1. The following graphs show reactant concentration as a function of time for reactions of the type Reactant $\rightarrow$ Product.

![Graphs](image)

a. What can you conclude about the rate of reaction in graph (a)? **Rate = 0** How do you know?
b. What can you conclude about the reaction order in of the reaction in graph (b)? **Zero order.** How do you know?
c. What can you conclude about the reaction order in of the reaction in graph (c)? **1st or 2nd order (would need to do a ln [Reactant] vs. time plot to distinguish between 1st and 2nd order).** How do you know?

2. For a reaction of the type R $\rightarrow$ P, it is found that when the concentration of reactant (R) is doubled, the rate increases by a factor of eight. What is the rate law for this reaction? **Rate = $k$ [Reactant]$^3$** (Note: A reaction order of 3 is very unlikely—can you think of a reason why?)

3. A past issue of *Scientific American* contains an article about the cleanup of radioactive waste at Hanford. According to the article, some of the waste is stored in containers that were designed to last for 25 years. The containers hold, among other things, radioactive Uranium, which decays following first order kinetics with a rate constant of $8.66 \times 10^{-4}$ yr$^{-1}$.

   a. What is the half life of this radioactive isotope? **8.00 x 10$^2$ years**
   b. How long will it take for the 90% of the Uranium to decompose? **2658 years** Will the tanks last this long? ☹

4. The redox reaction between KI and NaClO is first order with respect to both KI and NaClO.

   \[
   \text{KI}_{(aq)} + \text{NaClO}_{(aq)} \rightarrow \text{NaIO}_{(aq)} + \text{KCl}_{(aq)}
   \]

   Use the following data collected at 25 °C to answer the questions that follow. Be careful! These are volumes, *not* concentrations. Clearly show your work and explain your reasoning!

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Volume of 0.00100 M KI</th>
<th>Volume of 0.0250 M NaClO</th>
<th>Reaction time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75.0 mL</td>
<td>50.0 mL</td>
<td>25.0 s</td>
</tr>
<tr>
<td>2</td>
<td>150.0 mL</td>
<td>50.0 mL</td>
<td>40.0</td>
</tr>
<tr>
<td>3</td>
<td>75.0 mL</td>
<td>100.0 mL</td>
<td>17.5</td>
</tr>
</tbody>
</table>

a. As stated above, the reaction is first order with respect to both KI and NaClO. What is the rate law? **Rate = $k$ [KI] [NaClO]**

b. Assuming the reaction goes to completion, determine which reactant in trial #1 is limiting. **KI** (Show your work!!)

c. Calculate the rate of reaction in trial #1. **2.40 x 10$^{-5}$ M s$^{-1}$** (Show your work!!)

d. Use the data from trial #1 to calculate the rate constant for the reaction between KI and NaClO. **$k = 4.00 \text{ M}^{-1}\text{s}^{-1}$** (Show your work!!)

e. Calculate the reaction time for trial #2. **40.0 s** (Show your work!!)

f. Calculate the reaction time for trial #3. **17.5 s** (Show your work!!)
5. The decomposition of N\textsubscript{2}O takes place on the surface of a metal catalyst and is a zero\textsuperscript{th} order reaction. The reaction rate is 1.40 x 10\textsuperscript{-4} M/s at 300. K. How long will it take for the concentration of N\textsubscript{2}O to drop from 0.800 M to 0.200 M?

\[ t = 4286 \text{ s or 1.19 hr} \] (Show your work!!)

6. In the Iodine clock reaction, why does increasing the concentration of the thiosulfate ion (S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}), increase the time required for the solution to turn black?

7. The rate constant for the reaction: NO + O\textsubscript{3} \rightarrow NO\textsubscript{2} + O\textsubscript{2} is measured at a variety of temperatures. Below is a plot of ln k vs. 1/T for this reaction.

\[ \text{Ink vs. } 1/T \]
\[ y = -1435.7x + 28.071 \]
\[ R^2 = 0.9941 \]

\[ \begin{array}{cccc}
\text{1/T (K^{-1})} & 0.00200 & 0.00300 & 0.00400 & 0.00500 & 0.00600 \\
\text{ln k} & 25.0 & 24.0 & 23.0 & 22.0 & 21.0 \\
\end{array} \]

a. Determine the activation energy for the reaction in kJ/mol. **11.94 kJ/mol** (Show your work!!)

b. The reaction is exothermic with a ΔH of -65 kJ/mol. Use this information and your answer from part a to draw a reaction coordinate diagram for this reaction.

8. What is the importance of understanding the mechanism of a chemical reaction? Why isn’t it enough to know just the balanced equation (i.e. the relationship between reactants and products.) to determine the rate law of a reaction?

