Determining $\Delta H^\circ$, $\Delta G^\circ$, and $\Delta S^\circ$ from the effect of temperature on $K_c$

This experiment was largely adapted from an experiment used at the United States Naval Academy, Annapolis, MD. Special Thanks also go to Cheryl Ragan and the other TA’s who revised this lab for use at MU.

Beer’s Law states that the absorbance of a species is directly proportional to its concentration, shown by the equation 1.

$$ A = \varepsilon b c $$  \hspace{1cm} (eq. 1)

$A$ = absorbance  
$\varepsilon$ = molar extinction coefficient or the molar absorptivity  
$b$ = thickness of the sample (in our case, the width of the cuvette in centimeters)  
$c$ = concentration in molarity

Absorbances of solutions are easily measured and can be used to determine concentrations of absorbing species. As in the experiment *Determination of an Equilibrium Constant*, the addition of Fe(NO$_2$)$_3$ to a solution containing thiocyanate ions, SCN$^-$, yields a blood red solution due to the production of [Fe(SCN)]$^{2+}$.

$$ \text{Fe}^{3+} (aq) + \text{SCN}^- (aq) \rightleftharpoons \text{Fe(SCN)}^{2+} (aq) $$  \hspace{1cm} (eq. 2)

The equilibrium constant for the reaction above is:

$$ K_c = \frac{[\text{Fe(SCN)}^{2+}]_{eq}}{[\text{Fe}^{3+}]_{eq} [\text{SCN}^-]_{eq}} $$  \hspace{1cm} (eq. 3)

The maximum absorbance for Fe(SCN)$^{2+}$ is at 447 nm. Neither Fe$^{3+}$ nor SCN$^-$ ions absorb in this region.

The plot above shows the relationship between $K_c$ and temperature. From the linear regression of the data, we can determine the enthalpy of the reaction ($\Delta H^\circ$); the slope ($m$) of the regression line is equal to $-\Delta H^\circ/R$, where $R$ is just the gas constant. The formal expression (a version of the van’t Hoff equation) relating the equilibrium constant and the temperature is
\[ \ln K = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T}\right) + C \quad \text{(eq. 4)} \]

(C here is a constant).

The value of \( \Delta G \) lets us predict the spontaneous direction of a reaction, but we also know another way to make such a prediction. In particular, we can compare the reaction quotient (\( Q \)) to the equilibrium constant (\( K_c \)). These two ways of predicting reaction direction are related, as you might guess.

\[ \Delta G = RT \ln \frac{Q}{K} = RT \ln Q - RT \ln K \quad \text{(eq. 5)} \]

If we chose standard conditions for equation 5, at which all concentrations are 1M, the value of \( Q \) equals 1 and the \( RT \ln Q \) term goes to zero. We then have

\[ \Delta G^\circ = -RT \ln K \quad \text{(eq. 6)} \]

where, again, \( R \) is just the gas constant (8.314 J·mol\(^{-1}\)K\(^{-1}\)) and \( T \) is the absolute temperature.

Equation 7 then shows the relationship between the change in the entropy (\( \Delta S \)) and \( \Delta G \), \( \Delta H \), and \( T \).

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{(eq. 7)} \]

Using these relationships, you will calculate the change in enthalpy, entropy and Gibbs free energy from absorbance measurements.

**PROCEDURE**

You have performed the following procedure in the experiment *Determination of an Equilibrium Constant*. You will need to set up the OCEAN OPTICS spectrometers in exactly the same way as you did previously. Look over your earlier work to find the proper wavelength, the volumes of solutions used, etc.

1. Add 2.00 mL each of 0.50 M HNO\(_3\) and 0.00020 M KSCN solutions to a clean, dry test tube. Agitate the test tube to mix the solution well. Use this solution as the blank when calibrating the spectrometer at the selected wavelength of 447 nm.

2. Choose one of the following “recipes” for the solution in your test tube. Note that the test tube can hold a maximum volume of about 10 mL. Mix well and place the test tube in an ice bath until the solution temperature is around 3-4 °C. Add 3-4 mL of this solution to a clean cuvette.

<table>
<thead>
<tr>
<th>Recipe</th>
<th>Volume 0.0200 M Fe(NO(_3))(_3) solution</th>
<th>Volume 0.00020 M KSCN solution</th>
<th>Volume 0.50 M HNO(_3) solution</th>
<th>Volume H(_2)O</th>
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</table>
3. Dry off the cuvette, making sure that no condensation forms on the side. (Condensed water on the surface will scatter the light and alter your absorbance measurements.) Place the cuvette in the spectrophotometer, and with a thermometer measure the temperature at the bottom of the solution. Take absorbance readings after wiping the sides of the cuvette to remove the condensation that will form as the cuvette warms up. (Obviously, you will need to take the thermometer out of the cuvette before taking an absorbance reading.) Record the absorbance values at several (at least 5) different temperatures as the solution warms towards room temperature. Properly dispose of the solution.

4. Repeat steps 2 and 3 twice more with the same solution recipe. You should now have three good trials.

DATA ANALYSIS:

1) Enter your data into Excel, with one row showing how you calculated each column of values. Specifically, you will need the following.
   a. Calculate the concentration values as you did in the earlier experiment on this system.
   b. Enter your absorbances and your temperatures (to make this easy, enter one column in Celsius and calculate a second one in kelvins).
   c. Calculate $K_c$ from the absorbance at each temperature.
   d. Calculate $\ln K_c$ and $1/T$.

   NOTE: By entering appropriate equations in Excel, you can do all your calculations in the program itself. Make sure you show us which equations you are programming into Excel.

2) You will have 3 sets of data, with a minimum of 5 data points per each set (i.e., equilibrium constants for 5 temperatures). Make one graph with consisting of the three plots of $\ln K_c$ versus $1/T$ (in K$^{-1}$).

3) For each line, fit a linear trendline and obtain the fit equation and the corresponding $R^2$. Make sure that your trendlines are labeled so that you will know which fit corresponds to which data set.

4) Calculate $\Delta H^\circ$ for each set of data (eq. 4).

5) Using the equation obtained for the trendline, calculate $K_c$ at 298.15 K. Do this calculation for each trendline separately.

6) Using the value you calculated in Step 5, calculate $\Delta G^\circ$ (eq. 6). Do this calculation for each of your $K_c$ values.

7) Now, calculate $\Delta S^\circ$ (eq. 7) for each of your three trials.
8) You now should have three sets of $\Delta H^\circ$'s, $\Delta G^\circ$'s, and $\Delta S^\circ$'s. Average the results of the three trials and report both the average and the standard deviation for each of the three thermodynamic variables. The conventional way of reporting this data is to write variable = average ± σ [Units].

9) Look at your data and explain what happens, qualitatively, to $K_c$ as your temperature increases or decreases, and then write the correct equation for the equilibrium with heat as a reactant or product to explain this trend. Is the reaction as written endothermic or exothermic?