# CHAPTER 16 KINETICS: RATES AND MECHANISMS OF CHEMICAL REACTIONS

END–OF–CHAPTER PROBLEMS

16.1 Changes in concentrations of reactants (or products) as functions of time are measured to determine the reaction rate.

16.2 Rate is proportional to concentration. An increase in pressure will increase the number of gas molecules per unit volume. In other words, the gas concentration increases due to increased pressure, so the **reaction rate increases**. Increased pressure also causes more collisions between gas molecules.

16.3 The addition of more water will dilute the concentrations of all solutes dissolved in the reaction vessel. If any of these solutes are reactants, the **rate of the reaction will decrease**.

16.4 An increase in solid surface area would allow more gaseous components to react per unit time and thus would **increase the reaction rate**.

16.5 An increase in temperature affects the rate of a reaction by increasing the number of collisions, but more importantly, the energy of collisions increases. As the energy of collisions increases, more collisions result in reaction (i.e., reactants $\rightarrow$ products), so the **rate of reaction increases**.

16.6 The second experiment proceeds at the higher rate. I_2 in the gaseous state would experience more collisions with gaseous H_2.

16.7 The reaction rate is the change in the concentration of reactants or products per unit time. Reaction rates change with time because reactant concentrations decrease, while product concentrations increase with time.

16.8 a) For most reactions, the rate of the reaction changes as a reaction progresses. The instantaneous rate is the rate at one point, or instant, during the reaction. The average rate is the average of the instantaneous rates over a period of time. On a graph of reactant concentration vs. time of reaction, the instantaneous rate is the slope of the tangent to the curve at any one point. The average rate is the slope of the line connecting two points on the curve. The closer together the two points (shorter the time interval), the more closely the average rate agrees with the instantaneous rate.
b) The initial rate is the instantaneous rate at the point on the graph where time = 0, that is when reactants are mixed.

16.9 The calculation of the overall rate is the difference between the forward and reverse rates. This complication may be avoided by measuring the initial rate, where product concentrations are negligible, so the reverse rate is negligible. Additionally, the calculations are simplified as the reactant concentrations can easily be determined from the volumes and concentrations of the solutions mixed.

16.10 At time $t = 0$, no product has formed, so the B(g) curve must start at the origin. Reactant concentration (A(g)) decreases with time; product concentration (B(g)) increases with time. Many correct graphs can be drawn. Two examples are shown below. The graph on the left shows a reaction that proceeds nearly to completion, i.e., [products] >> [reactants] at the end of the reaction. The graph on the right shows a reaction that does not proceed to completion, i.e., [reactants] > [products] at reaction end.
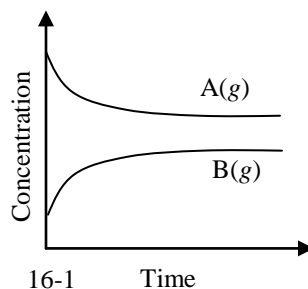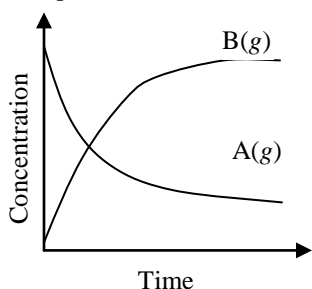
16.11   a) Calculate the slope of the line connecting $(0, [C]_o)$ and $(t_f, [C]_f)$ (final time and concentration). The negative of this slope is the average rate.
b) Calculate the negative of the slope of the line tangent to the curve at $t = x$.
c) Calculate the negative of the slope of the line tangent to the curve at $t = 0$.
d) If you plotted [D] vs. time, you would not need to take the negative of the slopes in a)-c) since [D] would increase over time.

16.12   Plan: The average rate is the total change in concentration divided by the total change in time.
Solution:
a) The average rate from $t = 0$ to $t = 20.0$ s is proportional to the slope of the line connecting these two points:

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[AX_2]}{\Delta t} = -\frac{1}{2}\frac{(0.0088 \text{ mol/L} - 0.0500 \text{ mol/L})}{(20.0 \text{ s} - 0 \text{ s})} = 0.00103 = \textbf{0.0010 mol/L•s}$$

The negative of the slope is used because rate is defined as the change in product concentration with time. If a reactant is used, the rate is the negative of the change in reactant concentration. The 1/2 factor is included to account for the stoichiometric coefficient of 2 for AX_2 in the reaction.
b)

[AX₂] vs time
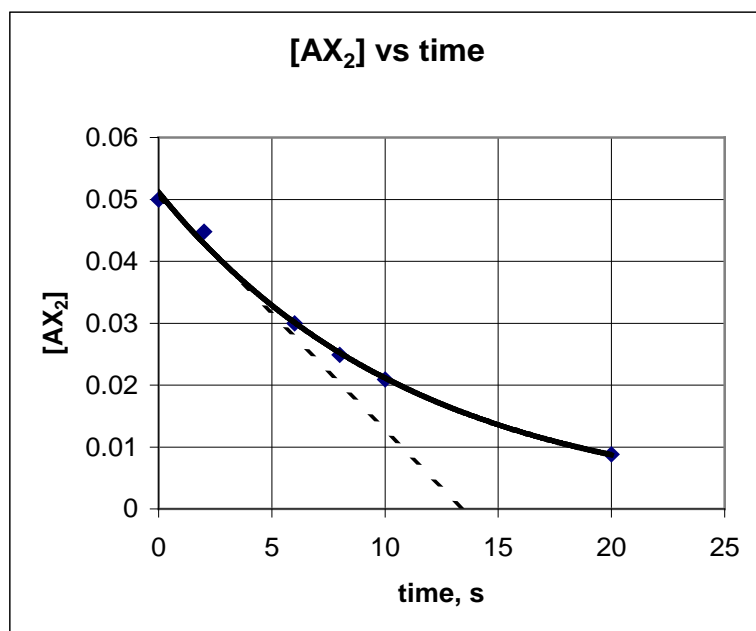
The slope of the tangent to the curve (dashed line) at $t = 0$ is approximately -0.004 mol/L•s. This initial rate is greater than the average rate as calculated in part a). The **initial rate is greater than the average rate** because rate decreases as reactant concentration decreases.
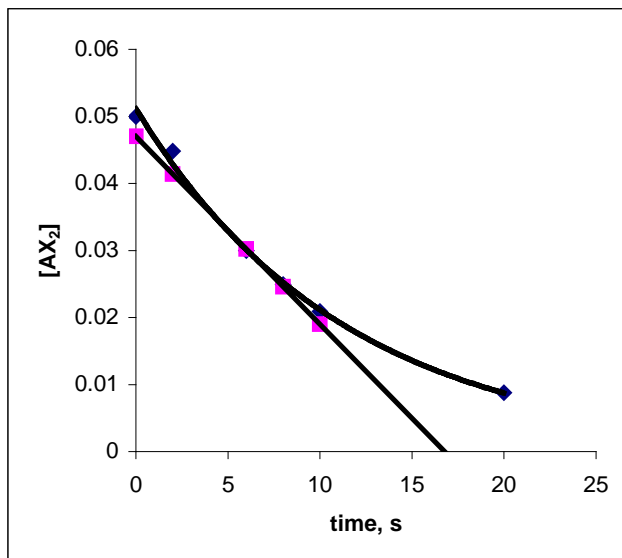
16.13   Plan: The average rate is the total change in concentration divided by the total change in time.
Solution:
a) $\text{Rate} = -\frac{1}{2}\frac{\Delta[AX_2]}{\Delta t} = -\frac{1}{2}\frac{(0.0088 \text{ mol/L} - 0.0249 \text{ mol/L})}{(20.0 \text{ s} - 8.0 \text{ s})} = 6.70833 \times 10^{-4} = \textbf{6.71} \times \textbf{10}^{\textbf{-4}} \textbf{ mol/L•s}$

b) The rate at exactly 5.0 s will be higher than the rate in part a).
The slope of the tangent to the curve at $t = 5.0$ s (the rate at 5.0 s) is approximately $\textbf{-2.8} \times \textbf{10}^{\textbf{-3}} \textbf{ mol/L•s}$.

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16.14   Plan: Use Equation 16.2 to describe the rate of this reaction in terms of reactant disappearance and product appearance. A negative sign is used for the rate in terms of reactants A and B since A and B are reacting and [A] and [B] are decreasing over time. A positive sign is used for the rate in terms of product C since C is being formed and [C] increases over time. The 1/2 factor is included for reactant B to account for the stoichiometric coefficient of 2 for B in the reaction. Reactant A decreases half as fast as reactant B decreases because one molecule of A disappears for every two molecules of B that disappear.
Solution:
Expressing the rate in terms of each component:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{1}{2}\frac{\Delta[B]}{\Delta t} = \frac{\Delta[C]}{\Delta t}$$

Calculating the rate of change of [A]:

$$\left(0.5\ \text{mol B/L•s}\right)\left(\frac{1\ \text{mol A/L•s}}{2\ \text{mol B/L•s}}\right) = -0.25\ \text{mol/L•s} = -0.2\ \text{mol/L•s}$$

The negative value indicates that [A] is decreasing as the reaction progresses. The rate of reaction is always expressed as a positive number, so [A] is decreasing at a rate of **0.2 mol/L•s**.

16.15   Plan: Use Equation 16.2 to describe the rate of this reaction in terms of reactant disappearance and product appearance. A negative sign is used for the rate in terms of reactants D, E, and F since these substances are reacting and [D], [E], and [F] are decreasing over time. Positive signs are used for the rate in terms of products G and H since these substances are being formed and [G] and [H] increase over time. Product H increases half as fast as reactant D decreases because one molecule of H is formed for every two molecules of D that disappear.
Solution:
Expressing the rate in terms of each component:

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[D]}{\Delta t} = -\frac{1}{3}\frac{\Delta[E]}{\Delta t} = -\frac{\Delta[F]}{\Delta t} = \frac{1}{2}\frac{\Delta[G]}{\Delta t} = \frac{\Delta[H]}{\Delta t}$$

Calculating the rate of change of [H]: $\left(0.1\ \text{mol D/L•s}\right)\left(\dfrac{1\ \text{mol H/L•s}}{2\ \text{mol D/L•s}}\right) = $ **0.05 mol/L•s**

16.16   Plan: A term with a negative sign is a reactant; a term with a positive sign is a product. The inverse of the fraction becomes the coefficient of the molecule.
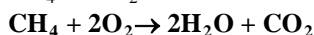Solution:
N_2O_5 is the reactant; NO_2 and O_2 are products.
$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

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16.17   Plan: A term with a negative sign is a reactant; a term with a positive sign is a product. The inverse of the fraction becomes the coefficient of the molecule.
Solution:
CH_4 and O_2 are the reactants; H_2O and CO_2 are products.
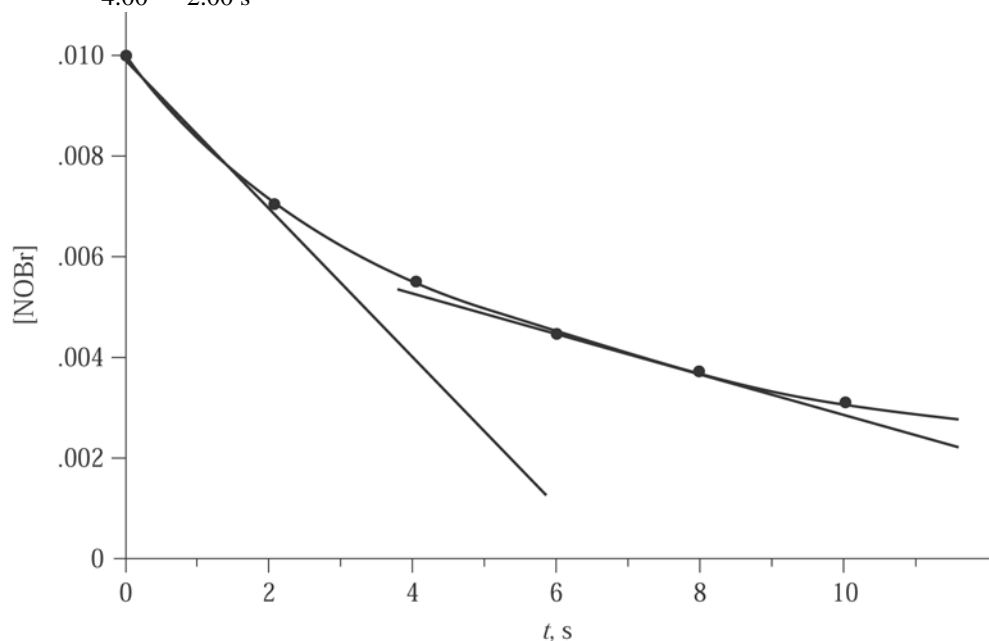**$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$**

16.18   Plan: The average rate is the total change in concentration divided by the total change in time. The initial rate is the slope of the tangent to the curve at $t = 0.0$ s and the rate at 7.00 s is the slope of the tangent to the curve at $t = 7.00$ s
Solution:

a) Rate $= -\dfrac{\Delta[\text{NOBr}]}{\Delta t}$ $-\dfrac{0.0033 - 0.0100 \text{ mol/L}}{10.00 - 0.00 \text{ s}}$ **$= 6.7\text{x}10^{-4}$ mol/L•s**

b) Rate $= -\dfrac{0.0055 - 0.0071 \text{ mol/L}}{4.00 - 2.00 \text{ s}}$ **$= 8.0\text{x}10^{-4}$ mol/L•s**

c)

Initial Rate $= -\Delta y/\Delta x = -[(0.0040 - 0.0100) \text{ mol/L}]/[4.00 - 0.00) \text{ s}] = \mathbf{1.5x10^{-3}}$ **mol/L•s**
d) Rate at 7.00 s $= -[(0.0030 - 0.0050) \text{ mol/L}]/[11.00 - 4.00) \text{ s}] = 2.857\text{x}10^{-4} = \mathbf{2.9x10^{-4}}$ **mol/L•s**
e) Average between $t = 3$ s and $t = 5$ s is:
Rate $= -[(0.0050 - 0.0063) \text{ mol/L}]/[5.00 - 3.00) \text{ s}] = 6.5\text{x}10^{-4}$ mol/L•s
Rate at 4 s $\approx 6.7\text{x}10^{-4}$ mol/L•s, thus the rates are equal at about **4 seconds**.

