

## EXPERIMENT

# Thermodynamics of the Borax – Borate Equilibrium

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The student will investigate an equilibrium system of a sparingly soluble salt in water. The thermodynamic quantities  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  for the solvation of borax in water are obtained by measuring the magnitude of the solubility product constant over a narrow temperature range.

### OBJECTIVE

#### A P P A R A T U S

Ring stand / buret clamp/ buret	Thermometer
Magnetic Stirrer / Stir Bar	150 (2) and 600 (1) mL Beaker
250 mL Erlenmeyer Flask (6)	10 mL Graduated Cylinder

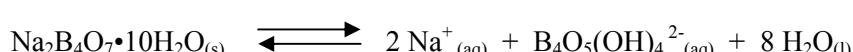
#### APPARATUS AND CHEMICALS

#### C H E M I C A L S

Na <sub>2</sub> CO <sub>3</sub>	Borax
~ 0.1 M HCl	Bromcresol Green

Borax, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> • 10H<sub>2</sub>O, is a naturally occurring mineral that was discovered in Death Valley in the late 1800's. Even today, it is sold under the name 20 Mule Team Borax after the trademark way it was removed from Death Valley. Borax is used as a detergent / cleanser and as an important buffer in biochemistry. The name "Borax" is derived from the fact that the mineral contains the element "Boron". The identity of Borax in the late 1800's was confirmed by a green flame test: after dark, the sample was mixed with sulfuric acid and alcohol and ignited – a green flame confirmed the presence of Boron.

The equilibrium of borax in water is given by Equation 1:



Equation 1

Inspection of **Equation 1** reveals that a solid material dissociates into three solvated ions and water when dissolved in water. The experimental procedure will specify that "some" solid borax must be present in the sample mixture before you remove an aliquot for

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analysis. The result of this requirement is that the  $[\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}_{(s)}]_{\text{eq}} = [\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}_{(s)}]_{\text{initial}}$ . This makes the  $[\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}_{(s)}]$  a constant which can be incorporated into the equilibrium constant. The same argument is used for the  $[\text{H}_2\text{O}_{(l)}]$  during the course of the reaction. These waters of hydration (water molecules which are part of borax's crystalline matrix) are released during the solvation process and become part of the aqueous environment. Since this “added amount of water” does not significantly change the concentration of water already present, this constant is also incorporated into the equilibrium constant,  $k_{\text{sp}}$ . The equilibrium expression for **Equation 1** is written as:

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

The solubility product constant can be calculated if either the concentration of sodium ions or borate ions is known. Titration of the borate ions with a known concentration of  $\text{HCl}_{(aq)}$  provides the  $[\text{B}_4\text{O}_5(\text{OH})_4^{2-}]_{\text{eq}}$  according to the following balanced equation:



This titration also provides the concentration of sodium ions in **Equation 2** since the reaction stoichiometry dictates that the  $[\text{Na}^+]_{\text{eq}} = 2 \times [\text{B}_4\text{O}_5(\text{OH})_4^{2-}]_{\text{eq}}$ . When the solvation of borax is analyzed at several different temperatures, one can determine the  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ .

The immediate relationship between free energy change ( $\Delta G^\circ$ ) and the solubility product constant ( $k_{\text{sp}}$ ) is given by

$$\Delta G^\circ = -RT \ln k_{\text{sp}} \quad \text{Equation 4}$$

where  $R$  is the ideal-gas constant, 8.314 J/mol-K and  $T$  is the absolute temperature in Kelvin. A reaction is thermodynamically favored if  $\Delta G^\circ < 0$ , a condition that occurs when  $k_{\text{sp}} > 1$ . By definition, the Free Energy change at a specified temperature expresses the net effect of two different thermodynamic quantities, Enthalpy and Entropy, and is represented by the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{Equation 5}$$

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This equation is routinely used to calculate  $\Delta G^\circ$  values because  $\Delta H$  and  $\Delta S$  values are relatively constant over small temperature ranges like the one in this lab. Combining the two Free Energy equations gives:

$$-RT \ln k_{sp} = \Delta H^\circ - T\Delta S^\circ$$

**Equation 6**

The *linear* form of Equation 6 is obtained when it is rearranged to

$$\ln k_{sp} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

**Equation 7**

A plot of  $\ln k_{sp}$  vs.  $1/T$  gives a line with a slope of  $-\Delta H^\circ/R$  and a y-intercept of  $\Delta S^\circ/R$ . The Enthalpy, Entropy and Free Energy values are easily determined from the graphed data. The literature values for the Enthalpy and Entropy of this process are 110 kJ/mole and 380 J/mole-K, respectively.

