**Name \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

**Determining Free Energy from Ksp**

**INTRODUCTION**

In this experiment you will determine the solubility product constant (Ksp) of borax, Na2B4O5(OH)4·8H2O, a slightly soluble sodium salt, in water at two different temperatures and evaluate the enthalpy, entropy and Gibbs free energy change for dissolving borax in water. The equilibrium expression for the process that gives two sodium ions, one borate ion, B4O5(OH)42-, and eight water molecules is:

Na2B4O5(OH)4·8H2O (s) ↔ 2 Na+(aq) + B4O5(OH)42-(aq) + 8 H2O (*l*) (1)

The reaction can be written in simplified form as:

borax (s) ↔ 2 Na+(aq) + borate (aq) + 8 H2O (*l*) (2)

Since liquid water and solid borax are not included in the Ksp expression, the solubility product expression associated with this reaction is:

Ksp = [Na+]2 [borate] (3)

The concentration of the borate ion in equilibrium with solid borax will be determined by titration with standardized HCl according to the equation:

B4O5(OH)42-(aq) + 2 HCl (aq) + 3 H2O (*l*) ↔ 4 H3BO3 (aq) + 2 Cl-(aq) (4)

According to equation 4, two moles of HCl are required for 1 mol of borate. The solubility product constant of borax can then be calculated from the values of [B4O5(OH)42-] and [Na+] after [Na+] is determined from the stoichiometric relationship, 1 mol borate **≡** 2 mol Na+.

The Ksp for borax will be evaluated at room temperature and at about 5 ºC . Knowing Ksp values at two temperatures allows the evaluation of the enthalpy change using Equation 5.

ln$\frac{Ksp1}{Ksp2}$ = $\frac{∆H}{R}$ ($\frac{1}{T2}$ - $\frac{1}{T1}$ ) (5)

Knowing the solubility product constant at two different temperatures also allows the evaluation of the Gibbs free energy change (ΔG°) at each of the two temperatures using Equation 6.

ΔG° = - RT lnKsp (6)

Remember that ΔH and ΔS are not supposed to change with temperature. On the other hand, ΔG usually does change appreciably with temperature. Once ΔH° and ΔG° values are known for each temperature, the values (which should be the same or very close) of the entropy change, ΔS, at each temperature can be evaluated using the Gibbs free energy expression, shown in Equation 7.

ΔG° = ΔH° - TΔS° (7)

**EXPERIMENTAL**

**Preparation of the Borax-Borate Equilibrium Mixtures:** These solutions will be prepared and shared by groups of four students. Each student will then take about 60 mL of each solution and work alone on the titrations.

To two separate 500 ml Erlenmeyer flasks containing magnetic stirring bars add about 20 g of borax and 400 mL of distilled water. Designate one flask as the room temperature system and one as the ice-water system. Stir the room temperature mixture gently on a magnetic stirrer (with no heating)for at least ten minutes. Shut off the stirrer, place a thermometer in the flask and leave it undisturbed to allow the excess undissolved borax to settle to the bottom. The solution portionshould become clear after a few minutes.

Place the second Erlenmeyer flask in an ice-water bath (be sure to use enough ice) on a magnetic stirrer and stir the mixture with no heating for at least 20 minutes. Shut off the stirrer, place a thermometer in the flask and allow the undissolved borax to settle to the bottom. This mixture temperature should be close to 5°C and the solution portion should become clear. Keep the flask undisturbed in the ice bath until aliquots are removed for titration.

**Preparation and Standardization of 0.1 M HCl Titrating Solution:** While the borax mixtures are stirring, add, in a fume hood, about 3.5 mL of conc. (12M) HCl to about 400 mL of distilled water in a 500 mL Erlenmeyer flask. This will give a solution of approximately 0.1 M HCl. Stir well. Use three 5-mL portions to rinse a clean 50 mL buret and then fill the buret with the solution. Weigh three approximately 0.15 g portions of Na2CO3 to 0.001g into separate clean but not necessarily dry Erlenmeyer flasks. To each flask add 3 drops of bromocresol green indicator and 50 mL of distilled water. The solution will turn blue. Titrate each portion of sodium carbonate to the yellow-green endpoint. Do more than three titrations if your instructor says your results are not consistent. Use the titration data to calculate the actual concentration of your HCl solution according to the equation:

Na2CO3(aq) + 2HCl(aq) → 2NaCl(aq) + CO2(g) + H2O(l) (8)

**Ksp of Borax at Room Temperature:** Record the temperature of the room temperature borax mixture. Without disturbing the solid at the bottom, carefully decant about 60 mL of the borate solution into a *clean* and *dry* beaker and pipet four 10.00 mL aliquots into four separate clean but not necessarily dry Erlenmeyer flasks. Add 20 mL of distilled water and 3 drops of bromothymol blue indicator to each flask. The solutions should turn blue. Titrate each sample with your standardized HCl solution until the solution changes from blue to yellow-green. Use your best three titrations to evaluate the Ksp of borax at room temperature.

