CHAPTER TWELVE

CHEMICAL KINETICS

Questions

9. The rate of a chemical reaction varies with time. Consider the general reaction:

\[ \text{A} \rightarrow \text{Products} \text{ where rate} = \frac{-\Delta [\text{A}]}{\Delta t} \]

If we graph [A] vs. t, it would roughly look like the dark line in the following plot.

An instantaneous rate is the slope of a tangent line to the graph of [A] vs. t. We can determine the instantaneous rate at any time during the reaction. On the plot, tangent lines at \( t = 0 \) and \( t = t_1 \) are drawn. The slope of these tangent lines would be the instantaneous rates at \( t = 0 \) and \( t = t_1 \). We call the instantaneous rate at \( t = 0 \) the initial rate. The average rate is measured over a period of time. For example, the slope of the line connecting points a and c is the average rate of the reaction over the entire length of time 0 to \( t_1 \) (average rate = \( \Delta [A]/\Delta t \)). An average rate is determined over some time period while an instantaneous rate is determined at one specific time. The rate which is largest is generally the initial rate. At \( t = 0 \), the slope of the tangent line is greatest, which means the rate is largest at \( t = 0 \).

10. a. An elementary step (reaction) is one in which the rate law can be written from the molecularity, i.e., from the coefficients in the balanced equation.
b. The mechanism of a reaction is the series of proposed elementary reactions that may occur to give the overall reaction. The sum of all the steps in the mechanism gives the balanced chemical reaction.

c. The rate-determining step is the slowest elementary reaction in any given mechanism.

11. a. The greater the frequency of collisions, the greater the opportunities for molecules to react, and, hence, the greater the rate.

b. Chemical reactions involve the making and breaking of chemical bonds. The kinetic energy of the collisions can be used to break bonds. So, as the kinetic energy of the collisions increases, the rate increases.

c. For a reaction to occur, it is the reactive portion of each molecule that must be involved in a collision. Only some of all the possible collisions have the correct orientation to convert reactants to products.

12. In a unimolecular reaction, a single reactant molecule decomposes to products. In a bimolecular reaction, two molecules collide to give products. The probability of the simultaneous collision of three molecules with enough energy and orientation is very small, making termolecular steps very unlikely.

13. A catalyst increases the rate of a reaction by providing reactants with an alternate pathway (mechanism) to convert to products. This alternate pathway has a lower activation energy, thus increasing the rate of the reaction.

A heterogeneous catalyst is in a different phase than the reactants. The catalyst is usually a solid, although a catalyst in a liquid phase can act as a heterogeneous catalyst for some gas phase reactions. Since the catalyzed reaction has a different mechanism than the uncatalyzed reaction, the catalyzed reaction most likely will have a different rate law.

14. Some energy must be added to get the reaction started, that is, to overcome the activation energy barrier. Chemically what happens is:

$$\text{Energy} + \text{H}_2 \rightarrow 2 \text{H}$$

The hydrogen atoms initiate a chain reaction that proceeds very rapidly. Collisions of $\text{H}_2$ and $\text{O}_2$ molecules at room temperature do not have sufficient kinetic energy to form hydrogen atoms and initiate the reaction.

15. a. Activation energy and $\Delta E$ are independent of each other. Activation energy depends on the path reactants to take to convert to products. The overall energy change, $\Delta E$, depends only on the initial and final energy states of the reactants and products. $\Delta E$ is path independent.

b. The rate law can be determined only from experiment, not from the overall balanced reaction.

c. Most reactions occur by a series of steps. The rate of the reaction is determined by the rate of the slowest step in the mechanism.
16. All of these choices would affect the rate of the reaction, but only b and c affect the rate by affecting the value of the rate constant $k$. The value of the rate constant is dependent on temperature. The value of the rate constant also depends on the activation energy. A catalyst will change the value of $k$ because the activation energy changes. Increasing the concentration (partial pressure) of either $H_2$ or NO does not affect the value of $k$, but it does increase the rate of the reaction because both concentrations appear in the rate law.

**Exercises**

**Reaction Rates**

17. The coefficients in the balanced reaction relate the rate of disappearance of reactants to the rate of production of products. From the balanced reaction, the rate of production of $P_4$ will be $1/4$ the rate of disappearance of $PH_3$, and the rate of production of $H_2$ will be $6/4$ the rate of disappearance of $PH_3$. By convention, all rates are given as positive values.

$$\text{Rate} = -\frac{\Delta [PH_3]}{\Delta t} = \frac{(0.0048 \text{ mol/L} \cdot 2.0 \text{ L})}{s} = 2.4 \times 10^{-3} \text{ mol/L} \cdot \text{s}$$

$$\frac{\Delta [P_4]}{\Delta t} = -\frac{1}{4} \frac{\Delta [PH_3]}{\Delta t} = 2.4 \times 10^{-3}/4 = 6.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}$$

$$\frac{\Delta [H_2]}{\Delta t} = -\frac{6}{4} \frac{\Delta [PH_3]}{\Delta t} = 6(2.4 \times 10^{-3})/4 = 3.6 \times 10^{-3} \text{ mol/L} \cdot \text{s}$$

18. $\frac{\Delta [H_2]}{\Delta t} = 3 \frac{\Delta [N_2]}{\Delta t}$ and $\frac{\Delta [NH_3]}{\Delta t} = -2 \frac{\Delta [N_2]}{\Delta t}$; So, $-\frac{1}{3} \frac{\Delta [H_2]}{\Delta t} = \frac{1}{2} \frac{\Delta [NH_3]}{\Delta t}$ or $\frac{\Delta [NH_3]}{\Delta t} = -\frac{2}{3} \frac{\Delta [H_2]}{\Delta t}$

Ammonia is produced at a rate equal to $2/3$ of the rate of consumption of hydrogen.

19. a. The units for rate are always mol/L$\cdot$ms.  
   b. Rate = $k$; $k$ must have units of mol/L$\cdot$ms.  
   c. Rate = $k[A]$, $\frac{\text{mol}}{\text{L} \cdot \text{s}} = k \left( \frac{\text{mol}}{\text{L}} \right)$  
   d. Rate = $k[A]^2$, $\frac{\text{mol}}{\text{L} \cdot \text{s}} = k \left( \frac{\text{mol}}{\text{L}} \right)^2$  
   e. L$^2$/mol$^2$·s

20. Rate = $k[Cl]^{1/2}[CHCl_3]$, $\frac{\text{mol}}{\text{L} \cdot \text{s}} = k \left( \frac{\text{mol}}{\text{L}} \right)^{1/2} \left( \frac{\text{mol}}{\text{L}} \right)$, $k$ must have units of L$^{1/2}$/mol$^{1/2}$·s.

**Rate Laws from Experimental Data: Initial Rates Method**
21. a. In the first two experiments, \([\text{NO}]\) is held constant and \([\text{Cl}_2]\) is doubled. The rate also doubled. Thus, the reaction is first order with respect to \([\text{Cl}_2]\). Or mathematically: 
\[\text{Rate} = k[\text{NO}] \cdot [\text{Cl}_2]^y\]

We can get the dependence on \(\text{NO}\) from the second and third experiments. Here, as the \(\text{NO}\) concentration doubles (\(\text{Cl}_2\) concentration is constant), the rate increases by a factor of four. Thus, the reaction is second order with respect to \(\text{NO}\). Or mathematically:

\[\frac{1.45}{0.36} = \frac{k(0.20)^{2}}{k(0.10)^{2}} = \frac{(0.20)^{2}}{(0.10)^{2}}, \quad 4.0 = 2.0^x, \quad x = 2; \quad \text{So, Rate} = k[\text{NO}]^2[\text{Cl}_2]^y\]

b. The rate constant \(k\) can be determined from the experiments. From experiment 1:

\[
\frac{0.18 \text{ mol}}{\text{L} \cdot \text{min}} = k \left( \frac{0.10 \text{ mol}}{\text{L}} \right)^2 \left( \frac{0.10 \text{ mol}}{\text{L}} \right), \quad k = 180 \text{ L}^2/\text{mol}^2 \cdot \text{min}
\]

From the other experiments:

\[k = 180 \text{ L}^2/\text{mol}^2 \cdot \text{min} \text{ (2nd exp.); } k = 180 \text{ L}^2/\text{mol}^2 \cdot \text{min} \text{ (3rd exp.)}\]

The average rate constant is \(k_{\text{mean}} = 1.8 \times 10^2 \text{ L}^2/\text{mol}^2 \cdot \text{min}\).

