EQUILIBRIUM AND THERMODYNAMICS
(ΔH° AND ΔS° THROUGH INDIRECT CALORIMETRY)

OBJECTIVES

1. Learn the mathematical relationship between the standard free energy for a system, $\Delta G°$, and the equilibrium constant.
2. Realize the thermodynamic variables $\Delta H°_{sys}$ and $\Delta S°_{sys}$ can be determined by measuring the temperature dependence of the thermodynamic equilibrium constant, K_{eq}.
3. Use titration techniques to determine the solubility and therefore the equilibrium constant for a salt near room temperature.

THEORY

From thermodynamics we can relate the equilibrium constant at any temperature to the standard free energy change at the same temperature through the equation

$$\Delta G° = -RT\ln(K_{eq}) \tag{1}$$

Where $\Delta G°$ is the standard Gibbs free energy change, R is the gas constant (8.3145 J/mol-K), T is the temperature (K), and K_{eq} is the equilibrium constant for the reaction under investigation. Remember from thermodynamics $\Delta G°$ is a temperature dependent quantity, just like the equilibrium constant, K_{eq}.

From equation 1 convince yourself that $\Delta G°$ will be a negative value when K_{eq} is > 1, a positive value when K_{eq} < 1 and zero when $K_{eq} = 1$.

Using the thermodynamic master equation

$$\Delta G° = \Delta H° - T\Delta S° \tag{2}$$

and substituting using equation 1 we have

$$-RT\ln(K_{eq}) = \Delta H° - T\Delta S° \tag{3}$$

If we rearrange equation 3 slightly, it becomes an equation for a straight line relating $\ln(K_{eq})$ to $1/T$:

$$\ln(K_{eq}) = \frac{-\Delta H°}{R}\left(\frac{1}{T}\right) + \frac{\Delta S°}{R} \tag{4}$$

Taking the antilog of each side of equation 4 reveals the nonlinear form of the temperature dependence of K_{eq}:

$$K_{eq} = e^{\left(\frac{-\Delta H°}{RT} + \frac{\Delta S°}{R}\right)} \tag{5}$$

Thus, the thermodynamic variables ΔH° and ΔS° can be determined by measuring the equilibrium constant, K_{eq}, as a function of temperature for any reaction. A nonlinear fit to the data using equation 5 can be done to find the constants $\Delta H°$ and $\Delta S°$. Indeed, for some systems the only way to determine $\Delta H°$ and $\Delta S°$ is through measurements of the equilibrium constant at various temperatures. This is a remarkable relationship showing equilibrium theory is really an extension of thermodynamics.

To use equations 2 through 5 we are assuming $\Delta H°$ and $\Delta S°$ do not change appreciably with temperature as we move away from 298.15 K, standard temperature. This is a good assumption for most systems. $\Delta H°$ and $\Delta S°$ may change enough to invalidate this assumption when we move too far from standard temperature, 25°C. For this reason our equilibrium studies will be made near room temperature.

APPLICATION OF THE THEORY: THE SODIUM TETRABORATE SOLUBILITY EQUILIBRIUM, K_{SP}

To demonstrate the application of equations 2 and 5 we will use a simple equilibrium system: **the dissolving of a soluble salt in water to reach saturation (equilibrium).** The salt we will use is **sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O(s)$**. This salt will dissolve until the solution becomes saturated, i.e., equilibrium is established between the solid and the dissolved sodium and tetraborate ions.

$$Na_2B_4O_7 \cdot 10H_2O(s) \rightleftarrows 2\,Na^+(aq) + B_4O_7^{2-}(aq) + 10\,H_2O(l) \tag{6}$$
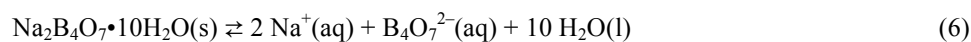
The equilibrium constant expression for this simple system is:

$$K_{eq} = K_c = [Na^+]^2[B_4O_7^{2-}] = K_{sp} \quad\quad\quad (7)$$

Where K_{sp} is called the **s**olubility **p**roduct equilibrium constant for a salt. Experimentally if the equilibrium concentrations of the sodium and tetraborate ions can be measured we can calculate K_{sp}. Repeating this solubility measurement at various temperatures near 25 °C we can use eqn 5 (nonlinear fit) to find $\Delta H°$ and $\Delta S°$ for this simple equilibrium process of solubility.

PROCEDURE

Materials

Solid sodium tetraborate decahydrate $Na_2B_4O_7 \cdot 10H_2O(s)$ ($\approx$ 70 g per student or group)
Standardized $\approx$ 1 M HCl (80 mL per student or group)
methyl red indicator
1 LabQuest with temp probe
1 50-mL buret
1 600-mL beaker
1 250-mL beaker
5 250-mL Erlenmeyer flask
1 10-mL graduated cylinder
1 100-mL graduated cylinder
1 stirring rod
1 hot plate
1 dropper

Safety

1. Wear safety goggles.
2. 1 M HCl is corrosive. Avoid contact with your skin and eyes. Immediately wash any exposed areas with water. Spills should be cleaned up immediately. Discard in an appropriate waste container.

