

## Experiment 7B

# THE TEMPERATURE DEPENDENCE OF THE EQUILIBRIUM CONSTANT

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### PURPOSE

To investigate the relationship between the equilibrium constant and the temperature and to determine the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for a reaction.

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### K vs. T

Since reactions proceed more rapidly at higher temperatures, it is natural to assume that as we raise the temperature more product will form, resulting in a larger value for the equilibrium constant,  $K$ . However, this is not necessarily true.

$K$  gives the relationship that exists between the amounts of reactants and products once the reaction stops (reaches equilibrium). Speeding up the rate at which a reaction gets to equilibrium does not, by itself, change the relative amounts present at equilibrium.

The value of  $K$  depends upon  $\Delta G^\circ$  which, in turn, depends upon  $\Delta H^\circ$  and  $\Delta S^\circ$ . Starting with

$$K = e^{-\Delta G^\circ/RT} \quad (1)$$

which can be rewritten as

$$\ln K = -\frac{\Delta G^\circ}{RT} \quad (2)$$

and substituting

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

finally yields

$$\ln K = \left(-\frac{\Delta H^\circ}{R}\right)\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R} \quad (4)$$

Therefore, we see that the effect of changing  $T$  upon  $K$  depends on the sign of  $\Delta H^\circ$ . If  $\Delta H^\circ$  is positive, then as  $T$  increases,  $\ln K$  (and, hence,  $K$ )

increases. Conversely, if  $\Delta H^\circ$  is negative, then as  $T$  increases,  $K$  decreases.

This is consistent with Le Châtelier's principle. If  $\Delta H^\circ$  is positive, then heat/enthalpy is a reactant and raising the temperature is equivalent to adding more of a reactant. Le Châtelier's principle predicts that when more reactant is added, the equilibrium will shift to favor products. In this case, that means  $K$  will increase.

Finally, note that equation (4) is the equation of a line. If  $\ln K$  is plotted vs.  $1/T$ , the slope of the line equals  $-\Delta H^\circ/R$  and the y-intercept equals  $\Delta S^\circ/R$ , where  $R=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ . (This assumes  $\Delta H^\circ$  and  $\Delta S^\circ$  are constant and independent of temperature, usually a good approximation.) This gives us an indirect method for actually measuring the entropy change during a reaction.

### SPONTANEITY

A reaction will be spontaneous if  $\Delta G^\circ$  is negative. By looking at equation (3), you should be able to convince yourself that the following table accurately predicts the sign of  $\Delta G^\circ$  for all of the possible combinations of  $\Delta H^\circ$  and  $\Delta S^\circ$ .

In two of the cases, the sign of  $\Delta G^\circ$  depends upon  $T$ . The temperature where the spontaneity changes can be determined by setting  $\Delta G^\circ=0$  in equation (3) and solving for  $T$ .

$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ$
Negative	Positive	Negative
Negative	Negative	Negative, at low T Positive, at high T
Positive	Positive	Positive, at low T Negative, at high T
Positive	Negative	Positive

**IN THIS EXPERIMENT**

$\text{Fe}^{3+}(\text{aq})$  and  $\text{SCN}^{-}(\text{aq})$  will be mixed to produce  $\text{FeSCN}^{2+}(\text{aq})$ . The absorbance will be measured at each of five different temperatures, from which the concentrations of all species may be calculated and the value of  $K_c$  determined at each temperature. A plot of  $\ln K_c$  vs.  $1/T$  will be generated and used to calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  for the reaction.

**PRE-LABORATORY PREPARATION**

1. Read the background, procedure, and data analysis sections of the experiment.
2. There is no PRELAB assignment in Canvas for this experiment.

**EXPERIMENTAL SECTION****REAGENTS PROVIDED**

**$\text{Fe}(\text{NO}_3)_3(\text{aq})$ , 0.010 M.** This is prepared using 0.10 M  $\text{HNO}_3$  as the solvent, since the acid stops insoluble iron hydroxides from forming.

**$\text{KSCN}(\text{aq})$ , 0.010 M.**

**Hazardous Chemicals**

$\text{Fe}(\text{NO}_3)_3(\text{aq})$  and  $\text{KSCN}(\text{aq})$  are both toxic and irritants. Wash thoroughly if you come into contact with either solution.

**WASTE DISPOSAL**

All solutions should be discarded into a waste container in the hood.

**PROCEDURE**

Unless told otherwise, you will work with a partner.

**PREPARATION OF EQUILIBRIUM MIXTURE**

1. Pour 10-20 mL of the 0.010 M potassium thiocyanate into a clean, dry 50-mL beaker.
2. Pour about 10-20 mL of the 0.010 M iron(III) nitrate into a clean, dry 100-mL beaker.
3. Pipet 2.00 mL from each beaker into a clean 25-mL volumetric flask. Fill the volumetric flask to the line with distilled water, cap it, and then invert several times to mix thoroughly.