22. a. \(\text{Rate} = k[I]^x[S_2\text{O}_5^{2-}]\); 
\[
\frac{12.5 \times 10^{-6}}{6.25 \times 10^{-6}} = \frac{k(0.080)^y(0.040)^y}{k(0.040)^y(0.040)^y}, \quad 2.00 = 2.0^x, \quad x = 1
\]

b. For the first experiment:

\[
\frac{12.5 \times 10^{-6} \text{ mol}}{\text{L}s} = k \left( \frac{0.080 \text{ mol}}{\text{L}} \right) \left( \frac{0.040 \text{ mol}}{\text{L}} \right), \quad k = 3.9 \times 10^3 \text{ L/mol} \cdot \text{s}
\]

Each of the other experiments also gives \(k = 3.9 \times 10^3 \text{ L/mol} \cdot \text{s}\), so \(k_{\text{mean}} = 3.9 \times 10^3 \text{ L/mol} \cdot \text{s}\).

23. a. \(\text{Rate} = k[\text{NOCl}]^n\); Using experiments two and three:
b. \( \frac{5.98 \times 10^4 \text{ molecules}}{\text{cm}^3} = k \left( \frac{3.0 \times 10^4 \text{ molecules}}{\text{cm}^3} \right)^2 \), \( k = 6.6 \times 10^{-29} \text{ cm}^3/\text{molecules s} \)

The other three experiments give \((6.7, 6.6 \text{ and } 6.6) \times 10^{-29} \text{ cm}^3/\text{molecules s}, \) respectively.

The mean value for \( k \) is \( 6.6 \times 10^{-29} \text{ cm}^3/\text{molecules s} \).

c. \( \frac{6.6 \times 10^{-29} \text{ cm}^3}{\text{molecules s}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} \times \frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol}} = 4.0 \times 10^{-4} \text{ L/mol s} \)

24. Rate = \( k[N_2O_3] \); The rate laws for the first two experiments are:

\( 2.26 \times 10^{-3} = k(0.190)^x \) and \( 8.90 \times 10^{-4} = k(0.0750)^x \)

Dividing: \( 2.54 = \frac{(0.190)^x}{(0.0750)^x} = (2.53)^x \), \( x = 1 \); Rate = \( k[N_2O_3] \)

\( k = \frac{\text{Rate}}{[N_2O_3]} = \frac{8.90 \times 10^{-4} \text{ mol/L-s}}{0.0750 \text{ mol/L}} = 1.19 \times 10^{-2} \text{ s}^{-1} \); \( k_{\text{mean}} = 1.19 \times 10^{-2} \text{ s}^{-1} \)

25. a. Rate = \( k[Hb][CO] \); Comparing the first two experiments, [CO] is unchanged, [Hb] doubles, and the rate doubles. Therefore, the reaction is first order in Hb. Comparing the second and third experiments, [Hb] is unchanged, [CO] triples and the rate triples. Therefore, \( y = 1 \) and the reaction is first order in CO.

b. Rate = \( k[Hb][CO] \)

c. From the first experiment:

\( 0.619 \mu\text{mol/L-s} = k (2.21 \mu\text{mol/L})(1.00 \mu\text{mol/L}), \; k = 0.280 \text{ L/\mu mol\cdot s} \)

The second and third experiments give similar \( k \) values, so \( k_{\text{mean}} = 0.280 \text{ L/\mu mol\cdot s} \).

d. Rate = \( k[Hb][CO] = \frac{0.280 \text{ L}}{\mu\text{mol g}} \times \frac{3.36 \mu\text{mol}}{\text{L}} \times \frac{2.40 \mu\text{mol}}{\text{L}} = 2.26 \mu\text{mol/L\cdot s} \)

26. a. Rate = \( k[ClO_2^-][OH^-] \); From the first two experiments:

\( 2.30 \times 10^{-1} = k(0.100)^x(0.100)^y \) and \( 5.75 \times 10^{-2} = k(0.0500)^x(0.100)^y \)

Dividing the two rate laws: \( 4.00 = \frac{(0.100)^x}{(0.0500)^x} = 2.00^x \), \( x = 2 \)

Comparing the second and third experiments:
2.30 × 10^-3 = k(0.100)(0.100)^2 and 1.15 × 10^-3 = k(0.100)(0.0500)^2

Dividing: 2.00 = \frac{(0.100)^2}{(0.0500)^2} = 2.00, \quad y = 1

The rate law is: Rate = k[ClO_2]^2[OH^-]

2.30 × 10^-1 mol/L·s = k(0.100 mol/L)^2(0.100 mol/L), \quad k = 2.30 × 10^2 L^2/mol^2·s = k_{mean}

b. Rate = k[ClO_2]^2[OH^-] = \frac{2.30 × 10^2 L^2}{mol^2·s} \times \left( \frac{0.175 \text{ mol}}{L} \right)^2 \times \frac{0.0844 \text{ mol}}{L} = 0.594 \text{ mol/L·s}

Integrated Rate Laws

27. The first assumption to make is that the reaction is first order. For a first-order reaction, a graph of ln [H_2O_2] vs time will yield a straight line. If this plot is not linear, then the reaction is not first order and we make another assumption. The data and plot for the first-order assumption is below.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>H_2O_2 (mol/L)</th>
<th>ln [H_2O_2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00</td>
<td>0.000</td>
</tr>
<tr>
<td>120.</td>
<td>0.91</td>
<td>-0.094</td>
</tr>
<tr>
<td>300.</td>
<td>0.78</td>
<td>-0.25</td>
</tr>
<tr>
<td>600.</td>
<td>0.59</td>
<td>-0.53</td>
</tr>
<tr>
<td>1200.</td>
<td>0.37</td>
<td>-0.99</td>
</tr>
<tr>
<td>1800.</td>
<td>0.22</td>
<td>-1.51</td>
</tr>
<tr>
<td>2400.</td>
<td>0.13</td>
<td>-2.04</td>
</tr>
<tr>
<td>3000.</td>
<td>0.082</td>
<td>-2.50</td>
</tr>
<tr>
<td>3600.</td>
<td>0.050</td>
<td>-3.00</td>
</tr>
</tbody>
</table>

Note: We carried extra significant figures in some of the ln values in order to reduce round-off error. For the plots, we will do this most of the time when the ln function is involved.

The plot of ln [H_2O_2] vs. time is linear. Thus, the reaction is first order. The rate law and integrated rate law are: Rate = k[H_2O_2] and ln [H_2O_2] = -kt + ln [H_2O_2].

We determine the rate constant k by determining the slope of the ln [H_2O_2] vs time plot (slope = -k).

Using two points on the curve gives:

slope = -k = \frac{\Delta y}{\Delta x} = \frac{0 - (-3.00)}{3600 - 0} = -8.3 × 10^{-4} \text{ s}^{-1}, \quad k = 8.3 × 10^{-4} \text{ s}^{-1}

To determine [H_2O_2] at 4000. s, use the integrated rate law where at t = 0, [H_2O_2]_0 = 1.00 M.
\[
\ln [\text{H}_2\text{O}_2] = -kt + \ln [\text{H}_2\text{O}_2]_0 \quad \text{or} \quad \ln \left( \frac{[\text{H}_2\text{O}_2]}{[\text{H}_2\text{O}_2]_0} \right) = -kt
\]

\[
\ln \left( \frac{[\text{H}_2\text{O}_2]}{1.00} \right) = -8.3 \times 10^{-4} \text{ s}^{-1} \times 4000 \text{ s}, \quad \ln [\text{H}_2\text{O}_2] = -3.3, \quad [\text{H}_2\text{O}_2] = e^{-3.3} = 0.037 \text{ M}
\]

28. a. Since the \(\ln[A]\) vs. time plot was linear, the reaction is first order in \(A\). The slope of the \(\ln[A]\) vs. time plot equals \(-k\). Therefore, the rate law, the integrated rate law and the rate constant value are:

\[
\text{Rate} = k[A]; \quad \ln[A] = -kt + \ln[A]_0; \quad k = 2.97 \times 10^{-2} \text{ min}^{-1}
\]

b. The half-life expression for a first-order rate law is:

\[
t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}, \quad t_{1/2} = \frac{0.693}{2.97 \times 10^{-2} \text{ min}^{-1}} = 23.3 \text{ min}
\]

c. \(2.50 \times 10^{-3} \text{ M}\) is 1/8 of the original amount of \(A\) present initially, so the reaction is 87.5% complete. When a first-order reaction is 87.5% complete (or 12.5% remains), the reaction has gone through 3 half-lives:

\[
100\% \rightarrow 50.0\% \rightarrow 25\% \rightarrow 12.5\%; \quad t = 3 \times t_{1/2} = 3 \times 23.3 \text{ min} = 69.9 \text{ min}
\]

Or we can use the integrated rate law:

\[
\ln \left( \frac{[A]}{[A]_0} \right) = -kt, \quad \ln \left( \frac{2.50 \times 10^{-3} \text{ M}}{2.00 \times 10^{-2} \text{ M}} \right) = - (2.97 \times 10^{-2} \text{ min}^{-1}) t, \quad t = \frac{\ln (0.125)}{-2.97 \times 10^{-2} \text{ min}^{-1}} = 70.0 \text{ min}
\]

