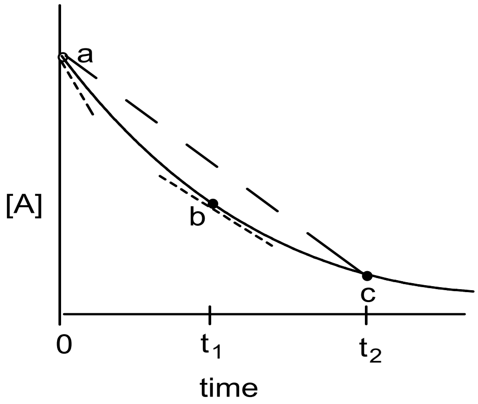
Chapter 11 Solutions to Review Questions and assigned Homework Questions

Review Questions

1. The reaction rate is defined as the change in concentration of a reactant or product per unit time. Consider the general reaction:

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

If we graph [A] vs. t, it would usually look like the solid 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 $t \approx 0$ and $t = t_1$ are drawn. The slope of these tangent lines would be the instantaneous rates at $t \approx 0$ and $t = t_1$. We call the instantaneous rate at $t \approx 0$ the initial rate. The average rate is measured over a period of time. For example, the slope of the dashed line connecting points a and c is the average rate of the reaction over the entire length of time 0 to t_2 (average rate = $\Delta[\mathrm{A}]/\Delta t$). An average rate is determined over some time period, whereas an instantaneous rate is determined at one specific time. The rate that is largest is generally the initial rate. At $t \approx 0$, the slope of the tangent line is greatest, which means the rate is largest at $t \approx 0$.

The initial rate is used by convention so that the rate of reaction only depends on the forward reaction; at $t \approx 0$, the reverse reaction is insignificant because no products are present yet.

2. The differential rate law describes the dependence of the rate on the concentration of reactants. The integrated rate law expresses reactant concentrations as a function of time. The differential rate law is generally just called the rate law. The rate constant k is a constant that allows one to equate the rate of a reaction to the concentration of reactants. The order is the exponent that the reactant concentrations are raised to in the rate equation.

3. The method of initial rates uses the results from several experiments where each experiment is carried out at a different set of initial reactant concentrations and the initial rate is determined. The results of the experiments are compared to see how the initial rate depends on the initial concentrations. If possible, two experiments are compared where only one reactant concentration changes. For these two experiments, any change in the initial rate must be due to the change in that one reactant concentration. The results of the experiments are compared until all of the orders are determined. After the orders are determined, then one can go back to any (or all) of the experiments and set the initial rate equal to the rate law using the concentrations in that experiment. The only unknown is k, which is then solved for. The units on k depend on the orders in the rate law. Because there are many different rate laws, there are many different units for k.

Rate = $k[\mathrm{A}]^n$; for a first-order rate law, $n = 1$. If [A] is tripled, then the rate is tripled. When [A] is quadrupled (increased by a factor of four), and the rate increases by a factor of 16, then A must be second order ($4^2 = 16$). For a third order reaction, as [A] is doubled, the rate will increase by a factor of $2^3 = 8$. For a zero order reaction, the rate is independent of the concentration of A. The only stipulation for zero order reactions is that the reactant or reactants must be present; if they are, then the rate is a constant value (rate = k).

5. The integrated rate laws can be put into the equation for a straight line, $y = mx + b$ where x and y are the x and y axes, m is the slope of the line, and b is the y-intercept.

Zero order:

$$\begin{array}{ccccc} [\mathrm{A}] & = & -kt & + & [\mathrm{A}] \\ y & = & mx & + & b \end{array}$$

A plot of [A] vs. time will be linear with a negative slope equal to $-k$ and a y-intercept equal to [A].

First order:

$$\begin{array}{ccccc} \ln[\mathrm{A}] & = & -kt & + & \ln[\mathrm{A}]_0 \\ y & = & mx & + & b \end{array}$$

A plot of ln[A] vs. time will be linear with a negative slope equal to $-k$ and a y-intercept equal to $\ln[\mathrm{A}]_0$.

