

**1. Steady-State Approximation: Decomposition of Dinitrogen Pentoxide (25 points)**

a) First make a table of all molecules in the mechanism and label them as reactant, product, or intermediate. This list of molecules is useful for bookkeeping purposes, and the label reminds you which molecules are appropriate for the steady-state approximation. Next, write the rate expressions, assuming that each step is an elementary step. (Remember: For elementary steps you assume the reaction is first-order for each reactant molecule.)

<i>Molecule</i>	<i>R, P, I</i>	<i>Rate Expression</i>
N <sub>2</sub> O <sub>5</sub>	Reactant	$\frac{d[\text{N}_2\text{O}_5]}{dt} = -k_1[\text{N}_2\text{O}_5] + k_{-1}[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}][\text{N}_2\text{O}_5]$
NO <sub>2</sub>	Product	$\frac{d[\text{NO}_2]}{dt} = k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] + 3k_3[\text{NO}][\text{N}_2\text{O}_5]$
O <sub>2</sub>	Product	$\frac{d[\text{O}_2]}{dt} = k_2[\text{NO}_2][\text{NO}_3]$
NO	Intermediate	$\frac{d[\text{NO}]}{dt} = k_2[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}][\text{N}_2\text{O}_5]$
NO <sub>3</sub>	Intermediate	$\frac{d[\text{NO}_3]}{dt} = k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}_2][\text{NO}_3]$

**(10 points total:** 2 points for each rate expression above. No credit if these equations are not in tabular form, since we explicitly asked you to do so! -0.5 for each Reactant/Product/Intermediate labeled incorrectly. Maximum overall deductions 10 pts.)

b) Now use the steady-state approximation for each intermediate:

$$\frac{d[\text{NO}]}{dt} = k_2[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}][\text{N}_2\text{O}_5] = 0,$$

**(3 points: for knowing to set this rate =0)**

$$\frac{d[\text{NO}_3]}{dt} = k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}_2][\text{NO}_3] = 0.$$

**(3 points: for knowing to set this rate=0)**

And use these expressions to solve for the intermediate concentrations in terms of products and reactants:

$$k_1[\text{N}_2\text{O}_5] - k_{-1}[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}_2][\text{NO}_3] = 0,$$

$$k_1[\text{N}_2\text{O}_5] = (k_{-1} + k_2)[\text{NO}_2][\text{NO}_3],$$

$$\frac{k_1[\text{N}_2\text{O}_5]}{(k_{-1} + k_2)[\text{NO}_2]} = [\text{NO}_3]. \quad [10]$$

**(3 points for calculating intermediate concentrations somewhere in solution)**

And:

$$\begin{aligned}
 k_2[NO_2][NO_3] - k_3[NO][N_2O_5] &= 0, \\
 k_2[NO_2][NO_3] &= k_3[NO][N_2O_5], \\
 \frac{k_2[NO_2]}{k_3[N_2O_5]}[NO_3] &= [NO], \\
 \frac{k_2[NO_2]}{k_3[N_2O_5]} \frac{k_1[N_2O_5]}{(k_{-1} + k_2)[NO_2]} &= [NO], \text{ (using Equation [10])} \\
 \frac{k_1 k_2}{(k_{-1} + k_2) k_3} &= [NO]. \tag{11}
 \end{aligned}$$

Substitute Equations [10] and [11] into the rate expression for dinitrogen pentoxide,

$$\begin{aligned}
 \frac{d[N_2O_5]}{dt} &= -k_1[N_2O_5] + k_{-1}[NO_2] \frac{k_1[N_2O_5]}{(k_{-1} + k_2)[NO_2]} - k_3 \frac{k_1 k_2}{(k_{-1} + k_2) k_3} [N_2O_5], \\
 \frac{d[N_2O_5]}{dt} &= -k_1[N_2O_5] + \frac{k_1 k_{-1} [N_2O_5]}{(k_{-1} + k_2)} - \frac{k_1 k_2}{(k_{-1} + k_2)} [N_2O_5], \\
 \frac{d[N_2O_5]}{dt} &= - \left( k_1 - \frac{k_1 k_{-1}}{(k_{-1} + k_2)} + \frac{k_1 k_2}{(k_{-1} + k_2)} \right) [N_2O_5], \\
 \frac{d[N_2O_5]}{dt} &= - \left( \frac{k_1 (k_{-1} + k_2)}{(k_{-1} + k_2)} - \frac{k_1 k_{-1}}{(k_{-1} + k_2)} + \frac{k_1 k_2}{(k_{-1} + k_2)} \right) [N_2O_5], \\
 \frac{d[N_2O_5]}{dt} &= - \left( \frac{2k_1 k_2}{(k_{-1} + k_2)} \right) [N_2O_5].
 \end{aligned}$$

