ENTHALPY AND ENTROPY CHANGES FOR BORAX DISSOLUTION

OBJECTIVES

Students will determine the enthalpy change ($\Delta H$) and entropy change ($\Delta S$) for the dissolution of borax (sodium tetraborate decahydrate) in water by using the equilibrium constant for the reaction determined at several temperatures.

SAFETY PRECAUTIONS

Safety goggles (chemical splash goggles), protective clothing and shoes which cover your feet must be worn at all times in the lab. Dilute solutions of acid can cause irritations and burns; wash contaminated areas thoroughly with cold water. Hot glassware can cause burns; handle carefully. When using volumetric pipets, always use a pipet bulb; NEVER pipet by mouth.

INTRODUCTION

Theoretically, the relationship between free energy change ($\Delta G$), enthalpy change ($\Delta H$), entropy change ($\Delta S$) and the equilibrium constant ($K$) for a chemical reaction at a specific temperature ($T$), is shown in equation (1) below. The Gas Constant, $R$, is equal to 8.31451 J mol$^{-1}$K$^{-1}$.

$$\Delta G^\circ = - R \, T \ln K = \Delta H^\circ - T \Delta S^\circ$$

Is this really true in practice?

A process at constant temperature and pressure will be spontaneous in the direction in which free energy decreases ($-\Delta G^\circ$). When equation (1) is rearranged to eliminate $\Delta G^\circ$, $\ln K$ is expressed in terms of $\Delta H^\circ$, $\Delta S^\circ$ and $T$ only:

$$\ln K = - \frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}$$

Note that equation (2) resembles the point-slope form of a line ($y = mx + b$). A plot of $\ln K$ versus $(1/T)$ should result in a straight line with a slope equal to $(-\Delta H^\circ/R)$ and a y-axis intercept equal to $(\Delta S^\circ/R)$. The enthalpy change, $\Delta H^\circ$, is determined from the slope but the entropy change, $\Delta S^\circ$, is usually calculated from (2) instead of the graph. The reason is that the intercept of the y-axis occurs when the ratio $(1/T) = 0$ (that is, when $T = \infty$). Since the temperature of the reaction will be ~310 to 340 K, the graph would have to be unusually large to show $T = \infty$.

The solubility of a salt is an example of an equilibrium reaction. The equilibrium solubility is dependent on the temperature of the solution. When equilibrium is established in a saturated solution at a specific temperature, the rate of formation of ions in solution is equal to the rate of deposition of solid. The equilibrium constant for the dissolution of a solid in a solvent is called the "solubility product constant" ($K_{sp}$). It is equal to the product of the concentration of ions in solution. Each ion concentration is raised to the power equal to its stoichiometric coefficient in the balanced solubility equation. Since the concentration of ions at saturation can change with temperature, the equilibrium constant for the reaction is $T$-dependent.
Sodium tetraborate decahydrate ("borax") (FW = 381.37) dissociates in water to form sodium ions, borate ions and water molecules:

\[ \text{Na}_2\text{B}_4\text{O}_7\cdot10\text{H}_2\text{O(s)} \rightleftharpoons 2 \text{Na}^+(aq) + \text{B}_4\text{O}_5(\text{OH})_4^{2-} (aq) + 8 \text{H}_2\text{O(l)} \]

The solubility product constant (equilibrium constant), \( K_{sp} \), is:

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

Note that there are two sodium ions produced for each borate ion \([\text{B}_4\text{O}_5(\text{OH})_4^{2-}]\) in the reaction. Therefore, (since we started with pure water) the concentration of \([\text{Na}^+]\) is TWICE the concentration of borate ion:

\[ [\text{Na}^+] = 2 \cdot [\text{B}_4\text{O}_5(\text{OH})_4^{2-}] \]

The equilibrium constant can now be expressed in terms of borate ion concentration alone by substituting the equality from (5) into equation (4), and can be calculated when the borate ion concentration at equilibrium is determined.

\[ K_{sp} = 4 \cdot [\text{B}_4\text{O}_5(\text{OH})_4^{2-}]^3 \]

This reaction is experimentally convenient, since borate ion is a weak base. This means that its concentration can easily be determined by a simple acid-base titration. The endpoint is signaled by the color change of bromocresol green indicator.