Preparation of the Saturated Solution of Sodium Tetraborate

These steps will prepare a saturated solution of sodium tetraborate in a 250-mL beaker.

1. Fill a 600-mL beaker with about 550 mL of tap water and heat to boiling using a ring-stand and Bunsen burner. Remove from the ring stand (WITH BEAKER TONGS) and let stand on your lab bench. **Place a 10-mL graduated cylinder into the hot water without submersing the cylinder.**

2. Weight about 70 g ± 5 g of sodium tetraborate into a 250-mL beaker. Add 150 mL of deionized water.

3. While stirring vigorously and continuously, heat the sodium tetraborate to 60 °C. DO NOT HEAT PAST 75 °C! **You must stir vigorously and continuously while heating**. This heating process is slow, so be patient!

4. When 60 °C is reached, turn off the heat and stop stirring. **There should be some undissolved sodium tetraborate in the beaker.** Remove the solution from the hot plate (WITH BEAKER TONGS). Place your 600-mL beaker with the 10-mL graduated cylinder back on the hot plate. Keep this water bath at 60+ °C.

5. Let your sodium tetraborate solution cool for about 5 minutes to let the solids settle. The solution should begin to separate into a **clear liquid on top (the supernatant)** and undissolved solids on the bottom of the beaker. This separation time will be several minutes. Don't worry if your supernatant is not completely clear. After 5 minutes, continuously, and gently, **stir the clear supernatant on top**, trying not to disturb the undissolved sodium tetraborate in the bottom of the beaker. Stirring only the supernatant establishes equilibrium between the dissolved and undissolved solid. Without stirring the equilibrium will not be established properly.

Removal of an Aliquot for Analysis

1. After a few minutes of stirring, **record the actual temperature of the supernatant** and immediately pour ≈10-mL of the supernatant **(NO SOLIDS)** into the preheated 10-mL graduated cylinder. If you get more than 10 mL remove some with a dropper. **Record the precise volume in your notebook**. Do not waste time trying to get exactly 10 mL. (Using a preheated graduated cylinder prevents the sodium tetraborate from prematurely crystallizing in the cylinder.)

2.   Transfer this 10-mL aliquot into one of the 250-mL Erlenmeyer flasks. **Rinse the 10-mL graduated cylinder several times (3x) with small amounts of deionized water, adding the rinse to the flask**. Make sure any sodium tetraborate that might have precipitated in the cylinder is completely rinsed from the cylinder into the flask.
3.   Give this flask to your partner for titration analysis (next step of this procedure).
4.   Dry the inside of the 10-mL graduated cylinder and place it back into the hot-water bath.
5.   **Continue letting the saturated solution of tetraborate cool while stirring the supernatant**. Repeat steps 1-4 at temperatures near 50, 45, 40, 35, and 30 °C. You should have five or six aliquots of saturated sodium tetraborate solution when complete. (As the solution nears 45 °C you can place the 250-mL beaker in an ice-water bath to hasten the cooling rate.)

Titration Analysis of an Aliquot

As the 10-mL aliquots are acquired, analysis to determine the concentration of the tetraborate and sodium ions can begin. Each aliquot is titrated with HCl(aq) to react with the tetraborate ion, since the tetraborate ion is a weakly basic ion. The titration of the tetraborate ion with HCl(aq) has the following stoichiometry with the boric acid product:

$$B_4O_7{}^{2-}(aq) + 2\ H_3O^+(aq) + 3\ H_2O(l) \longrightarrow 4\ H_3BO_3(aq)\ \text{or}\ 4\ B(OH)_3(aq) \tag{8}$$

The indicator used is methyl red. Methyl red is yellow in basic solutions and turns light pink when the endpoint is reached (slightly acidic).
1.   Rinse a 50-mL buret with the standardized HCl solution and then fill. **Record the precise molarity of the HCl in your notebook**.
2.   For each aliquot add 50-ml of deionized water to the Erlenmeyer flask and gently heat the solution to make sure any crystallized sodium tetraborate has dissolved. DO NOT BOIL! Add 3-4 drops of methyl red indicator to the flask.
3.   Record the initial buret reading and begin the titration. When the endpoint is reached (light pink) stop the titration and record the final buret reading. The titrated solution is disposed of in the waste container.
4.   Repeat steps 2 and 3 for each of the five aliquots.
5.   Show your data to your instructor before cleaning up. The volume of HCl used in the titration should decrease as the aliquot temperature decreases. To obtain good results for your graph of K_{eq} versus T you will need the class data. Your instructor should collect the data from each student and distribute to the class. **Be prepared to give the following information to your instructor: T (°C) of aliquot, V (mL) of aliquot, and V (mL) of HCl used to titrate the aliquot** for each of your samples.