Second order:

$$\begin{array}{ccccc} \dfrac{1}{[\mathrm{A}]} & = & kt & + & \dfrac{1}{[\mathrm{A}]_0} \\ y & = & mx & + & b \end{array}$$

A plot of 1/[A] vs. time will be linear with a positive slope equal to k and a y-intercept equal to $1/[\mathrm{A}]_0$.

When two or more reactants are studied, only one of the reactants is allowed to change during any one experiment. This is accomplished by having a large excess of the other reactant(s) as compared to the reactant studied; so large that the concentration of the other reactant(s) stays effectively constant during the experiment. The slope of the straight-line plot equals k (or $-k$) multiplied by the other reactant concentrations raised to the correct orders. Once all the orders are known for a reaction, then any (or all) of the slopes can be used to determine k.

6. At $t = t_{1/2}$, $[A] = 1/2[A]_0$; plugging these terms into the integrated rate laws yields the following half-life expressions:

zero order	first order	second order
$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

The first order half-life is independent of concentration, the zero order half-life is directly related to the concentration, and the second order half-life is inversely related to concentration. For a first order reaction, if the first half-life equals 20. s, the second half-life will also be 20. s because the half-life for a first order reaction is concentration independent. The second half-life for a zero order reaction will be 1/2(20.) = 10. s. This is because the half-life for a zero order reaction has a direct relationship with concentration (as the concentration decreases by a factor of 2, the half-life decreases by a factor of 2). For a second order reaction which has an inverse relationship between $t_{1/2}$ and $[A]_0$, the second half-life will be 40. s (twice the first half-life value).

7. a. An elementary step (reaction) is one for which the rate law can be written from the molecularity, i.e., from coefficients in the balanced equation.

b. The molecularity is the number of species that must collide to produce the reaction represented by an elementary step in a reaction mechanism.

c. 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.

d. An intermediate is a species that is neither a reactant nor a product but that is formed and consumed in the reaction sequence.

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

8. For a mechanism to be acceptable, the sum of the elementary steps must give the overall balanced equation for the reaction, and the mechanism must give a rate law that agrees with the experimentally determined rate law. A mechanism can never be proven absolutely. We can only say it is possibly correct if it follows the two requirements described above.

Most reactions occur by a series of steps. If most reactions were unimolecular, then most reactions would have a first order overall rate law, which is not the case.

9. The premise of the collision model is that molecules must collide to react, but not all collisions between reactant molecules result in product formation.

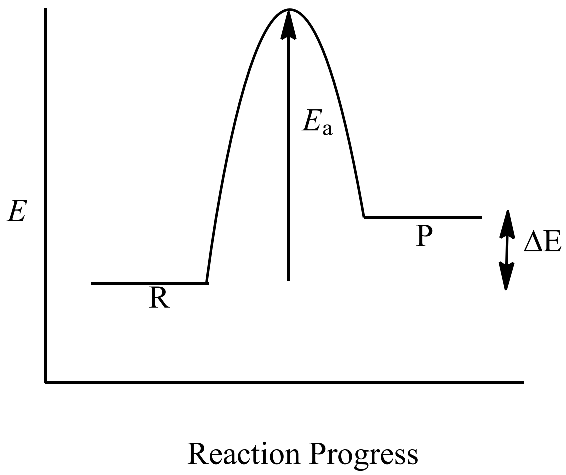
a. The larger the activation energy, the slower the rate.

b. The higher the temperature, the more molecular collisions with sufficient energy to convert to products and the faster the rate.