16.19   Plan: Use Equation 16.2 to describe the rate of this reaction in terms of reactant disappearance and product appearance. A negative sign is used for the rate in terms of the reactant O_2 since it is reacting and $[O_2]$ is decreasing over time. A positive sign is used for the rate in terms of the product O_3 since it is being formed and $[O_3]$ increases over time. O_3 increases 2/3 as fast as O_2 decreases because two molecules of O_3 are formed for every three molecules of O_2 that disappear.
Solution:

a) Rate $= -\dfrac{1}{3}\dfrac{\Delta[O_2]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[O_3]}{\Delta t}$

b) Use the mole ratio in the balanced equation:

$\left(\dfrac{2.17\text{x}10^{-5} \text{ mol } O_2 \text{ /L•s}}{}\right)\left(\dfrac{2 \text{ mol } O_3 \text{ /L•s}}{3 \text{ mol } O_2 \text{/L•s}}\right) = \mathbf{1.45x10^{-5}}$ **mol/L•s**

16.20 a) k is the rate constant, the proportionality constant in the rate law. k represents the fraction of successful collisions which includes the fraction of collisions with sufficient energy and the fraction of collisions with correct orientation. k is a constant that varies with temperature.

b) m represents the order of the reaction with respect to [A] and n represents the order of the reaction with respect to [B]. The order is the exponent in the relationship between rate and reactant concentration and defines how reactant concentration influences rate.

The order of a reactant does not necessarily equal its stoichiometric coefficient in the balanced equation. If a reaction is an elementary reaction, meaning the reaction occurs in only one step, then the orders and stoichiometric coefficients are equal. However, if a reaction occurs in a series of elementary reactions, called a mechanism, then the rate law is based on the slowest elementary reaction in the mechanism. The orders of the reactants will equal the stoichiometric coefficients of the reactants in the slowest elementary reaction but may not equal the stoichiometric coefficients in the overall reaction.

c) For the rate law rate $= k[A] [B]^2$ substitute in the units:

$$\text{Rate (mol/L·min)} = k[A]^1[B]^2$$

$$k = \frac{\text{rate}}{[A]^1[B]^2} = \frac{\text{mol/L•min}}{\left[\dfrac{\text{mol}}{L}\right]^1 \left[\dfrac{\text{mol}}{L}\right]^2} = \frac{\text{mol/L•min}}{\dfrac{\text{mol}^3}{L^3}}$$

$$k = \frac{\text{mol}}{L\text{•min}}\left(\frac{L^3}{\text{mol}^3}\right)$$

$$\mathbf{\mathit{k} = L^2/mol^2\text{•}min}$$

16.21 a) The **rate doubles**. If rate $= k[A]^1$ and [A] is doubled, then the rate law becomes rate $= k[2 \times A]^1$. The rate increases by 2^1 or 2.

b) The **rate decreases by a factor of four**. If rate $= k[B]^2$ and [B] is halved, then the rate law becomes rate $= k[1/2 \times B]^2$. The rate decreases to $(1/2)^2$ or 1/4 of its original value.

c) The **rate increases by a factor of nine**. If rate $= k[C]^2$ and [C] is tripled, then the rate law becomes rate $= k[3 \times C]^2$. The rate increases to 3^2 or 9 times its original value.

16.22 <u>Plan:</u> The order for each reactant is the exponent on the reactant concentration in the rate law. The individual orders are added to find the overall reaction order.

<u>Solution:</u>
The orders with respect to $[BrO_3^-]$ and to $[Br^-]$ are both 1 since both have an exponent of 1. The order with respect to $[H^+]$ is 2 (its exponent in the rate law is 2). The overall reaction order is $1 + 1 + 2 = 4$.
first order with respect to BrO_3^-, first order with respect to Br^-, second order with respect to H^+, fourth order overall

16.23 <u>Plan:</u> The order for each reactant is the exponent on the reactant concentration in the rate law. The individual orders are added to find the overall reaction order.

<u>Solution:</u>
The rate law may be rewritten as rate $= k[O_3]^2[O_2]^{-1}$. The order with respect to $[O_3]$ is 2 since it has an exponent of 2. The order with respect to $[O_2]$ is -1 since it has an exponent of -1. The overall reaction order is $2 + (-1) = 1$. **Second order with respect to O_3, (-1) order with respect to O_2, first order overall**

16.24 a) The rate is first order with respect to $[BrO_3^-]$. If $[BrO_3^-]$ is doubled, rate $= k[2 \times BrO_3^-]$, then rate increases to 2^1 or 2 times its original value. The rate **doubles**.

b) The rate is first order with respect to $[Br^-]$. If $[Br^-]$ is halved, rate $= k[1/2 \times Br^-]$, then rate decreases by a factor of $(1/2)^1$ or 1/2 times its original value. The rate is **halved**.

c) The rate is second order with respect to $[H^+]$. If $[H^+]$ is quadrupled, rate $= k[4 \times H^+]^2$, then rate increases to 4^2 or **16 times** its original value.

16.25 a) The rate is second order with respect to $[O_3]$. If $[O_3]$ is doubled, rate $= k[2 \times O_3]^2$, then rate increases to 2^2 or 4 times its original value. The rate **increases by a factor of 4**.

b) $[O_2]$ has an order of -1. If $[O_2]$ is doubled, rate $= k[2 \times O_2]^{-1}$, then rate decreases to 2^{-1} or 1/2 times its original value. The rate **decreases by a factor of 2**.

c) $[O_2]$ has an order of –1. If $[O_2]$ is halved, rate $= k[1/2 \times O_2]^{-1}$, then rate decreases by a factor of $(1/2)^{-1}$ or 2 times its original value. The rate **increases by a factor of 2**.

16.26   <u>Plan:</u> The rate law is rate $= [A]^m[B]^n$ where m and n are the orders of the reactants. To find the order of each reactant, take the ratio of the rate laws for two experiments in which only the reactant in question changes. Once the rate law is known, any experiment can be used to find the rate constant k.
<u>Solution:</u>
a) To find the order for reactant A, first identify the reaction experiments in which [A] changes but [B] is constant. Use experiments 1 and 2 (or 3 and 4 would work) to find the order with respect to [A]. Set up a ratio of the rate laws for experiments 1 and 2 and fill in the values given for rates and concentrations and solve for m, the order with respect to [A].

$$\frac{\text{rate}_{\text{exp 2}}}{\text{rate}_{\text{exp 1}}} = \left(\frac{[A]_{\text{exp 2}}}{[A]_{\text{exp 1}}}\right)^m$$

$$\frac{45.0 \text{ mol/L} \cdot \text{min}}{5.00 \text{ mol/L} \cdot \text{min}} = \left(\frac{0.300 \text{ mol/L}}{0.100 \text{ mol/L}}\right)^m$$

$$9.00 = (3.00)^m$$
$$\log (9.00) = m \log (3.00)$$
$$m = 2$$

Using experiments 3 and 4 also gives **second order with respect to [A]**.
To find the order for reactant B, first identify the reaction experiments in which [B] changes but [A] is constant. Use experiments 1 and 3 (or 2 and 4 would work) to find the order with respect to [B]. Set up a ratio of the rate laws for experiments 1 and 3 and fill in the values given for rates and concentrations and solve for n, the order with respect to [B].

$$\frac{\text{rate}_{\text{exp 3}}}{\text{rate}_{\text{exp 1}}} = \left(\frac{[B]_{\text{exp 3}}}{[B]_{\text{exp 1}}}\right)^n$$

$$\frac{10.0 \text{ mol/L} \cdot \text{min}}{5.00 \text{ mol/L} \cdot \text{min}} = \left(\frac{0.200 \text{ mol/L}}{0.100 \text{ mol/L}}\right)^n$$

$$2.00 = (2.00)^n$$
$$\log (2.00) = n \log (2.00)$$
$$n = 1$$

The reaction is **first order with respect to [B].**
b) The rate law, without a value for k, is **rate $= k[A]^2[B]$**.
c) Using experiment 1 to calculate k (the data from any of the experiments can be used):
Rate $= k[A]^2[B]$

$$k = \frac{\text{rate}}{[A]^2[B]} = \frac{5.00 \text{ mol/L} \cdot \text{min}}{[0.100 \text{ mol/L}]^2[0.100 \text{ mol/L}]} = \textbf{5.00x10}^3 \textbf{ L}^2\textbf{/mol}^2\textbf{•min}$$

16.27   <u>Plan:</u> The rate law is rate $= k [A]^m[B]^n[C]^p$ where m, n, and p are the orders of the reactants. To find the order of each reactant, take the ratio of the rate laws for two experiments in which only the reactant in question changes. Once the rate law is known, any experiment can be used to find the rate constant k.
<u>Solution:</u>
a) To find the order for reactant A, first identify the reaction experiments in which [A] changes but [B] and [C] are constant. Use experiments 1 and 2 to find the order with respect to [A]. Set up a ratio of the rate laws for experiments 1 and 2 and fill in the values given for rates and concentrations and solve for m, the order with respect to [A].

$$\frac{\text{rate}_{\text{exp 2}}}{\text{rate}_{\text{exp 1}}} = \left(\frac{[A]_{\text{exp 2}}}{[A]_{\text{exp 1}}}\right)^m$$

$$\frac{1.25\text{x}10^{-2} \text{ mol/L} \cdot \text{min}}{6.25\text{x}10^{-3} \text{ mol/L} \cdot \text{min}} = \left(\frac{0.1000 \text{ mol/L}}{0.0500 \text{ mol/L}}\right)^m$$

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$$2.00 = (2.00)^m$$
$$\log (2.00) = m \log (2.00)$$
$m = 1$ The order is **first order with respect to A**.

To find the order for reactant B, first identify the reaction experiments in which [B] changes but [A] and [C] are constant. Use experiments 2 and 3 to find the order with respect to [B]. Set up a ratio of the rate laws for experiments 2 and 3 and fill in the values given for rates and concentrations and solve for n, the order with respect to [B].

$$\frac{rate_{exp\ 3}}{rate_{exp\ 2}} = \left(\frac{[B]_{exp\ 3}}{[B]_{exp\ 2}} \right)^n$$

$$\frac{5.00 \times 10^{-2}\ mol/L{\cdot}min}{1.25 \times 10^{-2}\ mol/L{\cdot}min} = \left(\frac{0.1000\ mol/L}{0.0500\ mol/L} \right)^n$$

$$4.00 = (2.00)^n$$
$$\log (4.00) = n \log (2.00)$$
$n = 2$ The reaction is **second order with respect to B**.

To find the order for reactant C, first identify the reaction experiments in which [C] changes but [A] and [B] are constant. Use experiments 1 and 4 to find the order with respect to [C]. Set up a ratio of the rate laws for experiments 1 and 4 and fill in the values given for rates and concentrations and solve for p, the order with respect to [C].

$$\frac{rate_{exp\ 4}}{rate_{exp\ 1}} = \left(\frac{[C]_{exp\ 4}}{[C]_{exp\ 1}} \right)^p$$

$$\frac{6.25 \times 10^{-3}\ mol/L{\cdot}min}{6.25 \times 10^{-3}\ mol/L{\cdot}min} = \left(\frac{0.0200\ mol/L}{0.0100\ mol/L} \right)^p$$

$$1.00 = (2.00)^p$$
$$\log (1.00) = p \log (2.00)$$
$p = 0$ The reaction is **zero order with respect to C.**

b) Rate $= k[A]^1[B]^2[C]^0$
     Rate $= k[A][B]^2$

c) Using the data from experiment 1 to find k:
Rate $= k[A][B]^2$

$$k = \frac{rate}{[A][B]^2} = \frac{6.25 \times 10^{-3}\ mol/L{\cdot}min}{[0.0500\ mol/L][0.0500\ mol/L]^2} = \mathbf{50.0\ L^2/mol^2{\cdot}s}$$

16.28   <u>Plan:</u> The rate law is rate $= k\,[CO]^m[Cl_2]^n$ where m and n are the orders of the reactants. To find the order of each reactant, take the ratio of the rate laws for two experiments in which only the reactant in question changes. Once the rate law is known, the data in each experiment can be used to find the rate constant k.
<u>Solution:</u>
a) To find the order for CO, first identify the reaction experiments in which [CO] changes but [Cl_2] is constant. Use experiments 1 and 2 to find the order with respect to [CO]. Set up a ratio of the rate laws for experiments 1 and 2 and fill in the values given for rates and concentrations and solve for m, the order with respect to [CO].

$$\frac{rate_{exp\ 1}}{rate_{exp\ 2}} = \left(\frac{[CO]_{exp\ 1}}{[CO]_{exp\ 2}} \right)^m$$

$$\frac{1.29 \times 10^{-29}\ mol/L{\cdot}min}{1.33 \times 10^{-30}\ mol/L{\cdot}min} = \left(\frac{1.00\ mol/L}{0.100\ mol/L} \right)^m$$

$$9.699 = (10.0)^m$$
$$\log (9.699) = m \log (10.0)$$
$$m = 0.9867 = 1$$
The reaction is first order with respect to [CO].

