CHAPTER 16 KINETICS: RATES AND MECHANISMS OF CHEMICAL REACTIONS

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 increase, more collisions result in reaction (i.e., reactants → products), so the **rate of reaction increases**.

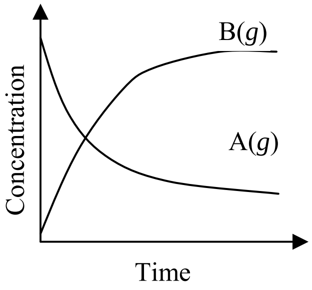
16.6 The second experiment proceeds at the higher rate. I_2 in the gaseous state would experience more collisions with gaseous H_2.

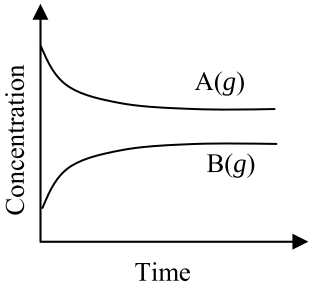
16.7 The reaction rate is the change in the concentration of reactants or products per unit time. Reaction rates change with time because reactant concentrations decrease, while product concentrations increase with time.

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 versus 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.





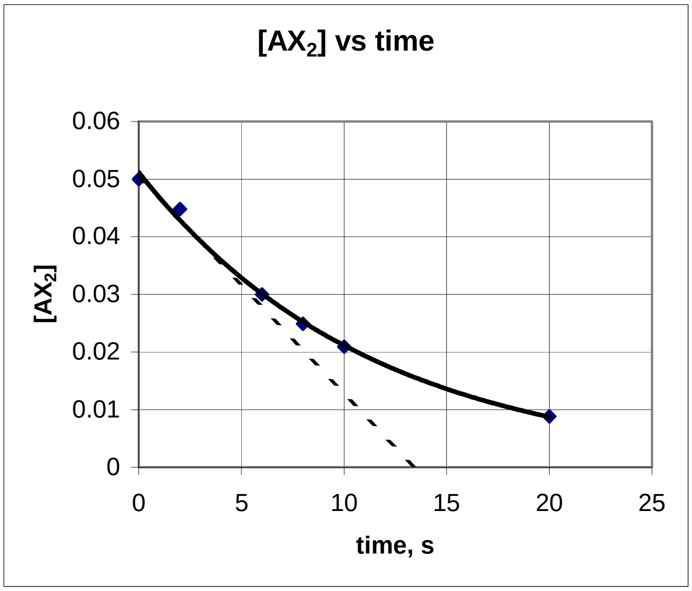
16.11 a) Calculate the slope of the line connecting (0, $[C]_o$) and (t_f, $[C]_f$) (final time and concentration). The negative of this slope is the average rate.
b) Calculate the negative of the slope of the line tangent to the curve at t = x.
c) Calculate the negative of the slope of the line tangent to the curve at t = 0.
d) If you plotted [D] versus time, you would not need to take the negative of the slopes in (a)–(c) since [D] would increase over time.

16.12 a) The average rate from t = 0 to t = 20.0 s is proportional to the slope of the line connecting these two points:

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[\text{AX}_2]}{\Delta t} = -\frac{1}{2}\frac{(0.0088\text{ mol/L} - 0.0500\text{ mol/L})}{(20.0\text{ s} - 0\text{ s})} = 0.00103 = \mathbf{0.0010\ mol/L \bullet s}$$

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.

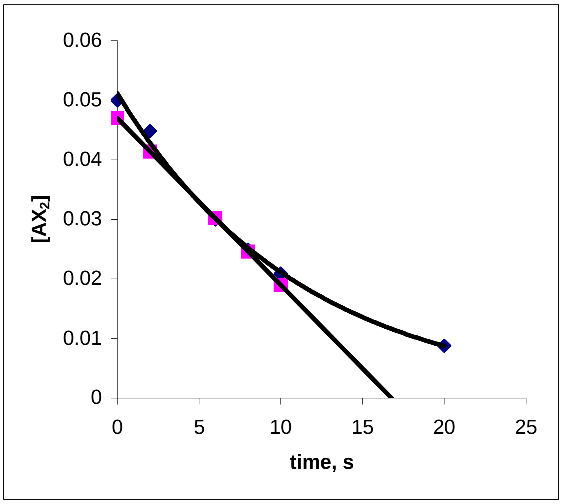
b)



The slope of the tangent to the curve (dashed line) at t = 0 is approximately –0.004 *M*/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 a) $$\text{Rate} = -\frac{1}{2}\frac{\Delta[\text{AX}_2]}{\Delta t} = -\frac{1}{2}\frac{(0.0088\text{ mol/L} - 0.0249\text{ mol/L})}{(20.0\text{ s} - 8.0\text{ s})} = 6.70833 \times 10^{-4} = \mathbf{6.71 \times 10^{-4}\ mol/L{\bullet}s}$$

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 **-2.8×10^{-3} mol/L•s**.

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

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 for reactant B to account for the stoichiometric coefficient of 2 for B in the reaction.

$-\dfrac{\Delta[A]}{\Delta t} = -\dfrac{1}{2}\dfrac{\Delta[B]}{\Delta t} = -\dfrac{1}{2}\dfrac{(0.50 \text{ mol/L})}{\text{s}}$ = –0.25 mol/L•s (unrounded)

[B] decreases twice as fast as [A], so [A] is decreasing at a rate of 1/2 (0.5 mol/L•s) or **0.2 mol/L • s**.