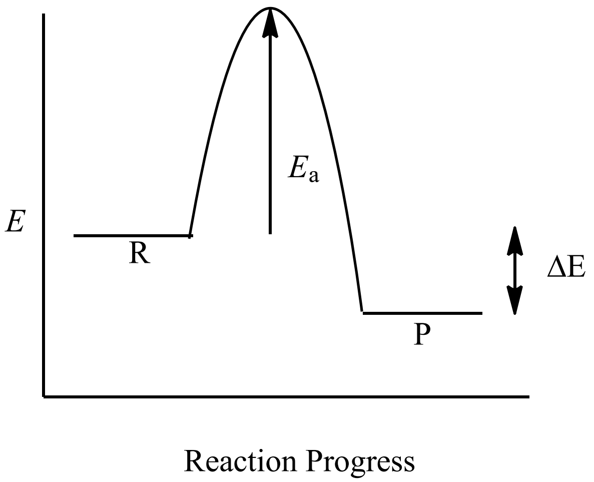
c. The greater the frequency of collisions, the greater the opportunities for molecules to react, and, hence, the greater the rate.

d. 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.

endothermic, $\Delta E > 0$



exothermic, $\Delta E < 0$



The activation energy for the reverse reaction will be the energy difference between the products and the transition state at the top of the potential energy “hill.” For an exothermic reaction, the activation energy for the reverse reaction ($E_{a,r}$) is larger than the activation energy for the forward reaction (E_a), so the rate of the forward reaction will be greater than the rate of the reverse reaction. For an endothermic reaction, $E_{a,r} < E_a$ so the rate of the forward reaction will be less than the rate of the reverse reaction (with other factors being equal).

11. 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 homogeneous catalyst is one that is in the same phase as the reacting molecules, and a heterogeneous catalyst is in a different phase than the reactants. The heterogeneous 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.

Text Homework

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

$$\text{Energy} + H_2 \rightarrow 2\,H$$

The hydrogen atoms initiate a chain reaction that proceeds very rapidly. Collisions of H_2 and O_2 molecules at room temperature do not have sufficient kinetic energy to form hydrogen atoms and initiate the reaction.

20. a. The blue plot is the catalyzed pathway. The catalyzed pathway has the lower activation. This is why the catalyzed pathway is faster.

b. ΔE_1 represents the activation energy for the uncatalyzed pathway.

c. ΔE_2 represents the energy difference between the reactants and products. Note that ΔE_2 is the same for both the catalyzed and the uncatalyzed pathways. It is the activation energy that is different for a catalyzed pathway versus an uncatalyzed pathway.

d. Because the products have a higher total energy as compared to reactants, this is an endothermic reaction.

26. 0.0120/0.0080 = 1.5; reactant B is used up 1.5 times faster than reactant A. This corresponds to a 3 to 2 mole ratio between B and A in the balanced equation. 0.0160/0.0080 = 2; product C is produced twice as fast as reactant A is used up, so the coefficient for C is twice the coefficient for A. A possible balanced equation is $2A + 3B \rightarrow 4C$.

34. Rate = $k[NO]^x[O_2]^y$; comparing the first two experiments, $[O_2]$ is unchanged, [NO] is tripled, and the rate increases by a factor of nine. Therefore, the reaction is second order in NO ($3^2 = 9$). The order of O_2 is more difficult to determine. Comparing the second and third experiments:

$$\frac{3.13 \times 10^{17}}{1.80 \times 10^{17}} = \frac{k(2.50 \times 10^{18})^2(2.50 \times 10^{18})^y}{k(3.00 \times 10^{18})^2(1.00 \times 10^{18})^y}$$

$$1.74 = 0.694(2.50)^y,\ \ 2.51 = 2.50^y,\ \ y = 1$$

Rate = $k[NO]^2[O_2]$; from experiment 1:

$$2.00 \times 10^{16}\ \text{molecules/cm}^3\text{•s} = k(1.00 \times 10^{18}\ \text{molecules/cm}^3)^2 \times (1.00 \times 10^{18}\ \text{molecules/cm}^3)$$