Therefore,

$$k_{obs} = \frac{2k_1 k_2}{(k_{-1} + k_2)} \cdot \text{(6 points, -2 if sign is incorrect)}$$

**Alternate solution to part b**

15 points For those students who found a simpler way to solve the problem:

Since we are assuming steady-state (i.e., that the concentrations of intermediates are constant and small), then we can write:

$$\frac{d[N_2O_5]}{dt} = -2 \frac{d[O_2]}{dt} \quad (2 \text{ points})$$

$$\frac{d[N_2O_5]}{dt} = -k_1[N_2O_5] + k_{-1}[NO_2][NO_3] - k_3[NO][N_2O_5] \quad (2 \text{ points})$$

$$\frac{d[O_2]}{dt} = k_2[NO_2][NO_3] \quad (2 \text{ points})$$

$$\frac{d[N_2O_5]}{dt} = -2k_2[NO_2][NO_3]$$

$$\frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][N_2O_5] = 0,$$

(1 points: for knowing to set this rate =0)

$$[NO_2][NO_3] = \frac{k_3}{k_2}[NO][N_2O_5],$$

$$\frac{d[N_2O_5]}{dt} = -2k_3[NO][N_2O_5]$$

$$\frac{k_1k_2}{(k_{-1} + k_2)k_3} = [NO].$$

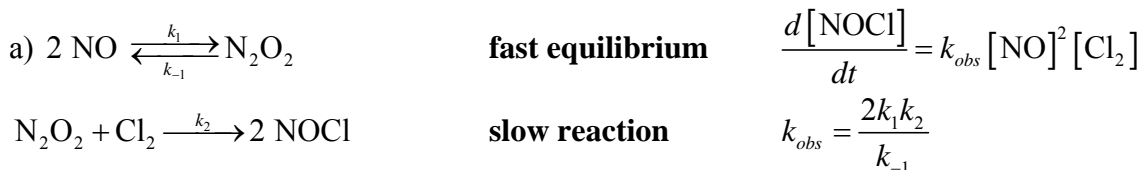
(2 points for calculating somewhere in solution)

see previous pages for details of calculation

$$\frac{d[N_2O_5]}{dt} = \frac{-2k_1k_2}{(k_{-1} + k_2)}[N_2O_5]$$

Therefore,

$$k_{obs} = \frac{2k_1k_2}{(k_{-1} + k_2)} \cdot (6 \text{ points, } -2 \text{ if sign is incorrect})$$

**2. Rate-Limiting Steps (18 points; 6 points each)**

**(2 points:  $k_{\text{obs}}$  factors; deduct 1 point for forgetting the factor of 2)**

**(2 points: reaction 1 as fast)**

**(2 points: reaction 2 as slow)**

The second reaction cannot be the fast reaction because the first reaction would *never* be at equilibrium. If the first reaction is fast, the second reaction must be slow.

Since the second reaction is slow, we can say that the overall rate is dominated by the rate law for the second reaction,

$$\text{rate} = k_2[\text{N}_2\text{O}_2][\text{Cl}_2].$$

But we don't want to include intermediate products in our rate law. (Rate laws should only include concentrations of products and reactants in the overall reaction.) We can eliminate the concentration of  $\text{N}_2\text{O}_2$  by using the fact the first reaction is at equilibrium,