29. Assume the reaction is first order and see if the plot of \(\ln [\text{NO}_2]\) vs. time is linear. If this isn’t linear, try the second-order plot of \(1/[\text{NO}_2]\) vs. time. The data and plots follow.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[\text{NO}_2] (M)</th>
<th>\ln [\text{NO}_2]</th>
<th>1/[\text{NO}_2] (M^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.500</td>
<td>-0.693</td>
<td>2.00</td>
</tr>
<tr>
<td>1.20 \times 10^3</td>
<td>0.444</td>
<td>-0.812</td>
<td>2.25</td>
</tr>
<tr>
<td>3.00 \times 10^3</td>
<td>0.381</td>
<td>-0.965</td>
<td>2.62</td>
</tr>
<tr>
<td>4.50 \times 10^3</td>
<td>0.340</td>
<td>-1.079</td>
<td>2.94</td>
</tr>
<tr>
<td>9.00 \times 10^3</td>
<td>0.250</td>
<td>-1.386</td>
<td>4.00</td>
</tr>
<tr>
<td>1.80 \times 10^4</td>
<td>0.174</td>
<td>-1.749</td>
<td>5.75</td>
</tr>
</tbody>
</table>
The plot of $1/\left[\text{NO}_2\right]$ vs. time is linear. The reaction is second order in NO$_2$. The rate law and integrated rate law are: 

$$ \text{Rate} = k[\text{NO}_2]^2 \quad \text{and} \quad \frac{1}{[\text{NO}_2]} = kt + \frac{1}{[\text{NO}_2]_0}.$$ 

The slope of the plot $1/[\text{NO}_2]$ vs. t gives the value of k. Using a couple of points on the plot:

$$\text{slope} = k = \frac{\Delta y}{\Delta x} = \frac{(5.75 - 2.00) \text{M}^{-1}}{(1.80 \times 10^4 - 0) \text{s}} = 2.08 \times 10^{-4} \text{L/mol}\cdot \text{s}$$

To determine $[\text{NO}_2]$ at $2.70 \times 10^4 \text{ s}$, use the integrated rate law where $1/[\text{NO}_2]_0 = 1/0.500 \text{ M} = 2.00 \text{ M}^{-1}$.

$$\frac{1}{[\text{NO}_2]} = kt + \frac{1}{[\text{NO}_2]_0} \quad \frac{1}{[\text{NO}_2]} = \frac{2.08 \times 10^{-4} \text{L}}{\text{mol} \cdot \text{s}} \times 2.70 \times 10^4 \text{ s} + 2.00 \text{ M}^{-1}$$

$$\frac{1}{[\text{NO}_2]} = 7.62, \quad [\text{NO}_2] = 0.131 \text{ M}$$

d. Since the $1/[\text{A}]$ vs. time plot was linear, the reaction is second order in A. The slope of the $1/[\text{A}]$ vs. time plot equals the rate constant k. Therefore, the rate law, the integrated rate law and the rate constant value are:

$$ \text{Rate} = k[A]^2; \quad \frac{1}{[A]} = kt + \frac{1}{[A]_0}; \quad k = 3.60 \times 10^{-2} \text{ L/mol}\cdot \text{s}$$

The half-life expression for a second-order reaction is: 

$$ t_{1/2} = \frac{1}{k[A]_0}$$

For this reaction: 

$$ t_{1/2} = \frac{1}{3.60 \times 10^{-2} \text{ L/mol}\cdot \text{s} \times 2.80 \times 10^{-3} \text{ mol/L}} = 9.92 \times 10^3 \text{ s}$$

Note: We could have used the integrated rate law to solve for $t_{1/2}$ where 

$[\text{A}] = (2.80 \times 10^{-3} /2) \text{ mol/L}$.

c. Since the half-life for a second-order reaction depends on concentration, we must use the
integrated rate law to solve.

\[
\frac{1}{[A]} = kt + \frac{1}{[A]_0}, \quad \frac{1}{7.00 \times 10^{-4} \text{M}} = \frac{3.60 \times 10^{-3} \text{L}}{\text{mol}\cdot\text{s}} \times t + \frac{1}{2.80 \times 10^{-3} \text{M}}
\]

\[1.43 \times 10^3 - 357 = 3.60 \times 10^{-2} \text{ t}, \quad t = 2.98 \times 10^4 \text{ s}\]

31. a. Since the \([\text{C}_2\text{H}_5\text{OH}]\) vs. time plot was linear, the reaction is zero order in \(\text{C}_2\text{H}_5\text{OH}\). The slope of the \([\text{C}_2\text{H}_5\text{OH}]\) vs. time plot equals \(-k\). Therefore, the rate law, the integrated rate law and the rate constant value are: \(\text{Rate} = k[\text{C}_2\text{H}_5\text{OH}] = k; \quad \text{[C}_2\text{H}_5\text{OH}] = -kt + [\text{C}_2\text{H}_5\text{OH}]_0;\)
   \[k = 4.00 \times 10^{-5} \text{ mol/L}\cdot\text{s}\]

b. The half-life expression for a zero-order reaction is: \(t_{1/2} = [A]_0/2k\).

\[t_{1/2} = \frac{[\text{C}_2\text{H}_5\text{OH}]_0}{2k} = \frac{1.25 \times 10^{-2} \text{mol/L}}{2 \times 4.00 \times 10^{-5} \text{mol/L}\cdot\text{s}} = 156 \text{ s}\]

Note: we could have used the integrated rate law to solve for \(t_{1/2}\) where \([\text{C}_2\text{H}_5\text{OH}] = (1.25 \times 10^{-2}/2) \text{ mol/L}\).

c. \([\text{C}_2\text{H}_5\text{OH}] = -kt + [\text{C}_2\text{H}_5\text{OH}]_0, \quad 0 \text{ mol/L} = -(4.00 \times 10^{-5} \text{ mol/L}\cdot\text{s}) t + 1.25 \times 10^{-2} \text{ mol/L}\]
   \[t = \frac{1.25 \times 10^{-2} \text{mol/L}}{4.00 \times 10^{-5} \text{mol/L}\cdot\text{s}} = 313 \text{ s}\]

32. From the data, the pressure of \(\text{C}_2\text{H}_5\text{OH}\) decreases at a constant rate of 13 torr for every 100. s. Since the rate of disappearance of \(\text{C}_2\text{H}_5\text{OH}\) is not dependent on concentration, the reaction is zero order in \(\text{C}_2\text{H}_5\text{OH}\).

\[k = \frac{13 \text{ torr}}{100. \text{ s}} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.7 \times 10^{-4} \text{ atm/s}\]

The rate law and integrated rate law are:

\[\text{Rate} = k = 1.7 \times 10^{-4} \text{ atm/s}; \quad P_{\text{C}_2\text{H}_5\text{OH}} = -kt + 250. \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = -kt + 0.329 \text{ atm}\]

At 900. s: \(P_{\text{C}_2\text{H}_5\text{OH}} = -1.7 \times 10^{-4} \text{ atm/s} \times 900. \text{ s} + 0.329 \text{ atm} = 0.176 \text{ atm} = 0.18 \text{ atm} = 130 \text{ torr}\)

33. The first assumption to make is that the reaction is first order. For a first-order reaction, a graph of \(\ln [\text{C}_2\text{H}_5]\) vs. \(t\) should yield a straight line. If this isn't linear, then try the second-order plot of \(1/[\text{C}_2\text{H}_5]\) vs. \(t\). The data and the plots follow.
The natural log plot is not linear, so the reaction is not first order. Since the second-order plot of $1/\left[C_4H_6\right]$ vs. $t$ is linear, we can conclude that the reaction is second order in butadiene. The rate law is:

$$\text{Rate} = k\left[C_4H_6\right]^2$$

For a second order reaction, the integrated rate law is:

$$\frac{1}{\left[C_4H_6\right]} = kt + \frac{1}{\left[C_4H_6\right]_o}$$

The slope of the straight line equals the value of the rate constant. Using the points on the line at 1000. and 6000. s:

$$k = \text{slope} = \frac{144 \text{ L/mol} - 73 \text{ L/mol}}{6000. \text{ s} - 1000. \text{ s}} = 1.4 \times 10^{-2} \text{ L/mol s}$$

34. a. First, assume the reaction to be first order with respect to O. A graph of ln $[O]$ vs. $t$ should be linear if the reaction is first order.