The waste from the rinsings can go into a 400-mL temporary waste beaker.

4. Rinse each of two cuvetts with the solution you have prepared. Rinse each cuvette a second time and then fill them with this solution. Cap the cuvetts.

It is much easier to avoid spills if you pour the solution from the volumetric flask into a clean, dry small beaker and then pour from the beaker into the cuvette.

Again, the waste from the rinsings can be poured into the 400-mL temporary waste beaker.

## SETUP THE SPECTROMETER

**5. Turn on the LabQuest2. Connect and calibrate a SpectroVis spectrometer using a distilled water blank.**

Tap on **Sensors**, then **Calibrate**, and then **USB: Spectrometer** to get to the calibration screen.

**6. Change the mode to Time-Based.**

While on the meter screen, tap on the **Mode** button and choose **Time Based** from the scroll box. Then tap **OK**.

**7. Choose to monitor absorbance at 470 nm.**

To do this, tap on the red meter box (which shows the measured absorbance), select **Choose Wavelength**, and enter 470. The LabQuest2 will select the closest available wavelength to 470 nm.

## SETUP THE TEMPERATURE BATHS AND MEASURE THE ABSORBANCES

*In the following steps, you will prepare five different temperature baths (at approximately 0°C, 10°C, 20°C, 30°C, and 40°C), equilibrate your solution in each bath, and then measure its absorbance.*

**8. Prepare a room temperature bath by adding 50-60 mL of cold tap water to a 100-mL beaker. Insert one of the cuvetts you have prepared and let it equilibrate for a few minutes before measuring its absorbance (step 13).**

The “cold” tap water is usually around room temperature. The cuvette should rest upright on the bottom of the beaker.

**9. Attach a temperature probe to the LabQuest2.**

You should see a temperature box appear on the meter screen after the probe is connected.

**10. Fill a 250-mL beaker with ice that you can use at your station for preparing cold/ice water baths.**

**11. Prepare an ice water bath by filling a 100-mL beaker with ice and then adding cold tap water until the total volume is about 50 mL.**

**12. Place your second cuvette containing your solution into the ice water bath. Let the cuvette sit in the solution for at least 5 minutes (10 is better).**

Add additional ice, as needed, so that there is always ice present in the bath.

**13. Measure the absorbance/temperature of the solution in the room temperature bath as follows:**

- Place the temperature probe in the bath and gently swirl it until the reading stops changing and then record it. *Do not rest the probe on the bottom of the beaker while actually taking the temperature reading since this can affect the reading.*
- Remove the cuvette from the beaker and thoroughly, but quickly, dry the outside with a Kimwipe.
- Insert the cuvette into the SpectroVis, wait a few seconds for the reading to stabilize, and then record the absorbance.

**14. Prepare a hot water bath by adding 60 mL of hot tap water to a 100-mL beaker.**

Run the hot water until it is as hot as it can get. This can take a couple of minutes. **Caution:** don't burn yourself. Usually it is somewhere around 40°C.

**15. Remove the cuvette from the SpectroVis and insert it into the hot water bath. Let it sit at least 5 minutes (10 is better) before reading the absorbance/temperature.**

**16. When the cuvette in the ice water bath has equilibrated, measure its temperature and absorbance as described in step 13.**

Since the cuvette is so far from room temperature, the absorbance will not totally stabilize. *For the ice/cold water solutions, you should record the maximum value of the absorbance that you observe.*

**17. Prepare a cold water bath (around 10°C) by adding about 25 mL of cold tap water and 30 mL of ice water to a 100-mL beaker.**

You can adjust the temperature by adding small amounts of ice water as needed.

**18. Remove the cuvet from the SpectroVis and insert it into the cold water bath. Let it sit for at least 5 minutes before reading the absorbance/temperature.**

**19. When the cuvet in the hot water bath has equilibrated, measure its temperature and absorbance as described in step 13.**

Again, since the cuvet is so far from room temperature, the absorbance will not stabilize. *For the hot/warm water solutions, you should record the minimum value of the absorbance that you observe after the readings have roughly stabilized.*

**20. Prepare a warm water bath (around 30°C) by adding about 25 mL of cold tap water and 30 mL of hot tap water to a 100-mL beaker.**

**21. Remove the cuvet from the SpectroVis and insert it into the warm water bath. Let it sit for at least 5 minutes before reading the absorbance/temperature.**

**22. When the cuvet in the cold water bath has equilibrated, measure its temperature and absorbance as described in step 13.**

*Reminder: For the ice/cold water solutions, you should record the maximum value of the absorbance you observe.*

**23. When the cuvet in the warm water bath has equilibrated, measure its temperature and absorbance as described in step 13.**

*Reminder: For the hot/warm water solutions, you should record the minimum value of the absorbance you observe after the readings have roughly stabilized.*

#### **CLEAN UP**

**24. Empty all cuvetts, beakers, and volumetric flasks containing your solutions into the 400-mL waste beaker. Dump the contents of the waste beaker into the waste bottle in the hood.**

**25. Dump your ice and temperature baths down the drain.**

**26. Rinse all of your glassware with distilled water. Dry it and put it away.**

**27. Wash your hands before leaving lab.**

Name \_\_\_\_\_

Station Used \_\_\_\_\_

Instructor/Day/Time \_\_\_\_\_

Partner \_\_\_\_\_

Station Checked &amp; Approved \_\_\_\_\_

**DATA SHEET**

Be sure to record all data with the proper number of significant figures (and units when needed).