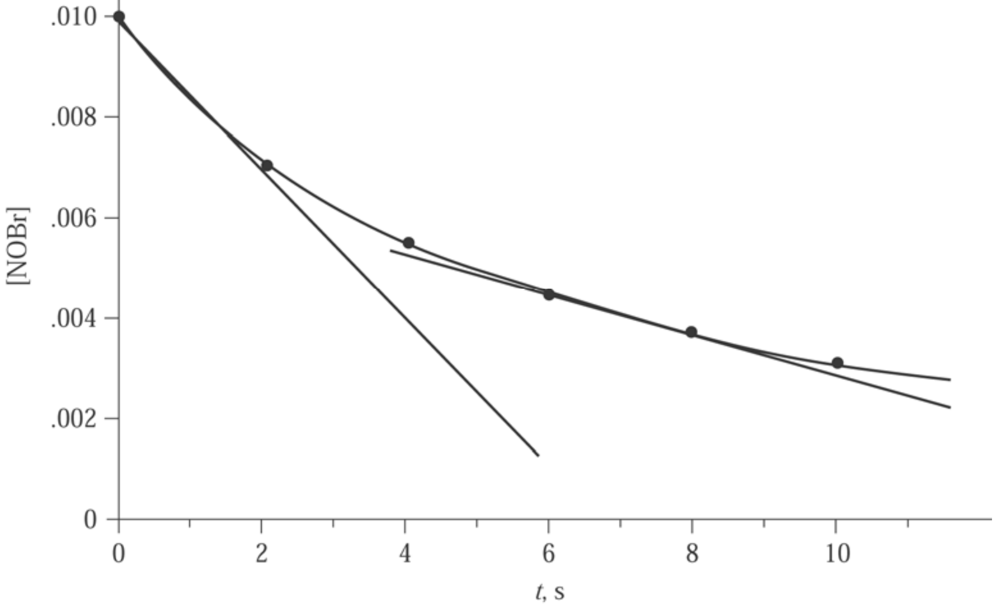
16.15 Rate = $-\dfrac{1}{2}\dfrac{\Delta[D]}{\Delta t} = -\dfrac{1}{3}\dfrac{\Delta[E]}{\Delta t} = -\dfrac{\Delta[F]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[G]}{\Delta t} = \dfrac{\Delta[H]}{\Delta t}$

$\dfrac{\Delta[H]}{\Delta t} = -\dfrac{1}{2}\dfrac{\Delta[D]}{\Delta t} = -\dfrac{1}{2}\dfrac{(-0.10 \text{ mol/L})}{\text{s}}$ = **0.05 mol/L • s**

16.16 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:
$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$

16.17 $CH_4 + 2\ O_2 \rightarrow 2\ H_2O + CO_2$

16.18 a) Rate = – [(0.0033 – 0.0100) mol/L] / [10.00 – 0.00) s] = **6.7×10^{-4} mol/L • s**
b) Rate = – [(0.0055 – 0.0071) mol/L] / [4.00 – 2.00) s] = **8.0×10^{-4} mol/L • s**
c)



Initial Rate = – Δ *y* / Δ *x* = – [(0.0040 – 0.0100) mol/L] / [4.00 – 0.00) s] = **1.5×10^{-3} mol/L • s**

d) Rate at 7.00 s = – [(0.0030 – 0.0050) mol/L] / [11.00 – 4.00) s] = 2.857×10^{-4} = **2.9×10^{-4} mol/L • s**

e) Average between *t* = 3 s and *t* = 5 s is:
Rate = – [(0.0050 – 0.0063) mol/L] / [5.00 – 3.00) s] = 6.5×10^{-4} mol/L • s
Rate at 4 s ≈ 6.7×10^{-4} mol/L•s thus the rates are equal at about **4 seconds**.

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

b) Use the mole ratio in the balanced equation:

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

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:

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

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

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

$$\mathbf{k = L^2/mol^2 \bullet min}$$

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

b) The **rate decreases by a factor of four**. If rate = $k[1/2 \text{ x } B]^2$, then rate decreases to $(1/2)^2$ or 1/4 of its original value.

c) The **rate increases by a factor of nine**. If rate = $k[3 \text{ x } C]^2$, then rate increases to 3^2 or 9 times its original value.

16.22 The order for each reactant is the exponent on the reactant concentration in the rate law. The orders with respect to $[BrO_3^-]$ and to $[Br^-]$ are both 1. The order with respect to $[H^+]$ is 2. The overall reaction order is the sum of each reactant order: 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 **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 = $k[2 \text{ x } BrO_3^-]$, 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 = $k[1/2 \text{ x } Br^-]$, 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 = $k[4 \text{ x } H^+]^2$, then rate increases to 4^2 or **16 times** its original value.

16.25 a) The rate **increases by a factor of 4**.

b) The rate **decreases by a factor of 2**.

c) The rate **increases by a factor of 2**.

16.26 a) To find the order for reactant A, first identify the reaction experiments in which [A] changes but [B] is constant. Set up a proportionality: $\frac{\text{rate}_{\text{exp 1}}}{\text{rate}_{\text{exp 2}}} = \left(\frac{[A]_{\text{exp 1}}}{[A]_{\text{exp 2}}}\right)^m$. Fill in the values given for rates and concentrations and solve for m, the order with respect to [A]. Repeat the process to find the order for reactant B.

Use experiments 1 and 2 (or 3 and 4 would work) to find the order with respect to [A].

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

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

$9.00 = (3.00)^m$

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

$m = 2$

Using experiments 3 and 4 also gives **2nd order with respect to [A]**.

Use experiments 1 and 3 with [A] = 0.100 *M* or 2 and 4 with [A] = 0.300 *M* to find order with respect to [B].

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

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

$2.00 = (2.00)^n$

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

$n = 1$

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*:

$$k = \frac{\text{rate}}{[A]^2[B]} = \frac{5.00 \text{ mol/L} \bullet \text{min}}{[0.100 \text{ mol/L}]^2[0.100 \text{ mol/L}]} = \mathbf{5.00 \times 10^3\ L^2/mol^2 \bullet min}$$

16.27 a) The rate law is rate = $k\,[A]^m[B]^n[C]^p$

Use experiments 1 and 2 to find the order with respect to [A].

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

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

$2.00 = (2.00)^m$

$\log (2.00) = m \log (2.00)$

$m = 1$ The order is **first order with respect to A**.

Use experiments 2 and 3 to find the order with respect to [B].

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

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

$4.00 = (2.00)^n$

$\log (4.00) = n \log (2.00)$

$n = 2$ The reaction is **second order with respect to B**.

Use experiments 1 and 4 to find the order with respect to [C].

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

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

$1.00 = (2.00)^{\text{p}}$

log (1.00) = p log (2.00)

p = 0

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

b) Rate = $k\,[\text{A}]^1[\text{B}]^2[\text{C}]^\circ$

Rate = k [A][B]^2

c) $k = \dfrac{\text{rate}}{[\text{A}][\text{B}]^2} = \dfrac{6.25 \text{ x } 10^{-3} \text{ mol/L} \bullet \text{min}}{[0.0500 \text{ mol/L}][0.0500 \text{ mol/L}]^2}$ = **50.0 L^2/mol^2•s**

16.28 a) Rate = $k\,[\text{CO}]^{\text{m}}[\text{Cl}_2]^{\text{n}}$

Use experiments 1 and 2 to find the order with respect to [CO].

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

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

$9.699 = (10.0)^{\text{m}}$

log (9.699) = m log (10.0)

m = 0.9867 = 1

The reaction is first order with respect to [CO].

