Take-Home Portion of Exam 3
CHEM 120
Fall 2009

Name: ____

Instructions:
Answer the questions in the space provided. You may use the back of any page for your work, if needed. If you need yet more space, you may insert additional pages, but you must do it so that they immediately follow the question in the order that you want me to read them. Do not attach them at the end of the entire packet. All final numerical answers and all essay-type questions must be hand-written in complete sentences, unless otherwise indicated. If a question requires a graph or spreadsheet output, tape the item in the provided space; do not use staples.

You may not consult with anyone, except the instructor, about specific questions regarding this exam. You may ask other faculty members general questions about topics and methods on this exam, but not about any specific question on the exam. You may not work on this portion of the exam with any one else.

Write your answers neatly and legibly in ink. Answers in pencil will be accepted, but you will not be able to appeal any apparent grading errors (except simple addition errors).

Give a brief description of what you are doing in each numerical problem. This description should give the reader an idea of what you are doing and some justification for your approach. You do not need to justify simple mathematical manipulations.

Problem	Possible Points	Points Received
1	30	
2	10	
3	39	
Total	79	

1. Sucrose, $C_{12}H_{22}O_{11}$, can be hydrolyzed in dilute acid solutions to form two simpler sugars, glucose and fructose, both of which have the chemical formula $C_6H_{12}O_6$. At 23.0 °C in a 0.5 M aqueous HCl solution, the following kinetics data were obtained for the reaction of sucrose.

Time (min)	**$[C_{12}H_{22}O_{11}]$ (M)**
0.	0.316
39.	0.274
80.	0.238
140.	0.190
210.	0.146

a. (8 Points) Prepare three graphs of the data with which to establish the order of the reaction with respect to sucrose. Tape each graph in the appropriate place below or on the next page.

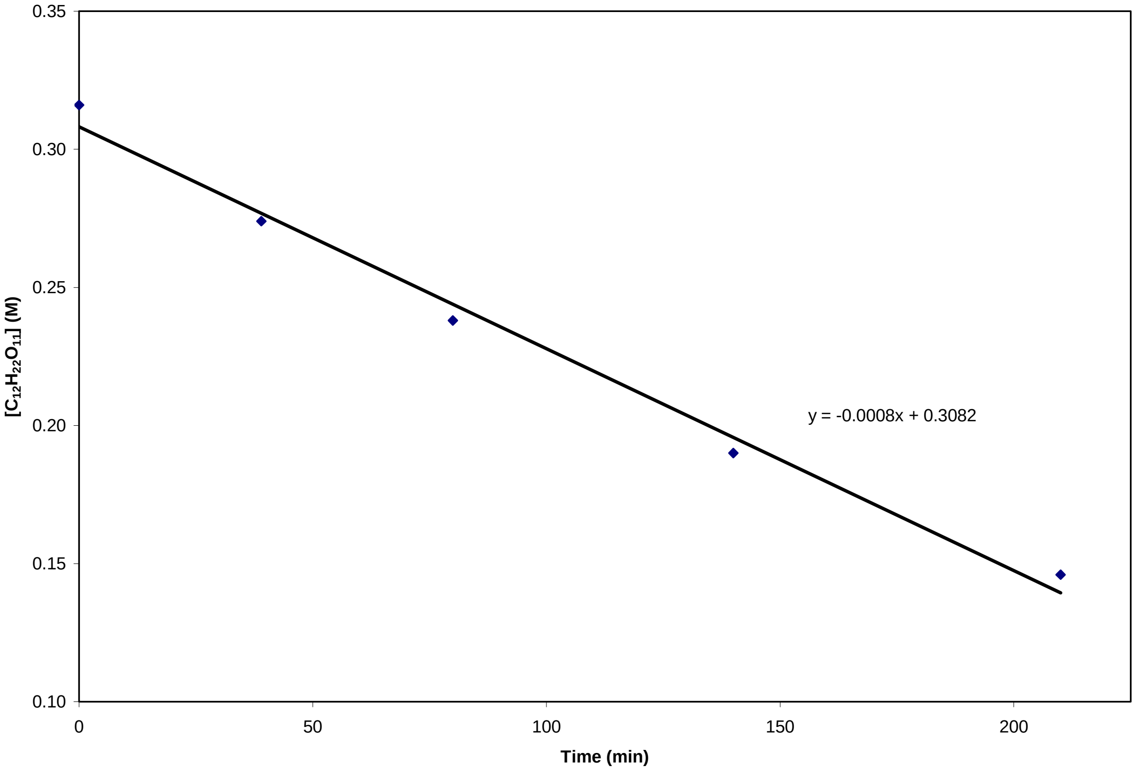

Figure 1. Graph of the data to a zeroth-order integrated rate law.

