

Name _____ Lab Day _____ Lab Time _____

Experiment 7 · Equilibrium

Pre-lab questions

Answer these questions and hand them to the TF before beginning work.

(1) What is the purpose of this experiment?

(2) You will measure the absorbance of a solution at 447 nm. What is the formula of the compound that is absorbing light at 447 nm?

(3) The Beer-Lambert Law states that the absorbance of a solution is proportional to what property of that solution?

(4) Define the term “equilibrium”.

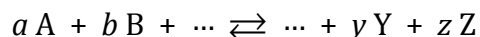
(5) You will measure the value of an equilibrium constant K_{eq} : what does a large value of K_{eq} imply about the relative amount of reactant versus product at equilibrium?

Equilibrium

Mathematical development

Measurement of the equilibrium constant K_{eq}

When a system reaches equilibrium, the macroscopic observables (e.g., temperature, pressure, concentration, color, mass, etc.) that characterize the system stop changing. The equilibrium state of the generic balanced reaction



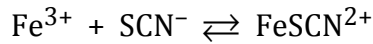
in which a mol of A react with b mol of B and so on to produce y mol of Y, z mol of Z and so on, can be quantified by an equilibrium constant K_{eq} such that

$$K_{eq} = \frac{\dots [Y]_{eq}^y [Z]_{eq}^z}{[A]_{eq}^a [B]_{eq}^b \dots}$$

where the quantities in brackets refer to the concentration in moles per liter of each substance at equilibrium. Note that the concentration of each species is exponentiated to a power equal to the stoichiometric coefficient pertaining to that species in the balanced reaction. The definition of the equilibrium constant suggests that, when $K_{eq} \gg 1$, a lot of product forms and little reactant remains when equilibrium is attained.

A system that both comes to equilibrium very quickly and has a respectably large K_{eq} is the reaction of ferric ion (Fe^{3+})

with thiocyanate ion (SCN^-) to produce ferric thiocyanate (FeSCN^{2+}):



The equilibrium constant of the reaction is given by

$$K_{eq} = \frac{[\text{FeSCN}^{2+}]_{eq}}{[\text{Fe}^{3+}]_{eq}[\text{SCN}^-]_{eq}} \quad (\text{Eqn. 7-1})$$

In this experiment we will measure the value of this K_{eq} .

Your lecture textbook presents a method of evaluating equilibrium constants that involves constructing tables such as Table 7-1. The table shows the concentrations of all species that occur in the equilibrium-constant expression before and after equilibrium is established. In terms of the quantities listed in Table 7-1, the equilibrium constant in Eqn. 7-1 can be expressed as

$$K_{eq} = \frac{[\text{FeSCN}^{2+}]_{eq}}{[\text{Fe}^{3+}]_{eq}[\text{SCN}^-]_{eq}} = \frac{[\text{FeSCN}^{2+}]_{eq}}{\left([\text{Fe}^{3+}]_i - [\text{FeSCN}^{2+}]_{eq}\right)\left([\text{SCN}^-]_i - [\text{FeSCN}^{2+}]_{eq}\right)} \quad (\text{Eqn. 7-2})$$

The quantities $[\text{Fe}^{3+}]_i$ and $[\text{SCN}^-]_i$ in Eqn. 7-2 are easy to measure. Ascertaining the value of $[\text{FeSCN}^{2+}]_{eq}$ is more involved.

We will determine $[\text{FeSCN}^{2+}]_{eq}$ by measuring the amount of light that FeSCN^{2+} absorbs (i.e., its absorbance) at a wavelength of 447 nm. According to the Beer-Lambert Law the concentration of a substance in solution is directly proportional to

Table 7-1 Equilibrium table pertaining to the reaction $\text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons \text{FeSCN}^{2+}$

Species	Initial concentration	Change	Concentration at equilibrium
FeSCN^{2+}	0	+x	$x = [\text{FeSCN}^{2+}]_{eq}$
Fe^{3+}	$[\text{Fe}^{3+}]_i$	-x	$[\text{Fe}^{3+}]_i - x = [\text{Fe}^{3+}]_i - [\text{FeSCN}^{2+}]_{eq} = [\text{Fe}^{3+}]_{eq}$
SCN^-	$[\text{SCN}^-]_i$	-x	$[\text{SCN}^-]_i - x = [\text{SCN}^-]_i - [\text{FeSCN}^{2+}]_{eq} = [\text{SCN}^-]_{eq}$

its absorbance at an arbitrarily chosen wavelength. Applied to the reaction we are to study,

$$A_{447} = \epsilon_{447}[\text{FeSCN}^{2+}]d$$

where A_{447} represents the absorbance of FeSCN^{2+} at 447 nm, ϵ_{447} (the “extinction coefficient” of FeSCN^{2+} at 447 nm) is a measure of how efficiently a substance absorbs light, and d is the diameter of the cell (called a “cuvet”) in which the absorbance is measured.