Use experiments 2 and 3 to find order with respect to [Cl_2].

$$\frac{\text{rate}_{\text{exp 3}}}{\text{rate}_{\text{exp 2}}} = \left(\frac{[\text{Cl}_2]_{\text{exp 3}}}{[\text{Cl}_2]_{\text{exp 2}}}\right)^{\text{n}}$$

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

$9.774 = (10.0)^{\text{n}}$

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

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

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

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

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

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

a) The reaction is **first order** since ln[reactant] versus time is linear.

b) The reaction is **second order** since 1/[reactant] versus time is linear.

c) The reaction is **zero order** since [reactant] versus time is linear.

16.30 The half-life ($t_{1/2}$) of a reaction is the time required for the reactant concentration to reach half its initial value. 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 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. ($[\text{AB}] = 1/3\ [\text{AB}]_0 = 1/3\ (1.50\ M) = 0.500\ M$)

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

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

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

$t = 6.6667 =$ **7 s**

16.32
$$\frac{1}{[\text{AB}]_t} - \frac{1}{[\text{AB}]_0} = kt$$

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

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

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

$[\text{AB}]_t = 0.375 =$ **$0.4\ M$**

16.33 a) The given information is the amount that has reacted in a specified amount of time. With this information, the integrated rate law must be used to find a value for the rate constant. For a first order reaction, the rate law is $\ln [\text{A}]_t = \ln [\text{A}]_0 - kt$. Using the fact that 50% has decomposed, let $[\text{A}]_0 = 1\ M$ and then $[\text{A}]_t = 1\ M/2$: $= 0.5\ M$:

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

$\ln [0.5] = \ln [1] - k(10.5\ \text{min})$

$-0.693147 = 0 - k(10.5\ \text{min})$

$0.693147 = k(10.5\ \text{min})$

$k = 0.0660\ \text{min}^{-1}$

Alternatively, 50.0% decomposition means that one half-life has passed. Thus, the first order half-life equation may be used:

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

b) Use the value for k calculated in part a. Let $[\text{A}]_0 = 1\ M$; since 75% of A has decomposed, 25% of A remains and $[\text{A}]_t =$ 25% of $[\text{A}]_0$ or $0.25[\text{A}]_0 = 0.25[1] = 0.25\ M$

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

$$\frac{\ln[\text{A}]_t - \ln[\text{A}]_0}{-k} = t = \frac{\ln[0.25] - \ln[1]}{-0.0660\ \text{min}^{-1}}$$

$t = 21.0045 =$ **21.0 min**

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

16.34 a) $t_{1/2} = \ln 2 / k = \ln 2 / (0.0012\ \text{yr}^{-1}) = 577.62 = \mathbf{5.8 \times 10^2\ yr}$

b) $\ln([\text{A}]_0 / [\text{A}]_t) = kt$

$[\text{A}]_0 = 100\%$ $[\text{A}]_t = 12.5\%$ $k = 0.0012\ \text{yr}^{-1}\ t$

$$\ln\left(\frac{100\%}{12.5\%}\right) = (0.0012\ \text{yr}^{-1})\ t$$

$t = 1732.86795 = \mathbf{1.7 \times 10^3\ yr}$

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 $k = Ae^{-Ea/RT}$

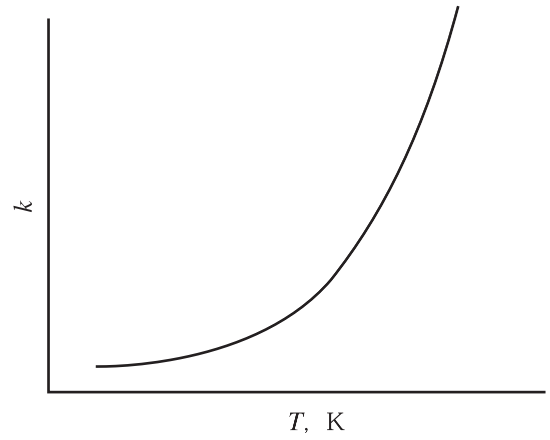
The Arrhenius equation indicates a negative exponential relationship between temperatures and the rate constant, *k*. In other words, the rate constant increases exponentially with temperature.

16.36 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* versus $1/T$. The slope equals $-E_a/R$.

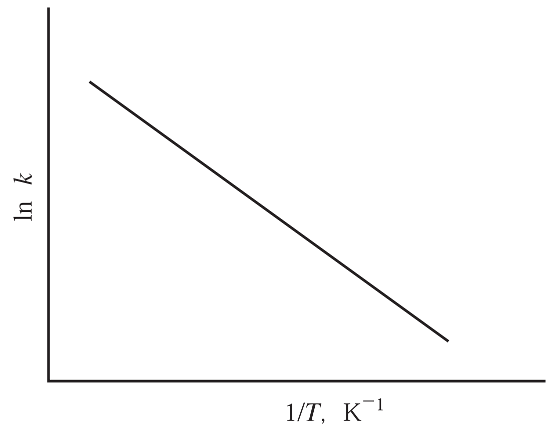
16.37 a) The value of *k* increases exponentially with temperature.

b) A plot of ln *k* versus $1 / T$ is a straight line whose slope is $-E_a / R$.

(a)



(b)



16.38 Substitute the given values into Equation 16.9 and solve for k_2.

$k_1 = 4.7 \text{ x } 10^{-3} \text{ s}^{-1}$ $T_1 = 25°\text{C} = (273 + 25) = 298 \text{ K}$

$k_2 = ?$ $T_2 = 75°\text{C} = (273 + 75) = 348 \text{ K}$

$E_a = 33.6 \text{ kJ/mol} = 33600 \text{ J/mol}$

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

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

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

$$\frac{k_2}{4.7 \text{ x } 10^{-3} \text{ s}^{-1}} = 7.0182577$$

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

16.39 Substitute the given values into Equation 16.9 and solve for E_a.

$k_1 = 4.50 \text{ x } 10^{-5} \text{ L/mol•s}$ $T_1 = 195°\text{C} = (273 + 195) = 468 \text{ K}$

$k_2 = 3.20 \text{ x } 10^{-3} \text{ L/mol•s}$ $T_2 = 258°\text{C} = (273 + 258) = 531 \text{ K}$

$E_a = ?$

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

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

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

16.40 Substitute the given values into Equation 16.9 and solve for E_a.

$k_1 = 0.76\text{/s}$ $T_1 = 727°\text{C} = (273 + 727) = 1000. \text{ K}$

$k_2 = 0.87\text{/s}$ $T_2 = 757°\text{C} = (273 + 757) = 1030. \text{ K}$

$E_a = ?$

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

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

$E_a = 3.8585 \text{ x } 10^4 \text{ J/mol} =$ **$3.9 \text{ x } 10^4 \text{ J/mol}$**

16.41 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.