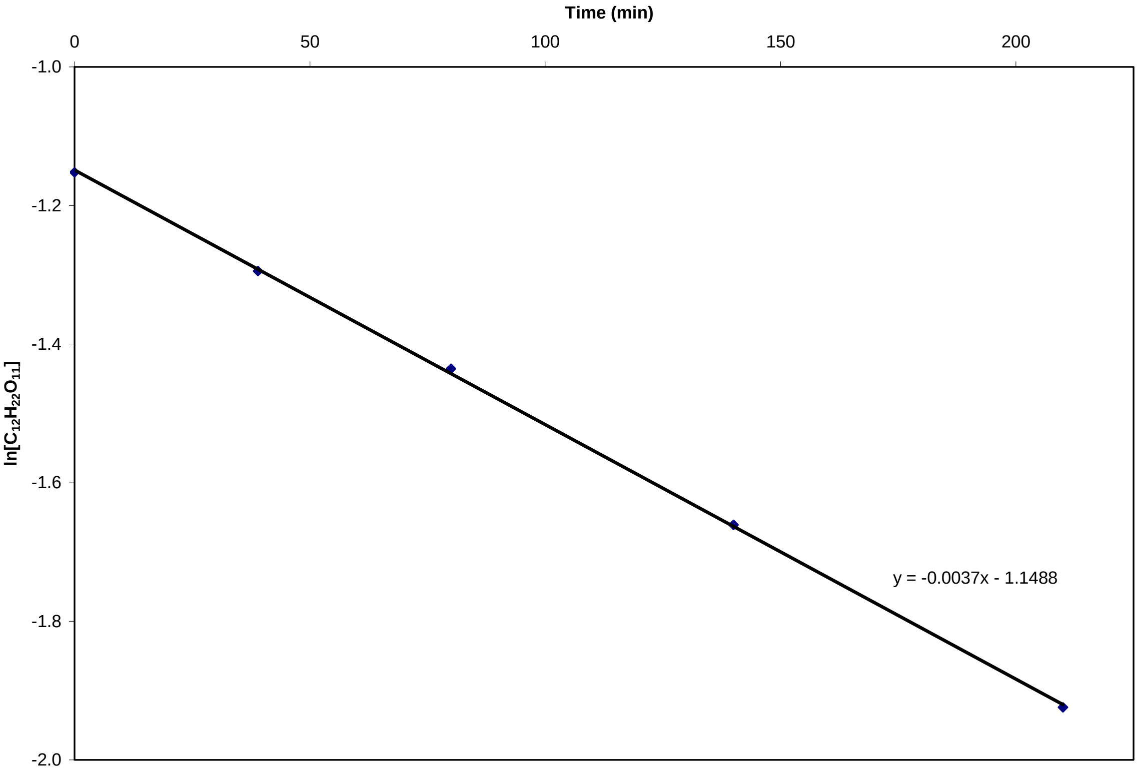

Figure 2. Graph of the data to a first-order integrated rate law.

