# CHAPTER 14 KINETICS: RATES AND MECHANISMS OF CHEMICAL REACTIONS

END–OF–CHAPTER PROBLEMS

14.2   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.

14.3   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**.

14.5   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 → products), so the **rate of reaction increases**.

14.8   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.

14.10   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.
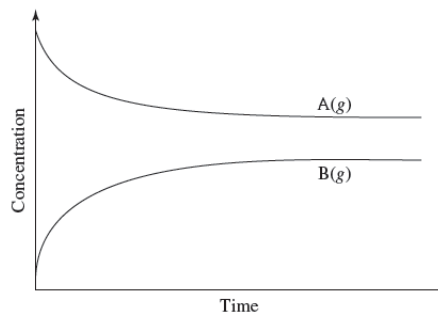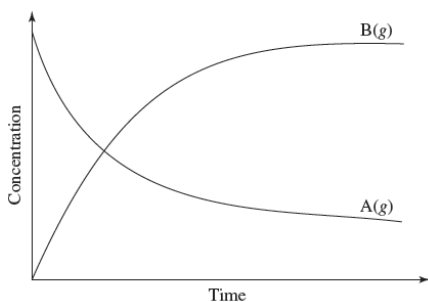
14.12   <u>Plan:</u> The average rate is the total change in concentration divided by the total change in time.
<u>Solution:</u>
a) The average rate from $t = 0$ s to $t = 20.0$ s is proportional to the slope of the line connecting these two points:

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

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)

[AX$_2$] vs Time
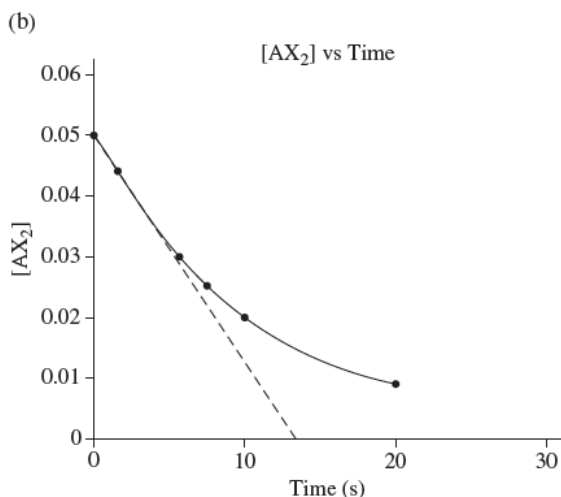
The slope of the tangent to the curve (dashed line) at $t = 0$ s is approximately –0.004 mol/L•s. This initial rate is greater than the average rate as calculated in part a). The **initial rate is greater than the average rate** because rate decreases as reactant concentration decreases.

14.14 Plan: Use Equation 14.2 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 reactant A since A is reacting and [A] is decreasing over time. Positive signs are used for the rate in terms of products B and C since B and C are being formed and [B] and [C] increase over time. Reactant A decreases twice as fast as product C increases because two molecules of A disappear for every molecule of C that appears.
Solution:
Expressing the rate in terms of each component:

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

Calculating the rate of change of [A]:

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

$$\left(2 \text{ mol C/L•s}\right)\left(\frac{2 \text{ mol A/L•s}}{1 \text{ mol C/L•s}}\right) = -4 \text{ mol/L•s}$$

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 **4 mol/L•s**.

14.16 Plan: Use Equation 14.2 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**.

14.18   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.
$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

14.21   Plan: Use Equation 14.2 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 N_2 and H_2 since these substances are reacting and $[N_2]$ and $[H_2]$ are decreasing over time. A positive sign is used for the rate in terms of the product NH_3 since it is being formed and $[NH_3]$ increases over time.
Solution:
$$\text{Rate} = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

14.22   Plan: Use Equation 14.2 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:
$$\left(\frac{2.17\text{x}10^{-5}\text{ mol } O_2 \text{ /L•s}}{}\right)\left(\frac{2 \text{ mol } O_3 \text{ /L•s}}{3 \text{ mol } O_2 \text{/L•s}}\right) = \textbf{1.45x10}^{-5}\textbf{ mol/L•s}$$