Measurement of ΔH° and ΔS°

One of the most important relationships in chemical thermodynamics is expressed by the equation

$$\Delta G^\circ = -RT \ln K_{eq} \quad (\text{Eqn. 7-3})$$

where ΔG° is the standard change in free energy, R is the gas constant (8.31 J/(mol·K)), and T is the temperature in units of degrees Kelvin. The value of ΔG° in Eqn. 7-3 indicates whether a reaction is spontaneous (i.e., takes place without any intervention on the part of the surroundings) at standard conditions and at the temperature T . If $\Delta G^\circ < 0$, the reaction is spontaneous at standard conditions; if $\Delta G^\circ > 0$, the reaction is not spontaneous at standard conditions. Combining Eqn. 7-3 with the definition

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where ΔH° represents the standard enthalpy change and ΔS° the standard entropy change, gives after some manipulation

$$\ln K_{eq} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (\text{Eqn. 7-4})$$

Eqn. 7-4 indicates that $\ln K_{eq}$ varies linearly with $1/T$: a plot of $\ln K_{eq}$ as a function of $1/T$ results in a straight line whose slope is equal to $-\Delta H^\circ/R$ and whose y -intercept is equal to $\Delta S^\circ/R$. We will measure K_{eq} at two temperatures and use Eqn. 7-4 to determine ΔH° , ΔS° and ΔG° of the reaction.

Procedure

Do not contaminate the stock solutions! Pour the approximate volumes of $\text{Fe}(\text{NO}_3)_3(\text{aq})$ and $\text{KSCN}(\text{aq})$ stock solutions that you need into appropriately sized beakers, take the beakers back to your lab bench and continue working with the solutions there. If you take too much solution, do not pour the excess back into the reagent bottle: dispose of the excess in a hazardous-waste receptacle.

Preliminaries

Using tape or a glass-marking pen, label eight dry 150-mm test tubes "Solution 1", "Solution 2", etc. In separate, dry beakers obtain 80 mL of 0.200 M $\text{Fe}(\text{NO}_3)_3(\text{aq})$ stock solution and 80 mL of 0.0005 M $\text{KSCN}(\text{aq})$ stock solution.

Obtain three burettes and clamp them to a ring stand using two burette holders. Prepare one burette to measure out $\text{KSCN}(\text{aq})$ stock solution and fill it with that stock solution. Prepare the second burette to measure out $\text{Fe}(\text{NO}_3)_3(\text{aq})$ stock solution and fill it with that stock solution. Prepare the third burette to measure out deionized water and fill it with water. Discard all rinses in a hazardous-waste receptacle.

Make up in the labeled test tubes the eight solutions described in Table 7-2. Measure all volumes using the appropriate prepared burette. **Do not use graduated cylinders!** – they're not accurate enough.

The solutions in the eight test tubes must be well mixed before continuing. Place a disposable dropper in each of the eight test tubes. Draw solution into the dropper by suction and gently squirt the solution back out into the test tube. Repeat this operation several times. Be careful not to lose any solution over the side of the test tube. Inspect each solution after the mixing process: if the color is not uniform, continue mixing.

Table 7-2 Initial make-up of the solutions required for the measurement of K_{eq}

Solution	Volume of 0.0005 M $\text{KSCN}(\text{aq})$ [mL]	Volume of 0.200 M $\text{Fe}(\text{NO}_3)_3(\text{aq})$ [mL]	Volume of H_2O [mL]
1	5.00	0.50	14.50
2	5.00	1.00	14.00
3	5.00	1.50	13.50
4	5.00	2.00	13.00
5	5.00	2.50	12.50
6	5.00	10.00	5.00
7	5.00	13.00	2.00
8	5.00	15.00	0.00

For each of the eight solutions you prepare, calculate $[\text{Fe}^{3+}]_i$ using the formula

$$[\text{Fe}^{3+}]_i = \frac{(\text{molarity of Fe}^{3+} \text{ stock sol'n})(\text{milliliters of Fe}^{3+} \text{ stock sol'n})}{20 \text{ mL}}$$

$[\text{Fe}^{3+}]_i$ will vary from

$$[\text{Fe}^{3+}]_i = \frac{(0.200)(0.50 \text{ mL})}{20 \text{ mL}} = 0.005 \text{ M}$$

in Solution 1 to

$$[\text{Fe}^{3+}]_i = \frac{(0.200)(15.00 \text{ mL})}{20 \text{ mL}} = 0.15 \text{ M}$$

in Solution 8.