<table>
<thead>
<tr>
<th>t(s)</th>
<th>[O] (atoms/cm³)</th>
<th>ln[O]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$5.0 \times 10^9$</td>
<td>22.33</td>
</tr>
<tr>
<td>$10. \times 10^{-3}$</td>
<td>$1.9 \times 10^9$</td>
<td>21.37</td>
</tr>
<tr>
<td>$20. \times 10^{-3}$</td>
<td>$6.8 \times 10^8$</td>
<td>20.34</td>
</tr>
<tr>
<td>$30. \times 10^{-3}$</td>
<td>$2.5 \times 10^8$</td>
<td>19.34</td>
</tr>
</tbody>
</table>
Since the graph is linear, we can conclude that the reaction is first order with respect to O.

b. The overall rate law is: \( \text{Rate} = k[\text{NO}_2][O] \)

Since \( \text{NO}_2 \) was in excess, its concentration is constant. So for this experiment, the rate law is: \( \text{Rate} = k'[O] \) where \( k' = k[\text{NO}_2] \). In a typical first-order plot, the slope equals \(-k\). For this experiment, the slope equals \(-k' = -k[\text{NO}_2] \). From the graph:

\[
\text{slope} = \frac{19.34 - 22.33}{(30 \times 10^{-3} - 0) \text{ s}} = -1.0 \times 10^2 \text{ s}^{-1}, \quad k' = -\text{slope} = 1.0 \times 10^2 \text{ s}^{-1}
\]

To determine \( k \), the actual rate constant:

\[
k' = k[\text{NO}_2], \quad 1.0 \times 10^2 \text{ s}^{-1} = k(1.0 \times 10^{13} \text{ molecules/cm}^3), \quad k = 1.0 \times 10^{-11} \text{ cm}^3/\text{molecules} \cdot \text{s}
\]

35. Since the \( 1/[A] \) vs. time plot is linear with a positive slope, the reaction is second order with respect to A. The y-intercept in the plot will equal \( 1/[A]_o \). Extending the plot, the y-intercept will be about 10, so \( 1/10 = 0.1 \text{ M} = [A]_o \).

36. The slope of the \( 1/[A] \) vs time plot in Exercise 12.35 with equal \( k \).

\[
\text{slope} = k = \frac{(60 - 20) \text{ L/mol}}{(5 - 1) \text{ s}} = 10 \text{ L/mol} \cdot \text{s}
\]

a. \[
\frac{1}{[A]} = k t + \frac{1}{[A]_o} = \frac{10 \text{ L}}{\text{mol} \cdot \text{s}} \times 9 \text{ s} + \frac{1}{0.1 \text{ M}} = 100, \quad [A] = 0.01 \text{ M}
\]

b. For a second-order reaction, the half-life does depend on concentration: \( t_{1/2} = \frac{1}{k[A]_o} \).

First half-life: \( t_{1/2} = \frac{1}{10 \text{ L} \times \frac{0.1 \text{ mol}}{\text{L}}} = 1 \text{ s} \)

Second half-life ([A]_o is now 0.05 M): \( t_{1/2} = 1/(10 \times 0.05) = 2 \text{ s} \)

Third half-life ([A]_o is now 0.025 M): \( t_{1/2} = 1/(10 \times 0.025) = 4 \text{ s} \)
37. a. \([A] = -kt + [A]_0\), \([A] = -(5.0 \times 10^{-2} \text{ mol/L} \cdot \text{s}) \cdot t + 1.0 \times 10^{-3} \text{ mol/L}\)

b. The half-life expression for a zero-order reaction is: \(t_{1/2} = \frac{[A]_0}{2k}\)

\[t_{1/2} = \frac{1.0 \times 10^{-2} \text{ mol/L}}{2 \times 5.0 \times 10^{-2} \text{ mol/L} \cdot \text{s}} = 1.0 \times 10^{-2} \text{ s}\]

c. \([A] = -5.0 \times 10^{-2} \text{ mol/L} \cdot \text{s} \cdot 5.0 \times 10^{-3} \text{ s} + 1.0 \times 10^{-3} \text{ mol/L} = 7.5 \times 10^{-4} \text{ mol/L}\)

Since \(7.5 \times 10^{-4} \text{ mol/L}\) of \(A\) remains, \(2.5 \times 10^{-4} \text{ mol/L}\) of \(A\) reacted, which means that \(2.5 \times 10^{-4} \text{ mol/L}\) of \(B\) has been produced.

38. \(\ln \left( \frac{[A]}{[A]_0} \right) = -kt; \quad k = \frac{\ln 2}{t_{1/2}} = \frac{0.6931}{14.3 \text{ d}} = 4.85 \times 10^{-2} \text{ d}^{-1}\)

If \([A] = 100.0\), then after 95.0% completion, \([A] = 5.0\).

\(\ln \left( \frac{5.0}{100.0} \right) = -4.85 \times 10^{-2} \text{ d}^{-1} \times t, \quad t = 62 \text{ days}\)

39. a. If the reaction is 38.5% complete, then 38.5% of the original concentration is consumed, leaving 61.5%.

\([A] = 61.5\% \text{ of } [A]_0 \text{ or } [A] = 0.615 \cdot [A]_0; \quad \ln \left( \frac{[A]}{[A]_0} \right) = -kt, \quad \ln \left( \frac{0.615 [A]_0}{[A]_0} \right) = -k(480. \text{ s})\)

\(\ln(0.615) = -k(480. \text{ s}), \quad -0.486 = -k(480. \text{ s}), \quad k = 1.01 \times 10^{-3} \text{ s}^{-1}\)

b. \(t_{1/2} = (\ln 2)/k = 0.6931/1.01 \times 10^{-3} \text{ s}^{-1} = 686 \text{ s}\)

c. 25% complete: \([A] = 0.75 [A]_0; \quad \ln(0.75) = -1.01 \times 10^{-3} (t), \quad t = 280 \text{ s}\)

75% complete: \([A] = 0.25 [A]_0; \quad \ln(0.25) = -1.01 \times 10^{-3} (t), \quad t = 1.4 \times 10^{3} \text{ s}\)

Or, we know it takes \(2 \times t_{1/2}\) for reaction to be 75% complete. \(t = 2 \times 686 \text{ s} = 1370 \text{ s}\)

95% complete: \([A] = 0.05 [A]_0; \quad \ln(0.05) = -1.01 \times 10^{-3} (t), \quad t = 3 \times 10^{3} \text{ s}\)

40. For a first-order reaction, the integrated rate law is: \(\ln([A]/[A]_0) = -kt\). Solving for \(k:\)

\(\ln \left( \frac{0.250 \text{ mol/L}}{1.00 \text{ mol/L}} \right) = -k \times 120. \text{ s}, \quad k = 0.0116 \text{ s}^{-1}\)

\(\ln \left( \frac{0.350 \text{ mol/L}}{2.00 \text{ mol/L}} \right) = -0.0116 \text{ s}^{-1} \times t, \quad t = 150. \text{ s}\)

41. For a second-order reaction: \(t_{1/2} = \frac{1}{k[A]_0}\) or \(k = \frac{1}{t_{1/2}[A]_0}\)
42. a. The integrated rate law for a second-order reaction is: \( \frac{1}{[A]} = kt + \frac{1}{[A]_0} \), and the half-life expression is: \( t_{1/2} = \frac{1}{k[A]_0} \). We could use either to solve for \( t_{1/2} \). Using the integrated rate law:

\[
\frac{1}{(0.900/2) \text{ mol/L}} = k \times 2.00 \text{ s} + \frac{1}{0.900 \text{ mol/L}}, \quad k = \frac{1.11 \text{ L/mol}}{2.00 \text{ s}} = 0.555 \text{ L/mol}\cdot\text{s}
\]

b. \( \frac{1}{0.100 \text{ mol/L}} = 0.555 \text{ L/mol}\cdot\text{s} \times t + \frac{1}{0.900 \text{ mol/L}}, \quad t = \frac{8.9 \text{ L/mol}}{0.555 \text{ L/mol}\cdot\text{s}} = 16 \text{ s} \)

43. Successive half-lives increase in time for a second-order reaction. Therefore, assume the reaction is second order in A.

\[
t_{1/2} = \frac{1}{k[A]_0}, \quad k = \frac{1}{t_{1/2}[A]_0} = \frac{1}{10.0 \text{ min} (0.10 \text{ M})} = 1.0 \text{ L/mol}\cdot\text{min}
\]

a. \( \frac{1}{[A]} = kt + \frac{1}{[A]_0} = \frac{1.0 \text{ L/mol min}}{80.0 \text{ min}} \times 80.0 \text{ min} + \frac{1}{0.10 \text{ M}} = 90. \text{ M}^{-1}, \quad [A] = 1.1 \times 10^{-2} \text{ M} \)

b. 30.0 min = 2 half-lives, so 25% of original A is remaining.

\[
[A] = 0.25(0.10 \text{ M}) = 0.025 \text{ M}
\]

44. Since \([B]_0 >> [A]_0\), the B concentration is essentially constant during this experiment, so rate = \( k[A] \) where \( k = k[B]^2 \). For this experiment, the reaction is a pseudo-first-order reaction in A.

a. \( \ln \left( \frac{[A]}{[A]_0} \right) = -kt, \quad \ln \left( \frac{3.8 \times 10^{-3} \text{ M}}{1.0 \times 10^{-2} \text{ M}} \right) = -k' \times 8.0 \text{ s}, \quad k' = 0.12 \text{ s}^{-1} \)