14.23   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:
$$\text{Rate (mol/L·min)} = k[A]^1[B]^2$$
$$k = \frac{\text{rate}}{[A]^1[B]^2} = \frac{\text{mol/L•min}}{\left[\dfrac{\text{mol}}{\text{L}}\right]^1\left[\dfrac{\text{mol}}{\text{L}}\right]^2} = \frac{\text{mol/L•min}}{\dfrac{\text{mol}^3}{\text{L}^3}}$$
$$k = \frac{\text{mol}}{\text{L•min}}\left(\frac{\text{L}^3}{\text{mol}^3}\right)$$
$k = \textbf{L}^2\textbf{/mol}^2\textbf{•min}$

14.25   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.

14.26   Plan: 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.
Solution:
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

14.28   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.

14.30   Plan: 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.
Solution:
The order with respect to **$[NO_2]$ is 2**, and the order with respect to **$[Cl_2]$ is 1**. The **overall order is:** $2 + 1 = 3$

14.32   a) The rate is second order with respect to $[NO_2]$. If $[NO_2]$ is tripled, rate $= k[3 \times NO_2]^2$, then rate increases to 3^2 or 9 times its original value. The rate **increases by a factor of 9.**
b) The rate is second order with respect to $[NO_2]$ and first order with respect to $[Cl_2]$. If $[NO_2]$ and $[Cl_2]$ are doubled, rate $= k[2 \times NO_2]^2[2 \times Cl_2]^1$, then the rate **increases by a factor of $2^2 \times 2^1 = 8$**.
c) The rate is first order with respect to $[Cl_2]$. If Cl_2 is halved, rate $= k[1/2 \times Cl_2]^1$, then rate decreases to 1/2 times its original value. The rate is **halved.**

14.34   Plan: 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.
Solution:
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].

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

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

$2.00 = (2.00)^n$

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

$n = 1$

The reaction is **first order with respect to [B].**

b) The rate law, without a value for k, is **rate $= k[\text{A}]^2[\text{B}]$**.

c) Using experiment 1 to calculate k (the data from any of the experiments can be used):

Rate $= k[\text{A}]^2[\text{B}]$

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

14.36   <u>Plan:</u> Write the appropriate rate law and enter the units for rate and concentrations to find the units of k. The units of k are dependent on the reaction orders and the unit of time.

<u>Solution:</u>

a) A first-order rate law follows the general expression, rate $= k[\text{A}]$. The reaction rate is expressed as a change in concentration per unit time with units of mol/L•time. Since [A] has units of mol/L, **k has units of time^{-1}**:

Rate $= k[\text{A}]$

$$\frac{\text{mol}}{\text{L} \cdot \text{time}} = k \frac{\text{mol}}{\text{L}}$$

$$k = \frac{\dfrac{\text{mol}}{\text{L} \cdot \text{time}}}{\dfrac{\text{mol}}{\text{L}}} = \frac{\text{mol}}{\text{L} \cdot \text{time}} \times \frac{\text{L}}{\text{mol}} = \frac{1}{\text{time}} = \textbf{time}^{-1}$$

b) A second-order rate law follows the general expression, rate $= k[\text{A}]^2$. The reaction rate is expressed as a change in concentration per unit time with units of mol/L•time. Since [A] has units of mol^2/L^2, **k has units of L/mol•time**:

Rate $= k[\text{A}]^2$

$$\frac{\text{mol}}{\text{L} \cdot \text{time}} = k \left(\frac{\text{mol}}{\text{L}}\right)^2$$

$$k = \frac{\dfrac{\text{mol}}{\text{L} \cdot \text{time}}}{\dfrac{\text{mol}^2}{\text{L}^2}} = \frac{\text{mol}}{\text{L} \cdot \text{time}} \times \frac{\text{L}^2}{\text{mol}^2} = \frac{\textbf{L}}{\textbf{mol•time}}$$

c) A third-order rate law follows the general expression, rate $= k[\text{A}]^3$. The reaction rate is expressed as a change in concentration per unit time with units of mol/L•time. Since [A] has units of mol^3/L^3, **k has units of L^2/mol^2•time**:

Rate $= k[\text{A}]^3$

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

$$k = \frac{\dfrac{\text{mol}}{\text{L} \cdot \text{time}}}{\dfrac{\text{mol}^3}{\text{L}^3}} = \frac{\text{mol}}{\text{L} \cdot \text{time}} \times \frac{\text{L}^3}{\text{mol}^3} = \frac{\textbf{L}^2}{\textbf{mol}^2\textbf{•time}}$$

d) A 5/2-order rate law follows the general expression, rate = $k[A]^{5/2}$. The reaction rate is expressed as a change in concentration per unit time with units of mol/L•time. Since [A] has units of $mol^{5/2}/L^{5/2}$, **k has units of $L^{3/2}/mol^{3/2}$•time**:

$$\frac{mol}{L\bullet time} = k\left(\frac{mol}{L}\right)^{5/2}$$

$$k = \frac{\dfrac{mol}{L\bullet time}}{\dfrac{mol^{5/2}}{L^{5/2}}} = \frac{mol}{L\bullet time} \times \frac{L^{5/2}}{mol^{5/2}} = \frac{\mathbf{L^{3/2}}}{\mathbf{mol^{3/2}\bullet time}}$$

14.39   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.

14.41   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 mol/L) = 0.500 mol/L), so we can solve for t.
Solution:

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

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

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

$$t = 6.6667 = \mathbf{7 \; s}$$

14.43   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 mol/Land then $[A]_t$ = 50% of 1 M = 0.5 mol/L. 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 mol/L and then $[A]_t$ = 25% of 1 mol/L = 0.25 mol/L.
Solution:
a) ln $[A]_t$ = ln $[A]_0 - kt$
ln $[0.5]$ = ln $[1] - k$(10.5 min)
$-0.693147 = 0 - k$(10.5 min)
$0.693147 = k$(10.5 min)
$k = 0.0660 \; min^{-1}$
Alternatively, 50.0% decomposition means that one half-life has passed. Thus, the first-order half-life equation may be used:

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

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

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

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

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

If you recognize that 75.0% decomposition means that two half-lives have passed, then

$t = 2$ (10.5 min) = **21.0 min.**

14.45 Plan: In a first-order reaction, ln [NH$_3$] vs. time is a straight line with slope equal to k. The half-life can be determined using the first-order half-life equation.
Solution:
a) A new data table is constructed: (Note that additional significant figures are retained in the calculations.)

x-axis (time, s)	[NH$_3$]	y-axis (ln [NH$_3$])
0	4.000 mol/L	1.38629
1.000	3.986 mol/L	1.38279
2.000	3.974 mol/L	1.37977
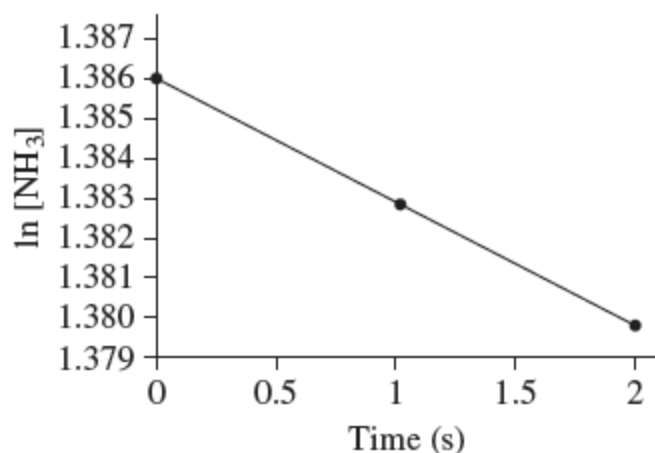
k = slope = rise/run = $(y_2 - y_1)/(x_2 - x_1)$
$k = (1.37977 - 1.38629)/(2.000 - 0) = (0.00652)/(2) = 3.260\text{x}10^{-3}\,\text{s}^{-1} = \mathbf{3\text{x}10^{-3}\,\text{s}^{-1}}$
(Note that the starting time is not exact, and hence, limits the significant figures.)

b) $t_{1/2} = \dfrac{\ln 2}{k} = \dfrac{\ln 2}{3.260\text{x}10^{-3}\,\text{s}^{-1}} = 212.62$ s= **2x10^2 s**

14.47 **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.