Clean-up

1.   The solid sodium tetraborate remaining in the 250-mL beaker is discarded. Add 100-mL deionized water to the solid and heat until the solid can easily be poured from the beaker into the sink.
2.   Discard any remaining HCl(aq) and the products of the titrations into an appropriate waste container.

DATA ANALYSIS

1. Create a data table in LoggerPro with the following headings. The first three columns are the class data. The remaining columns will be generated as New Calculated Columns (see steps below).

T (°C)	Vol. aliquot (mL)	Vol. HCl (mL)	mmole H_3O^+	mmole $B_4O_7^{2-}$	$[B_4O_7^{2-}]$ (M)	$[Na^+]$ (M)	K_{eq}	T (K)	$\Delta G°$ (kJ)

2. To find the mmoles of HCl, use the volume of HCl used in the titration and the precise molarity of the HCl(aq).
3. From the mmoles of HCl and the stoichiometry of equation 8 find the mmoles of tetraborate (TB^{2-}) ion titrated.
4. From the mmoles of tetraborate ion titrated and the volume of supernatant in the aliquot calculate the molarity of tetraborate ions in the titrated saturated solution of sodium tetraborate.
5. Using the stoichiometry of equation 6 calculate the molarity of sodium ions in equilibrium with the tetraborate ions.
6. Using equation 7 calculate K_{eq}.
7. Convert T (°C) to Kelvin.
8. Use K_{eq} and equation 1 to find $\Delta G°$. **While K_{eq} is reported without units, report $\Delta G°$ in kJ/rxn units.**

Nonlinear Graphing

Make and printout a nonlinear graph of K_{eq} versus T (K). Fit the equilibrium constant K_{eq} (y-axis) to the nonlinear function exp(−H/(8.3145*T)+S/8.3145) where H (enthalpy) and S (entropy) are the fitting constants, 8.3145 is the gas constant R with units of J/mol-K, and T is the x-axis short name. **Remember to show the errors in the fitting constants H and S.** What are the units of your fitting constants?

Thermodynamics Graph

Make and printout a linear graph of $\Delta G°$ versus T (K) using equation 2. Fit to a straight line and obtain the uncertainties in the fit.

REPORT SHEET: TETRABORATE EQUILIBRIUM & THERMODYNAMICS

Attach both your nonlinear graph of K_{eq} versus T and your linear graph of $\Delta G°$ versus T.
From your NONLINEAR GRAPH, report the following to the proper significant figures and with correct units:

ΔH˚ _____   ΔS˚ _____

1) Looking at your graph, is sodium tetraborate more soluble in hot or cold water? Explain.

2) Comment on the sign (+ or –) of $\Delta S°$. Is this what you would expect for this system (examine eqn 6)?

3) Calculate K_{eq} at 25 °C using your values of $\Delta H°$ and $\Delta S°$ and eqn 5.

4) Calculate $\Delta G°$ at 25°C using eqn 1.

   a) From the sign of $\Delta G°$, do you predict a net forward or reverse reaction starting at standard conditions (Q = 1) for the ion concentrations? Given your answer, is a standard solution of ions saturated (equilibrium, K_{eq} = 1), unsaturated (more salt will dissolve, K_{eq} > 1) or super saturated (some ions will precipitate, K_{eq} < 1)?

5) Calculate the equilibrium concentrations (M) of sodium and tetraborate ions at 25°C using your K_{eq} from above (use an ICE table). This produces a saturated solution of sodium tetraborate that determines the solubility of the sodium tetraborate salt at 25°C

    a)   From your ICE table, what is the MOLAR solubility (mol/L) of sodium tetraborate in water at 25°C? Note: This will be the value of "X" in the ICE table. Why is the molar solubility represented by "X"?

    b)   Convert the above molar solubility of sodium tetraborate to a mass solubility, g/mL. Use the anhydrous molar mass for sodium tetraborate.

6)   If the starting concentration of sodium ions is 0.30 M and the starting concentration of tetraborate ions is 0.30 M at 25°C, calculate ΔG (not $\Delta G°$). Hint: first calculate Q then use eqn 9 below.

$$\Delta G = \Delta G° + RT\ln(Q) = RT\ln(Q/K_{eq}) \tag{9}$$

    a)   Look at the sign of ΔG, with these ion concentrations, will more salt dissolve or will some of the ions precipitate? That is, is the solution saturated, unsaturated or super saturated under these conditions?

    b)   Use an ICE table to find the equilibrium concentrations of sodium and tetraborate ions using the initial concentration of ions given above.

7)   From your **_LINEAR GRAPH of $\Delta G°$ versus T,_** $\Delta G° = (-\Delta S°)T + \Delta H°$, at what temperature does $\Delta G°$ go through zero (i.e., what is the x-intercept)? Calculate this from your slope ($-\Delta S°$) and y-intercept ($\Delta H°$). This is called the system cross over temperature. Use proper significant figures.

    a)   Mathematically what is the value of K_{eq} at this cross over temperature where $\Delta G° = 0$?

    b)   At what temperature would the value of $\Delta G°$ be +10.0 kJ?, −10kJ? Use eqn (2) and solve for T.