For the reaction: \( k' = k[B]^2 \), \( k = 0.12 \text{ s}^{-1}/(3.0 \text{ mol/L})^2 = 1.3 \times 10^{-2} \text{ L}^2/\text{mol}^2\cdot\text{s} \)

b. \( t_{1/2} = \frac{\ln 2}{k'} = \frac{0.693}{0.12 \text{ s}^{-1}} = 5.8 \text{ s} \)

c. \( \ln \left( \frac{[A]}{1.0 \times 10^{-2} \text{ M}} \right) = -0.12 \text{ s}^{-1} \times 13.0 \text{ s}, \quad \frac{[A]}{1.0 \times 10^{-2} \text{ M}} = e^{-0.12(13.0)} = 0.21, \quad [A] = 2.1 \times 10^{-3} \text{ M} \)

d. \( [A]_{\text{reacted}} = 0.010 \text{ M} - 0.0021 \text{ M} = 0.008 \text{ M}; \quad [C]_{\text{reacted}} = 0.008 \text{ M} \times \frac{2 \text{ mol C}}{1 \text{ mol A}} = 0.016 \text{ M} \approx 0.02 \text{ M} \)

\( [C]_{\text{remaining}} = 2.0 \text{ M} - 0.02 \text{ M} = 2.0 \text{ M}; \) As expected, the concentration of C basically remains constant during this experiment since \([C]_0 >> [A]_0\).

**Reaction Mechanisms**
45. For elementary reactions, the rate law can be written using the coefficients in the balanced equation to determine orders.

a. Rate = $k[CH_3NC]$

b. Rate = $k[O_2][NO]$

c. Rate = $k[O_2]$

d. Rate = $k[O_2][O]$

46. The observed rate law for this reaction is: $Rate = k[NO]^2[H_2]$. For a mechanism to be plausible, the sum of all the steps must give the overall balanced equation (true for all the proposed mechanisms in this problem), and the rate law derived from the mechanism must agree with the observed mechanism. In each mechanism (I - III), the first elementary step is the rate-determining step (the slow step), so the derived rate law for each mechanism will be the rate of the first step. The derived rate laws follow:

Mechanism I: $Rate = k[H_2]^2[NO]^2$

Mechanism II: $Rate = k[H_2][NO]$

Mechanism III: $Rate = k[H_2][NO]^2$

Only in Mechanism III does the derived rate law agree with the observed rate law. Thus, only Mechanism III is a plausible mechanism for this reaction.

47. A mechanism consists of a series of elementary reactions where the rate law for each step can be determined using the coefficients in the balanced equations. For a plausible mechanism, the rate law derived from a mechanism must agree with the rate law determined from experiment. To derive the rate law from the mechanism, the rate of the reaction is assumed to equal the rate of the slowest step in the mechanism.

Since step 1 is the rate-determining step, the rate law for this mechanism is: $Rate = k[C_4H_9Br]$. To get the overall reaction, we sum all the individual steps of the mechanism.

Summing all steps gives:

- $C_4H_9Br \rightarrow C_4H_9^+ + Br$
- $C_4H_9^+ + H_2O \rightarrow C_4H_9OH^+$
- $C_4H_9OH^+ + H_2O \rightarrow C_4H_9OH + H_2O^+$
- $C_4H_9Br + 2H_2O \rightarrow C_4H_9OH + Br^- + H_2O^+$

Intermediates in a mechanism are species that are neither reactants nor products, but that are formed and consumed during the reaction sequence. The intermediates for this mechanism are $C_4H_9^+$ and $C_4H_9OH^+$.

48. Since the rate of the slowest elementary step equals the rate of a reaction, then:

$Rate = rate \ of \ step \ 1 = k[NO_2]^2$

The sum of all steps in a plausible mechanism must give the overall balanced reaction. Summing all steps gives:
\[ \text{NO}_2 + \text{NO} \rightarrow \text{NO}_3 + \text{NO} \]
\[ \text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2 \]
\[ \text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2 \]

**Temperature-Dependence of Rate Constants and the Collision Model**

49. In the following plot, R = reactants, P = products, \( E_a \) = activation energy and RC = reaction coordinate which is the same as reaction progress. Note for this reaction that \( \Delta E \) is positive since the products are at a higher energy than the reactants.

![Reaction diagram](image)

50. When \( \Delta E \) is positive, the products are at a higher energy relative to reactants and, when \( \Delta E \) is negative, the products are at a lower energy relative to reactants.

![Energy diagrams](image)
51. The activation energy for the reverse reaction is:

\[ E_{a,\text{reverse}} = 216 \text{ kJ/mol} + 125 \text{ kJ/mol} = 341 \text{ kJ/mol} \]

52. When \( \Delta E \) is negative, then \( E_{a,\text{reverse}} > E_{a,\text{forward}} \) (see energy profile in Exercise 12.51). When \( \Delta E \) is positive (the products have higher energy than the reactants as represented in the energy profile for Exercise 12.49), then \( E_{a,\text{forward}} > E_{a,\text{reverse}} \). Therefore, this reaction has a positive \( \Delta E \) value.

53. The Arrhenius equation is: 
\[ k = A \exp\left(-\frac{E_a}{RT}\right) \] or in logarithmic form, 
\[ \ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A. \] Hence, a graph of \( \ln k \) vs. \( 1/T \) should yield a straight line with a slope equal to \(-E_a/R\) since the logarithmic form of the Arrhenius equation is in the form of a straight line equation, \( y = mx + b \). Note: We carried extra significant figures in the following \( \ln k \) values in order to reduce round off error.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>1/T (K(^{-1}))</th>
<th>k (s(^{-1}))</th>
<th>( \ln k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>338</td>
<td>2.96 \times 10^{-3}</td>
<td>4.9 \times 10^{3}</td>
<td>-5.32</td>
</tr>
<tr>
<td>318</td>
<td>3.14 \times 10^{-3}</td>
<td>5.0 \times 10^{4}</td>
<td>-7.60</td>
</tr>
<tr>
<td>298</td>
<td>3.36 \times 10^{-3}</td>
<td>3.5 \times 10^{5}</td>
<td>-10.26</td>
</tr>
</tbody>
</table>

\[ \text{Slope} = \frac{-10.76 - (-5.85)}{(3.40 \times 10^{-3} - 3.00 \times 10^{-3})} = -1.2 \times 10^4 \text{ K} = -E_a/R \]

\[ E_a = -\text{slope} \times R = 1.2 \times 10^4 \text{ K} \times \frac{8.3145 \text{ J}}{\text{K mol}} = 1.0 \times 10^5 \text{ J/mol} = 1.0 \times 10^2 \text{ kJ/mol} \]

54. From the Arrhenius equation in logarithmic form (\( \ln k = -E_a/RT + \ln A \)), a graph of \( \ln k \) vs. \( 1/T \) should yield a straight line with a slope equal to \(-E_a/R\) and a y-intercept equal to \( \ln A \).
a. \( \text{slope} = -\frac{E_a}{R} \), \( E_a = 1.10 \times 10^4 \text{ K} \times \frac{8.3145 \text{ J}}{\text{mol} \cdot \text{K}} = 9.15 \times 10^4 \text{ J/mol} = 91.5 \text{ kJ/mol} \)

b. The units for \( A \) are the same as the units for \( k(\text{s}^{-1}) \).

y-intercept = \( \ln A \), \( A = e^{3.5} = 3.54 \times 10^{14} \text{ s}^{-1} \)

c. \( \ln k = -\frac{E_a}{RT} + \ln A \) or \( k = A \exp(-\frac{E_a}{RT}) \)

\[
k = 3.54 \times 10^{14} \text{ s}^{-1} \times \exp \left( -\frac{9.15 \times 10^4 \text{ J/mol}}{8.3145 \text{ J/K/mol} \times 298 \text{ K}} \right) = 3.24 \times 10^2 \text{ s}^{-1}
\]

55. \( k = A \exp(-\frac{E_a}{RT}) \) or \( \ln k = -\frac{E_a}{RT} + \ln A \) (the Arrhenius equation)

For two conditions: \( \ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \) (Assuming \( A \) is temperature independent.)