**Standardization of an aqueous HCl solution that is ~ 0.1 M:** A solution of HCl with **PROCEDURE** an approximate Molarity of 0.1 M has been prepared for use in this lab. Steps 1 – 12 will describe how to determine the **exact Molarity** of this solution.

1. Obtain  $400 \pm 10$  mL of the  $\sim 0.1$  M HCl solution in a 600 mL beaker.
2. Clean a 50 mL buret and rinse it with 5 - 10 mL of the HCl solution. Place the rinses in an empty beaker. Add 1 drop of the bromocresol green indicator to this beaker and record the color of this indicator in acid [**Data Sheet Q1**]. Fill the buret with the HCl solution.
3. Obtain two **clean** Erlenmeyer flasks (label them **FLASK 1** and **FLASK 2**) and add  $50 \pm 5$  mL distilled water and 4 drops bromocresol green indicator to each.
4. Add the HCl solution **dropwise** to **FLASK 1** until 1 drop turns the indicator yellow (no green color present). This should take 1 - 5 drops. Repeat for **FLASK 2**.
5. Place  $0.20 \pm .01$  grams of the primary standard,  $\text{Na}_2\text{CO}_3$ , onto a piece of weighing paper. Record its exact mass [**Data Sheet Q2 Trial 1**]. Transfer the  $\text{Na}_2\text{CO}_3$  to **FLASK 1**. Repeat for **FLASK 2** [**Data Sheet Q2 Trial 2**].
6. Record the color of the bromocresol green indicator in base ( $\text{Na}_2\text{CO}_3$  is a base) [**Data Sheet Q3**].
7. Record the initial buret reading [**Data Sheet Q4 Trial 1**] and titrate the  $\text{Na}_2\text{CO}_3$  solution in **FLASK 1** to a **green** endpoint – stir frequently or use a magnetic stirrer. At

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this point, add ~ 1 g solid NaCl to the flask and swirl vigorously – the indicator may turn blue again. Add HCl ***dropwise*** until 1 drop turns the indicator yellow (no green color present).

8. Record the final buret reading [**Data Sheet Q5 Trial 1**].
9. Repeat Steps 7 – 8 for **FLASK 2**. Record the initial [**Data Sheet Q4 Trial 2**] and final buret readings [**Data Sheet Q5 Trial 2**].
10. Calculate the Volume of HCl used in **FLASK 1** [**Online Report Sheet Q6 Trial 1**] and **FLASK 2** [**Online Report Sheet Q6 Trial 2**].
11. Calculate the Molarity of the HCl in **FLASK 1** [**Online Report Sheet Q7 Trial 1**] and **FLASK 2** [**Online Report Sheet Q7 Trial 2**]. The molar stoichiometry for this reaction is shown in Equation 8.



**Equation 8**

12. Calculate the Average Molarity of the HCl solution [**Online Report Sheet Q8**].

### Titration of the Borate ion with HCl:

13. Place two 150 mL (or 250 mL) beakers on a hot plate with 60 mL water in each. Heat the water in both beakers to 50°C.
14. Add just enough borax (~ 3 spoonfuls) to one of the beakers so that there is still solid borax in the bottom of the beaker. If all the borax dissolves, add more solid borax and stir – there MUST BE some solid in the bottom of the beaker. Gently stir the borax solution with your thermometer for 5 minutes to achieve equilibrium.
15. Keep the temperature of borax/water beaker at 50°C. The beaker containing only water can remain on the hot plate and get **hotter than 50°C**.
16. Add 40 mL distilled water and 4 drops bromocresol green indicator to **FLASKS 3** and **FLASKS 4**.

**The next 4 Steps must be performed quickly (< 1 minute) for best results!!**

17. Warm a 10 mL graduated cylinder by filling it with water from the beaker containing just hot water – the graduated cylinder must be hotter than the borax/water solution to prevent crystallization of the borax. After 10 seconds, pour the water in the graduated cylinder back into the beaker.
18. Shake any excess water out of the graduated cylinder.