14.50 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 pre-exponential factor, A, are known. However, the pre-exponential 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 $-E_a/R$.

14.53 **No**. For 4x10^{-5} moles of EF to form, every collision must result in a reaction and no EF molecule can decompose back to AB and CD. Neither condition is likely. All collisions will not result in product as some collisions will occur with an energy that is lower than the activation energy. In principle, all reactions are reversible, so some EF

molecules decompose. Even if all AB and CD molecules did combine, the reverse decomposition rate would result in an amount of EF that is less than 4×10^{-5} moles.

14.54   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 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.

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

14.57   Plan: The fraction of collisions with a specified energy is equal to the $e^{-E_a/RT}$ term in the Arrhenius equation.
Solution:
$f = e^{-E_a/RT}$ $T = 25°C + 273 = 298\ K$
$E_a = 100.\ kJ/mol$ $R = 8.314\ J/mol·K = 8.314 \times 10^{-3}\ kJ/mol·K$

$$-\frac{E_a}{RT} = -\frac{100.\ kJ/mol}{\left(8.314 \times 10^{-3}\ kJ/mol·K\right)\left(298\ K\right)} = -40.362096$$

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

14.59   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:
    $k_1 = 4.7 \times 10^{-3}\ s^{-1}$ $T_1 = 25°C + 273 = 298\ K$
    $k_2 = ?$ $T_2 = 75°C + 273 = 348\ K$
    $E_a = 33.6\ kJ/mol = 33,600\ J/mol$

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

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

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

$\dfrac{k_2}{4.7 \times 10^{-3}\ s^{-1}} = 7.0182577$

$k_2 = (4.7 \times 10^{-3}\ s^{-1})(7.0182577) = 0.0329858\ s^{-1} = \mathbf{0.033\ s^{-1}}$

14.61   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 $\Delta_r H = E_{a(fwd)} - E_{a(rev)}$ 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.
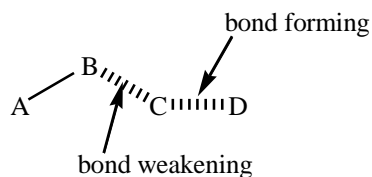Solution:
a)
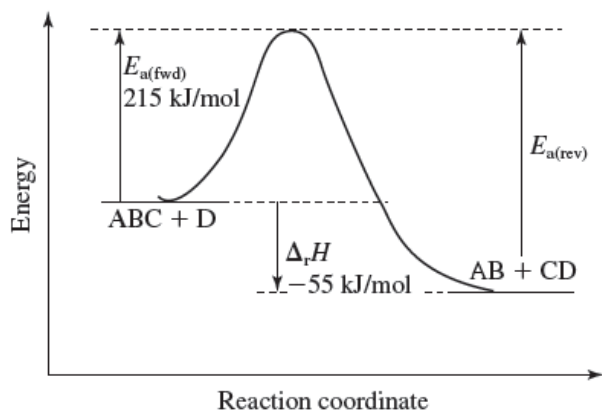
b) $\Delta_r H = E_{a(fwd)} - E_{a(rev)}$
$E_{a(rev)} = E_{a(fwd)} - \Delta_r H = 215$ kJ/mol $- (-55$ kJ/mol$) = \textbf{2.70x10}^2$ **kJ/mol**
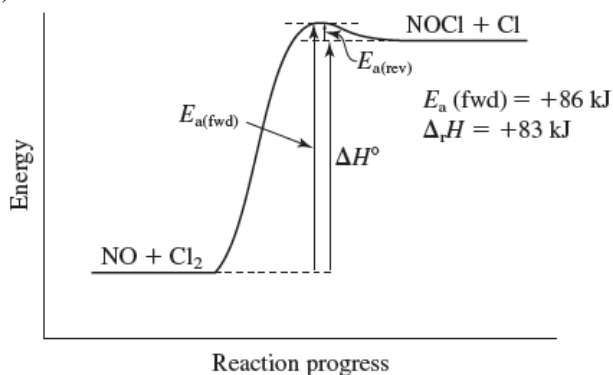c)