Let \( k_1 = 2.0 \times 10^3 \text{ s}^{-1}, T_1 = 298 \text{ K}; k_2 = ?, T_2 = 348 \text{ K}; E_a = 15.0 \times 10^3 \text{ J/mol} \)

\[
\ln \left( \frac{k_2}{2.0 \times 10^3} \right) = \frac{15.0 \times 10^3 \text{ J/mol}}{8.3145 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{298 \text{ K}} - \frac{1}{348 \text{ K}} \right) = 0.87
\]

\[
\ln \left( \frac{k_2}{2.0 \times 10^3} \right) = 0.87, \quad \frac{k_2}{2.0 \times 10^3} = e^{0.87} = 2.4, \quad k_2 = 2.4 \times 4.8 \times 10^3 \text{ s}^{-1}
\]

56. For two conditions: \( \ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \) (Assuming \( A \) factor is \( T \) independent.)

\[
\ln \left( \frac{8.1 \times 10^2 \text{ s}^{-1}}{4.6 \times 10^2 \text{ s}^{-1}} \right) = \frac{E_a}{8.3145 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{273 \text{ K}} - \frac{1}{293 \text{ K}} \right)
\]

0.57 = \( \frac{E_a}{8.3145} \) (2.5 \( \times 10^4 \)), \( E_a = 1.9 \times 10^4 \text{ J/mol} = 19 \text{ kJ/mol} \)

57. \( \ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \); \( \frac{k_2}{k_1} = 7.00, T_1 = 295 \text{ K}, E_a = 54.0 \times 10^3 \text{ J/mol} \)

\[
\ln (7.00) = \frac{54.0 \times 10^3 \text{ J/mol}}{8.3145 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{295 \text{ K}} - \frac{1}{T_2} \right), \quad \frac{1}{T_2} = 3.00 \times 10^{-4}
\]

\[
\frac{1}{T_2} = 3.09 \times 10^{-3}, T_2 = 324 \text{ K} = 51^\circ \text{C}
\]
58. \[
\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R \left( \frac{1}{T_1} - \frac{1}{T_2} \right)} ; \text{ Since the rate doubles, then } k_2 = 2k_1. \\
\ln (2.00) = \frac{5.3 \times 10^4 \text{ J/mol }}{8.3145 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{298 \text{ K}} - \frac{1}{308 \text{ K}} \right), \ E_a = 5.3 \times 10^4 \text{ J/mol } = 53 \text{ kJ/mol}
\]

59. \( \text{H}_2\text{O}^{+}(\text{aq}) + \text{OH}^{-}(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) \) should have the faster rate. \( \text{H}_2\text{O}^{+} \) and \( \text{OH}^{-} \) will be electrostatically attracted to each other; \( \text{Ce}^{4+} \) and \( \text{Hg}^{2+} \) will repel each other (so \( E_a \) is much larger).

60. Carbon cannot form the fifth bond necessary for the transition state because of the small atomic size of carbon and because carbon doesn’t have low energy d orbitals available to expand the octet.

Catalysts

61. a. \( \text{NO} \) is the catalyst. \( \text{NO} \) is present in the first step of the mechanism on the reactant side, but it is not a reactant since it is regenerated in the second step.

b. \( \text{NO}_2 \) is an intermediate. Intermediates also never appear in the overall balanced equation. In a mechanism, intermediates always appear first on the product side while catalysts always appear first on the reactant side.

c. \( k = A \exp(-E_a/RT) ; \frac{k_{\text{cat}}}{k_{\text{un}}} = \frac{A \exp \left( -E_a(\text{cat})/RT \right)}{A \exp \left( -E_a(\text{un})/RT \right)} = \exp \left( \frac{E_a(\text{un}) - E_a(\text{cat})}{RT} \right) \)

\[
\frac{k_{\text{cat}}}{k_{\text{un}}} = \exp \left( \frac{2100 \text{ J/mol}}{8.3145 \text{ J/mol} \cdot \text{K} \times 298 \text{ K}} \right) = e^{0.85} = 2.3
\]

The catalyzed reaction is 2.3 times faster than the uncatalyzed reaction at 25°C.

62. The mechanism for the chlorine catalyzed destruction of ozone is:

\[
\begin{align*}
\text{O}_3 + \text{Cl} & \rightarrow \text{O}_2 + \text{ClO} \quad \text{(slow)} \\
\text{ClO} + \text{O} & \rightarrow \text{O}_2 + \text{Cl} \quad \text{(fast)} \\
\text{O}_3 + \text{O} & \rightarrow 2 \text{ O}_2
\end{align*}
\]

Since the chlorine atom-catalyzed reaction has a lower activation energy, then the Cl-catalyzed rate is faster. Hence, Cl is a more effective catalyst. Using the activation energy, we can estimate the efficiency with which Cl atoms destroy ozone as compared to NO molecules (see Exercise 12.61c).

At 25°C: \[
\frac{k_{\text{Cl}}}{k_{\text{NO}}} = \exp \left( \frac{-E_a(\text{Cl})}{RT} + \frac{E_a(\text{NO})}{RT} \right) = \exp \left( \frac{\left( -2100 + 11,900 \right) \text{ J/mol}}{(8.3145 \times 298) \text{ J/mol}} \right) = e^{0.96} = 52
\]

At 25°C, the Cl-catalyzed reaction is roughly 52 times faster than the NO-catalyzed reaction, assuming the frequency factor \( A \) is the same for each reaction.

63. The reaction at the surface of the catalyst is assumed to follow the steps:
Thus, CH₃D–CH₂D should be the product. If the mechanism is possible, then the reaction must be:

\[ \text{C}_2\text{H}_4 + \text{D}_2 \rightarrow \text{CH}_2\text{DCH}_2\text{D} \]

If we got this product, then we could conclude that this is a possible mechanism. If we got some other product, e.g., CH₃CHD₂, then we would conclude that the mechanism is wrong. Even though this mechanism correctly predicts the products of the reaction, we cannot say conclusively that this is the correct mechanism; we might be able to conceive of other mechanisms that would give the same products as our proposed one.

64. a. W since it has a lower activation energy than the Os catalyst.

b. \( k_w = A_w \exp[-E_w/(RT)] \); \( k_{uncat} = A_{uncat} \exp[-E_{uncat}/RT] \); Assume \( A_w = A_{uncat} \)

\[
\frac{k_w}{k_{uncat}} = \exp \left( \frac{-E_w}{RT} + \frac{E_{uncat}}{RT} \right)
\]

\[
\frac{k_w}{k_{uncat}} = \exp \left( \frac{-163,000 \text{ J/mol} + 335,000 \text{ J/mol}}{8.3145 \text{ J/mol} \cdot \text{K} \times 298 \text{ K}} \right) = 1.41 \times 10^{10}
\]

The W-catalyzed reaction is approximately \( 10^{10} \) times faster than the uncatalyzed reaction.

c. Since \([\text{H}_2]\) is in the denominator of the rate law, then \( \text{H}_2 \) decreases the rate of the reaction. For the decomposition to occur, \( \text{NH}_3 \) molecules must be adsorbed on the surface of the catalyst. If \( \text{H}_2 \) is also adsorbed on the catalyst surface, then there are fewer sites for \( \text{NH}_3 \) molecules to be adsorbed and the rate decreases.

Additional Exercises

65. Rate \( = k[\text{NO}]^y[\text{O}_2]^z \); comparing the first two experiments, \([\text{O}_2]\) is unchanged, \([\text{NO}]\) is tripled, and the rate increases by a factor of nine. Therefore, the reaction is second order in \( \text{NO} (3^2 = 9) \).

The order of \( \text{O}_2 \) is more difficult to determine. Comparing the second and third experiments;

\[
\frac{3.13 \times 10^{17}}{1.80 \times 10^{17}} = \frac{k (2.50 \times 10^{16})^2 (2.50 \times 10^{16})^y}{k (3.00 \times 10^{16})^2 (1.00 \times 10^{18})^y} = 1.74 = 0.694 (2.50)^y, \quad 2.51 = 2.50^y, \quad y = 1
\]

Rate \( = k[\text{NO}]^y[\text{O}_2]^z \); From experiment 1:
2.00 \times 10^{16} \text{ molecules/cm}^3 \cdot \text{s} = k (1.00 \times 10^{18} \text{ molecules/cm}^3)^2 (1.00 \times 10^{19} \text{ molecules/cm}^3)

k = 2.00 \times 10^{-38} \text{ cm}^6/\text{molecules}^2 \cdot \text{s} = k_{\text{mean}}

\text{Rate} = \frac{2.00 \times 10^{-38} \text{ cm}^6}{\text{molecules}^2 \cdot \text{s}} \times \left( \frac{6.21 \times 10^{18} \text{ molecules}}{\text{cm}^3} \right)^2 \times \frac{7.36 \times 10^{18} \text{ molecules}}{\text{cm}^3} = 5.68 \times 10^{18} \text{ molecules/cm}^3 \cdot \text{s}

66. The pressure of a gas is directly proportional to concentration. Therefore, we can use the pressure data to solve the problem since \text{Rate} = -\Delta [\text{SO}_2\text{Cl}_2]/\Delta t \propto -\Delta P_{\text{SO}_2\text{Cl}_2}/\Delta t.

Assuming a first order equation, the data and plot follow.