16.42 **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 — 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.

16.43 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.

16.44 a) **rate increases** b) **rate increases**

16.45 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 trimethylamine ($N(CH_3)_3$) molecule has a greater mass than the ammonia molecule, so trimethylamine 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 trimethylamine 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 $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$ 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 trimethylamine and hydrogen chloride.

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

16.47 $[(1.01 \text{ mol A})(6.022 \times 10^{23} \text{ A/mol A})] \times [(2.12 \text{ mol B})(6.022 \times 10^{23} \text{ B/mol B})]$
$= 7.76495 \times 10^{47} = \mathbf{7.76 \times 10^{47}}$ **unique collisions**

16.48 The fraction of collisions with a specified energy is equal to the $e^{-Ea/RT}$ term in the Arrhenius equation.

$$f = e^{-Ea/RT} \qquad (25°\text{C} = 273 + 25 = 298 \text{ K}) \qquad -E_a/RT = -\frac{100 \text{ kJ/mol}}{(8.314 \text{ J/mol}\bullet\text{K})(298 \text{ K})}\left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right)$$

$$-E_a/RT = -40.362096$$

Fraction = $e^{-Ea/RT} = e^{-40.362096} = 2.9577689 \times 10^{-18} = \mathbf{2.96 \times 10^{-18}}$

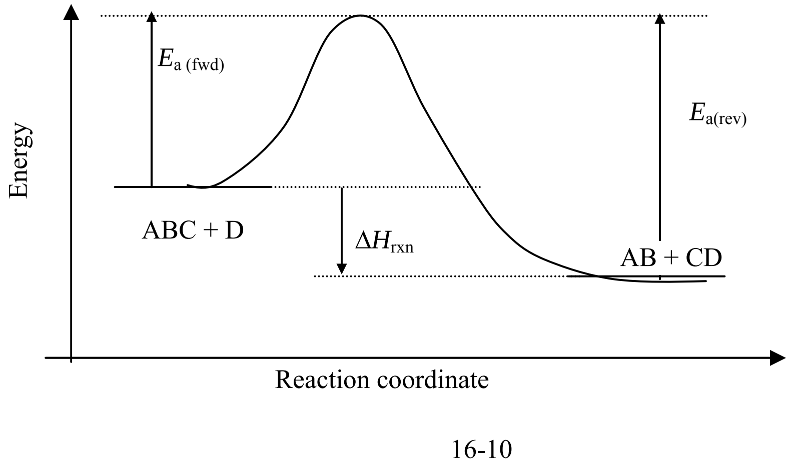
16.49 The fraction of collisions with a specified energy is equal to the $e^{-Ea/RT}$ term in the Arrhenius equation.

$$f = e^{-Ea/RT} \qquad (50.°\text{C} = 273 + 50. = 323 \text{ K}) \qquad -E_a/RT = -\frac{100 \text{ kJ/mol}}{(8.314 \text{ J/mol}\bullet\text{K})(323 \text{ K})}\left(\frac{10^3 \text{ J}}{1 \text{ kJ}}\right)$$

$$-E_a/RT = -37.238095$$

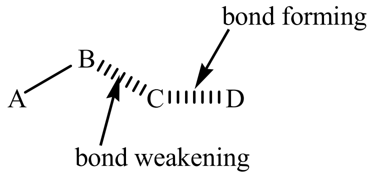
Fraction $= e^{-Ea/RT} = e^{-37.238095} = 6.725131 \times 10^{-17}$ (unrounded)
The fraction increased by $(6.725131 \times 10^{-17})/(2.9577689 \times 10^{-18}) = 22.737175 = \mathbf{22.7}$

16.50 a) The reaction is exothermic, so the energy of the reactants is higher than the energy of the products.

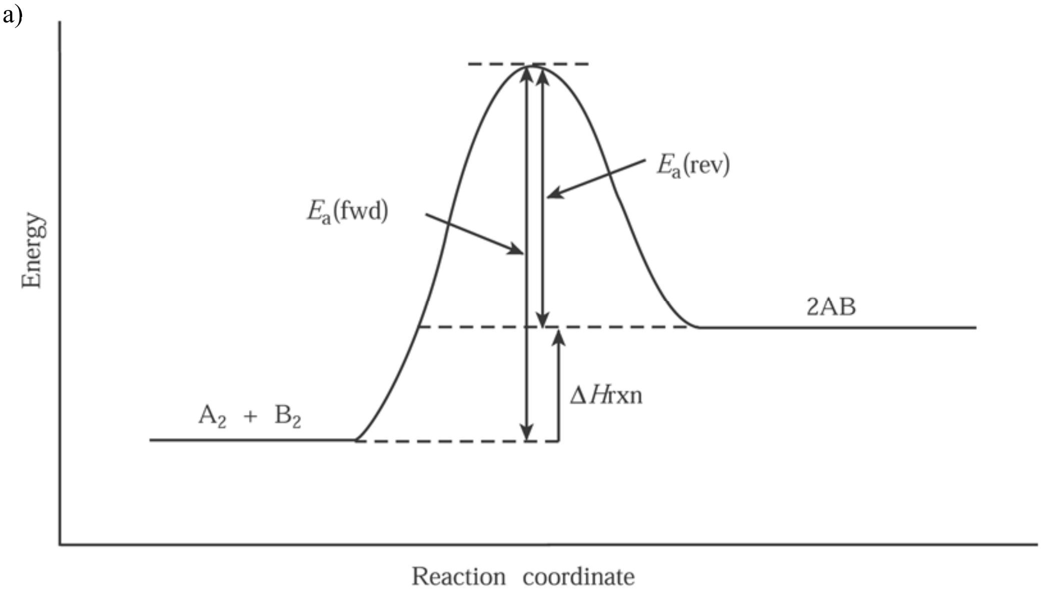


b) $E_{a(rev)} = E_{a(fwd)} - \Delta H_{rxn}$ = 215 kJ/mol – (–55 kJ/mol) = **2.70×10^2 kJ/mol**

c) Reaction coordinate



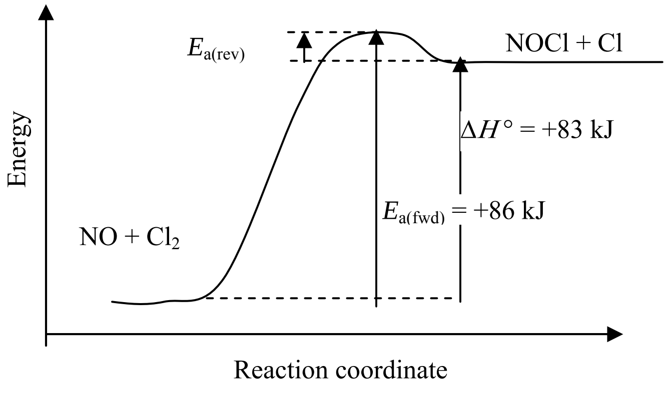
16.51 a)



b) $\Delta H_{rxn} = E_{a(fwd)} - E_{a(rev)}$ = 125 kJ/mol – 85 kJ/mol = **40 kJ/mol**