14.64   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 $\Delta_r H = E_{a(fwd)} - E_{a(rev)}$ 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.
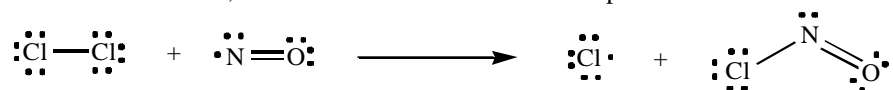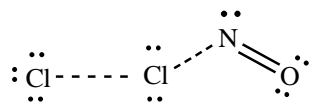Solution:
a)

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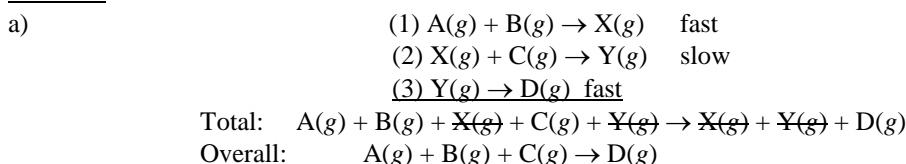

14-9

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.

14.65 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.

14.69 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.

14.70 **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.

14.72 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)
$$(1)\ A(g) + B(g) \rightarrow X(g) \quad \text{fast}$$
$$(2)\ X(g) + C(g) \rightarrow Y(g) \quad \text{slow}$$
$$\underline{(3)\ Y(g) \rightarrow D(g) \quad \text{fast}}$$
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$_{\text{forward rxn}}$ = 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 = ($k_2 k_1/k_{-1}$)[A][B][C] which is identical to the actual rate law with $k = k_2 k_1/k_{-1}$.
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.

14.74 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 $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$, 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 ($NOBr_2$). 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, rate$_{forward\ rxn}$ = rate$_{reverse\ rxn}$.

       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$_2$]

Rate of the slow step: Rate$_2$ = k_2[NOBr$_2$][NO]

Substitute the expression for [NOBr$_2$] into this equation, the slow step:

       Rate$_2$ = $k_2(k_1/k_{-1})$[NO][Br$_2$][NO]

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

       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.

14.77   **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.

14.78   a) **No**, by definition, a catalyst is a substance that increases reaction rate without being consumed. The spark provides energy that is absorbed by the H$_2$ and O$_2$ molecules to achieve the threshold energy needed for reaction.
b) **Yes**, the powdered metal acts like a heterogeneous catalyst, providing a surface upon which the reaction between O$_2$ and H$_2$ becomes more favorable because the activation energy is lowered.

14.83   <u>Plan:</u> An intermediate is a substance that is formed in one step and consumed in a subsequent step. The coefficients of the reactants in each elementary step are used as the orders in the rate law for the 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. Reactants that appear in the mechanism after the slow step do not determine the rate and therefore do not appear in the rate law.
<u>Solution:</u>
a) Water does not appear as a reactant in the rate-determining step.
Note that as a solvent in the reaction, the concentration of the water is assumed not to change even though some water is used up as a reactant. This assumption is valid as long as the solute concentrations are low (~1 M or less). So, even if water did appear as a reactant in the rate-determining step, it would not appear in the rate law. See rate law for step 2 below.
b)   Rate law for step (1):   rate$_1$ = k_1[(CH$_3$)$_3$CBr]
       Rate law for step (2):   rate$_2$ = k_2[(CH$_3$)$_3$C$^+$]
       Rate law for step (3):   rate$_3$ = k_3[(CH$_3$)$_3$COH$_2$$^+$]
c) The intermediates are (CH$_3$)$_3$C$^+$ and (CH$_3$)$_3$COH$_2$$^+$. (CH$_3$)$_3C^+$ is formed in step 1 and consumed in step 2; (CH$_3$)$_3$COH$_2$$^+$ is formed in step 2 and consumed in step 3.
d) The rate-determining step is the slow step, (1). The rate law for this step is rate = k_1[(CH$_3$)$_3$CBr] since the coefficient of the reactant in this slow step is 1. The rate law for this step agrees with the actual rate law with $k = k_1$.