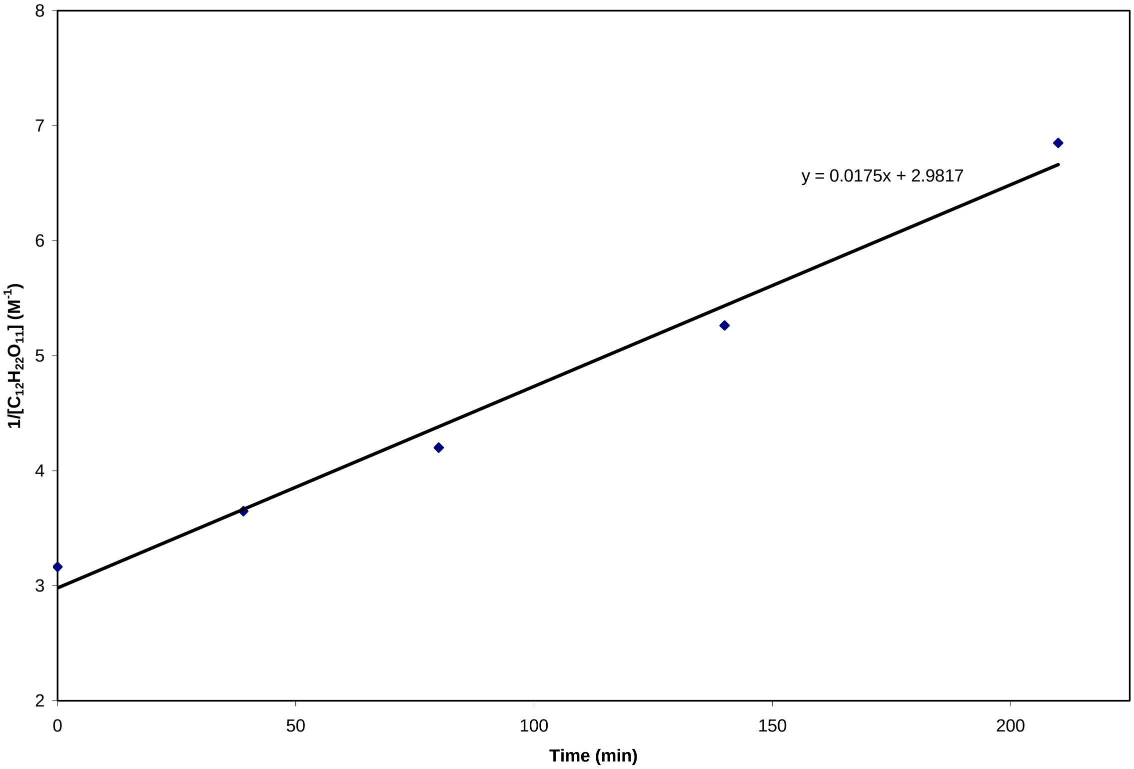

Figure 3. Graph of the data to a second-order integrated rate law.

b. (4 Points) What is the order of this reaction with respect to sucrose? Briefly defend your conclusion.

> **Of the three integrated rate law graphs, the ln[$C_{12}H_{22}O_{11}$] graph appears to be the most linear. The other two graphs clearly have a pattern of points above and below the line (the first and last points are above the line, the second point is on the line and the third and fourth points are below the line), which would indicate that they are not linear. Therefore, we conclude that the reaction is first order with respect to sucrose.**

c. (3 Points) What is the observed rate constant for the reaction in 0.5 M aqueous HCl?

> **The observed rate constant is the negative of the slope in a first order integrated rate law graph. Thus, the rate constant for this reaction is $3.7 \pm 0.1 \times 10^{-3}$ min^{-1} at 95% confidence.**

d. (4 Points) Given that this reaction only takes place under very acidic conditions (i. e., high [H^+]), describe how one would determine the order with respect to H^+.

> **We will vary the [H^+], but it will always be much higher than the [$C_{12}H_{22}O_{11}$], and measure the rate constant at the different [H^+], k_{obs} (sometimes this is referred to as a pseudo-first order rate constant because the rate law is only first order because we made [H^+] large and thus invariant). We will then take our k_{obs} as a function [H^+] data and prepare a graph with $\log k_{obs}$ as a function of $\log[H^+]$ (natural logs would work also). This graph should be a straight line with a slope equal to the order of the reaction with respect to H^+ and an intercept equal to $\log k$, where k is the reaction's actual rate constant.**

e. (9 Points) The following mechanism has been proposed for the hydrolysis of sucrose (Suc) in acidic solution to form fructose (Fruc) and glucose (Gluc). Is this mechanism consistent with what you know about the reaction so far? Note that I have defined an abbreviation for each sugar to simplify things. To solve the problem you will need to 1) write a balanced chemical equation for the reaction that occurs and 2) remember what roles H_2O (l) is playing in this reaction.

$$\text{Suc (aq)} + \text{H}^+\text{ (aq)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{HSuc}^+\text{ (aq)} \qquad \text{fast}$$

$$\text{HSuc}^+\text{ (aq)} + \text{H}_2\text{O (l)} \xrightarrow[k_2]{} \text{Gluc (aq)} + \text{Fruc (aq)} + \text{H}^+\text{ (aq)} \qquad \text{slow}$$

First we need to determine the overall balanced equation. Since this is a hydrolysis reaction (like the one we did in the *Oil of Wintergreen* laboratory exercise), we start by writing sucrose ($C_{12}H_{22}O_{11}$) reacting with water to form fructose ($C_6H_{12}O_6$) and glucose ($C_6H_{12}O_6$), as shown below. As this reaction is balanced, we are finished.