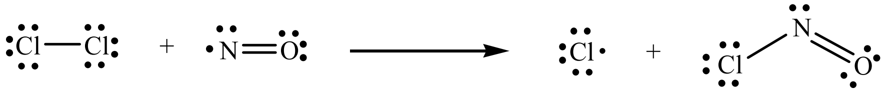
c)
A . . . . . B
| |
A . . . . . B

16.52 a) The reaction is endothermic since the enthalpy change is positive.

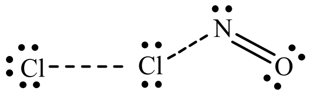


b) Activation energy for the reverse reaction: $E_{a(rev)} = E_{a(fwd)} - \Delta H°$ = 86 kJ – 83 kJ = **3 kJ**.

c) To draw the transition state, look at structures of reactants and products:



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



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.

16.59 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. $\mathbf{HCO_3^-}$ is an intermediate.

c)

Step:	Molecularity	Rate law
$CO_2(aq) + OH^-(aq) \rightarrow HCO_3^-(aq)$	bimolecular	$\text{rate}_1 = k_1[CO_2][OH^-]$
$HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$	bimolecular	$\text{rate}_2 = k_2[HCO_3^-][OH^-]$

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	$\text{rate}_1 = k_1[Cl_2][NO_2]$
$Cl(g) + NO_2(g) \rightarrow NO_2Cl(g)$	bimolecular	$\text{rate}_2 = k_2[Cl][NO_2]$

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 a) The overall reaction can be obtained by adding the three steps together:

(1) $A(g) + B(g) \leftrightarrows X(g)$ fast
(2) $X(g) + C(g) \rightarrow Y(g)$ slow
(3) $Y(g) \rightarrow D(g)$ fast

Total: $A(g) + B(g) + \cancel{X(g)} + C(g) + \cancel{Y(g)} \rightarrow \cancel{X(g)} + \cancel{Y(g)} + D(g)$
$A(g) + B(g) + C(g) \rightarrow D(g)$

b) Intermediates appear in the mechanism first as products, then as reactants. Both **X and Y** are intermediates in the given mechanism.

c)

Step:	Molecularity	Rate law
$A(g) + B(g) \leftrightarrows X(g)$	bimolecular	$\text{rate}_1 = k_1[A][B]$
$X(g) + C(g) \rightarrow Y(g)$	bimolecular	$\text{rate}_2 = k_2[X][C]$
$Y(g) \rightarrow D(g)$	unimolecular	$\text{rate}_3 = k_3[Y]$

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, $\text{rate}_{\text{forward rxn}} = \text{rate}_{\text{reverse rxn}}$. 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 a)
(1) $ClO^-(aq) + H_2O(l) \leftrightarrows HClO(aq) + OH^-(aq)$ fast
(2) $I^-(aq) + HClO(aq) \rightarrow HIO(aq) + Cl^-(aq)$ slow
(3) $OH^-(aq) + HIO(aq) \rightarrow H_2O(l) + IO^-(aq)$ fast
(overall) $ClO^-(aq) + I^-(aq) \rightarrow Cl^-(aq) + IO^-(aq)$

b) $HClO(aq)$, $OH^-(aq)$, and $HIO(aq)$

c)
(1) Bimolecular; $\text{Rate}_1 = k_1 [ClO^-] [H_2O]$
(2) Bimolecular; $\text{Rate}_2 = k_2 [I^-][HClO]$
(3) Bimolecular; $\text{Rate}_3 = k_3 [OH^-][HIO]$

d) **No**. For the slow step: Rate = $k[I^-][HClO]$

However, HClO is an intermediate, and should be replaced. From step (1), leaving out the water,

$[HClO] = [ClO^-]/[OH^-]$

Replacing [HClO] in the slow step rate law gives:

Rate = $k[I^-][ClO^-]/[OH^-]$

This is not the observed rate law.

16.63 Nitrosyl bromide is NOBr(*g*). The reactions sum to the equation 2 NO(*g*) + Br_2(*g*) → 2 NOBr(*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 ($NOBr_2$). Derive the rate law. The slow step in the mechanism is the second step with rate law: rate = $k_2[NOBr_2][NO]$. Since $NOBr_2$ is an intermediate, it must be replaced by using the first step. For an equilibrium like Step 1, $\text{rate}_{\text{forward rxn}} = \text{rate}_{\text{reverse rxn}}$.

(1) Rate_1 (forward) = $k_1[NO][Br_2]$
(2) Rate_1 (reverse) = $k_{-1}[NOBr_2]$
(3) Rate_2 (forward) = $k_2[NOBr_2][NO]$

Solve for $[NOBr_2]$ in Step 1:

Rate_1 (forward) = Rate_1 (reverse)
$k_1[NO][Br_2] = k_{-1}[NOBr_2]$
$[NOBr_2] = (k_1/k_{-1})[NO][Br_2]$

Substitute the expression for $[NOBr_2]$ into equation (3), the slow step:

Rate_2 (forward) = $k_2(k_1/k_{-1})[NO][Br_2][NO]$

Combine the separate constants into one constant: $k = k_2(k_1/k_{-1})$

$\text{Rate}_2 = k[NO]^2[Br_2]$

The derived rate law equals the known rate law, so criterion 3 is satisfied. The proposed mechanism is valid.