<table>
<thead>
<tr>
<th>Time (hour)</th>
<th>0.00</th>
<th>1.00</th>
<th>2.00</th>
<th>4.00</th>
<th>8.00</th>
<th>16.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{P}_{\text{SO}_2\text{Cl}_2} (\text{atm})</td>
<td>4.93</td>
<td>4.26</td>
<td>3.52</td>
<td>2.53</td>
<td>1.30</td>
<td>0.34</td>
</tr>
<tr>
<td>\ln \text{P}_{\text{SO}_2\text{Cl}_2}</td>
<td>1.595</td>
<td>1.449</td>
<td>1.258</td>
<td>0.928</td>
<td>0.262</td>
<td>-1.08</td>
</tr>
</tbody>
</table>

Since the \ln \text{P}_{\text{SO}_2\text{Cl}_2} vs. time plot is linear, the reaction is first order in \text{SO}_2\text{Cl}_2.

a. Slope of \ln(P) vs. t plot is -0.168 hour$^{-1}$ = -k, \( k = 0.168 \text{ hour}^{-1} = 4.67 \times 10^{-5} \text{ s}^{-1} \)

Since concentration units don’t appear in first-order rate constants, this value of k determined from the pressure data will be the same as if concentration data in molarity units were used.

b. \( t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k} = \frac{0.6931}{0.168 \text{ hour}^{-1}} = 4.13 \text{ hour} \)
c. \( \ln \left( \frac{P_{SO_{2}Cl_{2}}}{P_{o}} \right) = -kt = -0.168 \text{ h}^{-1} (20.0 \text{ hr}) = -3.36, \left( \frac{P_{SO_{2}Cl_{2}}}{P_{o}} \right) = e^{-3.36} = 3.47 \times 10^{-2} \)

Fraction left = 0.0347 = 3.47%

67. From 338 K data, a plot of \( \ln [N_{2}O_{5}] \) vs. \( t \) is linear and the slope = \(-4.86 \times 10^{-3} \) (plot not included). This tells us the reaction is first order in \( N_{2}O_{5} \) with \( k = 4.86 \times 10^{-3} \) at 338 K.

From 318 K data, the slope of \( \ln [N_{2}O_{5}] \) vs \( t \) plot is equal to \(-4.98 \times 10^{-4} \), so \( k = 4.98 \times 10^{-4} \) at 318 K. We now have two values of \( k \) at two temperatures, so we can solve for \( E_{a} \).

\[
\ln \left( \frac{k_{2}}{k_{1}} \right) = \frac{E_{a}}{R} \left( \frac{1}{T_{1}} - \frac{1}{T_{2}} \right), \quad \ln \left( \frac{4.86 \times 10^{-3}}{4.98 \times 10^{-4}} \right) = \frac{E_{a}}{8.3145 \text{ J/K mol}} \left( \frac{1}{318 \text{ K}} - \frac{1}{338 \text{ K}} \right)
\]

\( E_{a} = 1.0 \times 10^{5} \text{ J/mol} = 1.0 \times 10^{2} \text{ kJ/mol} \)

68. The Arrhenius equation is: \( k = A \exp (-E_{a}/RT) \) or in logarithmic form, \( \ln k = -E_{a}/RT + \ln A \). Hence, a graph of \( \ln k \) vs. \( 1/T \) should yield a straight line with a slope equal to \(-E_{a}/R\) since the logarithmic form of the Arrhenius equation is in the form of a straight line equation, \( y = mx + b \). Note: We carried one extra significant figure in the following \( \ln k \) values in order to reduce round off error.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( 1/T ) (K(^{-1} ))</th>
<th>( k ) (L/mol( \cdot )s)</th>
<th>( \ln k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>195</td>
<td>5.13 \times 10^{-3}</td>
<td>1.08 \times 10^{9}</td>
<td>20.80</td>
</tr>
<tr>
<td>230</td>
<td>4.35 \times 10^{-3}</td>
<td>2.95 \times 10^{9}</td>
<td>21.81</td>
</tr>
<tr>
<td>260</td>
<td>3.85 \times 10^{-3}</td>
<td>5.42 \times 10^{9}</td>
<td>22.41</td>
</tr>
<tr>
<td>298</td>
<td>3.36 \times 10^{-3}</td>
<td>12.0 \times 10^{9}</td>
<td>23.21</td>
</tr>
<tr>
<td>369</td>
<td>2.71 \times 10^{-3}</td>
<td>35.5 \times 10^{9}</td>
<td>24.29</td>
</tr>
</tbody>
</table>

From "eyeballing" the line on the graph:

\[
\text{slope} = \frac{20.95 - 23.65}{(5.00 \times 10^{-3} - 3.00 \times 10^{-3}) \text{ K}^{-1}} = -2.70 = -1.35 \times 10^{3} \text{ K} = \frac{-E_{a}}{R}
\]
$E_a = 1.35 \times 10^4 \text{ K} \times \frac{8.3145 \text{ J}}{\text{K mol}} = 1.12 \times 10^4 \text{ J/mol} = 11.2 \text{ kJ/mol}$

From a graphing calculator: slope = $-1.43 \times 10^3 \text{ K}$ and $E_a = 11.9 \text{ kJ/mol}$

69. At high $[S]$, the enzyme is completely saturated with substrate. Once the enzyme is completely saturated, the rate of decomposition of ES can no longer increase, and the overall rate remains constant.

70. $k = A \exp \left(\frac{-E_a}{RT}\right)$; 
\[\frac{k_{\text{cat}}}{k_{\text{mean}}} = \frac{A_{\text{cat}} \exp \left(\frac{-E_{a,\text{cat}}}{RT}\right)}{A_{\text{mean}} \exp \left(\frac{-E_{a,\text{mean}}}{RT}\right)} = \exp \left(\frac{-E_{a,\text{cat}} + E_{a,\text{mean}}}{RT}\right)\]

$2.50 \times 10^3 = \frac{k_{\text{cat}}}{k_{\text{mean}}} = \exp \left(\frac{-E_{a,\text{cat}} + 5.00 \times 10^4 \text{ J/mol}}{8.3145 \text{ J/K mol} \times 310, \text{ K}}\right)$

$\ln (2.50 \times 10^3) \times 2.58 \times 10^3 \text{ J/mol} = -E_{a,\text{cat}} + 5.00 \times 10^4 \text{ J/mol}$

$E_{a,\text{cat}} = 5.00 \times 10^4 \text{ J/mol} - 2.02 \times 10^4 \text{ J/mol} = 2.98 \times 10^4 \text{ J/mol} = 29.8 \text{ kJ/mol}$

**Challenge Problems**

71. Rate = $k[I^-][\text{OCI}^-][\text{OH}^-]^x$; Comparing the first and second experiments:
\[
\frac{18.7 \times 10^{-3}}{9.4 \times 10^{-3}} = \frac{k(0.0026)^x (0.012)^y (0.10)^x}{k(0.0013)^x (0.012)^y (0.10)^y}, \quad 2.0 = 2.0, \quad x = 1
\]

Comparing the first and third experiments:
\[
\frac{9.4 \times 10^{-3}}{4.7 \times 10^{-3}} = \frac{k(0.0013)^x (0.012)^y (0.10)^z}{k(0.0013)^x (0.0060)^y (0.10)^y}, \quad 2.0 = 2.0, \quad y = 1
\]

Comparing the first and sixth experiments:
\[
\frac{4.7 \times 10^{-5}}{9.4 \times 10^{-3}} = \frac{k(0.0013)^x (0.012)^y (0.20)^z}{k(0.0013)^x (0.012)^y (0.10)^y}, \quad 1/2 = 2.0, \quad z = -1
\]

Rate = $\frac{k[I^-][\text{OCI}^-]}{[\text{OH}^-]^x}$; The presence of OH$^-$ decreases the rate of the reaction.

For the first experiment:
\[
\frac{9.4 \times 10^{-3} \text{ mol}}{L s} = k \frac{(0.0013 \text{ mol/L}) (0.012 \text{ mol/L})}{(0.10 \text{ mol/L})}, \quad k = 60.3 \text{ s}^{-1} = 60. \text{ s}^{-1}
\]

For all experiments, $k_{\text{mean}} = 60. \text{ s}^{-1}$. 
72. For second order kinetics: \[ \frac{1}{[A]} - \frac{1}{[A]_o} = kt \text{ and } t_{1/2} = \frac{1}{k[A]_o} \]

a. \[ \frac{1}{[A]} = (0.250 \text{ L/mol}\cdot\text{s})t + \frac{1}{[A]_o}, \quad \frac{1}{[A]} = 0.250 \times 180. \text{ s} + \frac{1}{1.00 \times 10^{-2} \text{ M}} \]

\[ \frac{1}{[A]} = 145 \text{ M}^{-1}, \quad [A] = 6.90 \times 10^{-3} \text{ M} \]

Amount of A that reacted = 0.0100 - 0.00690 = 0.0031 M

\[ [A_2] = \frac{1}{2} (3.1 \times 10^{-3} \text{ M}) = 1.6 \times 10^{-3} \text{ M} \]

b. After 3.00 minutes (180. s): \[ [A] = 3.00 \text{ [B]}, \quad 6.90 \times 10^{-3} \text{ M} = 3.00 \text{ [B]}, \quad [B] = 2.30 \times 10^{-3} \text{ M} \]

\[ \frac{1}{[B]} = k_2 t + \frac{1}{[B]_o}, \quad \frac{1}{2.30 \times 10^{-3} \text{ M}} = k_2 (180. \text{ s}) + \frac{1}{2.50 \times 10^{-2} \text{ M}}, \quad k_2 = 2.19 \text{ L/mol}\cdot\text{s} \]

c. \[ t_{1/2} = \frac{1}{k[A]_o} = \frac{1}{0.250 \text{ L/mol}\cdot\text{s} \times 1.00 \times 10^{-2} \text{ mol/L}} = 4.00 \times 10^2 \text{ s} \]

73. a. We check for first-order dependence by graphing ln [concentration] vs. time for each set of data. The rate dependence on NO is determined from the first set of data since the ozone concentration is relatively large compared to the NO concentration, so \([O_3]\) is effectively constant.