$$C_{12}H_{22}O_{11}\text{ (aq)} + H_2O\text{ (l)} \rightarrow C_6H_{12}O_6\text{ (aq)} + C_6H_{12}O_6\text{ (aq)}$$

Or

$$\text{Suc (aq)} + H_2O\text{ (l)} \rightarrow \text{Fruc (aq)} + \text{Gluc (aq)}$$

Our first criterion is that the mechanism sum to the overall balanced chemical equation. If we add the two steps in the mechanism, and cancel $HSuc^+$ and H^+, which appear on both sides, we do, in fact, get the overall balanced chemical equation. Therefore, the mechanism passes the first test.

Our second test is does the mechanism give a rate law consistent with experimentally determined rate law. Since the second step is slow, we know that $rate = k_2[\text{HSuc}^+][\text{H}_2\text{O}]$, but as we want the rate law in terms of the reactants (Suc and H^+), and not in terms of any intermediates ($HSuc^+$), we need to eliminate [$HSuc^+$] from the expression. To do this we first write an expression for the change in [$HSuc^+$] with respect to time.

$$\frac{d[\text{HSuc}^+]}{dt} = k_1[\text{Suc}][\text{H}^+] - k_{-1}[\text{HSuc}^+] - k_2[\text{HSuc}^+][\text{H}_2\text{O}]$$

We can solve this for [$HSuc^+$] by making the steady state approximation (the concentration of an intermediate is small and doesn't change over time)

$$\frac{d[\text{HSuc}^+]}{dt} = k_1[\text{Suc}][\text{H}^+] - k_{-1}[\text{HSuc}^+] - k_2[\text{HSuc}^+][\text{H}_2\text{O}] = 0$$

$$k_1[\text{Suc}][\text{H}^+] = k_{-1}[\text{HSuc}^+] + k_2[\text{HSuc}^+][\text{H}_2\text{O}]$$

$$k_1[\mathrm{Suc}][\mathrm{H}^+] = \left(k_{-1} + k_2[\mathrm{H_2O}]\right)[\mathrm{HSuc}^+]$$

$$[\mathrm{HSuc}^+] = \frac{k_1[\mathrm{Suc}][\mathrm{H}^+]}{k_{-1} + k_2[\mathrm{H_2O}]}$$

Substituting this into the expression for the rate of slow step gives

$$rate = k_2\left(\frac{k_1[\mathrm{Suc}][\mathrm{H}^+]}{k_{-1} + k_2[\mathrm{H_2O}]}\right)[\mathrm{H_2O}] = \frac{k_1 k_2[\mathrm{Suc}][\mathrm{H}^+][\mathrm{H_2O}]}{k_{-1} + k_2[\mathrm{H_2O}]}$$

Since H_2O is the solvent, $[H_2O]$ is essentially constant. Our expression the simplifies to $rate = k[\mathrm{Suc}][\mathrm{H}^+]$, where $k = \frac{k_1 k_2[\mathrm{H_2O}]}{k_{-1} + k_2[\mathrm{H_2O}]}$.

This predicts that the reaction is first order in sucrose and first order in H^+. We have determined that the reaction is first order in sucrose, but have not determined the order with respect to H^+ (see part *d*). So, based on the evidence we have so far, this mechanism is consistent with the experimental data, but we would need more data to give more support to this mechanism before it could be accepted.

An alternate way to work this problem is to assume that the equilibrium in the first step is rapidly established, although the problem does not state explicitly that you could do so. However, if you did it this way, you would have then started with the following expression and rearranged it to solve for $[HSuc^+]$.

$$K = \frac{[\mathrm{Suc}][\mathrm{H}^+]}{[\mathrm{HSuc}^+]}$$

$$[\mathrm{HSuc}^+] = \frac{[\mathrm{Suc}][\mathrm{H}^+]}{K}$$

This expression can then be substituted into the rate expression for the second (slow) step.

$$rate = k_2\left(\frac{[\mathrm{Suc}][\mathrm{H}^+]}{K}\right)[\mathrm{H_2O}] = \frac{k_2[\mathrm{Suc}][\mathrm{H}^+][\mathrm{H_2O}]}{K}$$

We can again simplify this expression because the $[H_2O]$ is large and unchanging (because it is the solvent) to the rate law $rate = k_{overall}[\mathrm{Suc}][\mathrm{H}^+]$ where $k_{overall} = \frac{k_2[\mathrm{H_2O}]}{K}$. And as before, we can state that the mechanism is consistent with the data that we have because the mechanism's steps do sum to the overall balanced

chemical equation and it correctly predicts that the reaction is first order with respect to sucrose.

f. (2 Points) What role does H^+ play in the proposed mechanism?