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2}$$

Solving for the concentration of  $\text{N}_2\text{O}_2$ ,

$$[\text{N}_2\text{O}_2] = \frac{k_1}{k_{-1}} [\text{NO}]^2$$

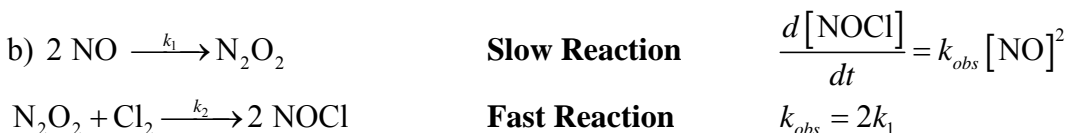
and substituting into the rate law above,

$$\text{rate} = \frac{k_1k_2}{k_{-1}} [\text{NO}]^2 [\text{Cl}_2].$$

This is the rate of reaction, not the rate of NOCl production, which is what we are looking for. Overall, this reaction produces TWO NOCl, so we need to multiply by two to get our final expression. (The same would hold true if we were obtaining an expression in terms of [NO])

$$\frac{d[\text{NOCl}]}{dt} = 2 \times \text{rate} = \frac{2k_1k_2}{k_{-1}} [\text{NO}]^2 [\text{Cl}_2].$$

**You may also award full credit for using the steady state approximation to obtain the same overall rate constant.**



**(2 points:  $k_{\text{obs}}$  factors; deduct 1 point for forgetting the factor of 2)**

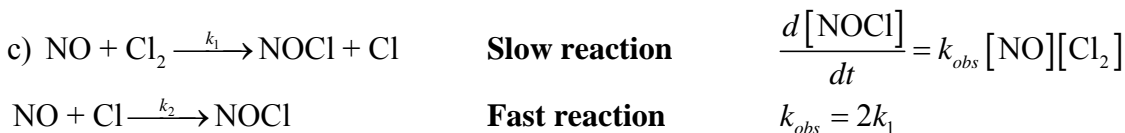
**(2 points: reaction 1 as slow)**

**(2 points: reaction 2 as fast)**

The rate law for the first elementary reaction is  $\text{rate} = k_1[\text{NO}]^2$ . Since the rate law for the first step is the same as the overall reaction, we can say that the first step is the rate-limiting step and must be the slow step. Similar to part a), we produce two NOCl per reaction, so we need to include the factor of 2.

**You may also award full credit for using the steady state approximation to obtain the same overall rate constant. Remember though, you would have to start off with**

$$\frac{1}{2} \frac{d[\text{NOCl}]}{dt} = k_2 [\text{N}_2\text{O}_2] [\text{Cl}_2]$$



**(2 points:  $k_{\text{obs}}$ , deduct 1 point for forgetting the factor of 2)**

**(2 point: reaction 1 as slow)**

**(2 point: reaction 2 as fast)**

Same reason as part (b). It's a little more subtle that two NOCl are produced (since it's listed twice), but it's true!

**You may also award full credit for using the steady state approximation to obtain the same overall rate constant.**

**3. Determine Reaction Order (22 points)**

a) Partial pressure is proportional to concentration. Since we will only analyze ratios of partial pressures, we do not need to find the constant of proportionality

Experiments #1–3 all occur at the same partial pressure of hydrogen.

- Looking at experiments #3 and #2, the initial rate quadruples when the partial pressure of NO doubles. This fact suggests the reaction is second order in NO.  
(2 points total: 1 pt for  $p_{\text{NO}}^2$ , 1 pt any reasonable justification)
- Verify by looking at experiments #2 and #1. When the partial pressure increases by a factor of 1.2, the rate should increase by  $(1.2)^2 = 1.44$ , which it does.

Experiments #4–6 all occur at the same partial pressure of nitrous oxide (NO).

- Looking at experiments #6 and #4, the initial rate doubles when the hydrogen concentration doubles. This fact suggest the reaction if first order in hydrogen.  
(2 points total: 1 point for  $p_{\text{H}_2}^1$ , 1 pt any reasonable justification)
- Verify by looking at experiments #5 and #6. When the concentration increases by ~33%, the initial rate also increases by ~33%.

Therefore, the rate law has the form:

$$\frac{dp_{\text{N}_2}}{dt} = k p_{\text{NO}}^2 p_{\text{H}_2} \quad (1 \text{ pt for final answer})$$

b) Since the reaction is a decomposition, only [NOBr] will appear in the rate law,

$$-\frac{d[\text{NOBr}]}{dt} = k[\text{NOBr}]^m,$$

where  $m$  is the unknown order of the reaction.