**Ksp of Borax at Ice Temperature:** Read the temperature of the iced borax mixture and carefully decant about 60 mL of the solution into a clean and dry beaker. Pipet four 10.00 mL aliquots into four separate Erlenmeyer flasks. To each flask, add 20 mL of distilled water and 3 drops of bromothymol blue indicator. Titrate each sample with HCl until the color changes to yellow-green. Use your best three titrations to evaluate the Ksp of borax at ice temperature.

**DATA PAGE**

**STANDARDIZATION OF 0.1 M HCl TITRATING SOLUTION:**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Check box if trial used to calculate [HCl]. | Trial 1 | Trial 2 | Trial 3 | Trial 4 | Trial 5 |
| Mass of container and Na2CO3 |  |  |  |  |  |
| Mass empty container |  |  |  |  |  |
| Mass of Na2CO3 weighed out |  |  |  |  |  |
| Final buret reading |  |  |  |  |  |
| Initial buret reading |  |  |  |  |  |
| Volume HCl dispensed |  |  |  |  |  |
| Endpoint Color |  |  |  |  |  |

**KSP OF BORAX AT ROOM TEMPERATURE:**

Temperature of borax solution (T2) as aliquots are removed: \_\_\_\_\_\_\_\_\_

Check box to right if trial

used to calculate the Ksp

Trial 1 Trial 2 Trial 3 Trial 4

Borate solution volume 10.00 mL 10.00 mL 10.00 mL 10.00 mL

Final buret reading \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_

Initial buret reading \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_

Volume HCl dispensed \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_

Endpoint color \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_

**KSP OF BORAX AT ICE TEMPERATURE:**

Temperature of borax solution (T2) as aliquots are removed: \_\_\_\_\_\_\_\_\_

Check box to right if trial

used to calculate the Ksp

Trial 1 Trial 2 Trial 3 Trial 4

Borate solution volume 10.00 mL 10.00 mL 10.00 mL 10.00 mL

Final buret reading \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_

Initial buret reading \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_

Volume HCl dispensed \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_

Endpoint color \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_

**1. Standardization of HCl Titrating Solution:** Using your best two or three standardization titrations, calculate the concentration of the HCl titrating solution. For full credit, show complete setups for all your answers. What is the average concentration of your HCl solution?

**2. Room Temperature Ksp Determination**: From your best three room temperature system titrations, calculate the room temperature Ksp for borax as follows: For full credit, show complete setups for all your answers.

a. From the HCl volume used in each titration and equation (4), calculate the concentration of borate in each room temperature aliquot.

b. From the stoichiometric relationship between borate and sodium ion, calculate [Na1+] in each aliquot.

c. Calculate the room temperature Ksp for each titration using equation (3) and calculate the average Ksp value.

**3. Ice Bath Temperature Ksp Determination**: For your best three ice temperature system titrations, calculate Ksp for borax as you did for the room temperature system. (4 points)

a. Calculate the concentration of borate in each ice temperature aliquot.

b. Calculate [Na1+] for each ice temperature aliquot.

c. Calculate each ice temperature Ksp and the average Ksp value.

**4.** Δ**H**° **Determination**: Dissolving borax in water is an endothermic process shown by:

heat + borax (s) ↔ 2 Na+(aq) + borate (aq) + 8 H2O (*l*) (8)

Evaluate ΔH° for the dissolving of borax using equation (5).

where Ksp2 is the borax solubility product at room temperature and T2 is room temperature in Kelvins, Ksp1 is the borax solubility product at ice temperature and T1 is the temperature of the borate solution in the ice-water bath. R = 8.314 J/mol⋅K. Organize your values in the chart. For full credit, show your calculation setups in the space below.

|  |  |  |  |
| --- | --- | --- | --- |
| **Temperature** | **Ksp** | **T (**°**C)** | **T (K)** |
| 1 (ice bath) |  |  |  |
| 2 (room temp) |  |  |  |

Δ**H**° = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

**4.** Δ**G**° **Determination**: Calculate ΔG° for each of the two temperatures using equation (6).

For full credit, show your calculation setups in the space below.

ΔG° = - RT lnKsp (6)

|  |  |  |  |
| --- | --- | --- | --- |
| **Temperature** | **Ksp** | **T (K)** | Δ**G**° **(kJ/mol)** |
| 1 (ice bath) |  |  |  |
| 2 (room temp) |  |  |  |

**Average** Δ**G**° **\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

**5.** Δ**S Determination** Calculate the entropy changes at the two temperatures using equation(7). For full credit, show your calculation setups.

ΔG° = ΔH° - TΔS° (7)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Temperature** | **T (K)** | Δ**G**° **(kJ/mol)** | Δ**H**° **(kJ/mol)** | Δ**S**° **(J/mol**⋅**K)** |
| 1 (cold) |  |  |  |  |
| 2 (room) |  |  |  |  |