9. The following mechanism is proposed for the reaction between NO\textsubscript{2} and CO:

\[
\begin{align*}
2 \text{ NO}_2(g) & \rightarrow \text{ NO}_3(g) + \text{ NO}(g) \quad \text{slow} \\
\text{NO}_3(g) + \text{ CO}(g) & \rightarrow \text{ NO}_2(g) + \text{ CO}_2(g) \quad \text{fast}
\end{align*}
\]

a. What is the balanced chemical equation for the reaction? **NO\textsubscript{2}(g) + CO(g) \rightarrow NO(g) + CO\textsubscript{2}(g)**

b. What rate law would be expected base on this mechanism? *Explain.* **Rate = k [NO\textsubscript{2}]^2**

c. What chemical species (if any) are reaction intermediates? **NO\textsubscript{3}**

d. Refer to the first step in the reaction mechanism. Draw the Lewis structure for NO\textsubscript{2} and think about how the molecules would have to collide in order for the collision to be effective (i.e. to produce the indicated products). Make a sketch showing the possible orientation of the molecules as they collide.

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10. For the reaction: \(2 \text{NO}_2(g) \rightarrow 2 \text{NO}(g) + \text{O}_2(g)\) each of the following curves corresponds to one of the species in the reaction shown above. Which curve represents the time dependence of the concentration of \(\text{O}_2\)? NO? \(\text{NO}_2\)?

A = __________________________
B = __________________________
C = __________________________

11. For the reaction:

\[
\text{BrO}_3^-(aq) + 5\text{Br}^-(aq) + 6\text{H}^+(aq) \rightarrow 3\text{Br}_2(l) + 3\text{H}_2\text{O}(l)
\]

The following initial rate data were obtained:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>([\text{BrO}_3^-]_0)</th>
<th>([\text{Br}^-]_0)</th>
<th>([\text{H}^+]_0)</th>
<th>Initial Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10M</td>
<td>0.10M</td>
<td>0.10M</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.20M</td>
<td>0.10M</td>
<td>0.10M</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>0.20M</td>
<td>0.20M</td>
<td>0.10M</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>0.10M</td>
<td>0.10M</td>
<td>0.20M</td>
<td>4</td>
</tr>
</tbody>
</table>

Which of the following rate laws is correct? The 2nd rate law (“B”) is correct. **Explain your reasoning.**

A. Rate = \(k[\text{BrO}_3^-]^1[\text{Br}^-]^2[\text{H}^+]^1\)

B. Rate = \(k[\text{BrO}_3^-]^1[\text{Br}^-]^1[\text{H}^+]^2\)

12. Which graph best describes the following reaction if it is first order in \(\text{N}_2\text{O}_4\)? Graph “C” is correct. **Explain your reasoning.**

\[
\text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g)
\]
13. The diagram below shows Arrhenius plots for two chemical reactions. Which reaction has the larger activation energy? **Reaction “B” has the larger $E_a$.**  *Explain your reasoning.*

14. The rate law for the reaction: $2 \text{NO}_2(g) + \text{F}_2(g) \rightarrow 2 \text{NO}_2\text{F}(g)$ is $\text{Rate} = k[\text{NO}_2][\text{F}_2]$. Which of the following mechanisms is consistent with this rate law? **Mechanism “b” is correct.**  *Explain your reasoning.*

a.) $\text{NO}_2(g) + \text{F}_2(g) \rightleftharpoons \text{NO}_2\text{F}(g) + \text{F}(g)$ (fast equilibrium)
$\text{NO}_2(g) + \text{F}(g) \rightarrow \text{NO}_2\text{F}(g)$ (slow)

b.) $\text{NO}_2(g) + \text{F}_2(g) \rightleftharpoons \text{NO}_2\text{F}(g) + \text{F}(g)$ (slow equilibrium)
$\text{NO}_2(g) + \text{F}(g) \rightarrow \text{NO}_2\text{F}(g)$ (fast)

c.) $\text{F}_2(g) \rightleftharpoons \text{F}(g) + \text{F}(g)$ (slow equilibrium)
$2 \text{NO}_2(g) + 2 \text{F}(g) \rightarrow 2 \text{NO}_2\text{F}(g)$ (fast)

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**Appendix**

**Integrated Rate Laws:**

<table>
<thead>
<tr>
<th>Reaction Order</th>
<th>Integrated Rate Law</th>
<th>Integrated Rate Law in the form $y = mx + b$</th>
<th>Half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>$[A]_o - [A]_t = kt$</td>
<td>$[A]_t = -kt + [A]_o$</td>
<td>$t_{1/2} = \frac{[A]_o}{2k}$</td>
</tr>
<tr>
<td>1$^{st}$</td>
<td>$Ln \frac{[A]_o}{[A]_t} = kt$</td>
<td>$Ln[A]_t = -kt + Ln[A]_o$</td>
<td>$t_{1/2} = \frac{Ln2}{k}$</td>
</tr>
<tr>
<td>2$^{nd}$</td>
<td>$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$</td>
<td>$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$</td>
<td>$t_{1/2} = \frac{1}{k[A]_o}$</td>
</tr>
</tbody>
</table>

$k = A e^{-\frac{E_a}{RT}}$  
$f = e^{-\frac{E_a}{RT}}$  
$R = 8.314 \frac{J}{\text{mol K}} = 0.0821 \frac{\text{L atm}}{\text{mol K}}$

$Ln k = Ln A - \frac{E_a}{RT}$  
$or$  
$Ln \left( \frac{k_2}{k_1} \right) = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$  
$or$  
$Ln \left( \frac{k_1}{k_2} \right) = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$