To find the order for Cl_2, first identify the reaction experiments in which $[Cl_2]$ changes but $[CO]$ is constant. Use experiments 2 and 3 to find the order with respect to $[Cl_2]$. Set up a ratio of the rate laws for experiments 2 and 3 and fill in the values given for rates and concentrations and solve for n, the order with respect to $[Cl_2]$.

$$\frac{rate_{exp\,3}}{rate_{exp\,2}} = \left(\frac{[Cl_2]_{exp\,3}}{[Cl_2]_{exp\,2}}\right)^n$$

$$\frac{1.30 \times 10^{-29} \text{ mol/L} \cdot \text{min}}{1.33 \times 10^{-30} \text{ mol/L} \cdot \text{min}} = \left(\frac{1.00 \text{ mol/L}}{0.100 \text{ mol/L}}\right)^n$$

$$9.774 = (10.0)^n$$
$$\log(9.774) = n \log(10.0)$$
$$n = 0.9901 = 1$$

The reaction is first order with respect to $[Cl_2]$.

Rate = $k[CO][Cl_2]$

b) $k = rate/[CO][Cl_2]$

Exp 1: $k_1 = (1.29 \times 10^{-29} \text{ mol/L} \cdot \text{s})/[1.00 \text{ mol/L}][0.100 \text{ mol/L}] = 1.29 \times 10^{-28}$ L/mol•s

Exp 2: $k_2 = (1.33 \times 10^{-30} \text{ mol/L} \cdot \text{s})/[0.100 \text{ mol/L}][0.100 \text{ mol/L}] = 1.33 \times 10^{-28}$ L/mol•s

Exp 3: $k_3 = (1.30 \times 10^{-29} \text{ mol/L} \cdot \text{s})/[0.100 \text{ mol/L}][1.00 \text{ mol/L}] = 1.30 \times 10^{-28}$ L/mol•s

Exp 4: $k_4 = (1.32 \times 10^{-31} \text{ mol/L} \cdot \text{s})/[0.100 \text{ mol/L}][0.0100 \text{ mol/L}] = 1.32 \times 10^{-28}$ L/mol•s

$k_{avg} = (1.29 \times 10^{-28} + 1.33 \times 10^{-28} + 1.30 \times 10^{-28} + 1.32 \times 10^{-28})$ L/mol•s/4 = **1.31×10^{-28} L/mol•s**

16.29   The integrated rate law can be used to plot a graph. If the plot of [reactant] vs. time is linear, the order is zero. If the plot of ln[reactant] vs. time is linear, the order is first. If the plot of inverse concentration (1/[reactant]) vs. time is linear, the order is second.
a) The reaction is **first order** since ln[reactant] vs. time is linear.
b) The reaction is **second order** since 1/[reactant] vs. time is linear.
c) The reaction is **zero order** since [reactant] vs. time is linear.

16.30   The half-life ($t_{1/2}$) of a reaction is the time required to reach half the initial reactant concentration. For a first-order process, no molecular collisions are necessary, and the rate depends only on the fraction of the molecules having sufficient energy to initiate the reaction.

16.31   Plan: The rate expression indicates that this reaction is second order overall (the order of [AB] is 2), so use the second-order integrated rate law to find time. We know k (0.2 L/mol•s), $[AB]_0$ (1.50 M), and $[AB]_t$ ($1/3[AB]_0 = 1/3(1.50 \ M) = 0.500 \ M$), so we can solve for t.
Solution:

$$\frac{1}{[AB]_t} - \frac{1}{[AB]_0} = kt$$

$$t = \frac{\left(\frac{1}{[AB]_t} - \frac{1}{[AB]_0}\right)}{k}$$

$$t = \frac{\left(\frac{1}{0.500 \ M} - \frac{1}{1.50 \ M}\right)}{0.2 \text{ L/mol} \cdot \text{s}}$$

$$t = 6.6667 = \textbf{7 s}$$

16.32   Plan: The rate expression indicates that this reaction is second order overall (the order of [AB] is 2), so use the second-order integrated rate law. We know k (0.2 L/mol•s), $[AB]_0$ (1.50 M), and t (10.0 s), so we can solve for $[AB]_t$.
Solution:

$$\frac{1}{[AB]_t} - \frac{1}{[AB]_0} = kt$$

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$$\frac{1}{[AB]_t} = kt + \frac{1}{[AB]_0}$$

$$\frac{1}{[AB]_t} = (0.2 \text{ L/mol•s}) (10.0 \text{ s}) + \frac{1}{1.50 \text{ } M}$$

$$\frac{1}{[AB]_t} = 2.66667 \frac{1}{M}$$

$$[AB]_t = 0.375 = \textbf{0.4 } \textbf{\textit{M}}$$

16.33   Plan: This is a first-order reaction so use the first-order integrated rate law. In part a), we know t (10.5 min). Let $[A]_0 = 1 \text{ } M$ and then $[A]_t = 50\%$ of $1 \text{ } M = 0.5 \text{ } M$. Solve for k. In part b), use the value of k to find the time necessary for 75.0% of the compound to react. If 75.0% of the compound has reacted, $100–75 = 25\%$ remains at time t. Let $[A]_0 = 1 \text{ } M$ and then $[A]_t = 25\%$ of $1 \text{ } M = 0.25 \text{ } M$.
Solution:
a) $\ln [A]_t = \ln [A]_0 - kt$
$\ln [0.5] = \ln [1] - k(10.5 \text{ min})$
$-0.693147 = 0 - k(10.5 \text{ min})$
$0.693147 = k(10.5 \text{ min})$
$k = 0.0660 \text{ min}^{-1}$
Alternatively, 50.0% decomposition means that one half-life has passed. Thus, the first-order half-life equation may be used:

$$t_{1/2} = \frac{\ln 2}{k} \qquad\qquad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{10.5 \text{ min}} = 0.066014 = \textbf{0.0660 min}^{-1}$$

b) $\ln [A]_t = \ln [A]_0 - kt$

$$\frac{\ln[A]_t - \ln[A]_0}{-k} = t$$

$$\frac{\ln[0.25] - \ln[1]}{-0.0660 \text{ min}^{-1}} = t$$

$t = 21.0045 = \textbf{21.0 min}$
If you recognize that 75.0% decomposition means that two half-lives have passed, then
$t = 2 \ (10.5 \text{ min}) = \textbf{21.0 min.}$

16.34   Plan: This is a first-order reaction so use the first-order integrated rate law (the units of k, yr^{-1}, indicates first order). In part a), the first-order half-life equation may be used to solve for half-life since k is known. In part b) use the value of k to find the time necessary for the reactant concentration to drop to 12.5% of the initial concentration. Let $[A]_0 = 1.00 \text{ } M$ and then $[A]_t = 12.5\%$ of $1 \text{ } M = 0.125 \text{ } M$.
Solution:

a) $t_{1/2} = \dfrac{\ln 2}{k} = \dfrac{\ln 2}{0.0012 \text{ yr}^{-1}} = 577.62 = \textbf{5.8x10}^{\textbf{2}} \textbf{ yr}$

b) $\ln [A]_t = \ln [A]_0 - kt$

$\ln \dfrac{[A]_0}{[A]_t} = kt$

$[A]_0 = 1.00 \text{ } M \qquad [A]_t = 0.125 \text{ } M \qquad k = 0.0012 \text{ yr}^{-1}$

$$\ln \left(\frac{1.00 \text{ } M}{0.125 \text{ } M} \right) = (0.0012 \text{ yr}^{-1}) \ t$$

$t = 1732.86795 = \textbf{1.7x10}^{\textbf{3}} \textbf{ yr}$
If the student recognizes that 12.5% remaining corresponds to three half-lives; then simply multiply the answer in part a) by three.

16.35   The central idea of collision theory is that reactants must collide with each other in order to react. If reactants must collide to react, the rate depends on the product of the reactant concentrations.

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16.36   **No**, collision frequency is not the only factor affecting reaction rate. The collision frequency is a count of the total number of collisions between reactant molecules. Only a small number of these collisions lead to a reaction. Other factors that influence the fraction of collisions that lead to reaction are the energy and orientation of the collision. A collision must occur with a minimum energy (activation energy) to be successful. In a collision, the orientation, that is, which ends of the reactant molecules collide, must bring the reacting atoms in the molecules together in order for the collision to lead to a reaction.

16.37   At any particular temperature, molecules have a distribution of kinetic energies, as will their collisions have a range of energies. As temperature increases, the fraction of these collisions which exceed the threshold energy, increases; thus, the reaction rate increases.

16.38 $k = Ae^{-E_a/RT}$
         The Arrhenius equation indicates a negative exponential relationship between temperatures and the rate constant, k. In other words, the rate constant increases exponentially with temperature.

16.39   The Arrhenius equation, $k = Ae^{-E_a/RT}$, can be used directly to solve for activation energy at a specified temperature if the rate constant, k, and the frequency factor, A, are known. However, the frequency factor is usually not known. To find E_a without knowing A, rearrange the Arrhenius equation to put it in the form of a linear plot: $\ln k = \ln A - E_a/RT$ where the y value is $\ln k$ and the x value is $1/T$. Measure the rate constant at a series of temperatures and plot $\ln k$ vs. $1/T$. The slope equals $-E_a/R$.

16.40   a) The value of k increases exponentially with temperature.
         b) A plot of $\ln k$ vs. $1/T$ is a straight line whose slope is $-E_a/R$.

a)

b)
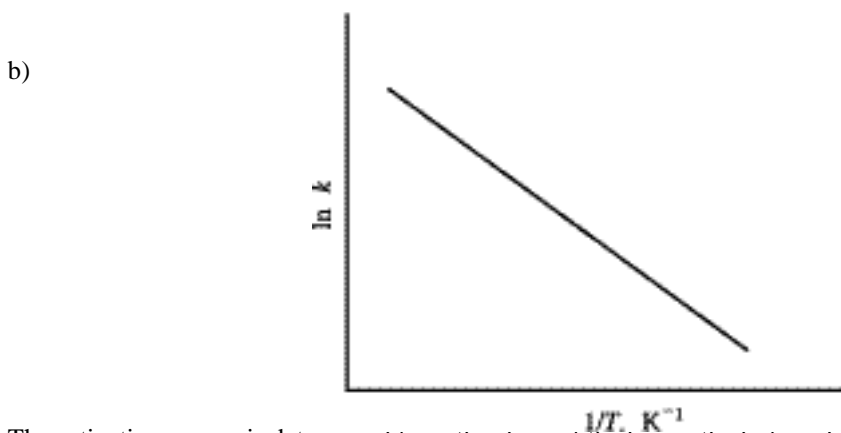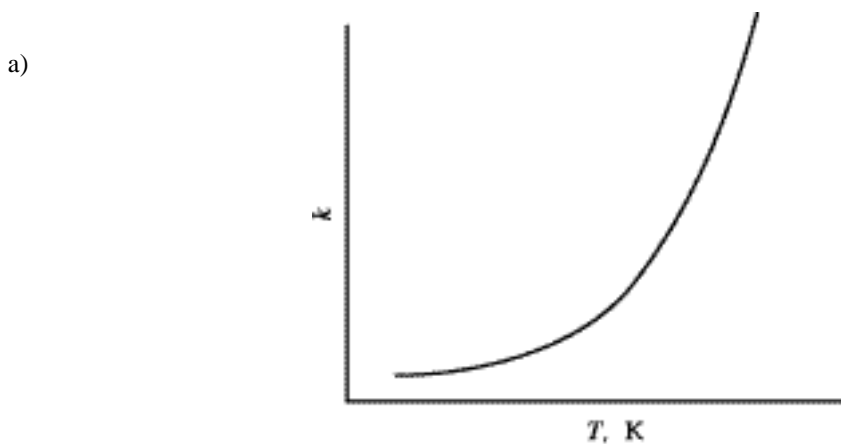
The activation energy is determined from the slope of the line in the $\ln k$ vs. $1/T$ graph. The slope equals $-E_a/R$.

16.41   a) As temperature increases, the fraction of collisions which exceed the activation energy increases; thus, the **reaction rate increases**.
b) A decrease in activation energy lowers the energy threshold with which collisions must take place to be effective. At a given temperature, more collisions occur with the lower energy so **rate increases.**

16.42   Collision frequency is proportional to the velocity of the reactant molecules. At the same temperature, both reaction mixtures have the same average kinetic energy, but not the same velocity. Kinetic energy equals $1/2\ mv^2$, where m is mass and v velocity. The methylamine ($N(CH_3)_3$) molecule has a greater mass than the ammonia molecule, so methylamine molecules will collide less often than ammonia molecules, because of their slower velocities. Collision energy thus is less for the $N(CH_3)_3(g) + HCl(g)$ reaction than for the $NH_3(g) + HCl(g)$ reaction. Therefore, the **rate of the reaction between ammonia and hydrogen chloride is greater** than the rate of the reaction between methylamine and hydrogen chloride.
The fraction of successful collisions also differs between the two reactions. In both reactions the hydrogen from HCl is bonding to the nitrogen in NH_3 or $N(CH_3)_3$. The difference between the reactions is in how easily the H can collide with the N, the correct orientation for a successful reaction. The groups (H) bonded to nitrogen in ammonia are less bulky than the groups bonded to nitrogen in trimethylamine (CH_3). So, collisions with correct orientation between HCl and NH_3 occur more frequently than between HCl and $N(CH_3)_3$ and the reaction $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$ occurs at a higher rate than $N(CH_3)_3(g) + HCl(g) \rightarrow (CH_3)_3NHCl(s)$. Therefore, the **rate of the reaction between ammonia and hydrogen chloride is greater** than the rate of the reaction between methylamine and hydrogen chloride.