H^+ is a homogeneous catalyst. *It plays a part in the reaction, but is not consumed in the reaction, and does not appear in the overall balanced chemical equation for the reaction.*

2. (9 Points) The rate constant for the reaction shown below was determined as a function of temperature (data are shown in the table). Prepare a graph of the data that will allow you to determine the reaction's activation energy (along with its uncertainty at 95% confidence) and tape it in the space provided. Given $\Delta E_a = \pm\left|-R\right|(\Delta slope)$.

$$CH_3COOC_2H_5\ (aq) + OH^-\ (aq) \rightarrow CH_3COO^-\ (aq) + C_2H_5OH\ (aq)$$

Temperature (°C)	***k* ($M^{-1}\cdot s^{-1}$)**
15.0	0.0521
25.1	0.101
34.9	0.184
45.2	0.332

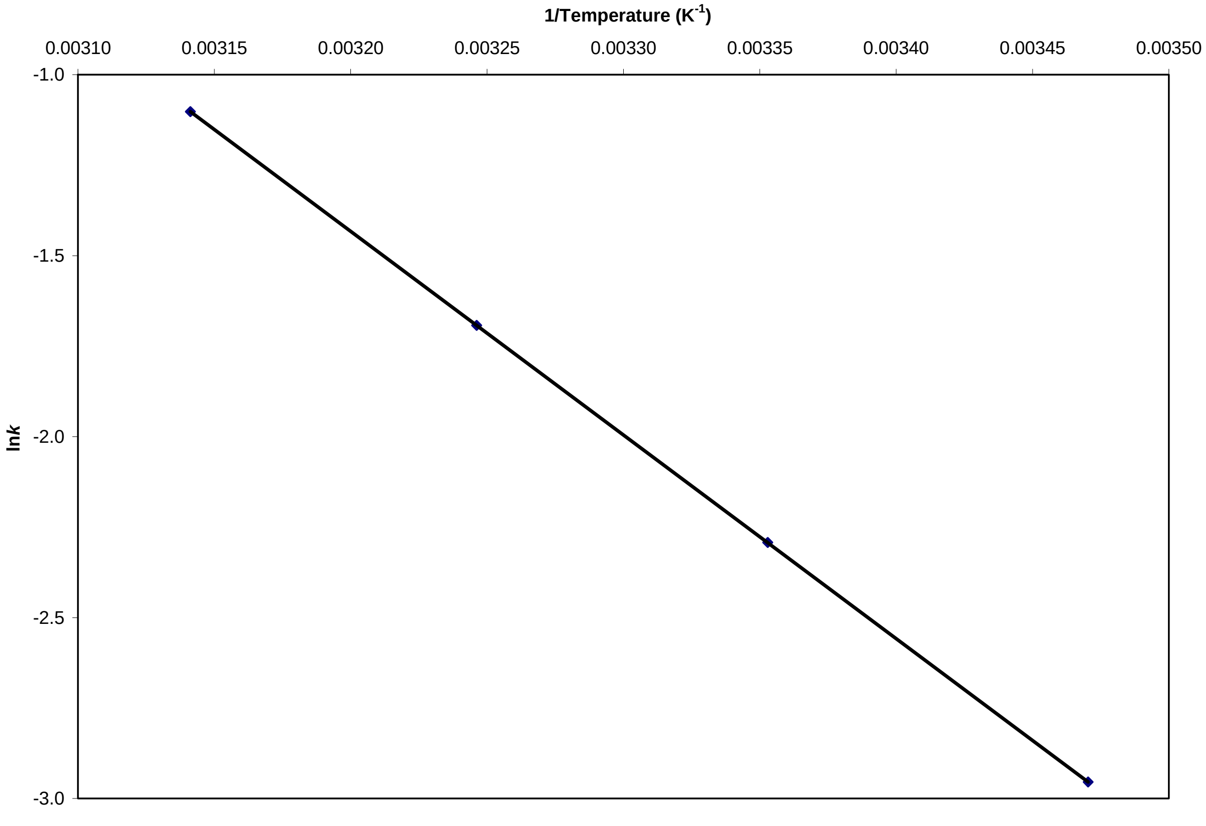

Figure 4. Graph to determine the activation energy of the reaction of ethyl acetate with OH^-. The activation energy for this reaction is **46.77±0.02 kJ/mole** at 95% confidence.