16.64 I. 2 NO(*g*) + O_2(*g*) → 2 NO_2(*g*)
Rate = $k[NO]^2[O_2]$

II. a) 2 NO(*g*) $\leftrightarrows$ N_2O_2(*g*)
b) N_2O_2(*g*) + O_2(*g*) → 2 NO_2(*g*)
Rate = $k[N_2O_2][O_2]$
$= k_b(k_a/k_{-a})\,[NO]^2[O_2]$
$= k[NO]^2[O_2]$

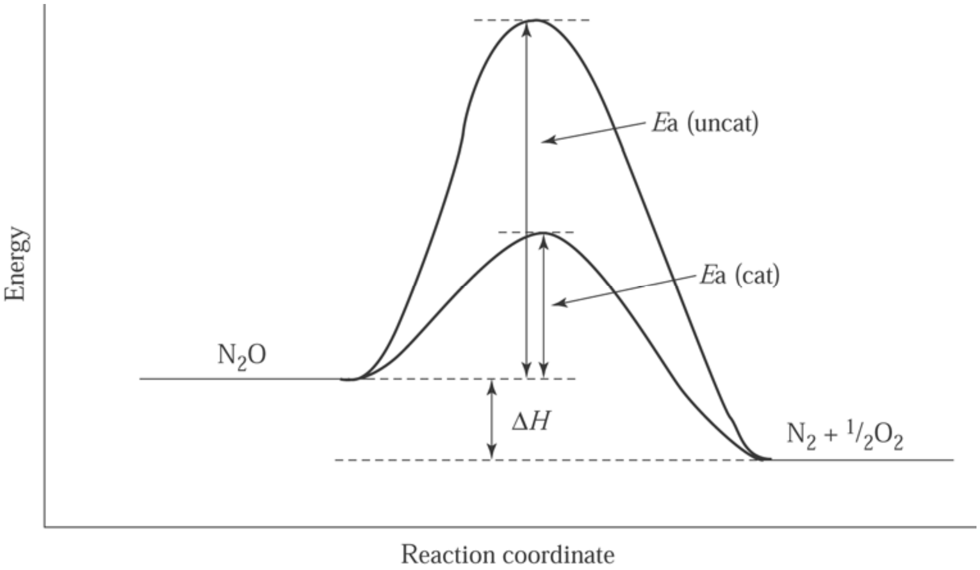
III. a) 2 NO(*g*) $\leftrightarrows$ N_2(*g*) + O_2(*g*)
b) N_2(*g*) + 2 O_2(*g*) → NO_2(*g*)
Rate = $k[N_2][O_2]^2$
$= k_b\,(k_a/k_{-a})\,[NO]^2[O_2]^{-1}[O_2]^2$
$= k[NO]^2[O_2]$

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.

16.65 a) Gold is a **heterogeneous catalyst**.

b)



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) **2** (two peaks) b) **the second step** (higher peak) c) **exothermic** (end below beginning)

16.68 a) Add the two equations:

(1) $X(g) + O_3(g) \rightarrow XO(g) + O_2(g)$

(2) $XO(g) + O(g) \rightarrow X(g) + O_2(g)$

Overall $O_3(g) + O(g) \rightarrow 2\ O_2(g)$

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.

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

$$= \mathbf{3 \text{ x } 10^{7} \text{ molecule/s}}$$

16.69 The activation energy can be calculated using Equation 16.9. 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 = (273 + 20) = 293 K, the rate of reaction is 1 apple/4 days while at T_2 = 0°C = (273 + 0) = 273 K, the rate is 1 apple/16 days. Therefore, rate_1 = 1 apple/4 days and rate_2 = 1 apple/16 days are substituted for k_1 and k_2, respectively.

$k_1 = 1/4$ $T_1 = 293$ K

$k_2 = 1/16$ $T_2 = 273$ K

$E_a = ?$

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

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

$E_a = 4.6096266 \text{ x } 10^4$ J/mol = $\mathbf{4.61 \text{ x } 10^4}$ **J/mol**

The significant figures are based on the Kelvin temperatures.

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

$k = \ln 2/9.8 \text{ x } 10^3 \text{ d} = 7.07293 \text{ x } 10^{-5} \text{ d}^{-1}$ (unrounded)

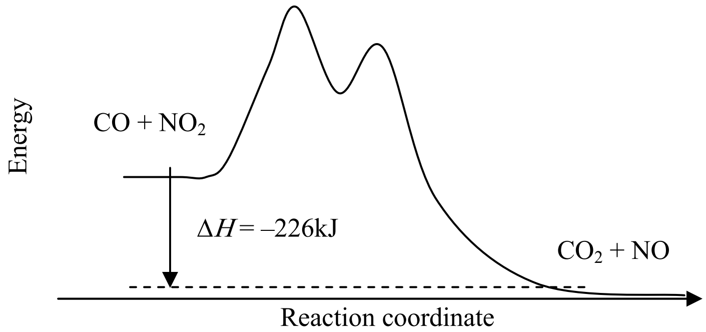
Use the first-order integrated rate law with BP = benzoyl peroxide:

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

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

$t = 725.2057 = \mathbf{7.3 \text{ x } 10^2 \text{ d}}$

16.71 a)



b) **Yes**, the alternative mechanism is consistent with the rate law since the rate of the mechanism is based on the slowest step, $2\ NO_2(g) \rightarrow N_2(g) + 2\ O_2(g)$. The rate law for this step is rate = $k_1[NO_2]^2$, the same as 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 Use the given rate law, and enter the given values:

rate = $k[H^+]$ [sucrose]

$[H^+]_i = 0.01\ M$ [sucrose]$_i = 1.0\ M$

The glucose and fructose are not in the rate law, so they may be ignored.

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 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 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) [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 x sucrose] = 1.0 times as fast. Thus, there will be **no change**.

16.73 A + B → Products. Assume the reaction is first order with respect to A and first order with respect to B.

Rate = k[A][B]

Mixture I:

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

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

Use the rate law to find the value of *k*, the rate constant:

Rate = *k*[A][B]

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

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

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

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

Rate = k[A][B]

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

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

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

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

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

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

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

t = 2.110 = **2.1 min**

16.75 $k_1 = Ae^{-E_{a1}/RT}$ and $k_2 = Ae^{-E_{a2}/RT}$

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

$$\ln\frac{k_2}{k_1} = \frac{E_{a1} - E_{a2}}{RT}$$

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

$$(8.314\ \text{J/mol•K})\ ((273 + 37)\text{K})\ \ln\frac{2.3 \times 10^{14}}{1} = E_{a1} - E_{a2}$$

$E_{a2} - E_{a1}$ = 8.5230 x 10^4 = **8.5 x 10^4 J/mol**

16.76 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.