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

$$\text{Rate} = \frac{2.00\times10^{-38}\ \text{cm}^6}{\text{molecules}^2\ \text{s}} \times \left(\frac{6.21\times10^{18}\ \text{molecules}}{\text{cm}^3}\right)^2 \times \frac{7.36\times10^{18}\ \text{molecules}}{\text{cm}^3}$$

Rate = 5.68×10^{18} molecules/cm^3•s

36. a. Rate = $k[ClO_2]^x[OH^-]^y$; 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: $4.00 = \dfrac{(0.100)^x}{(0.0500)^x} = 2.00^x$, $x = 2$

Comparing the second and third experiments:

$2.30 \times 10^{-1} = k(0.100)(0.100)^y$ and $1.15 \times 10^{-1} = k(0.100)(0.0500)^y$

Dividing: $2.00 = \dfrac{(0.100)^y}{(0.050)^y} = 2.0^y$, $y = 1$

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), k = 2.30×10^2 L^2/mol^2•s = k_{mean}

b. $$\text{Rate} = \frac{2.30\times10^2\ \text{L}^2}{\text{mol}^2\ \text{s}} \times \left(\frac{0.175\ \text{mol}}{\text{L}}\right)^2 \times \frac{0.0844\ \text{mol}}{\text{L}} = 0.594\ \text{mol/L•s}$$

38. a. Because the ln[A] versus time plot was linear, the reaction is first order in A. The slope of the ln[A] versus time plot equals –k. Therefore, the rate law, the integrated rate law, and the rate constant value are:

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

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

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k},\quad t_{1/2} = \frac{0.6931}{2.97\times10^{-2}\ \text{min}^{-1}} = 23.3\ \text{min}$$

c. 2.50×10^{-3} *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), then the reaction has gone through 3 half-lives:

$$100\% \xrightarrow[t_{1/2}]{} 50.0\% \xrightarrow[t_{1/2}]{} 25.0\% \xrightarrow[t_{1/2}]{} 12.5\%;\quad t = 3 \times t_{1/2} = 3 \times 23.3\ \text{min} = 69.9\ \text{min}$$

Or we can use the integrated rate law:

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt,\ \ln\left(\frac{2.50\times10^{-3}\ M}{2.00\times10^{-2}\ M}\right) = -(2.97\times10^{-2}\ \text{min}^{-1})t$$

$$t = \frac{\ln(0.125)}{-2.97\times10^{-2}\ \text{min}^{-1}} = 70.0\ \text{min}$$

40. a. Because the 1/[A] versus time plot was linear, the reaction is second order in A. The slope of the 1/[A] versus time plot equals the rate constant k. Therefore, the rate law, the integrated rate law, and the rate constant value are:

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

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

For this reaction: $t_{1/2} = \dfrac{1}{3.60 \times 10^{-2}\ \text{L/mol}\bullet\text{s} \times 2.80 \times 10^{-3}\ \text{mol/L}} = 9.92 \times 10^{3}\ \text{s}$

Note: We could have used the integrated rate law to solve for $t_{1/2}$, where $[A] = (2.80 \times 10^{-3}/2)$ mol/L.

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

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0},\quad \frac{1}{7.00 \times 10^{-4}\ M} = \frac{3.60 \times 10^{-2}\ \text{L}}{\text{mol s}} \times t + \frac{1}{2.80 \times 10^{-3}\ M}$$

$1.43 \times 10^{3} - 357 = (3.60 \times 10^{-2})t,\ t = 2.98 \times 10^{4}$ s

46. a. The slope of the 1/[A] versus time plot in Exercise 45 will equal k.

$$\text{Slope} = k = \frac{(60 - 20)\ \text{L/mol}}{(5 - 1)\ \text{s}} = 10\ \text{L/mol}\bullet\text{s}$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} = \frac{10\ \text{L}}{\text{mol s}} \times 9\ \text{s} + \frac{1}{0.1\ M} = 100,\ [A] = 0.01\ M$$

b. For a second-order reaction, the half-life does depend on concentration: $t_{1/2} = \dfrac{1}{k[A]_0}$