Concentration of the stock  $\text{Fe}(\text{NO}_3)_3$  solution: \_\_\_\_\_

Concentration of the stock KSCN solution: \_\_\_\_\_

**Absorbance/Temperature data and the calculated concentrations and  $K_c$  values:**

	Temperature (°C)	Absorbance	$[\text{FeSCN}^{2+}]$	$[\text{Fe}^{3+}]$	$[\text{SCN}^-]$	$K_c$
Ice Water Bath						
Cold Water Bath						
Room Temp Bath						
Warm Water Bath						
Hot Water Bath						

The  $[\text{FeSCN}^{2+}]$  values are calculated in data analysis step 1(b)The  $[\text{Fe}^{3+}]$  and  $[\text{SCN}^-]$  values are calculated in data analysis step 1(c)The  $K_c$  values are calculated in data analysis step 1(d)

Duplicate table (in case you mess up the first one, otherwise leave it blank):

	Temperature (°C)	Absorbance	$[\text{FeSCN}^{2+}]$	$[\text{Fe}^{3+}]$	$[\text{SCN}^-]$	$K_c$
Ice Water Bath						
Cold Water Bath						
Room Temp Bath						
Warm Water Bath						
Hot Water Bath						

## DATA ANALYSIS

All calculations should be clearly organized, make proper use of significant figures, and include the units.

**1. Calculate  $K_c$  for the reaction at each of the five temperatures utilizing the following procedure:**

- (a) Determine the initial concentration of each reactant in the reaction mixture. These are the concentrations of the reactants present after they are mixed together in the filled volumetric flask (and prior to any reaction occurring). This can be accomplished for each reactant via a dilution calculation. These values will be the same for all five temperatures.

[Fe<sup>3+</sup>] \_\_\_\_\_ [SCN<sup>-</sup>] \_\_\_\_\_

- (b) Using Beer's Law ( $A = \epsilon bc$ ), calculate the concentration of FeSCN<sup>2+</sup> formed at each of the five temperatures using the path length ( $b = 1 \text{ cm}$ ), the measured absorbance at each temperature, and the molar absorptivity ( $\epsilon = 4.80 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$ ). Record your results in the table on the data page. Show a sample calculation below using your room temperature data.

- (c) Determine the equilibrium concentrations of Fe<sup>3+</sup> and SCN<sup>-</sup> at each of the five temperatures and record them in the table on the data page. You may find the use of ICE tables helpful. In the ICE table below, show your calculation for the room temperature data. [Note: cells marked <sup>(a)</sup> should be filled with the results from part (a) and cells marked <sup>(b)</sup> should be filled with results from part (b).] You will need to construct a separate table for each temperature.

Net ionic reaction:  $\text{Fe}^{3+}(\text{aq}) + \text{SCN}^{-}(\text{aq}) \rightarrow \text{FeSCN}^{2+}(\text{aq})$

Initial (M)	(a)	(a)	0
Change (M)			
Equilibrium (M)			(b)

- (d) Use the equilibrium concentrations of the three species to calculate  $K_c$  at each of the five temperatures and record them in the table on the data page. Show your calculation for the room temperature data.

**2. Construct a graph of  $\ln K_c$  vs.  $1/T$  and then use linear regression to obtain the slope and y-intercept (with proper units).** You can enter your data into the Data Table of the LabQuest2 in order to make the graph. You can either (1) enter your  $K_c$  and  $T$  data and then convert it, as needed, using the functions in the LabQuest2, or (2) calculate the  $\ln K_c$  and  $1/T$  values with your calculator and then enter these values into the LabQuest2. If you do the latter, be sure to enter lots of digits to avoid rounding error. Also, be sure to convert your temperatures into Kelvin. Print your graph and include it with your report.

slope \_\_\_\_\_ y-intercept \_\_\_\_\_

**3. Use the slope and y-intercept to calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  for the reaction.** See the background section and the information regarding equation (4).

$\Delta H^\circ$  \_\_\_\_\_  $\Delta S^\circ$  \_\_\_\_\_

**4. At what temperatures will this reaction be spontaneous under standard state conditions? (See the background section on Spontaneity in this experiment.)**