

Complete the following individually. You may use your textbook and notes, but may not receive assistance from your classmates or anyone other than Dr. Lamp. This signed statement must accompany the completed assignment. By signing below, you certify that you completed the problems in accordance with these rules. No credit will be given to unsigned papers. Staple any additional sheets prior to turning the assignment in.

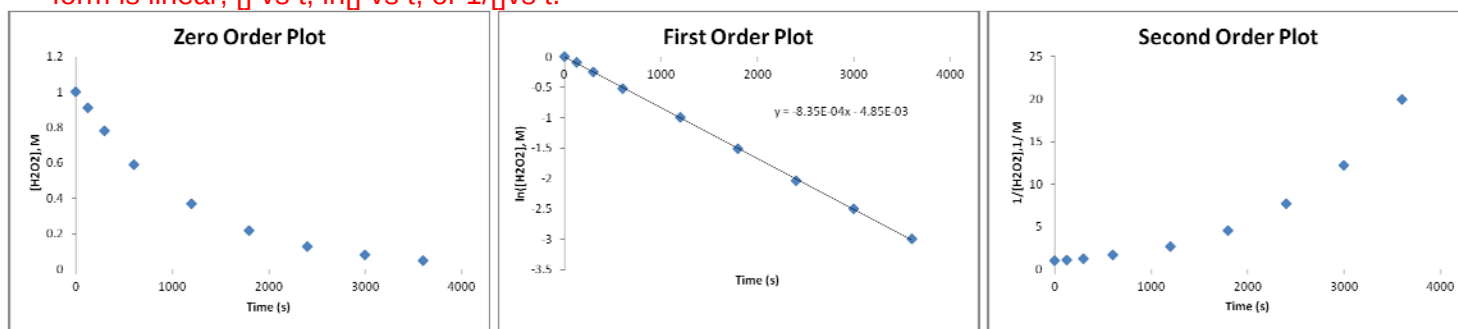
Signature _____ Date _____

Complete the following problems. **You must show your work to receive full credit.** Show your answers to the correct number of significant figures with the correct units.

- The decomposition of hydrogen peroxide was studied at a particular temperature, and the data below were obtained. Determine the order of reaction in H_2O_2 and the rate constant. If you use a spreadsheet, attach any plots or spreadsheet output. (9 pts)

Time (s)	$[\text{H}_2\text{O}_2]$ (M)	$\ln [\text{H}_2\text{O}_2]$	$1/[\text{H}_2\text{O}_2]$
0	1	0	1
121	0.91	-0.09431	1.098901
299	0.78	-0.24846	1.282051
601	0.59	-0.52763	1.694915
1201	0.37	-0.99425	2.702703
1799	0.22	-1.51413	4.545455
2399	0.13	-2.04022	7.692308
3001	0.082	-2.50104	12.19512
3601	0.05	-2.99573	20

To determine the reaction order, we plot the three forms of the integrated rate law and determine which form is linear, $[\text{A}]$ vs t , $\ln[\text{A}]$ vs t , or $1/[\text{A}]$ vs t .



From the plots, it is clear that the plot of $\ln[\text{H}_2\text{O}_2]$ versus time is linear. Since the integrated rate law is in the form: $\ln[\text{H}_2\text{O}_2]_t = -kt + \ln[\text{H}_2\text{O}_2]_0$, the slope of the line is $-k$. From the trendline, the slope is $-8.34 \times 10^{-4} \text{ s}^{-1}$, therefore the value for the rate constant is $k = 8.34 \times 10^{-4} \text{ s}^{-1}$ for this first-order reaction.

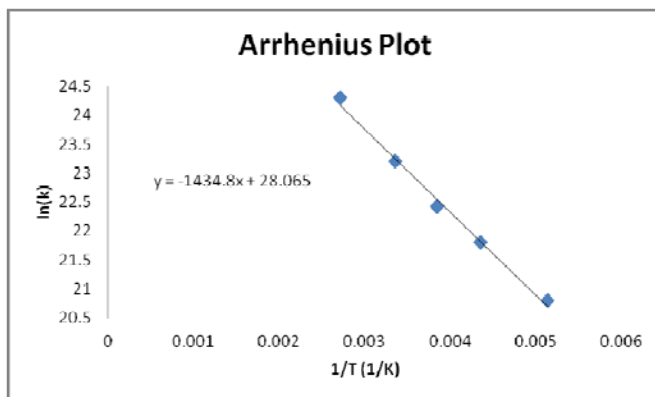
2. Experimental values for the temperature dependence of the rate constant for the gas phase reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ are shown below. Determine the activation energy and the frequency factor for this reaction. If you use a spreadsheet, attach any plots or spreadsheet output. (8 pts)