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

Second half-life ($[A]_0$ is now 0.05 *M*): $t_{1/2} = 1/(10 \times 0.05) = 2$ s

Third half-life ($[A]_0$ is now 0.025 *M*): $t_{1/2} = 1/(10 \times 0.025) = 4$ s

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

$$\frac{1}{(0.900/2)\ \text{mol/L}} = k \times 2.00\ \text{s} + \frac{1}{0.900\ \text{mol/L}},\ k = \frac{1.11\ \text{L/mol}}{2.00\ \text{s}} = 0.555\ \text{L/mol}\bullet\text{s}$$

b. $\dfrac{1}{0.100\ \text{mol/L}} = 0.555\ \text{L/mol}\bullet\text{s} \times t + \dfrac{1}{0.900\ \text{mol/L}},\ t = \dfrac{8.9\ \text{L/mol}}{0.555\ \text{L/mol}\bullet\text{s}} = 16$ s

58. Because $[B]_0 >> [A]_0$, 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. $\ln\left(\frac{[A]}{[A]_0}\right) = -k't,\ \ln\left(\frac{3.8 \times 10^{-3}\ M}{1.0 \times 10^{-2}\ M}\right) = -k' \times 8.0\ \text{s},\ \ k' = 0.12\ \text{s}^{-1}$

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

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

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

$[A] = 2.1 \times 10^{-3} M$

d. $[A]_{\text{reacted}} = 0.010\ M - 0.0021\ M = 0.008\ M$

$[C]_{\text{reacted}} = 0.008\ M \times \frac{2\ \text{mol C}}{1\ \text{mol A}} = 0.016\ M \approx 0.02\ M$

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

60. From experiment (Exercise 37), we know the rate law is Rate = $k[H_2O_2]$. 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 equation for each respective step. 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.

This mechanism will agree with the experimentally determined rate law only if step 1 is the slow step (called the rate-determining step). If step 1 is slow, then Rate = $k[H_2O]_2$ which agrees with experiment.

Another important property of a mechanism is that the sum of all steps must give the overall balanced equation. Summing all steps gives:

$$\begin{array}{c}
H_2O_2 \rightarrow 2\ OH \\
H_2O_2 + OH \rightarrow H_2O + HO_2 \\
HO_2 + OH \rightarrow H_2O + O_2 \\
\hline
2\ H_2O_2 \rightarrow 2\ H_2O + O_2
\end{array}$$

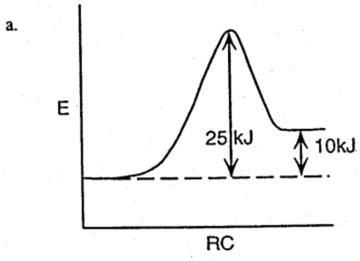
62. Because the rate of the slowest elementary step equals the rate of a reaction:

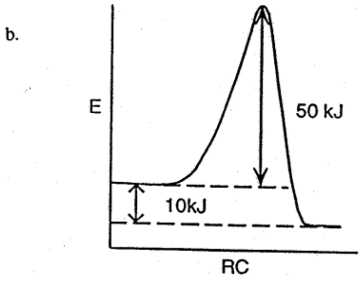
Rate = rate of step 1 = $k[NO_2]^2$

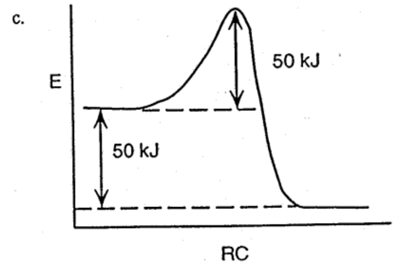
The sum of all steps in a plausible mechanism must give the overall balanced reaction. Summing all steps gives:

$$\begin{array}{c}
NO_2 + NO_2 \rightarrow NO_3 + NO \\
NO_3 + CO \rightarrow NO_2 + CO_2 \\
\hline
NO_2 + CO \rightarrow NO + CO_2
\end{array}$$