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19. Pour 10.0 mL of the borax solution (**DON'T TRANSFER ANY SOLID BORAX**) in the graduated cylinder and transfer it to **FLASK 3**. Rinse the graduated cylinder twice with hot water and add these rinses to **FLASK 3** also.
20. Shake any excess water out of the graduated cylinder. Add 10.0 mL of the borax solution (**DON'T TRANSFER ANY SOLID BORAX**) to the graduated cylinder and transfer it to **FLASK 4**. Rinse the graduated cylinder twice with hot water and add these rinses to **FLASK 4**.
21. Record the temperature of the saturated borax solution in Step 15 [**Data Sheet Q9**].
22. Record the initial buret reading [**Data Sheet Q10 Trials 1 & 2**].
23. Titrate with the freshly standardized HCl solution to a yellow endpoint – stir frequently or use a magnetic stirrer. Record the final buret reading [**Data Sheet Q11 Trials 1 & 2**]. *You will have to refill the buret (1 or 2 times) before reaching the endpoint. If that is necessary, refill the buret to the 0.0 mL mark and enter 50 plus (or 100 plus if you refilled it twice) the volume shown on the buret at the equivalence point as the final buret reading.*
24. Calculate the volume of HCl used in **FLASK 3** [**Online Report Sheet Q12 Trial 1**] and **FLASK 4** [**Online Report Sheet Q12 Trial 2**].
25. Calculate the  $[B_4O_5(OH)_4]_{eq}^{2-}$  [**Online Report Sheet Q13 Trials 1 & 2**]. Recall that the volume of the borate solution titrated is 10.0 mL - do not include the 40 mL of distilled water added in the titration.
26. Calculate the average  $[B_4O_5(OH)_4]_{eq}^{2-}$  [**Online Report Sheet Q14**].
27. Calculate the  $k_{sp}$  of the Borax – Borate equilibrium [**Online Report Sheet Q15**].
28. Calculate  $\ln k_{sp}$  [**Online Report Sheet Q16**].
29. Calculate  $1/T$  [**Online Report Sheet Q17**].
30. Add ice to the beaker containing the 50°C saturated borax solution and stir gently with a thermometer - remove any ice present in the solution when it reaches room temperature. Gently stir the saturated borax solution with your thermometer for 5 minutes.
31. Add 40 mL distilled water and 4 drops bromocresol green indicator to **FLASKS 5** and **FLASKS 6**.
32. Add 10.0 mL of the borax solution (**DON'T TRANSFER ANY SOLID BORAX**) to the graduated cylinder and transfer it to **FLASK 5**. Rinse the graduated cylinder twice with hot water and add these rinses to **FLASK 5**.
33. Repeat for **FLASK 6**.
34. Record the temperature of the saturated borax solution [**Data Sheet Q18**].

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35. Record the initial buret reading [**Data Sheet Q19 Trials 1 & 2**].
36. Record the final buret reading [**Data Sheet Q20 Trials 1 & 2**].
37. Calculate the volume of HCl used [**Online Report Sheet Q21 Trials 1 & 2**]
38. Calculate the  $[B_4O_5(OH)_4]_{eq}^{2-}$  [**Online Report Sheet Q22 Trials 1 & 2**]
39. Calculate the average  $[B_4O_5(OH)_4]_{eq}^{2-}$  [**Online Report Sheet Q23**].
40. Calculate the  $k_{sp}$  [**Online Report Sheet Q24**].
41. Calculate  $\ln k_{sp}$  [**Online Report Sheet Q25**].
42. Calculate  $1/T$  [**Online Report Sheet Q26**].
  
43. Add ice to the beaker containing the room temperature saturated borax solution and stir gently with a thermometer - remove any ice present in the solution when it reaches 0°C. Gently stir the saturated borax solution with your thermometer for 5 minutes keeping the temperature at ~ 5°C by adding ice (1 piece at a time).
44. Add 40 mL distilled water and 4 drops bromocresol green indicator to **FLASKS 7** and **FLASKS 8**.
45. Add 10.0 mL of the borax solution (**DON'T TRANSFER ANY SOLID BORAX**) to the graduated cylinder and transfer it to **FLASK 7**. Rinse the graduated cylinder twice with room temperature water and add these rinses to **FLASK 7**.
46. Repeat for **FLASK 8**.
47. Record the temperature of the solution [**Data Sheet Q27**].
48. Record the initial buret reading [**Data Sheet Q28 Trials 1 & 2**].
49. Record the final buret reading [**Data Sheet Q29 Trials 1 & 2**].
50. Volume of HCl used [**Online Report Sheet Q30 Trials 1 & 2**]
51. Calculate the  $[B_4O_5(OH)_4]_{eq}^{2-}$  [**Online Report Sheet Q31 Trials 1 & 2**]
52. Calculate the average  $[B_4O_5(OH)_4]_{eq}^{2-}$  [**Online Report Sheet Q32**].
53. Calculate the  $k_{sp}$  [**Online Report Sheet Q33**].
54. Calculate  $\ln k_{sp}$  [**Online Report Sheet Q34**].
55. Calculate  $1/T$  [**Online Report Sheet Q35**].
  
56. Graph  $\ln k_{sp}$  vs  $1/T$  using Excel: During the submission of your Online Lab Report, you will need to graph the data collected above. A description of how to graph this data using Excel is provided below – if your university uses a different graphing program, your instructor will provide details for that graphing program.