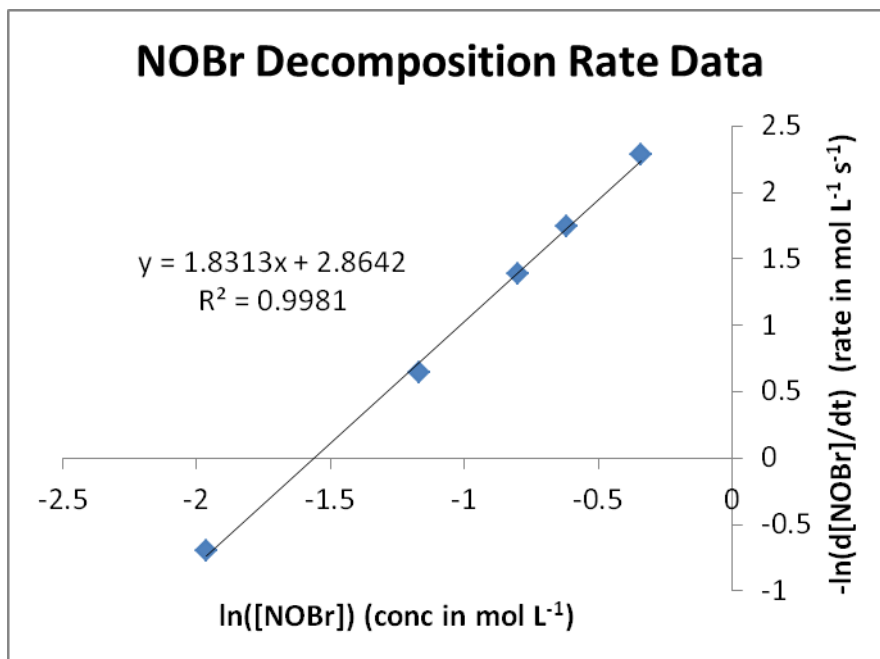
Take the natural logarithm of both sides,

$$\ln\left(-\frac{d[\text{NOBr}]}{dt}\right) = \ln(k) + m \ln([\text{NOBr}]) \quad (1 \text{ point})$$

First, convert our data into  $\ln([\text{NOBr}])$  and  $\ln\left(-\frac{d[\text{NOBr}]}{dt}\right)$ . By doing this, we can

generate a plot of  $\ln\left(-\frac{d[\text{NOBr}]}{dt}\right)$  vs.  $\ln([\text{NOBr}])$  that will be linear. Performing linear

regression gives us the slope (order of the reaction) and intercept (rate constant). You may do these in any program; this solution uses Excel 2010. (2 points for plot)



Using the LINEST function on Excel, we obtain a slope of  $m=1.83\pm0.05$  and an intercept of  $\ln(k)=2.86\pm0.05$  (and therefore  $k=17 \text{ L}^{0.83} \text{ mol}^{-0.83} \text{ s}^{-1}$ ). The rate law would be

$$-\frac{d[\text{NOBr}]}{dt} = (17 \text{ L}^{0.83} \text{ mol}^{-0.83} \text{ s}^{-1}) [\text{NOBr}]^{1.83}$$

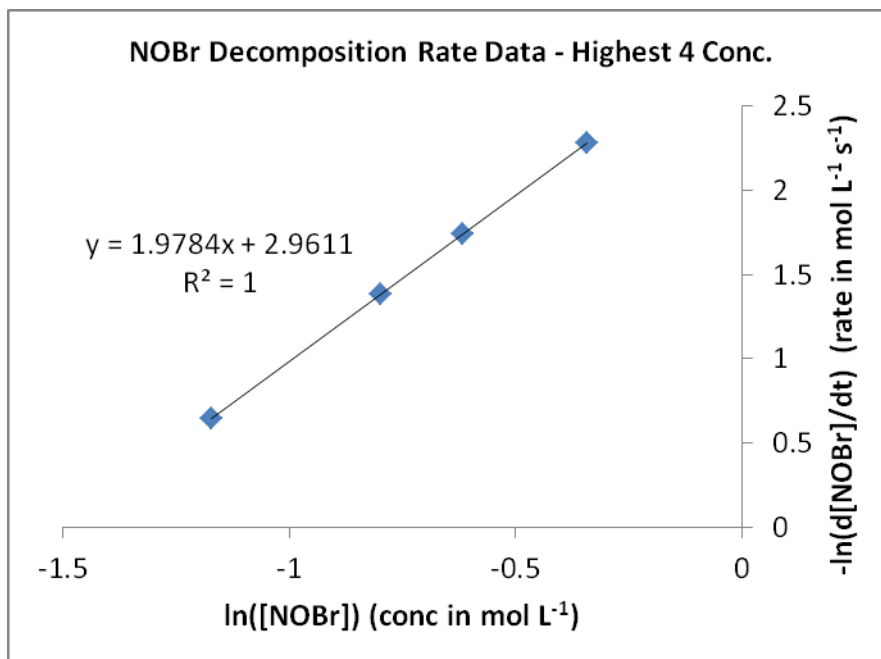
(3 points for regression. No need to plug in a numerical value of  $k$ . Sigfigs are ambiguous because of the regression, so we'll accept anything reasonable. You would really need more advanced error analysis to figure this out)