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

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

Use the first-order integrated rate law:

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

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

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

t = 57.3765798 = **57 yr**

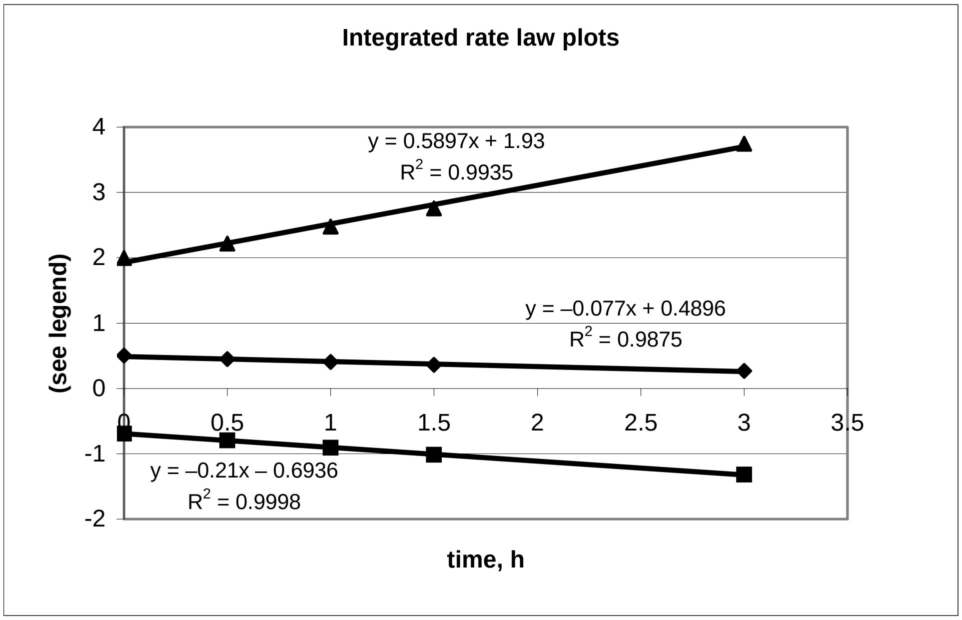
16.77 Rearrange $t_{1/2} = \ln 2/k$ to $k = \ln 2/t_{1/2}$

$k = \ln 2/8.0\text{min} = 8.6643 \times 10^{-2}\ \text{min}^{-1}$ (unrounded)

The problem states that the interval $t = 1/k$:

$t = 1/(8.6643 \times 10^{-2}\ \text{min}^{-1})$ = 11.5416 = **12 min**

16.78 a) 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] versus time – linear for zero order, 2) ln[sucrose] versus time – linear for first order, and 3) 1/[sucrose] versus time – linear for second order.



Legend: ♦ *y*–axis is [sucrose]
■ – axis is ln[sucrose]
▲ – *y*–axis is 1/[sucrose]

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] versus t equals $-k$. The equation for the straight line in the first order plot is $y = -0.21x - 0.6936$.

So, $k = -(-0.21\ h^{-1}) = \mathbf{0.21\ h^{-1}}$.

Half-life for a first-order reaction equals ln 2/*k*, so $t_{1/2} = \ln 2/0.21\ h^{-1} = 3.3007 = \mathbf{3.3\ h}$.

b) If 75% of the sucrose has been reacted, 25% of the sucrose remains. The time to hydrolyze 75% of the sucrose can be calculated by substituting 1.0 *M* for $[A]_0$ and 0.25 *M* for $[A]_t$ in the integrated rate law equation:

$\ln[A]_t = (-0.21\ h^{-1})t + \ln[A]_0$.
$\ln[A]_t - \ln[A]_0 = (-0.21\ h^{-1})t$
$\ln[0.25] - \ln[1.0] = (-0.21\ h^{-1})t$
$t = 6.6014 = \mathbf{6.6\ h}$

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.

16.79 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 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 a) After 60 minutes, one-fourth of the initial amount of cyclopropane remains unreacted. Therefore, 60 minutes represents two half-lives. The half-life is **30 minutes**.
b) $k = \ln 2/t_{1/2}$
$k = \ln 2/30\ \text{min}$
$\boldsymbol{k = 0.023\ \text{min}^{-1}}$

16.81 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): $k_2[\text{H}_2][\text{I}] = k_{-2}[\text{H}_2\text{I}]$; $[\text{H}_2\text{I}] = k_2/k_{-2}[\text{H}_2][\text{I}]$
Rate law for slow step
Rate = $k_3[\text{H}_2\text{I}][\text{I}]$
Substituting for $[\text{H}_2\text{I}]$:
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]:
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's:
Rate = $k[\text{H}_2][\text{I}_2]$

16.82 a) Rearrange $t_{1/2} = \ln 2/k$ to $k = \ln 2/t_{1/2}$
$k = \ln 2/90\ \text{min} = 7.7016 \times 10^{-3}\ \text{min}^{-1}$ (unrounded)

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

$$\ln\frac{[\text{Aspirin}]_t}{[2\ \text{mg}/100\ \text{mL}]_0} = -(7.7016 \times 10^{-3}\ \text{min}^{-1})\ (2.5\ \text{h})\ (60\ \text{min}/1\ \text{h}) = -1.15524$$

$$\frac{[\text{Aspirin}]_t}{[2\ \text{mg}/100\ \text{mL}]_0} = 0.31498 \text{ (unrounded)}$$

$[\text{Aspirin}]_t = (2\ \text{mg} / 100\ \text{mL})\ (0.31498) = 0.62996\ \text{mg}/100\ \text{mL} =$ **0.6 mg/100 mL**
b) The rate constant must be determined first:
SEC = secobarbital sodium

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

$$\ln\frac{[18\%]_t}{[100\%]_0} = -k\ (8.0\ \text{h})$$

$k = 0.2143\ \text{h}^{-1}$ (unrounded)

$t_{1/2} = \ln 2/k = \ln 2\ (0.2143\ \text{h}^{-1}) = 3.23447 =$ **3.2 h**

c) The rate constant must be determined first:

PHE = phenobarbital sodium

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

$$\ln \frac{[59\%]_t}{[100\%]_0} = -\,k\ (20.\ \text{h})$$

$k = 0.02638\ \text{h}^{-1}$ (unrounded)

$t_{1/2} = \ln 2/k = \ln 2/(0.02638\ \text{h}^{-1}) = 26.275 =$ **26 h**

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

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

$$\ln \frac{[2/3\ \text{PILL}]_t}{[1\text{PILL}]_0} = -\,(3.9 \times 10^{-5}\ \text{s}^{-1})\ t\ (3600\ \text{s}/1\ \text{h})$$

$t = 2.887928 =$ **2.9 h**

Pills should be taken at about three hour intervals.

e) Convert the temperatures to°C then to K.