$[\text{SCN}^-]_i$ for each of the eight solutions is calculated using the formula

$$[\text{SCN}^-]_i = \frac{(\text{molarity of SCN}^- \text{ stock sol'n})(\text{milliliters of SCN}^- \text{ stock sol'n})}{20 \text{ mL}}$$

but, because the volume of $\text{KSCN}(\text{aq})$ stock solution (5.00 mL) added to each test tube is the same, $[\text{SCN}^-]_i$ in all eight solutions is

$$[\text{SCN}^-]_i = \frac{(0.0005)(5.00 \text{ mL})}{20 \text{ mL}} = 1.25 \times 10^{-4} \text{ M}$$

Obtain eight cuvetts (these are really just small test tubes). Using a glass-marking pen, label each cuvette "Solution 1", "Solution 2", etc.; be sure to place the mark quite near the top of the cuvette because marks down low on the cuvette's body interfere with measurement. Using the droppers for mixing in each big test tube and being careful to avoid cross-contamination, fill each cuvette with the appropriate solution to within a centimeter of the top of the cuvette.

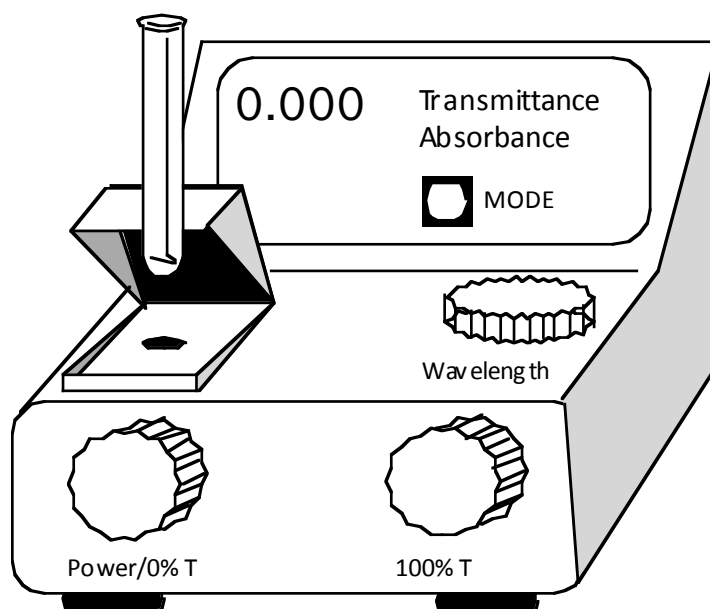
Using the Spec-20 spectrophotometer

You will use the Spec-20 spectrophotometer (see Figure 7-1) to measure the amount of light absorbed by $[\text{FeSCN}^{2+}]$. Before taking measurements on actual samples, the response of the Spec-20 must be calibrated in a process called “zeroing against the blank”. The blank is a solution identical to the actual sample whose absorbance you will measure except that the blank does not contain any substances that absorb light at the wavelength of interest.

To zero the Spec-20 against the blank, follow these steps:

- Turn on the Spec-20 and allow it to warm up for 15 min. Make sure that the sample compartment is empty and that it is closed.
- Press the MODE button to select transmittance mode. Some spectrophotometers have a lever located on the lower left of the front panel: be sure that the lever is set to the appropriate wavelength range, that is, to read 447 nm.
- Twirl the wavelength adjust knob to the desired wavelength (447 nm); on digital models, enter 447 nm.