Ever hear of a decomposition reaction involving 1.83 molecules? No? I haven't either. Is the reaction order really 1.83? Or could it be something else?

The curve fit looks good; so the unexpected value for the slope (and the reaction order) is not caused by a calculation error.

The reaction order is very likely something else. At best you'll be measuring to the nearest half-order (1.5 or 2.0). (You can end up with half order reactions from more complicated mechanisms with multiple intermediate elementary reactions or three-body steps.) You can immediately see one of the main issues using concentration data – you need a lot of experiments and you need a measurement of uncertainty (error bars) to get a more realistic estimate.

The uncertainty in the concentration (error bars along the x-axis) and the uncertainty in the rate (error bars along the y-axis) are often largest at small concentrations. (By our sigfig rules, the lowest concentration point would have 6% error on the conc.) Let's eliminate the point at the smallest concentration and do the linear regression again.



Now when we use LINEST, we obtain a slope of  $m=1.98\pm0.01$  and an intercept of  $\ln(k)=2.96\pm0.01$ , or  $k=19 \text{ L mol}^{-1} \text{ s}^{-1}$ . Not only are the standard errors much lower, we essentially have a physically reasonable order for the reaction (2 with respect to NOBr).

Based on this analysis, we *hypothesize* that the *reaction is second order with respect to NOBr* and that

$$-\frac{d[\text{NOBr}]}{dt} = (19 \text{ L mol}^{-1} \text{ s}^{-1})[\text{NOBr}]^2$$

but we should perform additional experiments and pose a mechanism to confirm the hypothesis.

(1 point for recognizing that the reaction order is probably NOT 1.83)

(1 point for throwing out the lowest concentration and providing any reasonable explanation)

(2 points for repeating the regression and obtaining an order of 2. No need for an actual numerical value of  $k$ . Sigfigs are ambiguous because of the regression, so we'll accept anything reasonable. You would really need more advanced error analysis to figure this out)

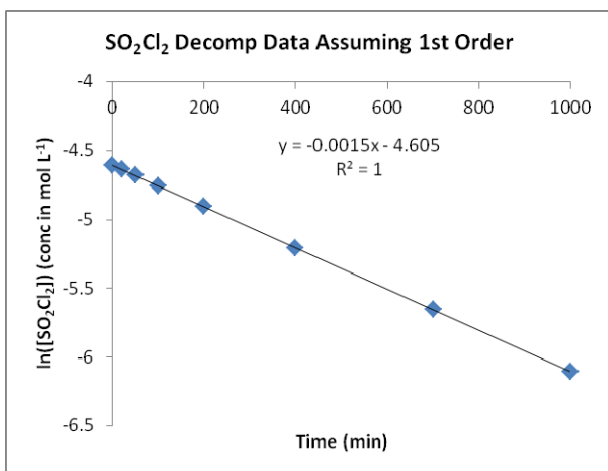
c) The integrated first-order rate equation is:

$$[\text{SO}_2\text{Cl}_2] = [\text{SO}_2\text{Cl}_2]_0 e^{-kt}, \text{ (OGC6, Equation [18.2], p.758) (1 point)}$$

If the decomposition is first order, a plot of  $\ln([\text{SO}_2\text{Cl}_2])$  vs.  $t$  will be linear with a slope of  $-k$  and an intercept of  $\ln([\text{SO}_2\text{Cl}_2]_0)$ .