\[ \text{B}_4\text{O}_5(\text{OH})_4^{2-} + 2 \text{H}^+ + 3 \text{H}_2\text{O} \rightarrow 4 \text{B(OH)}_3 \]

Example: A student equilibrated solid borax with an aqueous solution at 59.2°C. 5.00-mL of the aqueous solution at 59.2°C was removed, added to a flask, and diluted with enough distilled water so that no precipitate appeared on cooling. This solution in the flask was titrated to an endpoint with 27.05 mL of 0.500 M HCl. Calculations are shown below.

\[
\begin{align*}
0.500 \text{ mol L}^{-1} \cdot 0.02705 \text{ L} \cdot \frac{1 \text{ mol B}_4\text{O}_5(\text{OH})_4^{2-}}{2 \text{ mol H}^+} &= 1.352_{50} \text{ M B}_4\text{O}_5(\text{OH})_4^{2-} \\
\ln K_{sp} &= \ln [4(1.352_{50})^3] = 2.292_{16} \quad \frac{1}{T} = \frac{1}{59.2 + 273.15 \text{ K}} = \frac{1}{332.35 \text{ K}} = 3.008_{88} \times 10^{-3} \text{ K}^{-1}
\end{align*}
\]

When graphing \( \ln K_{sp} \) one must use inverse Kelvin temperature, \( 3.008_{88} \times 10^{-3} \text{ K}^{-1} \).

KEEP AT LEAST FOUR SIGNIFICANT FIGURES.

In today's experiment, students will prepare 5 saturated borax solutions at temperatures between 15 °C and 65 °C. Each solution will be titrated with dilute HCl to determine borate ion concentration and \( K_{sp} \).
The enthalpy change \((\Delta H^\circ)\) will be determined from a plot of \(\ln K_{sp}\) versus \(1/T\), and the entropy change \((\Delta S^\circ)\) will be calculated from equation (2).

**PRE-LAB QUESTIONS**

(1) Define: saturated solution, enthalpy, entropy, free energy, and spontaneity.

(2) In your textbook, read the section on "Free Energy" and complete the table below.

| Reaction Conditions | Sign of \(\Delta H\) | Sign of \(\Delta S\) | Sign of \(\Delta G\) | Spontaneous Reaction?
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>(a) at high (T)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>Yes or No</td>
</tr>
<tr>
<td>(b) at low (T)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>(c) at high (T)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>(d) at low (T)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>(e) at all (T)</td>
<td>+</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>(f) at all (T)</td>
<td>–</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
</tbody>
</table>

(3) When solid borax is dissolved in water, do you expect entropy of the system to increase or decrease? Explain your answer. Will the sign of \(\Delta S_{sys}\) be positive or negative?

(4) Assuming the dissolution of borax in water is a spontaneous reaction, do you expect the change in enthalpy to be positive or negative or are both signs possible? Explain your answer.

(5) Show how equation (2) can be derived from: \(\Delta G = \Delta G^\circ + RT \ln Q\).

**EXPERIMENTAL PROCEDURE**

Work in pairs. For best results, allow saturated solutions to stand at each temperature for at least 10 minutes to establish equilibrium between ions and solids at that temperature. Do NOT transfer any solids when pouring the saturated solution into the graduated cylinder. If a "scum" forms on the top of the solution, use a disposable pipet to transfer the clear liquid from the middle of the solution to the graduated cylinder.

In a 250-mL beaker, dissolve approx. 25-30 g of borax in 50-75-mL of DI (deionized) water. Heat gently with stirring to 65 °C. Do not exceed 65 °C, because the borate ion may start to decompose. If all solid dissolves, add a LITTLE more borax to the solution until a TINY amount of excess solid is present and the solution is COMPLETELY SATURATED. Allow the solution to cool to approximately 60°C and keep the temperature constant for about 10 minutes, with stirring, to equilibrate ions and solids. Additional solids may precipitate out at the lower temperature but this is expected. At the end of 10 minutes, draw the solution into a calibrated 10 mL pipet until the level exactly reaches the 5.00-mL mark. Be very careful not to transfer any of the solid borax from the beaker to the pipet. Note the exact temperature of the solution in the beaker.