16.43   Each A particle can collide with three B particles, so (4 x 3) = **12 unique collisions** are possible.

16.44   Plan: Use Avogadro's number to convert moles of particles to number of particles. The number of unique collisions is the product of the number of A particles and the number of B particles.
Solution:

Number of particles of A $= \left(1.01 \text{ mol A}\right)\left(\dfrac{6.022 \text{x} 10^{23} \text{ A particles}}{1 \text{ mol A}}\right) = 6.08222 \text{x} 10^{23}$ particles of A

Number of particles of B $= \left(2.12 \text{ mol B}\right)\left(\dfrac{6.022 \text{x} 10^{23} \text{ B particles}}{1 \text{ mol B}}\right) = 1.279997 \text{x} 10^{24}$ particles of B

Number of collisions $= (6.08222 \text{ x } 10^{23}$ particles of A$)(1.279997 \text{ x } 10^{24}$ particles of B$)$
        $= 7.76495 \text{x} 10^{47} = $ **$7.76 \text{x} 10^{47}$ unique collisions**

16.45   Plan: The fraction of collisions with a specified energy is equal to the $e^{-E_a/RT}$ term in the Arrhenius equation.
Solution:

$f = e^{-E_a/RT}$ $T = 25°C + 273 = 298$ K
$E_a = 100.$ kJ/mol $R = 8.314$ J/mol•K $= 8.314 \text{x} 10^{-3}$ kJ/mol•K

$-\dfrac{E_a}{RT} = -\dfrac{100. \text{ kJ/mol}}{\left(8.314 \text{x} 10^{-3} \text{ kJ/mol•K}\right)\left(298 \text{ K}\right)} = -40.362096$

Fraction $= e^{-E_a/RT} = e^{-40.362096} = 2.9577689 \text{x} 10^{-18} = $ **$2.96 \text{x} 10^{-18}$**

16.46   Plan: The fraction of collisions with a specified energy is equal to the $e^{-E_a/RT}$ term in the Arrhenius equation.
Solution:

$f = e^{-E_a/RT}$ $T = 50.°C + 273 = 323$ K
$E_a = 100.$ kJ/mol $R = 8.314$ J/mol•K $= 8.314 \text{x} 10^{-3}$ kJ/mol•K

$-\dfrac{E_a}{RT} = -\dfrac{100. \text{ kJ/mol}}{\left(8.314 \text{x} 10^{-3} \text{ kJ/mol•K}\right)\left(323 \text{ K}\right)} = -37.238095$

Fraction $= e^{-E_a/RT} = e^{-37.238095} = 6.725131 \text{x} 10^{-17}$
The fraction increased by $(6.725131 \text{x} 10^{-17})/(2.9577689 \text{x} 10^{-18}) = 22.737175 = $ **22.7**

16.47 Plan: You are given one rate constant k_1 at one temperature T_1 and the activation energy E_a. Substitute these values into the Arrhenius equation and solve for k_2 at the second temperature.

Solution:
$$k_1 = 4.7\text{x}10^{-3}\text{ s}^{-1} \qquad\qquad T_1 = 25°C + 273 = 298\text{ K}$$
$$k_2 = ? \qquad\qquad T_2 = 75°C + 273 = 348\text{ K}$$
$$E_a = 33.6\text{ kJ/mol} = 33{,}600\text{ J/mol}$$

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{k_2}{4.7\text{x}10^{-3}\text{ s}^{-1}} = -\frac{33{,}600\text{ J/mol}}{8.314\text{ J/mol•K}}\left(\frac{1}{348\text{ K}} - \frac{1}{298\text{ K}}\right)$$

$$\ln\frac{k_2}{4.7\text{x}10^{-3}\text{ s}^{-1}} = 1.948515\text{ (unrounded)} \qquad\text{Raise each side to } e^x$$

$$\frac{k_2}{4.7\text{x}10^{-3}\text{ s}^{-1}} = 7.0182577$$
$$k_2 = (4.7\text{x}10^{-3}\text{ s}^{-1})(7.0182577) = 0.0329858 = \textbf{0.033 s}^{-1}$$

16.48 Plan: You are given the rate constants, k_1 and k_2, at two temperatures, T_1 and T_2. Substitute these values into the Arrhenius equation and solve for E_a.

Solution:
$$k_1 = 4.50\text{x}10^{-5}\text{ L/mol•s} \qquad\qquad T_1 = 195°C + 273 = 468\text{ K}$$
$$k_2 = 3.20\text{x}10^{-3}\text{ L/mol•s} \qquad\qquad T_2 = 258°C + 273 = 531\text{ K}$$
$$E_a = ?$$

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = -\frac{R\left(\ln\dfrac{k_2}{k_1}\right)}{\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)} = -\frac{\left(8.314\dfrac{\text{J}}{\text{mol•K}}\right)\left(\ln\dfrac{3.20\text{x}10^{-3}\text{ L/mol•s}}{4.50\text{x}10^{-5}\text{ L/mol•s}}\right)}{\left(\dfrac{1}{531\text{ K}} - \dfrac{1}{468\text{ K}}\right)}$$

$$E_a = 1.3984658\text{x}10^5\text{ J/mol} = \textbf{1.40x10}^5\textbf{ J/mol}$$

16.49 Plan: The reaction is exothermic (ΔH is negative), so the energy of the products must be lower than that of the reactants. Use the relationship $\Delta H_{rxn} = E_{a(fwd)} - E_{a(rev)}$ to solve for $E_{a(rev)}$. To draw the transition state, note that the bond between B and C will be breaking while a bond between C and D will be forming.
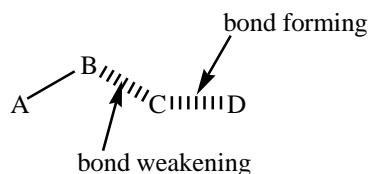
Solution:

a)
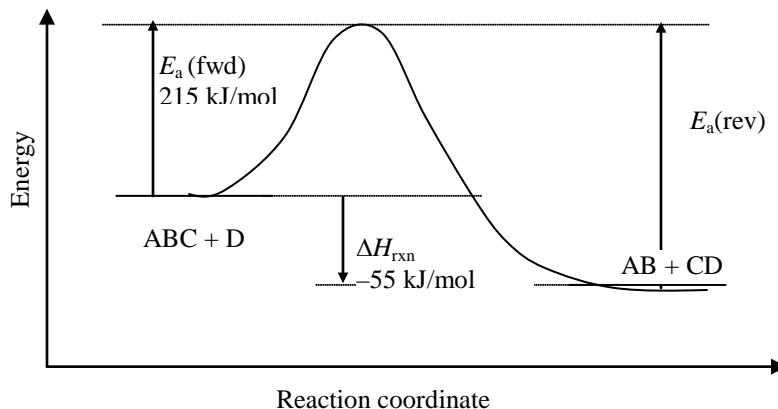
b) $\Delta H_{rxn} = E_{a(fwd)} - E_{a(rev)}$
$E_{a(rev)} = E_{a(fwd)} - \Delta H_{rxn} = 215\text{ kJ/mol} - (-55\text{ kJ/mol}) = \textbf{2.70x10}^2\textbf{ kJ/mol}$

c)

bond forming

B⫶⫶⫶⫶C⫶⫶⫶⫶D
A

bond weakening

16.50 <u>Plan:</u> The forward activation energy $E_{a(fwd)}$ is larger than the reverse activation energy $E_{a(rev)}$ which indicates that the energy of the products must be higher than that of the reactants. Use the relationship $\Delta H_{rxn} = E_{a(fwd)} - E_{a(rev)}$ to solve for ΔH_{rxn}. To draw the transition state, note that the bonds in the A_2 and B_2 molecules will be breaking while bonds between A and B will be forming.
<u>Solution:</u>
a)
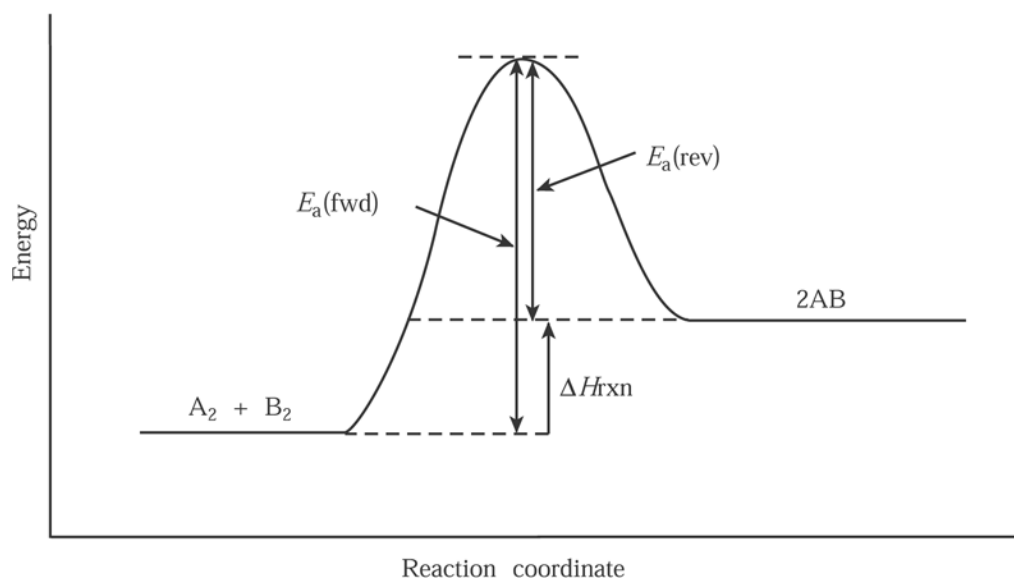
b) $\Delta H_{rxn} = E_{a(fwd)} - E_{a(rev)} = 125$ kJ/mol $- 85$ kJ/mol $= $ **40 kJ/mol**
c)   A . . . . . B
         | |
         A . . . . . B
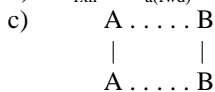
16.51 <u>Plan:</u> You are given the rate constants, k_1 and k_2, at two temperatures, T_1 and T_2. Substitute these values into the Arrhenius equation and solve for E_a.
<u>Solution:</u>

$k_1 = 0.76$/s $T_1 = 727°C + 273 = 1000.$ K
$k_2 = 0.87$/s $T_2 = 757°C + 273 = 1030.$ K
$E_a = ?$

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = -\frac{R\left(\ln\frac{k_2}{k_1}\right)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = -\frac{\left(8.314\frac{J}{mol\bullet K}\right)\left(\ln\frac{0.87\,/\,s}{0.76\,/\,s}\right)}{\left(\frac{1}{1030.\ K} - \frac{1}{1000.\ K}\right)}$$

$E_a = 3.8585 \times 10^4$ J/mol $= $ **3.9x10^4 J/mol**

16.52   Plan: The reaction is endothermic (ΔH is positive), so the energy of the products must be higher than that of the reactants. Use the relationship $\Delta H_{rxn} = E_{a(fwd)} - E_{a(rev)}$ to solve for $E_{a(rev)}$. To draw the transition state, note that the bond in Cl_2 will be breaking while the bond between N and Cl will be forming.
Solution:
a)
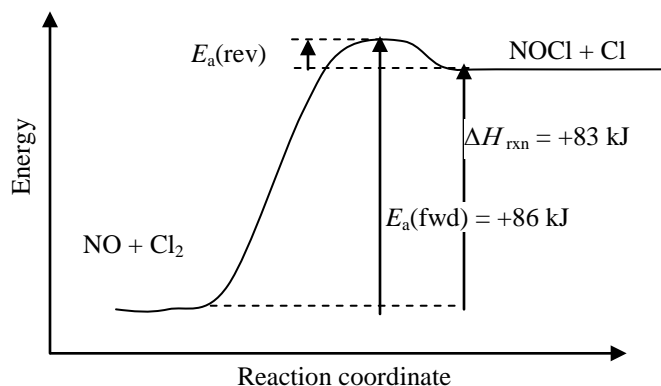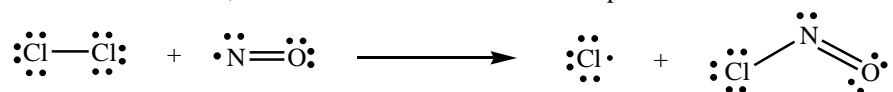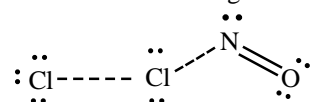

b) $\Delta H_{rxn} = E_{a(fwd)} - E_{a(rev)}$
$E_{a(rev)} = E_{a(fwd)} - \Delta H_{rxn} = 86\ kJ - 83\ kJ = \textbf{3 kJ}$.
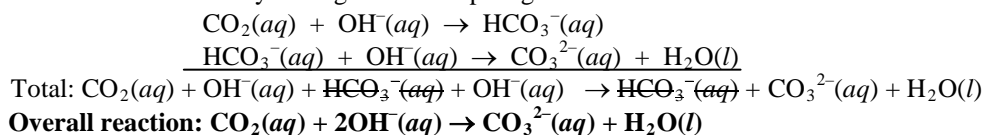c) To draw the transition state, look at structures of reactants and products:

The collision must occur between one of the chlorine atoms and the nitrogen. The transition state would have weak bonds between the nitrogen and chlorine and between the two chlorine atoms.

16.53   The rate of an overall reaction depends on the slowest step. Each individual step's reaction rate can vary widely, so the rate of the slowest step, and hence the overall reaction, will be **slower than the average of the individual rates** because the average contains faster rates as well as the rate-determining step.

16.54   An elementary step is a single molecular event, such as the collision of two molecules. Since an elementary step occurs in one step, its rate must be proportional to the product of the reactant concentrations. Thus, the exponents in the rate of an elementary step are identical to the coefficients in the equation for the step. Since an overall reaction is generally a series of elementary steps, it is not necessarily proportional to the product of the overall reactant concentrations.

16.55   **Yes**, it is often possible to devise more than one mechanism since the rate law for the slowest step determines the rate law for the overall reaction. The preferred mechanism will be the one that seems most probable, where molecules behave in their expected fashion.

16.56   Reaction intermediates have some stability, however limited, but transition states are inherently unstable. Additionally, unlike transition states, intermediates are molecules with normal bonds.

16.57   A bimolecular step (a collision between two particles) is more reasonable physically than a termolecular step (a collision involving three particles) because the likelihood that two reactant molecules will collide with the proper energy and orientation is much greater than the likelihood that three reactant molecules will collide simultaneously with the proper energy and orientation.