T (°C)	k (L mol ⁻¹ s ⁻¹)	1/T (1/K)	lnk
-78.1	1.08 × 10 ⁹	0.005127	20.80023
-43.2	2.95 × 10 ⁹	0.004349	21.80507
-12.9	5.42 × 10 ⁹	0.003842	22.41336
25.0	12.0 × 10 ⁹	0.003354	23.20817
96.1	35.5 × 10 ⁹	0.002708	24.2928

Here we can take advantage of the linearized form of the Arrhenius equation:

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

If we plot $\ln k$ as a function of $1/T$, we expect a line with slope of $-E_a/R$ and intercept of $\ln A$. It is important that we convert temperatures to Kelvin first!



From the plot, we find the slope is -1434.8 K^{-1} , so the activation energy is:

$$E_a = -\text{slope}/R = -(-1434 \text{ K}^{-1}/8.1345 \text{ Jmol}^{-1}\text{K}^{-1}) = 11,930 \text{ Jmol}^{-1} \text{ or } \mathbf{11.9 \text{ kJmol}^{-1}}$$

The frequency factor, A , comes from the intercept, 28.065. Since the intercept is equal to $\ln A$,

$$A = e^{\text{intercept}} = e^{28.065} = \mathbf{1.54 \times 10^{12} \text{ M}^{-1}\text{s}^{-1}}$$

You may also have chosen to take the two-point approach, shown in equation 14.22 in your book. This allows you to calculate E_a based on any two rate constants measured at two temperatures. If you took this approach, your E_a and A values will vary slightly from those above, but should be of the same order of magnitude.

3. The reaction $2\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}$ exhibits the rate law: $\text{Rate} = k[\text{CO}]^2[\text{O}_2]$. Two proposed mechanisms for this reaction are listed below. Determine if one, both, or neither mechanisms are consistent with this rate law. Justify your answer. (8 pts)

<u>Mechanism 1:</u>	<u>Mechanism 2</u>
Step 1: $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$ (slow)	Step 1: $\text{CO} + \text{O}_2 \rightleftharpoons \text{CO}_3$ (fast equilibrium)
Step 2: $\text{O} + \text{CO} \rightarrow \text{CO}_2$ (fast)	Step 2: $\text{CO}_3 + \text{CO} \rightarrow 2\text{CO}_2$ (slow)

For mechanism 1, since the slow step is the first step in the reaction, any subsequent steps will not contribute to the rate law. Therefore we can write the overall rate law as the rate law for the slow first step:

$$\text{Rate} = k[\text{CO}][\text{O}_2]$$

Since this does not correspond to the experimentally-determined rate law, we conclude that the proposed mechanism is not consistent with the reaction.

For mechanism 2, we start by writing the rate law for the slow step:

$$\text{Rate} = k_2[\text{CO}_3][\text{CO}]$$

Since CO_3 is an intermediate, we need to find a way to get its concentration in terms of reactants and/or products. Since step 1 is a fast equilibrium, we take advantage of the fact that at equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction:

$$k_1[\text{CO}][\text{O}_2] = k_{-1}[\text{CO}_3]$$

We now rearrange to solve for $[\text{CO}_3]$

$$[\text{CO}_3] = k_1[\text{CO}][\text{O}_2]/k_{-1}$$

Plugging in to the rate law for the second elementary step (the slow step):

$$\text{Rate} = k_2[\text{CO}_3][\text{CO}] = k_2(k_1[\text{CO}][\text{O}_2]/k_{-1})[\text{CO}] = (k_2k_1/k_{-1})[\text{CO}]^2[\text{O}_2] = k[\text{CO}]^2[\text{O}_2]$$

So, the rate law for this mechanism is $\text{Rate} = k[\text{CO}]^2[\text{O}_2]$, which is consistent with the experimentally-determined rate law. Therefore, mechanism 2 is a plausible mechanism for this reaction.

Possibly Useful Information

$k = Ae^{-E_a/RT}$	$\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$	$R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ $R = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$
$\text{rate} = k[\text{A}]^1$	$[\text{A}]_t = -kt + [\text{A}]_0$	$t_{1/2} = [\text{A}]_0/2k$
$\text{rate} = k[\text{A}]^2$	$\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$	$t_{1/2} = 1/(k[\text{A}]_0)$
$\text{rate} = k[\text{A}]^0$	$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0}$	$t_{1/2} = 0.693/k$