To solve this problem we need to put the Arrhenius equation in the form of a straight line, which we do by taking the natural logarithm of both sides.

$$k = Ae^{-E_a / RT}$$

$$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$$

Thus, a graph of the natural log of the rate constant as a function of one over the absolute temperature gives a slope equal to $-\frac{E_a}{R}$**.**

From a regression analysis of the data, the slope is -5625. ± 9 K (a standard error of 2.). Rearrange the expression for the slope to solve for E_a**.**

$$slope = -\frac{E_a}{R}$$

$$E_a = -R \cdot slope = -\left(8.31447\ \mathrm{J \cdot K^{-1} \cdot mole^{-1}}\right)\left(-5625.\ \mathrm{K}\right) = 46.77\ \mathrm{kJ \cdot mole^{-1}}$$

To find the uncertainty in this number we take the standard error and substitute it into the given propagation of error equation.

$$\Delta E_a = \pm\left|-R\right|\left(\Delta slope\right) = \pm\left(8.31447\ \mathrm{J \cdot K^{-1} \cdot mole^{-1}}\right)\left(2.\ \mathrm{K}\right) = \pm 0.02\ \mathrm{kJ \cdot mole^{-1}}$$

If you used the uncertainty at 95% confidence for the slope, you would have calculated the uncertainty in the activation energy to be ±0.08 kJ/mole, which was also accepted.

b. (1 Point) The overall order of this reaction is **second** ***(based on the units on k).***

3. The equilibrium CO (g) + Cl_2 (g) $\leftrightarrows$ COCl (g) + Cl (g) is believed to occur as written in both directions (i. e., both the forward reaction and the reverse reaction is an elementary step).

a. (4 Points) If the rate constant for the forward reaction, k_f, is $1.4\text{x}10^{-28}\ \mathrm{M^{-1} \cdot s^{-1}}$ and the rate constant for the reverse reaction, k_r, is $9.3\text{x}10^{10}\ \mathrm{M^{-1} \cdot s^{-1}}$ at 25.00 °C, what is the equilibrium constant, *K*, for the reaction?

In general $K = \frac{k_{forward}}{k_{reverse}}$**. So,** $K = \frac{k_{forward}}{k_{reverse}} = \frac{1.40x10^{-28}\ \mathrm{M^{-1} \cdot s^{-1}}}{9.3x10^{10}\ \mathrm{M^{-1} \cdot s^{-1}}} = 1.5x10^{-39}$**.**

The equilibrium constant for this reaction is $\mathbf{1.5x10^{-39}}$**.**

b. (7 Points) Using the following thermodynamic data, determine whether heating this reaction will increase the amount of COCl formed.

	ΔH_f^0 (kJ/mole)	**S^0 ($J\cdot K^{-1}\cdot mole^{-1}$)**	**ΔG_f^0 (kJ/mole)**
CO (g)	-110.5	197.7	-137.2
Cl_2 (g)	0	223.1	0
COCl (g)	-62.76	265.97	-----
Cl (g)	+121.7	165.2	+105.7

To know how heating will affect the equilibrium, we need to know Δ*H* for the reaction.

ΔH^0 = (1 mole COCl)(-62.76 kJ/mole) + (1 mole Cl)(+121.7 kJ/mole) – (1 mole CO)(–110.5 kJ/mole) – (1 mole Cl_2)(0)

ΔH^0 = –62.76 kJ + 121.7 kJ + 110.5 kJ = +169.4 kJ

This reaction is endothermic. So, by the van't Hoff equation, $\frac{d\ln K}{dT} = \frac{\Delta H^0}{RT^2}$, we see when ΔH^0 is positive that an increase in temperature increases *K*. If *K* increases, then the amount of products form will also increase.

You could also have used the short cut and said that, if we treat heat as a reactant, heating this reaction stresses the reaction by adding a reactant. Then by LeChâtelier's principle the reaction will react to the stress by shifting toward products, and so more COCl will be formed. Remember that this is only a short cut and that the real reason is because *K* changes according to the van't Hoff equation.

c. (7 Points) Does Δ*H* or Δ*S* play a larger role in determining the sign of Δ*G* for this reaction?