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- ✓ Open Excel by clicking on Start, All Programs, Microsoft Office, Microsoft Office Excel
- ✓ Rows 1, 2 and 3 correspond to the  $\sim 5^{\circ}\text{C}$ , room temperature and  $\sim 50^{\circ}\text{C}$  solutions, respectively. Place  $\ln k_{\text{sp}}$  in cells A1 – A3 (click the cell and type the **number** then press ENTER – **enter only numbers in the spreadsheet**).
- ✓ Place  $1/T$  in cells B1 – B3.
- ✓ Go to INSERT then place your mouse over the SCATTER section in the CHARTS area. Click on the Scatter icon and then click on the SCATTER WITH ONLY MARKERS icon.
- ✓ This will place a chart on the page with your data. Right-click in the white area on the right side of the chart and click the Select Data link.
- ✓ Click Series 1 to highlight it and then click the Edit button. Make sure the X values are “=Sheet1! \$B\$1:\$B\$3” and the Y values are “=Sheet1! \$A\$1:\$A\$3”.
- ✓ Click OK and then click OK again.
- ✓ Click in the white area to the right of the chart and then click the LAYOUT tab at the top of the page. Under the ANALYSIS group, click on the TRENDLINE icon (you may need to click it again to see the Trendline options).
- ✓ Click MORE TRENDLINE OPTIONS and then click “Display Equation on Chart” and “Display R squared Value on Chart”.
- ✓ Click Close.

57. Your graph will be displayed along with the equation of the line [Equation 7]. Enter the slope [**On-line Report Sheet Q36**], y-intercept [**On-line Report Sheet Q37**] and R-squared value [[**On-line Report Sheet Q38**]].

58. Determine the  $\Delta H$  for the solvation of Borax [**Online Report Sheet Q39**].

59. Determine the percent error in the experimentally determined value for  $\Delta H$  [**Online Report Sheet Q40**].

$$\text{Percent Error} = \frac{|\text{Theoretical} - \text{Experimental}|}{\text{Theoretical}} \times 100$$

60. Determine the  $\Delta S$  for the solvation of Borax [**Online Report Sheet Q41**].

61. Determine the percent error in the experimentally determined value for  $\Delta S$  [**Online Report Sheet Q42**].

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62. Determine the  $\Delta G$  for the solvation of Borax [[Online Report Sheet Q43](#)].

**Waste Disposal:** Flush all titration solutions down the sink with plenty of water.

**Lab Report:** Once you have turned in your Instructor Data Sheet, lab attendance will be entered and lab attendees will be permitted to access the online data / calculation submission part of the lab report (click on **Lab 22 – Thermodynamics of the Borax – Borate Equilibrium**). Enter your data accurately to avoid penalty. The lab program will take you in order to each calculation. If there is an error, you will be given additional submissions (the number and penalty to be determined by your instructor) to correct your calculation.

## Laboratory 22

### Student Data Sheet

	Trial 1	Trial 2
1. Record the color of the indicator in acid		
2. Mass of $\text{Na}_2\text{CO}_3$	_____ g	_____ g
3. Record the color of the indicator in base		
4. Initial volume of HCl	_____ mL	_____ mL
5. Final volume of HCl	_____ mL	_____ mL
9. Exact Temperature at $\sim 50^\circ\text{C}$	_____ $^\circ\text{C}$	
10. Initial volume of HCl	_____ mL	_____ mL
11. Final volume of HCl	_____ mL	_____ mL
18. Exact Temperature at room temperature	_____ $^\circ\text{C}$	
19. Initial volume of HCl	_____ mL	_____ mL
20. Final volume of HCl	_____ mL	_____ mL
27. Exact Temperature at $\sim 5^\circ\text{C}$	_____ $^\circ\text{C}$	
28. Initial volume of HCl	_____ mL	_____ mL
29. Final volume of HCl	_____ mL	_____ mL



## Laboratory 22

### Instructor Data Sheet

	Trial 1	Trial 2
1. Record the color of the indicator in acid		
2. Mass of $\text{Na}_2\text{CO}_3$	_____ g	_____ g
3. Record the color of the indicator in base		
4. Initial volume of HCl	_____ mL	_____ mL
5. Final volume of HCl	_____ mL	_____ mL
9. Exact Temperature at $\sim 50^\circ\text{C}$	_____ $^\circ\text{C}$	
10. Initial volume of HCl	_____ mL	_____ mL
11. Final volume of HCl	_____ mL	_____ mL
18. Exact Temperature at room temperature	_____ $^\circ\text{C}$	
19. Initial volume of HCl	_____ mL	_____ mL
20. Final volume of HCl	_____ mL	_____ mL
27. Temperature at $\sim 5^\circ\text{C}$	_____ $^\circ\text{C}$	
28. Initial volume of HCl	_____ mL	_____ mL
29. Exact Final volume of HCl	_____ mL	_____ mL