Immediately transfer the contents of the graduated pipet to a clean 125-mL Erlenmeyer flask. Rinse the pipet with several portions of warm (60 °C) DI water, adding the rinsings to the flask. Make certain that no crystallized solid remains in the pipet. Add sufficient DI H₂O to the flask to keep the borax completely dissolved. Add 2-3 d (drops) of bromocresol green indicator to the flask. The borate ion is a base. What color is your indicator in base?
Clean the graduated pipet and repeat the steps above using the original solution (less the amount withdrawn) cooled to ~50°C, ~40°C, ~30°C and ~20°C. Be sure to record ACTUAL temperatures at the time the solution is initially placed in the graduated pipet and label the 125 mL Erlenmeyer flasks containing the solutions accordingly. Note that you need to prepare only one 50 – 75 mL Borax solution for the five temperatures and five 5.00 mL samples.

When you are finished with this step, wash the beaker and pipet thoroughly. Solidified borax is difficult to remove if ignored too long.

For the solution in each 125 mL Erlenmeyer flask, fill a clean 50-mL buret with a standardized 0.500 M HCl solution. Drain a few mL of the acid into a large beaker (>800 mL) to remove air bubbles trapped in the stopcock. Add one drop of bromocresol green to the acid in the beaker and set aside. What color is your indicator in acid? Once you've determined what the indicator colors are in acid and base solution, titrate the borate ion solution to an endpoint with HCl. (If any solid has appeared, add small amounts of DI H₂O to redissolve before titration.) When you finish each titration, pour the solution in the Erlenmeyer flask into 1000 mL beaker and set aside.

When you have completed all titrations, add the remaining HCl from your buret to the large beaker containing titrated solutions. The solution will be acidic. Place about 1 inch of solid NaHCO₃ in the bottom of another 1000 mL beaker, add water until it barely covers the NaHCO₃, stir to make a slurry. Now slowly pour the diluted acidic solution from the first 1000 mL beaker into the bicarbonate slurry and stir. When foaming stops, check the solution with pH paper. If pH = 7, pour the neutralized solution into a collection bottle in the hood. If the pH of the solution is less than 7, prepare a new slurry and neutralize the solution again in the same manner. The neutralization reaction is:

\[ \text{H}^+(\text{aq}) + \text{NaHCO}_3(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O(ℓ)} \]

Clean workspace and glassware thoroughly before leaving lab.

(1) Calculate the concentration of borate ion from the volume of 0.500 M HCl used in each titration. Use the borate ion concentration to determine \( K_{sp} \) at each temperature. Convert Celsius temperatures to inverse Kelvin temperatures (1/T) and summarize your data and calculated values in a table with 6 columns: °C, K, 1/T, [borate ion], \( K_{sp} \), and ln \( K_{sp} \). It is best to use a spreadsheet for this.

(2) Use a Graphical Analysis program to plot ln \( K_{sp} \) vs 1/T (use T in Kelvin) and find the slope and intercept of the resulting line. If you use Excel, you must choose “X-Y Scatter” as the “Chart Type”. Record slope and intercept in your notebook. (Give your TA the duplicate pages of pre-lab and in-lab data before leaving lab.) Print a copy of the graph to use in your post lab calculations. Adjust the scale of the axes so that the data points are spread out over at least two inches horizontally and vertically. The post lab (and graph) is due next week.
CALCULATIONS

(1) Use the plot of ln $K_{sp}$ vs $1/T$ and determine $\Delta H^o$ (kJ mol$^{-1}$).
(2) Use the plot of ln $K_{sp}$ vs $1/T$ and determine $\Delta S^o$ (J mol$^{-1}$ K$^{-1}$) or select a point on the best-fit line and determine $\Delta S^o$ using equation (2).
(3) The literature values for enthalpy change and entropy change for the dissolution of borax in water are 110 kJ mol$^{-1}$ and 380 J mol$^{-1}$ K$^{-1}$ respectively. Determine the percent error in your experimentally determined values. If your values deviate significantly from the literature value, discuss the possible sources of error and ways that these errors can be avoided or corrected.

POST-LAB QUESTIONS

(1) Does the solubility of borax in water increase or decrease as temperature increases? What experimental evidence supports your answer?
(2) Is the dissolution of borax in water an exothermic or endothermic process? What experimental evidence supports your answer?
(3) Did $\Delta S^o_{sys}$ increase or decrease in this reaction? What experimental evidence supports your answer?
(4) Is the dissolution of borax in water a temperature dependent reaction or is it spontaneous at all temperatures at which water is liquid? Briefly explain.