Figure 7.1 The Spec-20



- With the sample compartment empty and closed. Twirl the power/0% T knob until the pointer (or digital display) reads 0% transmittance (0% T).
- Open the sample compartment, insert a cuvet filled with water, close the sample compartment, and twirl the 100% T knob until the pointer (or digital display) reads 100% T .
- Remove the cuvet and ensure that the instrument still reads 0% T when the sample compartment is empty and closed; if it does not, twirl the power/0% T knob until it does so.
- Open the sample compartment, re-insert the cuvet filled with water and ensure that the instrument still reads 100% T ; if it does not, twirl the 100% T knob until it does so.
- Repeat the zeroing procedure until the instrument reproducibly reads 0% T when the sample compartment is empty and 100% T when the cuvet filled with water is inserted.
- After you have zeroed the Spec-20, press the MODE button to select absorbance mode. The instrument is now ready to measure the absorbance of a sample. Although it is a nuisance to do so, good technique requires that you zero the instrument after every five or six measurements. In order to minimize experimental errors, it's also advisable to insert the cuvet the same way every time: try making an inconspicuous mark near the top of the cuvet and thereafter always insert the cuvet such that the mark faces you.

The relationship between percent transmittance (% T) and absorbance (A) is:

$$\% T = 10^{2-A}$$

$$A = 2 - \log_{10} (\% T)$$

Measurement of K_{eq} at room temperature

Measure the absorbance of Solutions 1–8 at 447 nm. Remember to measure the diameter d of the cuvet in units of centimeter and remember to record the air temperature T_1 . Do not discard the cuvet filled with Solutions 1–8: you will need them later.

Measurement of K_{eq} at low temperature

Prepare a 50:50 mixture of ice and water in a beaker large enough to accommodate all eight cuvetts holding Solutions 1–8.

Place the eight cuvetts in the ice bath for at least 20 min. During the 20-min interval, occasionally monitor the temperature of the ice bath; refresh it by adding more ice and pouring out water if the temperature rises above 6 °C. Re-zero the Spec-20 against the water blank while you are waiting for the 20-min interval to elapse.

At the end of the 20-min interval, wipe down the thermometer probe with a clean paper towel, measure and record in your notebook the temperature T_2 of the solution that has been in the ice bath for the least amount of time. You want the temperature to be as low as possible, preferably below 6 °C. Do not measure the temperature of any other solution: this risks cross-contamination, especially if you don't scrupulously clean the thermometer tip.

Measure the absorbance of Solutions 1–8 at 447 nm. The cuvet will be wet when you withdraw it from the ice bath: quickly wipe it dry with a clean paper towel before inserting the cuvet into the Spec-20: water will damage the instrument.

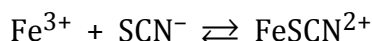
Clean-up

The 150-mm test tubes are not disposable. Rinse out any liquid remaining in each test tube by adding a few milliliters of water. Be sure to catch the rinse water in a hazardous waste receptacle: do not dump it down the drain.

Data analysis

Evaluation of the K_{eq} s

The Beer–Lambert Law says that the absorbance of FeSCN^{2+} is proportional to the amount of FeSCN^{2+} present in solution. We will assume that the solution that exhibits the maximum value of A_{447} contains the maximum equilibrium concentration of FeSCN^{2+} . Given the one-to-one stoichiometry of the reaction



and given that Fe^{3+} is present in excess in all eight solutions, we conclude that SCN^- is the limiting reagent. The maximum possible equilibrium concentration of FeSCN^{2+} is thus

$$[\text{FeSCN}^{2+}]_{eq,max} = [\text{SCN}^-]_i = 1.25 \times 10^{-4} M$$

In other words, we assume that all of the SCN^- present initially reacts in the solution that exhibits $A_{447,max}$. Because the Beer-Lambert Law says that the absorbance of FeSCN^{2+} is directly proportional to its concentration, for those solutions in which $A_{447} < A_{447,max}$

$$\frac{[\text{FeSCN}^{2+}]_{eq}}{[\text{FeSCN}^{2+}]_{eq,max}} = \frac{A_{447}}{A_{447,max}}$$

and

$$\begin{aligned} [\text{FeSCN}^{2+}]_{eq} &= [\text{FeSCN}^{2+}]_{eq,max} \left(\frac{A_{447}}{A_{447,max}} \right) \\ &= (1.25 \times 10^{-4} M) \left(\frac{A_{447}}{A_{447,max}} \right) \end{aligned} \quad (\text{Eqn. 7-5})$$

