15.33 mL of a prepared hydrochloric acid solution. What is the molar concentration of the HCl solution?

5. Consider the Experimental Procedure.

a. How many samples of a saturated borax solution are to be titrated?

b. Each sample is to be titrated at a different temperature. How many trials are completed at each temperature?

c. What titrant and what indicator are used for the analysis of the saturated borax solutions in the experiment?

e. How many data points are collected for the plot of $\ln K_{sp}$ versus $1/T$ in the experiment?