<table>
<thead>
<tr>
<th>Time (ms)</th>
<th>[NO] (molecules/cm³)</th>
<th>ln [NO]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.0 \times 10^6</td>
<td>20.21</td>
</tr>
<tr>
<td>100.</td>
<td>5.0 \times 10^6</td>
<td>20.03</td>
</tr>
<tr>
<td>500.</td>
<td>2.4 \times 10^6</td>
<td>19.30</td>
</tr>
<tr>
<td>700.</td>
<td>1.7 \times 10^6</td>
<td>18.95</td>
</tr>
<tr>
<td>1000.</td>
<td>9.9 \times 10^7</td>
<td>18.41</td>
</tr>
</tbody>
</table>

![Graph of ln [NO] vs. time (ms)](image-url)
Since \( \ln [\text{NO}] \) vs. \( t \) is linear, the reaction is first order with respect to NO.

We follow the same procedure for ozone using the second set of data. The data and plot are:

<table>
<thead>
<tr>
<th>Time (ms)</th>
<th>([\text{O}_3]) (molecules/cm(^3))</th>
<th>(\ln [\text{O}_3])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0 ( \times 10^{10})</td>
<td>23.03</td>
</tr>
<tr>
<td>50.</td>
<td>8.4 ( \times 10^9)</td>
<td>22.85</td>
</tr>
<tr>
<td>100.</td>
<td>7.0 ( \times 10^9)</td>
<td>22.67</td>
</tr>
<tr>
<td>200.</td>
<td>4.9 ( \times 10^9)</td>
<td>22.31</td>
</tr>
<tr>
<td>300.</td>
<td>3.4 ( \times 10^9)</td>
<td>21.95</td>
</tr>
</tbody>
</table>

The plot of \( \ln [\text{O}_3] \) vs. \( t \) is linear. Hence, the reaction is first order with respect to ozone.

b. Rate = \( k[\text{NO}][\text{O}_3] \) is the overall rate law.

c. For NO experiment, Rate = \( k'[\text{NO}] \) and \( k' = -(\text{slope from graph of } \ln [\text{NO}] \text{ vs. } t) \).

\[
k' = -\text{slope} = \frac{18.41 - 20.21}{(1000 - 0) \times 10^{-3}} = 1.8 \text{ s}^{-1}
\]

For ozone experiment, Rate = \( k''[\text{O}_3] \) and \( k'' = -(\text{slope from } \ln [\text{O}_3] \text{ vs. } t) \).

\[
k'' = -\text{slope} = \frac{21.95 - 23.03}{(300 - 0) \times 10^{-3}} = 3.6 \text{ s}^{-1}
\]

d. From NO experiment, Rate = \( k[\text{NO}][\text{O}_3] = k'[\text{NO}] \) where \( k' = k[\text{O}_3] \).

\[
k' = 1.8 \text{ s}^{-1} = k(1.0 \times 10^{14} \text{ molecules/cm}^3), \quad k = 1.8 \times 10^{-14} \text{ cm}^3/\text{molecules} \cdot \text{s}
\]

We can check this from the ozone data. Rate = \( k''[\text{O}_3] = k[\text{NO}][\text{O}_3] \) where \( k'' = k[\text{NO}] \).
\[ k'' = 3.6 \text{ s}^{-1} = k(2.0 \times 10^{14} \text{ molecules/cm}^3), \quad k = 1.8 \times 10^{-14} \text{ cm}^3/\text{molecules} \cdot \text{s} \]

Both values of \( k \) agree.

74. On the energy profile to the right, \( R = \) reactants, \( P = \) products, \( E_a = \) activation energy, \( \Delta E = \) overall energy change for the reaction and \( I = \) intermediate.

a - d. See plot to the right.

e. This is a two-step reaction since an intermediate plateau appears between the reactant and the products. This plateau represents the energy of the intermediate. The general reaction mechanism for this reaction is:

\[
\begin{align*}
R & \rightarrow I \\
I & \rightarrow P \\
R & \rightarrow P
\end{align*}
\]

In a mechanism, the rate of the slowest step determines the rate of the reaction. The activation energy for the slowest step will be the largest energy barrier that the reaction must overcome. Since the second hump in the diagram is at the highest energy, the second step has the largest activation energy and will be the rate-determining step (the slow step).

75. a. If the interval between flashes is 16.3 sec, then the rate is:

\[
1 \text{ flash}/16.3 \text{ s} = 6.13 \times 10^{-2} \text{ s}^{-1} = k
\]

<table>
<thead>
<tr>
<th>Interval</th>
<th>( k )</th>
<th>( T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.3 s</td>
<td>( 6.13 \times 10^{-2} \text{ s}^{-1} )</td>
<td>21.0°C (294.2 K)</td>
</tr>
<tr>
<td>13.0 s</td>
<td>( 7.69 \times 10^{-2} \text{ s}^{-1} )</td>
<td>27.8°C (301.0 K)</td>
</tr>
</tbody>
</table>

\[
\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) ; \quad \text{Solving: } E_a = 2.5 \times 10^4 \text{ J/mol} = 25 \text{ kJ/mol}
\]

b. \[
\ln \left( \frac{k}{6.13 \times 10^{-2}} \right) = \frac{2.5 \times 10^4 \text{ J/mol}}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{294.2 \text{ K}} - \frac{1}{303.2 \text{ K}} \right) = 0.30
\]

\( k = e^{0.30} \times 6.13 \times 10^{-2} = 8.3 \times 10^{-2} \text{ s}^{-1} \); Interval = \( 1/k = 12 \text{ seconds} \)

c. | \( T \) | Interval | 54-2(Interval) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>21.0 °C</td>
<td>16.3 s</td>
<td>21 °C</td>
</tr>
<tr>
<td>27.8 °C</td>
<td>13.0 s</td>
<td>28 °C</td>
</tr>
<tr>
<td>30.0 °C</td>
<td>12 s</td>
<td>30 °C</td>
</tr>
</tbody>
</table>
This rule of thumb gives excellent agreement to two significant figures.

76. We need the value of $k$ at 500. K.  
\[
\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

\[
\ln \left( \frac{k_2}{2.3 \times 10^{-12} \text{ L/mol s}} \right) = 1.11 \times 10^5 \text{ J/mol} \left( \frac{1}{273 \text{ K}} - \frac{1}{500 \text{ K}} \right) = 22.2
\]

\[
\frac{k_2}{2.3 \times 10^{-12}} = e^{22.2}, \quad k_2 = 1.0 \times 10^{-2} \text{ L/mol s}
\]

Since the decomposition reaction is an elementary reaction, then the rate law can be written using the coefficients in the balanced equation. For this reaction: \( \text{Rate} = k[\text{NO}_2]^2 \). To solve for the time, we must use the integrated rate law for second-order kinetics. The major problem now is converting units so they match. Rearranging the ideal gas law gives \( \frac{n}{V} = \frac{P}{RT} \). Substituting \( \frac{P}{RT} \) for concentration units in the second-order integrated rate law equation:

\[
\frac{1}{[\text{NO}_2]} = k_t + \frac{1}{[\text{NO}_2]_0}, \quad \frac{1}{P/RT} = k_t + \frac{1}{P_o/RT}, \quad \frac{RT}{P} - \frac{RT}{P_o} = k_t, \quad t = \frac{RT}{k} \left( \frac{P_o - P}{P \times P_o} \right)
\]

\[
t = \frac{(0.08206 \text{ L atm/K mol})(500 \text{ K})}{1.0 \times 10^{-2} \text{ L/mol s}} \times \left( \frac{2.5 \text{ atm} - 1.5 \text{ atm}}{1.5 \text{ atm} \times 2.5 \text{ atm}} \right) = 1.1 \times 10^7 \text{ s}
\]