16.58   **No**, the overall rate law must contain reactants only (no intermediates) and is determined by the slow step. If the first step in a reaction mechanism is slow, the rate law for that step is the overall rate law.

16-14

16.59   a) The overall reaction can be obtained by adding the two steps together:
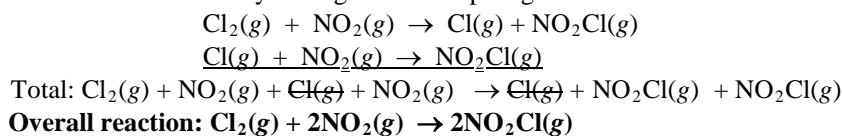$$CO_2(aq) + OH^-(aq) \rightarrow HCO_3^-(aq)$$
$$\underline{HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)}$$
Total: $CO_2(aq) + OH^-(aq) + \cancel{HCO_3^-(aq)} + OH^-(aq) \rightarrow \cancel{HCO_3^-(aq)} + CO_3^{2-}(aq) + H_2O(l)$
Overall reaction: $CO_2(aq) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$
b) Intermediates appear in the mechanism first as products, then as reactants. **HCO_3^-** is an intermediate.
c)

Step:	Molecularity	Rate law
$CO_2(aq) + OH^-(aq) \rightarrow HCO_3^-(aq)$	bimolecular	$rate_1 = k_1[CO_2][OH^-]$
$HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$	bimolecular	$rate_2 = k_2[HCO_3^-][OH^-]$

d) **Yes**, the mechanism is consistent with the actual rate law. The slow step in the mechanism is the first step with the rate law: rate = $k_1[CO_2][OH^-]$. This rate law is the same as the actual rate law.

16.60   a) The overall reaction can be obtained by adding the two steps together:
$$Cl_2(g) + NO_2(g) \rightarrow Cl(g) + NO_2Cl(g)$$
$$\underline{Cl(g) + NO_2(g) \rightarrow NO_2Cl(g)}$$
Total: $Cl_2(g) + NO_2(g) + \cancel{Cl(g)} + NO_2(g) \rightarrow \cancel{Cl(g)} + NO_2Cl(g) + NO_2Cl(g)$
Overall reaction: $Cl_2(g) + 2NO_2(g) \rightarrow 2NO_2Cl(g)$
b) Intermediates appear in the mechanism first as products, then as reactants. **Cl** is an intermediate.
c)

Step:	Molecularity	Rate law
$Cl_2(g) + NO_2(g) \rightarrow Cl(g) + NO_2Cl(g)$	bimolecular	$rate_1 = k_1[Cl_2][NO_2]$
$Cl(g) + NO_2(g) \rightarrow NO_2Cl(g)$	bimolecular	$rate_2 = k_2[Cl][NO_2]$

d) **Yes**, the mechanism is consistent with the actual rate law. The slow step in the mechanism is the first step with the rate law: rate = $k_1[Cl_2][NO_2]$. This rate law is the same as the actual rate law.

16.61   Plan: The overall reaction can be obtained by adding the three steps together. An intermediate is a substance that is formed in one step and consumed in a subsequent step. The molecularity of each step is the total number of reactant particles; the molecularities are used as the orders in the rate law for each step. The overall rate law for the mechanism is determined from the slowest step (the rate-determining step) and can be compared to the actual rate law.
Solution:
a)   (1) $A(g) + B(g) \rightarrow X(g)$ fast
            (2) $X(g) + C(g) \rightarrow Y(g)$ slow
            $\underline{(3)\ Y(g) \rightarrow D(g)\ \ fast}$
Total: $A(g) + B(g) + \cancel{X(g)} + C(g) + \cancel{Y(g)} \rightarrow \cancel{X(g)} + \cancel{Y(g)} + D(g)$
Overall: $A(g) + B(g) + C(g) \rightarrow D(g)$
b) Both **X and Y** are intermediates in the given mechanism. Intermediate X is produced in the first step and consumed in the second step; intermediate Y is produced in the second step and consumed in the third step. Notice that neither X nor Y were included in the overall reaction.
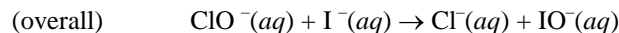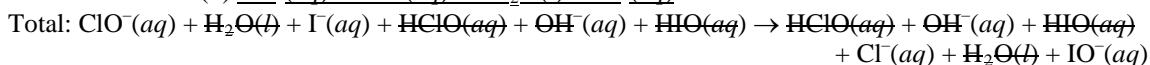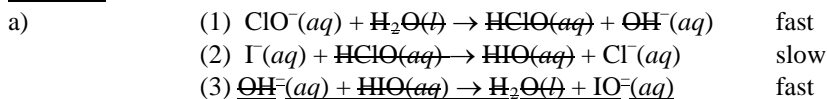c)

Step	Molecularity	Rate law
$A(g) + B(g) \rightarrow X(g)$	bimolecular	$rate_1 = k_1[A][B]$
$X(g) + C(g) \rightarrow Y(g)$	bimolecular	$rate_2 = k_2[X][C]$
$Y(g) \rightarrow D(g)$	unimolecular	$rate_3 = k_3[Y]$

d) **Yes**, the mechanism is consistent with the actual rate law. The slow step in the mechanism is the second step with rate law: rate = $k_2[X][C]$. Since X is an intermediate, it must be replaced by using the first step. For an equilibrium, $rate_{forward\ rxn} = rate_{reverse\ rxn}$. For step 1 then, $k_1[A][B] = k_{-1}[X]$. Rearranging to solve for [X] gives $[X] = (k_1/k_{-1})[A][B]$. Substituting this value for [X] into the rate law for the second step gives the overall rate law as rate = $(k_2k_1/k_{-1})[A][B][C]$ which is identical to the actual rate law with $k = k_2k_1/k_{-1}$.
e) **Yes**, The one step mechanism $A(g) + B(g) + C(g) \rightarrow D(g)$ would have a rate law of rate = $k[A][B][C]$, which is the actual rate law.

16.62   Plan: The overall reaction can be obtained by adding the three steps together. An intermediate is a substance
        that is formed in one step and consumed in a subsequent step. The molecularity of each step is the total number of
        reactant particles; the molecularities are used as the orders in the rate law for each step. The overall rate law for
        the mechanism is determined from the slowest step (the rate-determining step) and can be compared to the actual
        rate law.
        Solution:
        a)   (1) ClO⁻(aq) + H̶₂̶O̶(̶l̶)̶ → H̶C̶l̶O̶(̶a̶q̶)̶ + O̶H̶⁻(aq)   fast
                        (2) I⁻(aq) + H̶C̶l̶O̶(̶a̶q̶)̶ → HIO(aq) + Cl⁻(aq)   slow
                        (3) O̶H̶⁻(aq) + H̶I̶O̶(̶a̶q̶)̶ → H̶₂̶O̶(̶l̶)̶ + IO⁻(aq)   fast
        Total: ClO⁻(aq) + H̶₂̶O̶(̶l̶)̶ + I⁻(aq) + H̶C̶l̶O̶(̶a̶q̶)̶ + O̶H̶⁻(aq) + H̶I̶O̶(̶a̶q̶)̶ → H̶C̶l̶O̶(̶a̶q̶)̶ + O̶H̶⁻(aq) + H̶I̶O̶(̶a̶q̶)̶
                                                                                    + Cl⁻(aq) + H̶₂̶O̶(̶l̶)̶ + IO⁻(aq)
                 (overall)   ClO⁻(aq) + I⁻(aq) → Cl⁻(aq) + IO⁻(aq)
        b) **HClO(aq), OH⁻(aq), and HIO(aq)** are intermediates in the given mechanism. HClO(aq) is produced in the
        first step and consumed in the second step; OH⁻(aq) is produced in the first step and consumed in the third step;
        HIO(aq) is produced in the second step and consumed in the third step. Notice that the intermediates were not
        included in the overall reaction.
        c)   (1) Bimolecular; $Rate_1 = k_1 [ClO^-] [H_2O]$
                        (2) Bimolecular; $Rate_2 = k_2 [I^-][HClO]$
                        (3) Bimolecular; $Rate_3 = k_3 [OH^-][HIO]$
        d) The slow step in the mechanism is the second step with rate law: rate = $k_2[I^-][HClO]$. Since HClO is an
        intermediate, it must be replaced by using the first step. For an equilibrium, $rate_{forward\ rxn}$ = $rate_{reverse\ rxn}$. For step 1
        then, leaving out the water, $k_1[ClO^-] = k_{-1}[HClO][OH^-]$. Rearranging to solve for [HClO] gives
        [HClO] = $(k_1/k_{-1})[ClO^-]/[OH^-]$. Substituting this value for [HClO] into the rate law for the second step gives the
        overall rate law as rate = $(k_2k_1/k_{-1})[I^-][ClO^-]/[OH^-]$ or rate = $k[I^-][ClO^-]/[OH^-]$.
        This is not the observed rate law. **The mechanism is not consistent with the actual rate law**.

16.63   Plan: Use the rate-determining step to find the rate law for the mechanism. The concentration of the
        intermediate in the rate law must be expressed in terms of a true reactant which is then substituted into the rate
        law for the concentration of the intermediate.
        Solution:
        Nitrosyl bromide is NOBr(g). The reactions sum to the equation 2NO(g) + Br₂(g) → 2NOBr(g), so criterion
        1 (elementary steps must add to overall equation) is satisfied. Both elementary steps are bimolecular and
        chemically reasonable, so criterion 2 (steps are physically reasonable) is met. The reaction rate is determined by
        the slow step; however, rate expressions do not include reaction intermediates (NOBr₂). The slow step in the
        mechanism is the second step with rate law: rate = $k_2[NOBr_2][NO]$. Since NOBr₂ is an intermediate, it must be
        replaced by using the first step. For an equilibrium like step 1, $rate_{forward\ rxn}$ = $rate_{reverse\ rxn}$.
                Solve for [NOBr₂] in step 1:
                Rate₁ (forward) = rate₁ (reverse)
                $k_1[NO][Br_2] = k_{-1}[NOBr_2]$
                $[NOBr_2] = (k_1/k_{-1})[NO][Br_2]$
        Rate of the slow step: Rate₂ = $k_2[NOBr_2][NO]$
        Substitute the expression for [NOBr₂] into this equation, the slow step:
                Rate₂ = $k_2(k_1/k_{-1})[NO][Br_2][NO]$
   Combine the separate constants into one constant: $k = k_2(k_1/k_{-1})$
   Rate₂ = $k[NO]^2[Br_2]$
        The derived rate law equals the known rate law, so criterion 3 is satisfied. The proposed mechanism is valid.
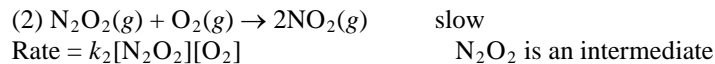
16.64   Plan: Use the rate-determining step to find the rate law for each mechanism. If there is an intermediate in the
        rate law, the concentration of the intermediate must be expressed in terms of a true reactant which is then
        substituted into the rate law for the concentration of the intermediate.
        Solution:
        I.   2NO(g) + O₂(g) → 2NO₂(g)
                Rate = $k[NO]^2[O_2]$
        II.   (1) 2NO(g) → N₂O₂(g)

16-16
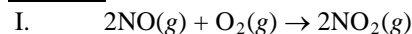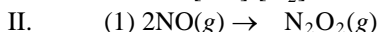
(2) $N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$ slow
Rate = $k_2[N_2O_2][O_2]$ N_2O_2 is an intermediate
$Rate_1$ (forward) = $rate_1$ (reverse)
$k_1[NO]^2 = k_{-1}[N_2O_2]$
$[N_2O_2] = (k_1/k_{-1})[NO]^2$
 Substitute this for $[N_2O_2]$ in the rate law:
Rate = $k[N_2O_2][O_2]$
Rate = $k_2(k_1/k_{-1})[NO]^2[O_2]$
Rate = $k[NO]^2[O_2]$
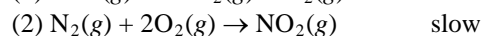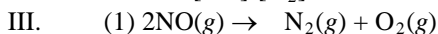
III.   (1) $2NO(g) \rightarrow$ $N_2(g) + O_2(g)$
     (2) $N_2(g) + 2O_2(g) \rightarrow NO_2(g)$ slow
     Rate = $k_2[N_2][O_2]^2$ N_2 is an intermediate
     $Rate_1$ (forward) = $rate_1$ (reverse)
     $k_1[NO]^2 = k_{-1}[N_2][O_2]$
     $[N_2] = (k_1/k_{-1})[NO]^2/[[O_2] = (k_1/k_{-1})[NO]^2[O_2]^{-1}$
     Substitute this for $[N_2]$ in the rate law:
     Rate = $k_2[N_2][O_2]^2$
     Rate = $k_2(k_1/k_{-1})[NO]^2 [O_2]^{-1}[O_2]^2$
     Rate = $k[NO]^2[O_2]$

a) All the mechanisms are consistent with the rate law.
b) The most reasonable mechanism is II, since none of its elementary steps are more complicated than being bimolecular. Mechanism I and III have steps that are termolecular.