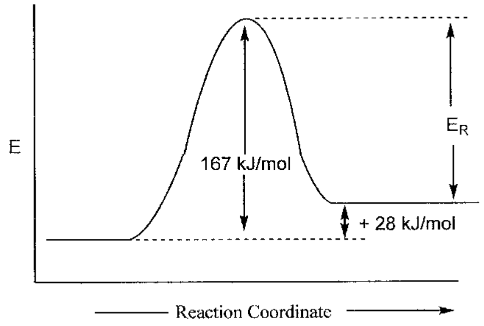
64. When ΔE is positive, the products are at a higher energy relative to reactants, and when ΔE is negative, the products are at a lower energy relative to reactants. RC = reaction coordinate, which is the same as reaction progress.







66.



The activation energy for the reverse reaction is E_R in the diagram.

E_R = 167 – 28 = 139 kJ/mol

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

$$\begin{array}{ll} O_3 + Cl \rightarrow O_2 + ClO & \text{(slow)} \\ ClO + O \rightarrow O_2 + Cl & \text{(fast)} \\ \hline O_3 + O \rightarrow 2\,O_2 & \end{array}$$

Because the chlorine atom-catalyzed reaction has a lower activation energy, the Cl-catalyzed rate is faster. Hence Cl is a more effective catalyst. Using the activation energy, we can estimate the efficiency that Cl atoms destroy ozone compared to NO molecules (see Exercise 75c).

At 25°C: $\frac{k_{Cl}}{k_{NO}} = \exp\left[\frac{-E_a(Cl)}{RT} + \frac{E_a(NO)}{RT}\right] = \exp\left[\frac{(-2100 + 11{,}900)\ J/mol}{(8.3145 \times 298)\ J/mol}\right] = e^{3.96} = 52$

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.

98. Rate = $k[DNA]^x[CH_3I]^y$; comparing the second and third experiments:

$$\frac{1.28 \times 10^{-3}}{6.40 \times 10^{-4}} = \frac{k(0.200)^x(0.200)^y}{k(0.100)^x(0.200)^y},\ 2.00 = 2.00^x,\ x = 1$$

Comparing the first and second experiments:

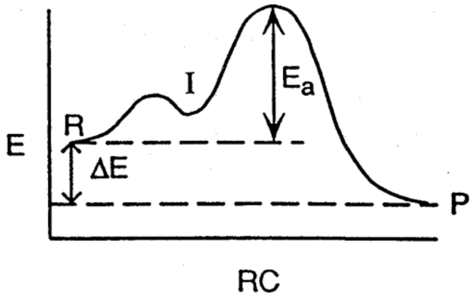
$$\frac{6.40 \times 10^{-4}}{3.20 \times 10^{-4}} = \frac{k(0.100)(0.200)^y}{k(0.100)(0.100)^y},\ 2.00 = 2.00^y,\ y = 1$$

The rate law is Rate = $k[DNA][CH_3I]$.

Mechanism I is possible because the derived rate law from the mechanism (Rate = $k[DNA][CH_3I]$) agrees with the experimentally determined rate law. The derived rate law for Mechanism II will equal the rate of the slowest step. This is step 1 in the mechanism giving a derived rate law that is Rate = $k[CH_3I]$. Because this rate law does not agree with experiment, Mechanism II would not be a possible mechanism for the reaction.

108. On the energy profile to the right, R = reactants, P = products, E_a = activation energy, ΔE = overall energy change for the reaction, I = intermediate, and RC = reaction coordinate, which is the same as reaction progress.

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:

$$\begin{array}{l} R \rightarrow I \\ \underline{I \rightarrow P} \\ R \rightarrow P \end{array}$$

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).