When we apply Eqn. 7-5 to the equilibrium-constant expression in Eqn. 7-2, we obtain a formula that allows us to determine the equilibrium constant of all eight solutions **except that solution in which $A_{447,max}$ is attained:**

$$\begin{aligned} K_{eq} &= \frac{[\text{FeSCN}^{2+}]_{eq}}{[\text{Fe}^{3+}]_{eq}[\text{SCN}^-]_{eq}} = \frac{[\text{FeSCN}^{2+}]_{eq}}{\left([\text{Fe}^{3+}]_i - [\text{FeSCN}^{2+}]_{eq} \right) \left([\text{SCN}^-]_i - [\text{FeSCN}^{2+}]_{eq} \right)} \\ &= \frac{(1.25 \times 10^{-4}) \left(\frac{A_{447}}{A_{447,max}} \right)}{\left([\text{Fe}^{3+}]_i - (1.25 \times 10^{-4}) \left(\frac{A_{447}}{A_{447,max}} \right) \right) \left([\text{SCN}^-]_i - (1.25 \times 10^{-4}) \left(\frac{A_{447}}{A_{447,max}} \right) \right)} \end{aligned}$$

Because $[\text{SCN}^-]_i = 1.25 \times 10^{-4} M$ in all eight solutions, the expression for K_{eq} simplifies to

$$K_{eq} = \frac{\left(\frac{A_{447}}{A_{447,max}}\right)}{\left([\text{Fe}^{3+}]_i - (1.25 \times 10^{-4})\left(\frac{A_{447}}{A_{447,max}}\right)\right)\left(1 - \left(\frac{A_{447}}{A_{447,max}}\right)\right)} \quad (\text{Eqn. 7-6})$$

Evaluation of ΔH° and ΔS°

As was pointed out in the “Mathematical development” section, ΔH° and ΔS° of the reaction can be determined by graphical methods. To expedite the procedure, we choose instead to evaluate these thermodynamic quantities using the following formulas derived from the point-slope equation of a straight line:

$$\Delta H^\circ = \left(\frac{RT_1T_2}{T_1 - T_2}\right) \ln\left(\frac{K_{eq,T1}}{K_{eq,T2}}\right)$$

$$\Delta S^\circ = \frac{R}{T_1 - T_2} (T_1 \ln K_{eq,T1} - T_2 \ln K_{eq,T2})$$

In these formulas, T_1 corresponds to your measurement of room temperature in degrees Kelvin; T_2 corresponds to the temperature in degrees Kelvin of the solutions after cooling in the ice bath for at least 20 min; $K_{eq,T1}$ represents the value of K_{eq} at T_1 ; $K_{eq,T2}$ represents the value of K_{eq} at T_2 ; R is the universal gas constant (8.31 J/(mol·K)). Recall that degrees Kelvin = degrees Celsius + 273.15.

Name _____ Lab Day _____ Lab Time _____

Experiment 7 · Equilibrium

Lab report form

Page 1

(I) Report the data items and calculated quantities required to determine the equilibrium constant $K_{eq,T1}$ at T_1 (room temperature) from Eqn. 7-6. Calculate $[FeSCN^{2+}]_{eq}$ from Eqn. 7-5; calculate ϵ_{447} from the Beer-Lambert Law

$$A_{447} = \epsilon_{447}[FeSCN^{2+}]_{eq} d$$

Draw a prominent arrow (\Leftarrow) in the right-hand margin to indicate the solution that exhibited $A_{447,max}$; $K_{eq,T1}$ cannot be calculated for that solution. Calculate the mean, standard deviation of the mean, and the 95% confidence interval about the mean of ϵ_{447} and $K_{eq,T1}$.

$T_1 =$ _____ °C

$d =$ _____ cm

Sol'n	$[Fe^{3+}]_i$ [mol/L]	A_{447}	$[FeSCN^{2+}]_{eq}$ [mol/L]	ϵ_{447} [units?]	$K_{eq,T1}$ [units?]
1					
2					
3					
4					
5					
6					
7					
8					

mean		
standard deviation		
95% confidence interval		

Experiment 7 · Equilibrium**Lab report form****Page 2**

(II) Report the data items and calculated quantities required to determine the equilibrium constant K_{eq,T_2} at T_2 (the temperature of the cold bath) from Eqn. 7-6. Calculate $[\text{FeSCN}^{2+}]_{eq}$ from Eqn. 7-5; calculate ϵ_{447} from the Beer-Lambert Law

$$A_{447} = \epsilon_{447}[\text{FeSCN}^{2+}]_{eq} d$$

Draw a prominent arrow (\Leftarrow) in the right-hand margin to indicate the solution that exhibited $A_{447,max}$; K_{eq,T_2} cannot be calculated for that solution. Calculate the mean, standard deviation of the mean, and the 95% confidence interval about the mean of ϵ_{447} and K_{eq,T_2} .