16.65   Plan: Review the definitions of homogeneous vs. heterogeneous catalysts. To draw the reaction energy diagrams, recall that addition of a catalyst to a reaction results in a lower activation energy.
Solution:
a) A heterogeneous catalyst speeds up a reaction that occurs in a different phase. Gold is a **heterogeneous catalyst** since it is a solid and is catalyzing a reaction in the gas phase.
b) The activation energy for the uncatalyzed reaction must be greater than the activation for the catalyzed reaction.
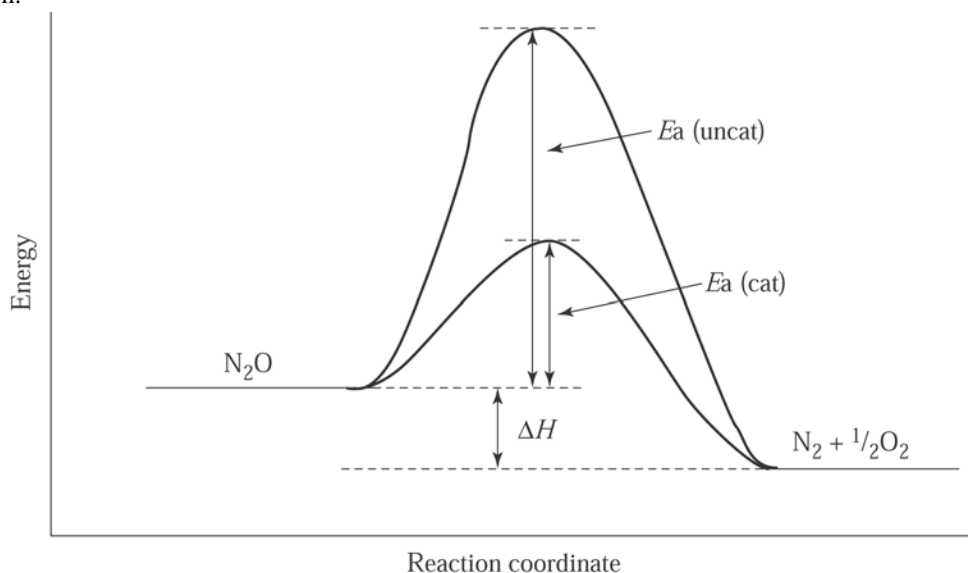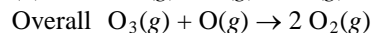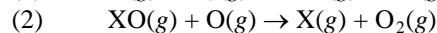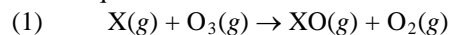

16.66   **No**, a catalyst changes the mechanism of a reaction to one with lower activation energy. Lower activation energy means a faster reaction. An increase in temperature does not influence the activation energy, but instead increases the fraction of collisions with sufficient energy to react.

16.67   a) There are **two** elementary steps since there are two different values of activation energy.
b) The **second step** is the rate-limiting step since it has the greater activation energy and would therefore be the slower of the two steps.

c) The reaction is **exothermic** since a loss of energy results in the products having lower energy than the reactants.

16.68   a) Add the two equations:

$$(1) \qquad X(g) + O_3(g) \rightarrow XO(g) + O_2(g)$$
$$(2) \qquad XO(g) + O(g) \rightarrow X(g) + O_2(g)$$
$$\text{Overall} \quad O_3(g) + O(g) \rightarrow 2\,O_2(g)$$

   b) Step (1) $\text{rate}_1 = k_1[X][O_3]$
   Step (2) $\text{rate}_2 = k_2[XO][O]$

   c) X acts as a **catalyst**, and XO acts as an **intermediate**.

   d) Step (1) is the rate-determining (slow) step, so use its rate law with NO = X.

   $\text{rate}_1 = k_1[NO][O_3] = (6\text{x}10^{-15}\ cm^3/\text{molecule}\bullet s)(1.0\text{x}10^9\ \text{molecule}/cm^3)(5\text{x}10^{12}\ \text{molecule}/cm^3)$
   $= \textbf{3x10}^{\textbf{7}}\ \textbf{molecule/s}$

16.69   <u>Plan:</u> The activation energy can be calculated using the Arrhenius equation. Although the rate constants, k_1 and k_2, are not expressly stated, the relative times give an idea of the rate. The reaction rate is proportional to the rate constant. At $T_1 = 20°C$, the rate of reaction is 1 apple/4 days while at $T_2 = 0°C$, the rate is 1 apple/16 days. Therefore, $\text{rate}_1 = 1$ apple/4 days and $\text{rate}_2 = 1$ apple/16 days are substituted for k_1 and k_2, respectively.

<u>Solution:</u>

$k_1 = 1/4$ \qquad\qquad\qquad $T_1 = 20°C + 273 = 293\ K$
$k_2 = 1/16$ \qquad\qquad\qquad $T_2 = 0°C + 273 = 273\ K$
$E_a = ?$

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = -\frac{R\left(\ln\dfrac{k_2}{k_1}\right)}{\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)} = -\frac{\left(8.314\dfrac{J}{\text{mol}\bullet K}\right)\left(\ln\dfrac{1/16}{1/4}\right)}{\left(\dfrac{1}{273\ K} - \dfrac{1}{293\ K}\right)}$$

$E_a = 4.6096266\text{x}10^4\ J/mol = \textbf{4.61x10}^{\textbf{4}}\ \textbf{J/mol}$ The significant figures are based on the Kelvin temperatures.

16.70   <u>Plan:</u> Use the first-order integrated rate law. First use the first-order half-life equation to solve for k since the half-life is given. Since 95% of the benzoyl peroxide (BP) remains at time t, let $[BP]_0 = 100\%$ and then $[BP]_t = 95\%$.

<u>Solution:</u>

$$t_{1/2} = \frac{\ln 2}{k} \qquad\qquad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{9.8\text{x}10^3\ d} = 7.07293\text{x}10^{-5}\ d^{-1}$$

Use the first-order integrated rate law with BP = benzoyl peroxide:

$$\ln\frac{[BP]_t}{[BP]_0} = -kt$$

$$\ln\frac{[95\%]_t}{[100\%]_0} = -(7.07293\text{x}10^{-5}\ d^{-1})\,t$$

$$t = 725.2057 = \textbf{7.3x10}^{\textbf{2}}\ \textbf{d}$$

16.71   <u>Plan:</u> The reaction is exothermic (ΔH is negative), so the energy of the products must be lower than that of the reactants in the reaction energy diagram. Since there are two steps in the proposed mechanism, the diagram must show two transition states. The first step in the mechanism is the slower step so its E_a value is larger than the E_a value of the second step in the mechanism. The overall rate law for the alternative mechanism is determined from the slowest step (the rate-determining step) and can be compared to the actual rate law.

16-18

Solution:
a)
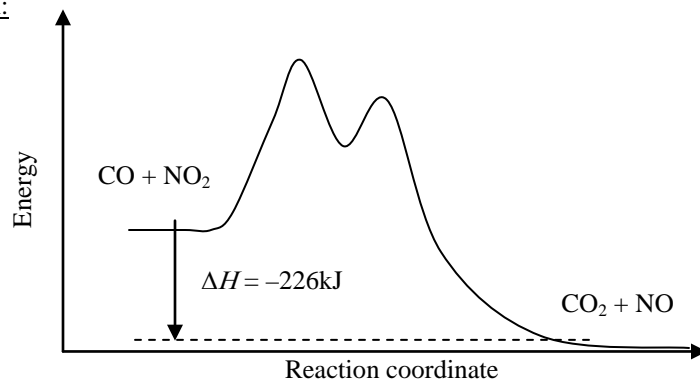
b) The rate of the mechanism is based on the slowest step, $2NO_2(g) \rightarrow N_2(g) + 2O_2(g)$. The rate law for this step is rate $= k_1[NO_2]^2$ which is consistent with the actual rate law. The alternative mechanism includes an elementary reaction (step 2) that is a termolecular reaction. Thus, the original mechanism given in the text is more reasonable physically since it involves only bimolecular reactions.

16.72   Plan: Use the given rate law, rate $= k[H^+][sucrose]$, and enter the given values. The glucose and fructose are not in the rate law, so they may be ignored.
Solution:
a) The rate is first order with respect to [sucrose]. The [sucrose] is changed from 1.0 M to 2.5 M, or is increased by a factor of 2.5/1.0 or 2.5. Then the rate $= k[H^+][2.5 \text{ x sucrose}]$; the rate **increases by a factor of 2.5.**
b) The [sucrose] is changed from 1.0 M to 0.5 M, or is decreased by a factor of 0.5/1.0 or 0.5. Then the rate $= k[H^+][0.5 \text{ x sucrose}]$; the rate decreases by a factor of ½ or **half the original rate**.
c) The rate is first order with respect to [H$^+$]. The [H$^+$] is changed from 0.01 M to 0.0001 M, or is decreased by a factor of 0.0001/0.01 or 0.01. Then the rate $= k[0.01 \text{ x } H^+][sucrose]$; the rate **decreases by a factor of 0.01**. Thus, the reaction will decrease to **1/100 the original**.
d) The [sucrose] decreases from 1.0 M to 0.1 M, or by a factor of (0.1 M/1.0 M) = 0.1. [H$^+$] increases from 0.01 M to 0.1 M, or by a factor of (0.1 M/0.01 M) = 10. Then the rate will increase by $k[10 \text{ x } H^+][0.1 \text{ x sucrose}]= 1.0$ times as fast. Thus, there will be **no change**.

16.73   Plan: The reaction is A + B $\rightarrow$ products. Assume the reaction is first order with respect to A and first order with respect to B. Find the concentration of each reactant in Mixture I and use those values and the initial rate to calculate k, the rate constant, for the reaction. Knowing k, the initial rate in Mixture II can be calculated using the rate law and the reactant concentrations.
Solution:
Rate $= k[A][B]$
Mixture I:

$$\text{Concentration of A} = \frac{(6 \text{ spheres A})\left(\dfrac{0.010 \text{ mol A}}{1 \text{ sphere}}\right)}{0.50 \text{ L}} = 0.12 \text{ mol/L}$$

$$\text{Concentration of B} = \frac{(5 \text{ spheres B})\left(\dfrac{0.010 \text{ mol B}}{1 \text{ sphere}}\right)}{0.50 \text{ L}} = 0.10 \text{ mol/L}$$

Use the rate law to find the value of k, the rate constant:
Rate $= k[A][B]$

$$k = \frac{\text{rate}}{[A][B]} = \frac{8.3 \text{x} 10^{-4} \text{ mol/L} \bullet \text{min}}{[0.12 \text{ mol/L}][0.10 \text{ mol/L}]} = 0.069167 \text{ L/mol} \cdot \text{min}$$

Use this value of k to find the initial rate in Mixture II:

$$\text{Concentration of A} = \frac{(7 \text{ spheres A})\left(\dfrac{0.010 \text{ mol A}}{1 \text{ sphere}}\right)}{0.50 \text{ L}} = 0.14 \text{ mol/L}$$

16-19

$$\text{Concentration of B} = \frac{(8 \text{ spheres B})\left(\dfrac{0.010 \text{ mol B}}{1 \text{ sphere}}\right)}{0.50 \text{ L}} = 0.16 \text{ mol/L}$$

Rate = k[A][B]

Rate = 0.069167 L/mol·min[0.14 mol/L][0.16 mol/L]

Rate = 1.5493×10^{-3} = **1.5×10^{-3} mol/L•min**

16.74   Rearrange $t_{1/2} = \ln 2/k$ to $k = \ln 2/t_{1/2}$

$k = \ln 2/9.0$ min $= 7.7016 \times 10^{-2}$ min^{-1}

Use the first-order integrated rate law with BA = biacetyl:

$$\ln\frac{[BA]_t}{[BA]_0} = -kt$$

$$\ln\frac{[85\%]_t}{[100\%]_0} = -(7.7016 \times 10^{-2} \text{ min}^{-1})\,t$$

$t = 2.110 = $ **2.1 min**

16.75   <u>Plan:</u> First, find the rate constant, k, for the reaction by solving the first-order half-life equation for k. Then use the first-order integrated rate law expression to find t, the time for decay.
<u>Solution:</u>

Rearrange $t_{1/2} = \dfrac{\ln 2}{k}$ to $k = \dfrac{\ln 2}{t_{1/2}}$

$$k = \frac{\ln 2}{12 \text{ yr}} = 5.7762 \times 10^{-2} \text{ yr}^{-1}$$

Use the first-order integrated rate law: $\ln\dfrac{[DDT]_t}{[DDT]_0} = -kt$

$$\ln\frac{[10. \text{ ppbm}]_t}{[275 \text{ ppbm}]_0} = -(5.7762 \times 10^{-2} \text{ yr}^{-1})\,t$$

$t = 57.3765798 = $ **57 yr**

16.76   <u>Plan:</u> The rate constant can be determined from the slope of the integrated rate law plot. To find the correct order, the data should be plotted as 1) [sucrose] vs. time – linear for zero order, 2) ln [sucrose] vs. time – linear for first order, and 3) 1/[sucrose] vs. time – linear for second order. Once the order is established, use the appropriate integrated rate law to find the time necessary for 75.0% of the sucrose to react. If 75.0% of the sucrose has reacted, 100–75 = 25% remains at time t. Let [sucrose]$_0$ = 100% and then [sucrose]$_t$ = 25%.
<u>Solution:</u>
a) All three graphs are linear, so picking the correct order is difficult. One way to select the order is to compare correlation coefficients (R^2) — you may or may not have experience with this. The best correlation coefficient is the one closest to a value of 1.00. Based on this selection criterion, the plot of ln [sucrose] vs. time for the first-order reaction is the best.
Another method when linearity is not obvious from the graphs is to examine the reaction and decide which order fits the reaction. For the reaction of one molecule of sucrose with one molecule of liquid water, the rate law would most likely include sucrose with an order of one and would not include water.
The plot for a first-order reaction is described by the equation ln [A]$_t$ = $-kt$ + ln [A]$_0$. The slope of the plot of ln [sucrose] vs. t equals $-k$. The equation for the straight line in the first-order plot is $y = -0.21x - 0.6936$.
So, $k = -(-0.21 \text{ h}^{-1}) = $ **0.21 h^{-1}**.
Solve the first-order half-life equation to find $t_{1/2}$:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{0.21 \text{ hr}^{-1}} = 3.3007 = \textbf{3.3 h}$$