°C = [T(°F) – 32] (5/9)

K = 273.15 +°C = 273.15 + [T(°F) – 32] (5/9)

$k_1 = 3.1 \times 10^{-5}\ \text{s}^{-1}$ $\quad T_1 = 273.15 + [98.6°\text{F} - 32]\ (5/9) = 310.15$ K (unrounded)

$k_2 = 3.9 \times 10^{-5}\ \text{s}^{-1}$ $\quad T_2 = 273.15 + [101.9°\text{F} - 32]\ (5/9) = 311.98$ K (unrounded)

$E_a = ?$

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

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

$E_a = 1.0092 \times 10^5$ J/mol = **1 x 10^5 J/mol**

The subtraction of the $1/T$ terms leaves only one significant figure.

16.83 $k_1 = 1$ egg/4.8 min $\quad T_1 = (273.2 + 90.0)\ \text{K} = 363.2\ \text{K}$

$k_2 = 1$ egg/4.5 min $\quad T_2 = (273.2 + 100.0)\ \text{K} = 373.2\ \text{K}$

$E_a = ?$

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

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

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

$E_a = 7.2730 \times 10^3$ J/mol = **7.3 x 10^3 J/mol**

16.84 a) 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].

$\text{rate}_1 = \text{rate}_2$

$k_1[NO_2] = k_2[O][O_2]$

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

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

$\text{rate}_2 = k_2[O][O_2] = (1.0 \text{ x } 10^6 \text{ L/mol} \bullet \text{s})(2.4 \text{ x } 10^{-15}\, M)(1.0 \text{ x } 10^{-2}\, M) = \mathbf{2.4 \text{ x } 10^{-11}\text{ mol/L} \bullet \text{s}}$

16.85 a) Calculate the concentrations of A and B in each flask.

Flask I

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

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

Flask II

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

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

Flask III

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

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

$$\frac{\text{Rate}_{\text{II}}}{\text{Rate}_{\text{I}}} = \frac{k_2[A]^m[B]^n}{k_1[A]^m[B]^n}$$ Molarity of B is constant

$$\frac{5.6 \text{ x } 10^{-4}\, M\text{s}^{-1}}{3.5 \text{ x } 10^{-4}\, M\text{s}^{-1}} = \frac{[0.16]^m}{[0.10]^m}$$

$1.6 = (1.6)^m$

$m = 1$

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

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

$$\frac{5.6 \text{ x } 10^{-4}\, M\text{s}^{-1}}{5.6 \text{ x } 10^{-4}\, M\text{s}^{-1}} = \frac{[0.14]^m}{[0.10]^m}$$

$1 = (1.4)^m$

$m = 0$

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

Rate law: Rate = $\boldsymbol{k[A][B]^0 = k[A]}$

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

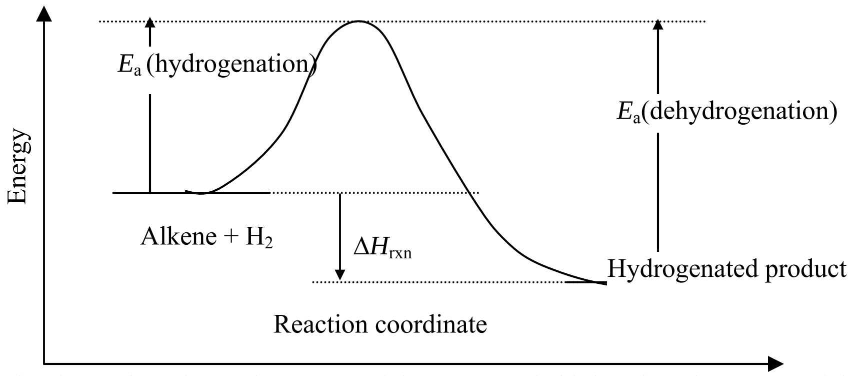
c) Use Flask I:
rate = k[A]
$3.5 \times 10^{-4}\ M\text{s}^{-1} = k[0.10\ M]$
k = **3.5×10^{-3} s^{-1}**
d) The catalyst was used in Flask IV.

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

$$\text{Concentration of B} = (8\ \text{spheres})\left(\frac{0.01\ \text{mol}}{1\ \text{sphere}}\right)\left(\frac{1}{0.50\ \text{L}}\right) = 0.16\ M\ \text{B}$$

Rate = k[A]
$4.9 \times 10^{-4} = k[0.10\ M]$
$k = 4.9 \times 10^{-3}\ \text{s}^{-1}$
Yes, the gray pellets had a catalytic effect. The rate of reaction and the rate constant are greater with the pellets than without.

16.86 a) 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.



The reaction is exothermic, so the energy of the reactants is higher than the energy of the products.
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 a) At time = 0.00 min assume $[\text{A}]_0 = 1.00$, thus at time = 3.00 min, $[\text{A}]_t = 0.001$ (from the equation for % inactivation). Using this information:

$$\ln [\text{A}]_t / [\text{A}]_0 = -k\,t$$

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

b) From the equation for % inactivation, 95% inactivation results in $[\text{A}]_t = 0.05$:

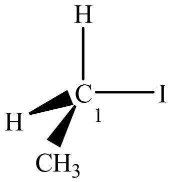
$$\ln [\text{A}]_t / [\text{A}]_0 = -k\,\text{t}$$

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

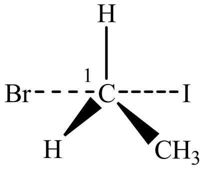
16.88

I.	$\text{Rate} = k_1[N_2O_5]^2$	No
II.	$\text{Rate} = k_1[N_2O_5]^2$	No
III.	$\text{Rate} = k_2[NO_2][N_2O_5] = k_2K_{eq_1}[N_2O_5]^2[NO_3]^{-1} = k[N_2O_5]^2[NO_3]^{-1}$	No
IV.	$\text{Rate} = k_2[N_2O_3][O] = k_2K_{eq_1}{}^{1/3}[N_2O_5]^{2/3}[NO_2]^{-2/3}[N_2O_3]^{2/3}$	No
V.	$\text{Rate} = k_1[N_2O_5]^2$	No

16.89 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.

16.90

$H_2(g) \rightarrow \cancel{H_2(ads)}$

$\cancel{H_2(ads)} + \cancel{2M} \rightarrow \cancel{2\ M\text{–}H}$

$C_2H_4(g) \rightarrow \cancel{C_2H_4(ads)}$

$\cancel{C_2H_4(ads)} + \cancel{M\text{–}H} \rightarrow \cancel{C_2H_5(ads)} + \cancel{M}$

$\underline{\cancel{C_2H_5(ads)} + \cancel{M\text{–}H} \rightarrow C_2H_6(g) + \cancel{M}}$

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

16.91 a)

$B \rightarrow \cancel{C}$

$\underline{\cancel{C} \rightarrow A}$

$B \rightarrow A$

b) C is an **intermediate**.