$T_2 =$ _____ °C

$d =$ _____ cm

Sol'n	$[\text{Fe}^{3+}]_i$ [mol/L]	A_{447}	$[\text{FeSCN}^{2+}]_{eq}$ [mol/L]	ϵ_{447} [units?]	K_{eq,T_2} [units?]
1					
2					
3					
4					
5					
6					
7					
8					

mean		
standard deviation		
95% confidence interval		

Experiment 7 • Equilibrium**Lab report form****Page 3**

(III) On separate sheets present plots of the absorbance data as a function of $[\text{Fe}^{3+}]_i$ collected during the runs at T_1 and T_2 . Include the origin $\{0,0\}$ as a data point. Prepare a separate plot for each run. Give each plot a truly informative title (i.e., don't just call it "Plot 1"), label the axes, and include appropriate units and divisions of those axes. Do not submit small plots: use a whole sheet of paper. Scale the horizontal and vertical axes so that the data points occupy most of the area of the plot.

(IV.A) Using the formulas

$$\Delta H^\circ = \left(\frac{RT_1T_2}{T_1 - T_2} \right) \ln \left(\frac{K_{eq,T1}}{K_{eq,T2}} \right) \quad \text{and} \quad \Delta S^\circ = \frac{R}{T_1 - T_2} (T_1 \ln K_{eq,T1} - T_2 \ln K_{eq,T2})$$

evaluate ΔH° and ΔS° of the reaction. Use the mean values of $K_{eq,T1}$ and $K_{eq,T2}$ from the tables in (I) and (II), the Kelvin temperatures T_1 and T_2 (degrees Kelvin = degrees Celsius + 273.15), $R = 0.00831 \text{ kJ}/(\text{mol}\cdot\text{K})$ in the calculation of ΔH° and $R = 8.31 \text{ J}/(\text{mol}\cdot\text{K})$ in the calculation of ΔS° .

T_1 [° C]	T_1 [K]	T_2 [° C]	T_2 [K]	$K_{eq,T1}$ [units?]	$K_{eq,T2}$ [units?]	ΔH° [kJ/mol]	ΔS° [J/(mol·K)]

(IV.B) Using the definition $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, where ΔG° is the standard free energy change and T is in units of degree Kelvin, evaluate ΔG° in units of kilojoule per mole at T_1 and T_2 . Pay attention to units!

$$\Delta G^\circ_{T1} = \text{_____} \text{ kJ/mol}$$

$$\Delta G^\circ_{T2} = \text{_____} \text{ kJ/mol}$$

Name _____ Lab Day _____ Lab Time _____

Experiment 7 · Equilibrium

Lab report form

Page 4

Post-lab questions

(1.a) What is the percent yield of FeSCN^{2+} at equilibrium in the solution that exhibited $A_{447, \text{max}}$ at room temperature?

(1.b) What is the percent yield of FeSCN^{2+} at equilibrium at room temperature in Solution 2? Show the calculation.

(2.a) Absorbance A has no units; however, the extinction coefficient ϵ *does* have units. What are the units of ϵ ? Show how you arrived at your answer.

(2.b) Although equilibrium constants are usually reported without units, in fact they *do* have units. What are the units of the K_{eq} measured in this experiment? Show how you arrived at your answer.

Name _____ Lab Day _____ Lab Time _____

Experiment 7 · Equilibrium

Lab report form

Page 5

(3) Do your data indicate that the reaction studied in this experiment releases heat or absorbs heat under the experimental conditions you employed? Explain your answer.

(4) You should obtain a value of ΔS° in units of joule per mole–degree Kelvin that is close to zero. Interpret the algebraic sign (positive or negative) of the ΔS° value you reported in (IV.A).

(5) Is the reaction studied in this experiment more spontaneous or less spontaneous at low temperature? Explain your answer.

Experiment 7 · Equilibrium

Lab report form

Page 6

(5) The plot of your room-temperature data submitted in (III) probably resembles the curve marked by circles (“Actual data”) in the figure below. But suppose the plot of your room-temperature data looked like the curve marked by squares (“Hypothetical data”). What would the hypothetical data imply about the magnitude of K_{eq} ? What would the hypothetical data imply about the percent yield of the reaction?