(2 points for plot, no need for any regression,  $R^2$ , or other statistics. They are provided for informational purposes only)





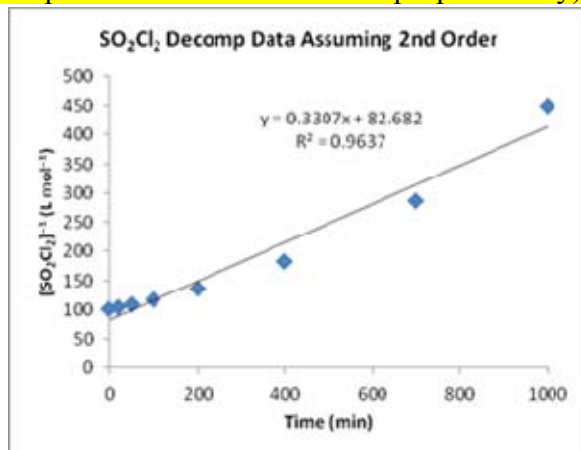
Our fit gives us  $k = 1.5 \times 10^{-3} \pm 3.8 \times 10^{-7} \text{ min}^{-1}$  and  $[\text{SO}_2\text{Cl}_2]_0 = 0.0100 \pm 0.0001 \text{ M}$ . Very good agreement!

The integrated second-order rate equation is:

$$\frac{1}{[\text{SO}_2\text{Cl}_2]} = \frac{1}{[\text{SO}_2\text{Cl}_2]_0} + 2kt, \text{ (OGC6, Equation [18.4]) (1 point)}$$

(If you're wondering about that 2 in front of the  $kt$ , it's because in order to have a second order decomposition, you necessarily need two SO<sub>2</sub>Cl<sub>2</sub> molecules...)

If the decomposition is second order, a plot of  $[\text{SO}_2\text{Cl}_2]^{-1}$  vs.  $t$  will be linear with a slope of  $2k$  and an intercept of  $[\text{SO}_2\text{Cl}_2]_0^{-1}$ . (2 points for plot, no need for any regression,  $R^2$ , or other statistics. They are provided for informational purposes only)



This “fit” gives us a rate constant of  $k = (0.17 \pm 0.01) \text{ L mol}^{-1} \text{ s}^{-1}$  and  $[\text{SO}_2\text{Cl}_2]_0$  of  $(0.012 \pm 0.002) \text{ M}$ . You should use the term “fit” loosely: the data certainly are not linear! Again, sigfigs are ambiguous because of the regression. You would really need more advanced error analysis to figure this out

Whether you quantitatively went through the statistics or qualitatively looked at the plots, you should draw the same conclusion: **the reaction is first order in SO<sub>2</sub>Cl<sub>2</sub>**. (1 pt for this conclusion)

**4. Thermal Decomposition of Cycloalkanes (20 points)**

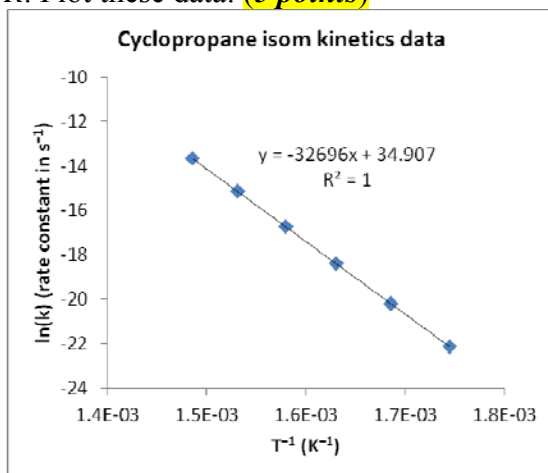
a) The Arrhenius Equation is

$$k = A \exp \left[ \frac{-E_a}{RT} \right].$$

(OGN5: Equation [13.5]; OGC6: Equation [18.5]; Parsons p. 54)

Take the natural log of both sides,

$$\ln[k] = \ln[A] - \frac{E_a}{RT}.$$

(OGN5, Equation [13.6]; OGC6: Equation [18.6]) **(1 point)**A plot of  $\ln(k)$  vs.  $1/T$  (after converting temperature to Kelvin) will have an intercept of  $\ln(A)$  and a slope of  $E_a/R$ . Plot these data: **(5 points)**Performing linear regression, we obtain a slope of  $(-32696 \pm 3)$  K and an intercept of  $(34.907 \pm 0.006)$ . (With such small errors, the sigfigs in our final answers will be limited by our initial data).