Integrated rate law plots
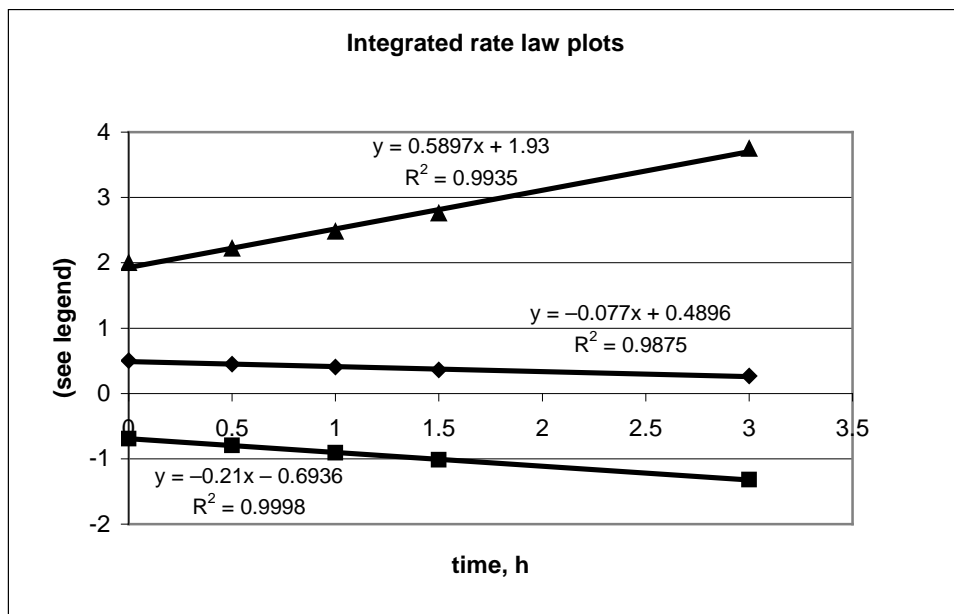
Legend: ♦ *y*-axis is [sucrose]
■ *y*-axis is ln [sucrose]
▲ *y*-axis is 1/[sucrose]

b) If 75% of the sucrose has been reacted, 25% of the sucrose remains. Let $[\text{sucrose}]_0 = 100\%$ and $[\text{sucrose}]_t = 25\%$ in the first-order integrated rate law equation:

$$\ln \frac{[\text{sucrose}]_t}{[\text{sucrose}]_0} = -kt$$

$$\ln \frac{[25\%]_t}{[100\%]_0} = -(0.21 \text{ h}^{-1})\, t$$

$$t = 6.6014 = \textbf{6.6 h}$$

c) The reaction might be second order overall with first order in sucrose and first order in water. If the concentration of sucrose is relatively low, the concentration of water remains constant even with small changes in the amount of water. This gives an apparent zero-order reaction with respect to water. Thus, the reaction appears to be first order overall because the rate does not change with changes in the amount of water.

16.77   Rearrange $t_{1/2} = \ln 2/k$ to $k = \ln 2/t_{1/2}$
$\qquad k = \ln 2/8.0\text{min} = 8.6643 \times 10^{-2} \text{ min}^{-1}$
The problem states that the interval $t = 1/k$:
$\qquad t = 1/(8.6643 \times 10^{-2} \text{ min}^{-1}) = 11.5416 = \textbf{12 min}$

16.78   <u>Plan:</u> You are given the ratio of the rate constants, k_1 and k_2, at a particular temperature and you want to find the difference in E_a between the uncatalyzed and catalyzed processes. Write the Arrhenius equation twice, once for the uncatalyzed process and once for the catalyzed process and divide the two equations so that the constant A factor divides out.
<u>Solution:</u>

$$\frac{k_2}{k_1} = 2.3 \times 10^{14} \qquad\qquad T = 37°C + 273 = 310 \text{ K}$$

$$\Delta E_a = ?$$

16-21

$$k_1 = \text{Ae}^{-E_{a1}/RT} \quad \text{and} \quad k_2 = \text{Ae}^{-E_{a2}/RT}$$

$$\frac{k_2}{k_1} = \frac{\text{Ae}^{-E_{a2}/RT}}{\text{Ae}^{-E_{a1}/RT}} = e^{(E_{a1} - E_{a2})/RT}$$

$$\ln\frac{k_2}{k_1} = \frac{E_{a1} - E_{a2}}{RT} \qquad \text{or} \qquad RT\left(\ln\frac{k_2}{k_1}\right) = E_{a1} - E_{a2}$$

$$(8.314 \text{ J/mol·K})\,(310 \text{ K})\,\ln\frac{2.3\text{x}10^{14}}{1} = E_{a1} - E_{a2}$$

$$E_{a1} - E_{a2} = 8.5230\text{x}10^4 = \textbf{8.5x10}^4 \textbf{ J/mol}$$

16.79 a) **False**, at any particular temperature, molecules have a range of kinetic energies.
b) **False**, at reduced pressure, the number of collisions per unit time is reduced, as is the reaction rate.
c) **True**
d) **False**, the increase in rate depends on the activation energy for the reaction. Also, biological catalysts (enzymes) may decompose on heating, reducing their effectiveness.
e) **False**, they also must have the correct orientation.
f) **False**, the activation energy is unique to the mechanism of a particular reaction.
g) **False**, since most reaction rates depend to some extent on the reactant concentrations, as these decrease during the course of the reaction, the reaction rate also decreases.
h) **False**, see part f).
i) **False**, a catalyst speeds up the reaction by lowering the activation energy.
j) **False**, the speed of a reaction (kinetics) is separate from the stability of the products (thermodynamics).
k) **False**, the frequency factor, A, is the product of the collision frequency which is affected by temperature and an orientation probability factor.
l) **True**
m) **False**, the catalyst changes the activation energy, not ΔH of reaction.
n) **True**
o) **True**
p) **False**, bimolecular and unimolecular refer to the molecularity or the number of reactant particles involved in the reaction step. There is no direct relationship to the speed of the reaction.
q) **False**, molecularity and molecular complexity are not related.

16.80 Plan: The overall rate law for the mechanism is determined from the slowest step (the rate-determining step). An overall rate law can only include reactants and products; intermediates cannot be included in the rate law. Express [intermediate] in terms of [reactant]. Compare the resulting rate law from the mechanism to the actual rate law.
Solution:
Rate law for slow step (*Step 3*):
   Rate = $k_3[\text{H}_2\text{I}][\text{I}]$
Both H_2I and I are intermediates and cannot be in the final rate law. For an equilibrium, rate$_{\text{forward rxn}}$ = rate$_{\text{reverse rxn}}$.

From first two steps:
   From step 1: $k_1[\text{I}_2] = k_{-1}[\text{I}]^2$; $[\text{I}] = (k_1/k_{-1})^{1/2}[\text{I}_2]^{1/2}$
   From step 2: $k_2[\text{H}_2][\text{I}] = k_{-2}[\text{H}_2\text{I}]$; $[\text{H}_2\text{I}] = k_2/k_{-2}[\text{H}_2][\text{I}]$
Substituting for $[\text{H}_2\text{I}]$ in rate = $k_3[\text{H}_2\text{I}][\text{I}]$:
   Rate = $k_3[k_2/k_{-2}[\text{H}_2][\text{I}]][\text{I}]$
   Rate = $k_3k_2/k_{-2}[\text{H}_2][\text{I}]^2$
Substituting for [I] in rate = $k_3k_2/k_{-2}[\text{H}_2][\text{I}]^2$:
   Rate = $k_3k_2/k_{-2}[\text{H}_2][(k_1/k_{-1})^{1/2}[\text{I}_2]^{1/2}]^2$
   Rate = $k_3k_2/k_{-2}(k_1/k_{-1})[\text{H}_2][\text{I}_2]$
Combining k values:
   Rate = $k[\text{H}_2][\text{I}_2]$ which is consistent with the known rate law.

16.81 Plan: For part a), first use the first-order half-life equation to find the rate constant k for the reaction. Then use the first-order integrated rate law to find concentration of reactant at a later time, given the initial concentration.

16-22

Since the time unit in the rate constant is minutes, t must be expressed in units of minutes. For part b), use the first-order integrated rate law to solve for the time required for 2/3 of the pill to decompose, leaving 1/3 pill at time t. For part c) use the Arrhenius equation to calculate E_a.

Solution:

a) Rearrange $t_{1/2} = \dfrac{\ln 2}{k}$ to $k = \dfrac{\ln 2}{t_{1/2}}$

$$k = \frac{\ln 2}{90 \text{ min}} = 7.7016 \times 10^{-3} \text{ min}^{-1}$$

Converting t from h to min: $(2.5 \text{ h})\left(\dfrac{60 \text{ min}}{1 \text{ h}}\right) = 150 \text{ min}$

$$\ln \frac{[\text{aspirin}]_t}{[\text{aspirin}]_0} = -kt \text{ or}$$

$\ln [\text{aspirin}]_t = \ln [\text{aspirin}]_0 - kt$
$\ln [\text{aspirin}]_t = \ln [2 \text{ mg}/100 \text{ mL}] - (7.7016 \times 10^{-3} \text{ min}^{-1})(150 \text{ min})$
$\ln [\text{aspirin}]_t = -5.06729$
$[\text{aspirin}]_t = 6.29964 \times 10^{-3}$ mg/mL or

$$\frac{6.29964 \times 10^{-3} \text{ mg}}{\text{mL}} \text{ x } 100 \text{ mL} = 0.62996 \text{ mg}/100 \text{ mL} = \textbf{0.6 mg/100 mL}$$

b) The antibiotic pill = PILL. The pill is taken at the fever temperature, so use the fever k.

$$\ln \frac{[\text{PILL}]_t}{[\text{PILL}]_0} = -kt$$

$$\ln \frac{[1/3 \text{ PILL}]_t}{[1 \text{ PILL}]_0} = -(3.9 \times 10^{-5} \text{ s}^{-1})\, t$$

$$t = 28169.55 \text{ s} \quad \text{or} \quad (28169.55 \text{ s})\left(\frac{1 \text{ h}}{3600 \text{ s}}\right) = 7.8 \text{ h}$$

Pills should be taken at about eight hour intervals.

c) $k_1 = 3.1 \times 10^{-5}$ s^{-1} $\qquad\qquad$ $T_1 = [98.6°\text{F} - 32](5/9) + 273.15 = 310.15$ K
$k_2 = 3.9 \times 10^{-5}$ s^{-1} $\qquad\qquad$ $T_2 = [101.9°\text{F} - 32](5/9) + 273 = 311.98$ K
$E_a = ?$

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = -\frac{R\left(\ln \dfrac{k_2}{k_1}\right)}{\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)} = -\frac{\left(8.314\dfrac{\text{J}}{\text{mol} \bullet \text{K}}\right)\left(\ln \dfrac{(3.9 \times 10^{-5} \text{ s}^{-1})}{(3.1 \times 10^{-5} \text{ s}^{-1})}\right)}{\left(\dfrac{1}{311.98 \text{ K}} - \dfrac{1}{310.15 \text{ K}}\right)}$$

$E_a = 1.0092 \times 10^5$ J/mol = $\textbf{1x10}^\textbf{5}$ **J/mol**
The subtraction of the $1/T$ terms leaves only one significant figure.

16.82   Plan: Starting with the fact that rate of formation of O (rate of step 1) equals the rate of consumption of O (rate of step 2), set up an equation to solve for [O] using the given values of k_1, k_2, [NO$_2$], and [O$_2$].

Solution:

a)   Rate$_1$ = k_1[NO$_2$] $\qquad$ Rate$_2$ = k_2[O][O$_2$}
        Rate$_1$ = rate$_2$
        k_1[NO$_2$] = k_2[O][O$_2$]

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$$[O] = \frac{k_1[NO_2]}{k_2[O_2]} = \frac{\left(6.0 \times 10^{-3}\,s^{-1}\right)\left[4.0 \times 10^{-9}\,M\right]}{\left(1.0 \times 10^{6}\,L/mol \cdot s\right)\left[1.0 \times 10^{-2}\,M\right]} = \mathbf{2.4 \times 10^{-15}\,M}$$

b) Since the rate of the two steps is equal, either can be used to determine rate of formation of ozone.

$$Rate_2 = k_2[O][O_2] = (1.0 \times 10^{6}\,L/mol \cdot s)(2.4 \times 10^{-15}\,M)(1.0 \times 10^{-2}\,M) = \mathbf{2.4 \times 10^{-11}\,mol/L \cdot s}$$

16.83 Plan: The activation energy can be calculated using the Arrhenius equation. Although the rate constants, k_1 and k_2, are not expressly stated, the relative times give an idea of the rate. The reaction rate is proportional to the rate constant. At $T_1 = 90.0°C$, the rate of reaction is 1 egg/4.8 min while at $T_2 = 100.0°C$, the rate is 1 egg/4.5 min. Therefore, rate$_1$ = 1 egg/4.8 min and rate$_2$ = 1 egg/4.5 min are substituted for k_1 and k_2, respectively.

Solution:

k_1 = 1 egg/4.8 min $T_1 = (273.2 + 90.0)\,K = 363.2\,K$
k_2 = 1 egg/4.5 min $T_2 = (273.2 + 100.0)\,K = 373.2\,K$
E_a = ?

The number of eggs (1) is exact, and has no bearing on the significant figures.

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = -\frac{R\left(\ln\dfrac{k_2}{k_1}\right)}{\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)} = -\frac{\left(8.314\dfrac{J}{mol \cdot K}\right)\left(\ln\dfrac{(1\,egg/4.5\,min)}{(1\,egg/4.8\,min)}\right)}{\left(\dfrac{1}{373.2\,K} - \dfrac{1}{363.2\,K}\right)}$$

$$E_a = 7.2730 \times 10^{3}\,J/mol = \mathbf{7.3 \times 10^{3}\,J/mol}$$

16.84 Plan: At time = 0.00 min, assume $[A]_0 = 1.00$; use the given equation for % inactivation to calculate $[A]_t$ at 3.00 min. Now knowing $[A]_0$ and $[A]_t$, use the first-order integrated rate law to calculate the rate constant, k in part a). For part b), use the equation for % inactivation to calculate $[A]_t$ and then use the k value from part a) to calculate time, t.