Because *K* is a number less than one, we know that Δ*G* is positive for this reaction. To determine whether Δ*H* or Δ*S* is more important in determining the sign of Δ*G*, we need to know that these parameters are related by the equation $\Delta G = \Delta H - T\Delta S$. Now we need to determine the relative magnitudes of the Δ*H* and the *T*Δ*S* terms.

In this reaction we start with 2 moles of gas and end up with 2 moles of gas. So, we expect Δ*S* to be relatively small because *S* of different gases tend to be similar (except for differences due to their internal arrangement). Thus, we may conclude that the moderately large, positive Δ*H* that we calculated is playing a dominant role in determining the sign of Δ*G* because at this temperature the *T*Δ*S* term is small because Δ*S* is small.

An alternate solution is to calculate Δ*S* from the given information. In this case, you would find Δ*S* to be +10.4 J/K, which means the *T*Δ*S* term is only 3.10 kJ/mole at 298.15 K, which is only about 2% of Δ*H*.

d. (8 Points) Using your answer to part *a*, and the thermodynamic data on the previous page, determine ΔG_f^0 for COCl (g).

Since $K = 1.5\text{x}10^{-39}$ **from part *a*, we can calculate** ΔG^0 **for the reaction using** $\Delta G = -RT\ln K$**.**

$$\Delta G = -RT\ln K = -\left(8.31447\ \text{J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}\right)\left(298.1_5\ \text{K}\right)\ln\left(1.5x10^{-39}\right)$$

$$\Delta G = -\left(8.31447\ \text{J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}\right)\left(298.1_5\ \text{K}\right)\left(-89.39\right) = +221.6\ \text{kJ}\cdot\text{mole}^{-1}$$

Note that this is +221.6 kJ for the reaction as written (per mole of each reactant, in this case).

With ΔG^0 **for the reaction, we can then determine** ΔG_f^0 **for COCl.**

ΔG_{rxn}^0 = (1 mole Cl) ΔG_f^0(Cl, g) + (1 mole COCl) ΔG_f^0(COCl, g)
– (1 mole CO) ΔG_f^0(CO, g) – (1 mole Cl_2) ΔG_f^0(Cl_2, g)

ΔG_{rxn}^0 – (1 mole Cl) ΔG_f^0(Cl, g) + (1 mole CO) ΔG_f^0(CO, g) = (1 mole COCl) ΔG_f^0(COCl, g)

221.6 kJ – 105.7 kJ + 137.2 kJ = (1 mole COCl) ΔG_f^0(COCl, g)

ΔG_f^0(COCl, g) = -21.3 kJ/mole

So, ΔG_f^0(COCl, g) **is -21.3 kJ/mole.**

e. (8 Points) Determine the partial pressure of COCl at equilibrium at 25.00 °C when the initial partial pressures of CO and Cl_2 are both 0.500 atm.

Since this is a gas phase reaction, the K that we calculated is a K_p. We can then set up a table to summarize the problem.

	CO (g)	Cl_2 (g)	COCl (g)	Cl (g)
Initial	0.500	0.500	0	0
Change	-x	-x	+x	+x
Equilibrium	0.500 – x	0.500 – x	x	x

Because there are no products present, we know that the reaction must proceed to the right to reach equilibrium.

The equilibrium constant expression is thus

$$K = \frac{p_{COCl}\,p_{Cl}}{p_{CO}\,p_{Cl_2}} = \frac{x^2}{\left(0.500 - x\right)^2} = 1.5x10^{-39}$$

We can simplify this expression by taking the square root of both sides. The expression can then be further simplified by recognizing that, because K **is so small, this equilibrium lies almost entirely toward reactants. Thus,** x **will be very small with respect to 0.500 and** $0.500 - x \approx 0.500$**.**

$$\frac{x}{(0.500 - x)} = 3.8_7 x 10^{-20}$$

$$x = 3.8_7 x 10^{-20}(0.500 - x) = 3.8_7 x 10^{-20}(0.500) = 1.9_4 x 10^{-20}$$

By inspection we can verify that our assumption was valid.

The partial pressure of COCl is 1.9x10^{-20} atm at equilibrium.

f. (5 Points) Draw a reaction profile for this reaction and label the important features.

From the information given in part *a*, we know that this reaction takes place in one step. This, and the result from part *b*, allows us to draw the following reaction profile.