Use these values to obtain the activation energy and Arrhenius pre-factor.

$$m = -\frac{E_a}{R} \longrightarrow E_a = -mR,$$

$$E_a = -(-32696 \text{ K}) \left( 8.31447 \times 10^{-3} \frac{\text{kJ}}{\text{mol} \times \text{K}} \right),$$

$$E_a = 272 \text{ kJ mol}^{-1} \text{. (2 points, no credit for incorrect units or sigfigs)}$$

$$A = \exp[\text{intercept}] = \exp[34.907] = 1.45 \times 10^{15} \text{ s}^{-1}$$

**(2 points, no credit for incorrect sigfigs or units)**

b) Using the Arrhenius Equation:

$$k_{350^\circ\text{C}} = (1.45 \times 10^{15} \text{ s}^{-1}) \exp \left[ \frac{-32696 \text{ K}}{623 \text{ K}} \right] = 2.34 \times 10^{-8} \text{ s}^{-1}$$

The half-life of a reaction is defined as the time it takes for half of the reactants to be left over. Define cyclopropane to be  $(\text{CH}_2)_3$ . We are dealing with a unimolecular reaction, so the differential and integrated rate laws are

$$\frac{d[(\text{CH}_2)_3]}{dt} = -k[(\text{CH}_2)_3]$$

$$\ln \left( \frac{[(\text{CH}_2)_3]}{[(\text{CH}_2)_3]_{t=0}} \right) = -kt$$

If we then rearrange the integrated rate law, we can determine the time at which we obtain a certain concentration of the cyclopropane.

$$t = \frac{1}{k} \ln \left( \frac{[(\text{CH}_2)_3]_{t=0}}{[(\text{CH}_2)_3]_t} \right)$$

For the half-life, our equation reduces to (you may simply use this expression from OGC)

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{2.34 \times 10^{-8} \text{ s}^{-1}} = 2.96 \times 10^7 \text{ s}$$

**(2 pts equation, 3 points answer, no credit for an answer with incorrect units or sigfigs)**

c)  $k$  at  $400^\circ\text{C} = 1.15 \times 10^{-6} \text{ s}^{-1}$  (given in data table)

30.0000% completion means that fraction 0.700000 of cyclopropane is left. We already derived an equation to use, so simply use it again.

$$t = \frac{\ln \frac{1}{0.700000}}{k} = \frac{\ln \frac{1}{0.700000}}{1.15 \times 10^{-6} \text{ s}^{-1}} = 3.10 \times 10^5 \text{ s}$$

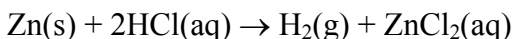
**(2 pts equation, 3 points answer, no credit for an answer with incorrect units or sigfigs)**

**5. Electrode Potentials (15 points)**

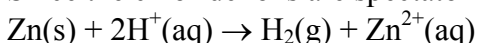
a) The standard electrode potential for zinc is less than that of hydrogen but the standard electrode potential for copper is greater than that of hydrogen. OR zinc is a reducing agent and copper is an oxidizing agent. OR any other valid and simple reason. **(6 points)**

Side Note: The following analysis is definitely not required and is meant for instructional purposes:

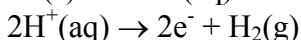
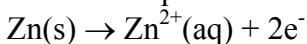
The balanced chemical reaction between zinc and hydrochloric acid:



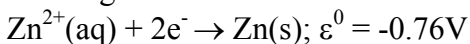
Since the chloride ions are spectator ions,



From this equation we find the ionic half-equations,

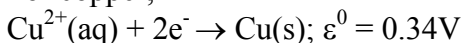


Relating these to the standard electrode potentials that were presented in lecture,



Electrons flow from the half-cell with the more negative potential to the other half-cell; so zinc metal is oxidized and hydrogen ions are reduced.

For copper,



Electrons flow from the half-cell with the more negative potential to the other half-cell. Electrons flow the wrong direction to reduce hydrogen ions into hydrogen gas.

b) Magnesium **(2 points)**

Same reasoning as part (a). Magnesium has a standard electrode potential that is less than that of iron while lead has a standard electrode potential that is greater than that of iron. Since magnesium has a more negative electrode potential, it will give up its electrons more easily than iron. **(2 points)**

c) Calcium tends to react at a *slower rate* than the other metals having similar electrode potential. This is because in order to react, because in displacement reactions (for example), two electrons must be removed from Ca, whereas only one must be removed from Na. **(5 points)**