Solution:

a) Calculating $[A]_t$ at 3.00 min (99.9% inactivation):

% inactivation = 100 x (1 – $[A]_t/[A]_0$)

At 3.00 min: 99.9% = 100 x (1 – $[A]_t/1.00$)

99.9% = 100 – 100$[A]_t$

$[A]_t$ = 0.001

$$\ln\frac{[A]_t}{[A]_0} = -kt$$

$$k = -\frac{\ln\dfrac{[A]_t}{[A]_0}}{t} = -\frac{\ln\dfrac{[0.001]_t}{[1.00]_0}}{3.00\,min} = 2.302585 = \mathbf{2.3\,min^{-1}}$$

b) Calculating $[A]_t$ at 95% inactivation:

% inactivation = 100 x (1 – $[A]_t/[A]_0$)

95% = 100 x (1 – $[A]_t/1.00$)

95% = 100 – 100$[A]_t$

$[A]_t$ = 0.05

$$\ln\frac{[A]_t}{[A]_0} = -kt$$

$$t = -\frac{\ln\dfrac{[A]_t}{[A]_0}}{k} = -\frac{\ln\dfrac{[0.05]_t}{[1.00]_0}}{2.302585\,min^{-1}} = 1.30103 = \mathbf{1.3\,min}$$

16.85 Plan: The overall rate law for the mechanism is determined from the slowest step (the rate-determining step). An overall rate law can only include reactants and products; intermediates cannot be included in the rate law. Express [intermediate] in terms of [reactant]. Compare the resulting rate law from the mechanism to the actual rate law.
Solution:
I. Since there is only one step in the mechanism, it must be the rate-determining step:

$$\text{Rate} = k_1[N_2O_5]^2$$

This rate law does not match the actual rate law so the proposed mechanism is not valid.
II. The first step is the rate-determining step. From step 1:

$$\text{Rate} = k_1[N_2O_5]^2$$

This rate law does not match the actual rate law so the proposed mechanism is not valid.
III. The second step is the rate-determining step. From step 2:

$$\text{Rate} = k_2[NO_2][N_2O_5]$$

NO_2 is an intermediate and cannot be in the final rate law. For an equilibrium, $\text{rate}_{\text{forward rxn}} = \text{rate}_{\text{reverse rxn}}$.
From step 1:

$$k_1[N_2O_5] = k_{-1}[NO_3][NO_2]; \quad [NO_2] = (k_1/k_{-1})[N_2O_5]/[NO_3]$$

Substituting for $[NO_2]$:

$$\text{Rate} = k_2(k_1/k_{-1})[N_2O_5]^2[NO_3]^{-1} = k[N_2O_5]^2[NO_3]^{-1}$$

This rate law does not match the actual rate law so the proposed mechanism is not valid.
IV. The second step is the rate-determining step. From step 2:

$$\text{Rate} = k_2[N_2O_3][O]$$

N_2O_3 and O are intermediates and cannot be in the final rate law. For an equilibrium, $\text{rate}_{\text{forward rxn}} = \text{rate}_{\text{reverse rxn}}$.
From step 1:

$$k_1[N_2O_5]^2 = k_{-1}[NO_2]^2[N_2O_3][O]^3; \qquad [O] = (k_1/k_{-1})^{1/3}[N_2O_5]^{2/3}/[NO_2]^{2/3}[N_2O_3]^{1/3}$$

Substituting for $[O]$:

$$\text{Rate} = k_2(k_1/k_{-1})^{1/3}[N_2O_5]^{2/3}[NO_2]^{-2/3}[N_2O_3]^{2/3}$$

This rate law does not match the actual rate law so the proposed mechanism is not valid.
V. The first step is rate determining:

$$\text{Rate} = k_1[N_2O_5]^2$$

This rate law does not match the actual rate law so the proposed mechanism is not valid.

16.86 a) The reaction is $C{=}C + H_2(g) \leftrightarrow C{-}C$. Since the hydrogenation and dehydrogenation reactions are reversible, the direction of reaction is determined by the hydrogen pressure.
b) Dehydrogenation will require a higher temperature. Hydrogenation, adding hydrogen to the double bond in the alkene, is exothermic. The hydrogenated product is of lower energy than the dehydrogenated reactant. The reaction pathways are the same but in reverse order so the hydrogenated material has a larger activation energy and thus a higher temperature is needed to obtain a useful reaction rate for dehydrogenation.
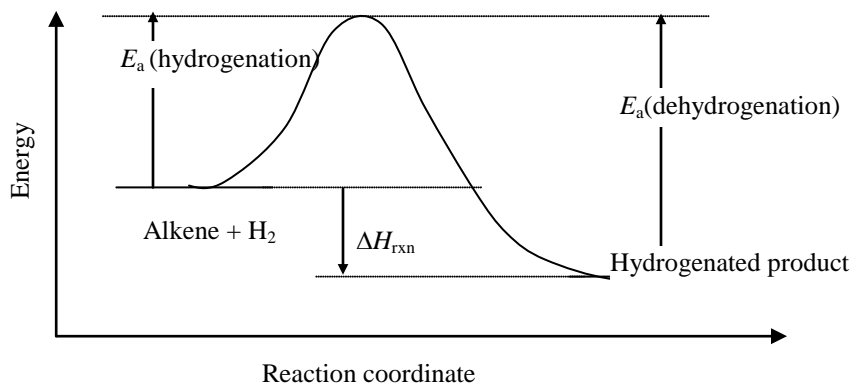
c) In the hydrogenation process, when the double bond has been broken and one hydrogen atom has been added to the bond, the molecule can rotate around the resulting single bond and then lose a hydrogen atom (since hydrogenation and dehydrogenation are reversible) to restore the double bond and produce the *trans* fat.

16.87   Plan: The half-life is the time required for one-half of the reactant to be consumed. Count the reactant molecules
in the three scenes to determine the number of molecules remaining after each time period. This information is
used to determine the half-life. Once $t_{1/2}$ is known, use the first-order half-life equation to calculate the rate
constant, k.
Solution:
a) There are twelve molecules of reactant at $t = 0$, eight reactant molecules after 20 min, and three reactant
molecules after 60 min. After 60 min, one-fourth (three of twelve molecules) of the initial amount of
cyclopropane remains unreacted. Therefore, 60 min represents two half-lives. The half-life is **30 min**.

b) $t_{1/2} = \dfrac{\ln 2}{k}$ $k = \dfrac{\ln 2}{t_{1/2}} = \dfrac{\ln 2}{30 \text{ min}} = 0.023104906 = \textbf{0.023 min}^{-1}$

16.88   a) The shape is **tetrahedral** and the hybridization of C_1 is sp^3.
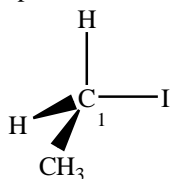
b) The shape is **trigonal bipyramidal**. Because an unhybridized p orbital is needed to overlap p orbitals on I and
Br, the hybridization around C_1 is sp^2.
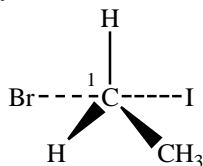
c) After Br^- is replaced with I^- in the initial replacement reaction, the ethyl iodide is optically active. However, as
other I^- ions react with the ethyl iodide by the same mechanism the molecules change from one isomer to the
other. Eventually, equal portions of each isomer exist and the ethyl iodide is optically inactive.

16.89   Plan: The rate law is rate = $k[A]^m[B]^n$ where m and n are the orders of the reactants. The initial rate for each
reaction mixture is given. Calculate the concentration of A and B in each mixture. To find the order of each
reactant, take the ratio of the rate laws for two experiments in which only the reactant in question changes. Once
the rate law is known, Reaction Mixture I, II, or III can be used to find the rate constant k for the reactions without
the solid and Reaction Mixture IV can be used to find the rate constant k for the reaction with a solid present.
Solution:
a) Reaction Mixture I

$\text{Concentration of A} = (5 \text{ spheres})\left(\dfrac{0.01 \text{ mol}}{1 \text{ sphere}}\right)\left(\dfrac{1}{0.50 \text{ L}}\right) = 0.10 \text{ mol/L A}$

$\text{Concentration of B} = (5 \text{ spheres})\left(\dfrac{0.01 \text{ mol}}{1 \text{ sphere}}\right)\left(\dfrac{1}{0.50 \text{ L}}\right) = 0.10 \text{ mol/L B}$

Reaction Mixture II

$\text{Concentration of A} = (8 \text{ spheres})\left(\dfrac{0.01 \text{ mol}}{1 \text{ sphere}}\right)\left(\dfrac{1}{0.50 \text{ L}}\right) = 0.16 \text{ mol/L A}$

$\text{Concentration of B} = (5 \text{ spheres})\left(\dfrac{0.01 \text{ mol}}{1 \text{ sphere}}\right)\left(\dfrac{1}{0.50 \text{ L}}\right) = 0.10 \text{ mol/L B}$

Reaction Mixture III

$\text{Concentration of A} = (8 \text{ spheres})\left(\dfrac{0.01 \text{ mol}}{1 \text{ sphere}}\right)\left(\dfrac{1}{0.50 \text{ L}}\right) = 0.16 \text{ mol/L A}$

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Concentration of B = $(7 \text{ spheres})\left(\dfrac{0.01 \text{ mol}}{1 \text{ sphere}}\right)\left(\dfrac{1}{0.50 \text{ L}}\right) = 0.14$ mol/L B

To find the order for A, use Mixtures I and II in which [B] is constant while [A] changes. Set up a ratio of the rate laws for Mixtures I and II and fill in the values given for rates and concentrations and solve for m, the order with respect to [A].

$$\frac{\text{Rate}_{II}}{\text{Rate}_I} = \frac{k_2[A]^m[B]^n}{k_1[A]^m[B]^n} \qquad \text{The concentration of B is constant}$$

$$\frac{5.6 \times 10^{-4} \text{ mol/L} \cdot \text{s}}{3.5 \times 10^{-4} \text{ mol/L} \cdot \text{s}} = \frac{[0.16]^m}{[0.10]^m}$$

$$1.6 = (1.6)^m$$
$$m = 1$$

The reaction is **first order with respect to A**.

To find the order for B, use Mixtures II and III in which [A] is constant while [B] changes. Set up a ratio of the rate laws for Mixtures II and III and fill in the values given for rates and concentrations and solve for n, the order with respect to [B].

$$\frac{\text{Rate}_{III}}{\text{Rate}_{II}} = \frac{k_2[A]^m[B]^n}{k_1[A]^m[B]^n} \qquad \text{The concentration of A is constant.}$$

$$\frac{5.6 \times 10^{-4} \text{ mol/L} \cdot \text{s}}{5.6 \times 10^{-4} \text{ mol/L} \cdot \text{s}} = \frac{[0.14]^n}{[0.10]^n}$$

$$1 = (1.4)^n$$
$$n = 0$$

The reaction is **zero order with respect to B**.

Rate law: Rate = $k[A][B]^0 = k[A]$

b) The overall reaction order is 1 + 0 = **1**.

c) Use Reaction Mixture I:

Rate = $k[A]$

3.5×10^{-4} mol/L$\cdot$s = $k[0.10]$

$k = \mathbf{3.5 \times 10^{-3} \text{ s}^{-1}}$

d) The catalyst was used in Reaction Mixture IV.

Concentration of A = $(5 \text{ spheres})\left(\dfrac{0.01 \text{ mol}}{1 \text{ sphere}}\right)\left(\dfrac{1}{0.50 \text{ L}}\right) = 0.10$ mol/L A

Concentration of B = $(8 \text{ spheres})\left(\dfrac{0.01 \text{ mol}}{1 \text{ sphere}}\right)\left(\dfrac{1}{0.50 \text{ L}}\right) = 0.16$ mol/L B
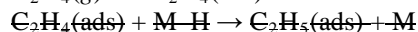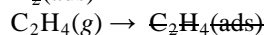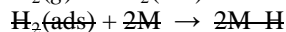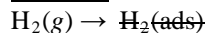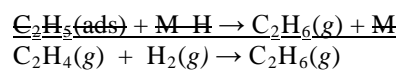
Rate = $k[A]$

$4.9 \times 10^{-4} = k[0.10]$

$k = 4.9 \times 10^{-3} \text{ s}^{-1}$

Yes, the gray pellets had a catalytic effect. The rate of reaction and the rate constant are greater with the pellets than without.

16.90   Plan: The figure shows the H_2 molecule adsorbing to the metal surface with H_2 bond breakage. The individual H atoms form bonds to the metal catalyst atoms. Ethylene also adsorbs to the metal catalyst and then the two C–H bonds form, one at a time. The resulting C_2H_6 leaves the metal surface. The overall reaction can be obtained by adding the steps of the mechanism together.
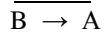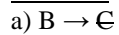Solution:
$H_2(g) \rightarrow$ ~~$H_2(ads)$~~
~~$H_2(ads)$~~ $+$ ~~$2M$~~ $\rightarrow$ ~~$2M–H$~~
$C_2H_4(g) \rightarrow$ ~~$C_2H_4(ads)$~~
~~$C_2H_4(ads)$~~ $+$ ~~$M–H$~~ $\rightarrow$ ~~$C_2H_5(ads)$~~ $+$ ~~M~~

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$$\begin{array}{l} \underline{C_2H_5(ads) + M-H \rightarrow C_2H_6(g) + M} \\ C_2H_4(g) \ + \ H_2(g) \rightarrow C_2H_6(g) \end{array}$$

16.91 Plan: The reaction begins with B as the reactant; the final product is A. Isomer C is formed during the reaction but is not a final product.
Solution:
a) B → C
  C → A
  B → A
b) C is an **intermediate**.

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