14.85   <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, rate$_1$ = 1 apple/4 days and rate$_2$ = 1 apple/16 days are substituted for k_1 and k_2, respectively.
<u>Solution:</u>

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

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

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

$E_a = 4.6096266\text{x}10^4$ J/mol = **4.61x10⁴ J/mol**   The significant figures are based on the Kelvin temperatures.

14.89   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 mol/L to 2.5 mol/L , 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 mol/L to 0.5 mol/L , 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 mol/L to 0.0001 mol/L , or is decreased by a factor of 0.0001/0.01 or 0.01. Then the rate = $k[0.01$ 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 mol/L to 0.1 mol/L , or by a factor of (0.1 mol/L /1.0 mol/L) = 0.1. [H⁺] increases from 0.01 mol/L to 0.1 mol/L , or by a factor of (0.1 mol/L /0.01 mol/L) = 10. Then the rate will increase by $k[10$ x H⁺][0.1 x sucrose]= 1.0 times as fast. Thus, there will be **no change**.

14.90   Plan: The overall order is equal to the sum of the individual orders. Since the reaction is eleventh order overall, the sum of the exponents equals eleven. Add up the known orders and subtract that sum from eleven to find the unknown order.
Solution:
Sum of known orders = 1 + 4 + 2 + 2 = 9
Overall order – sum of known orders = 11 – 9 = 2.
The reaction is **second order** with respect to NAD.

14.93   Plan: 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.
Solution:
Rearrange $t_{1/2} = \dfrac{\ln 2}{k}$ to $k = \dfrac{\ln 2}{t_{1/2}}$

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

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

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

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

14.96   Plan: 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%.
Solution:
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.
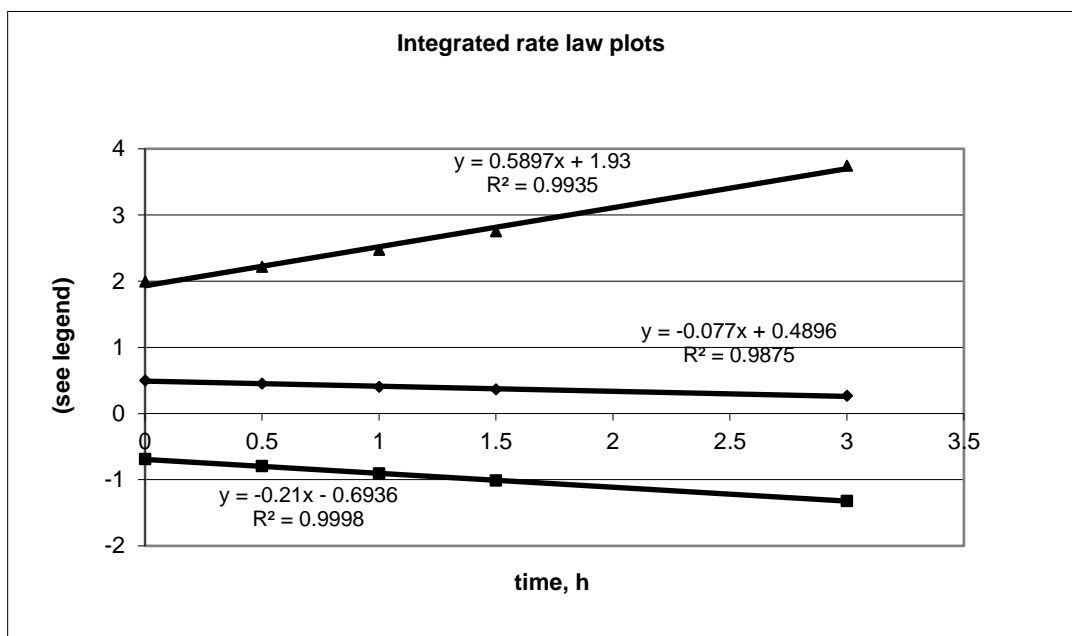
Another method when linearity is not obvious from the graphs is to examine the reaction and decide which order fits the reaction. For the reaction of one molecule of sucrose with one molecule of liquid water, the rate law would most likely include sucrose with an order of one and would not include water.

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

Solve the first-order half-life equation to find $t_{1/2}$:

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

Integrated rate law plots

$y = 0.5897x + 1.93$
$R^2 = 0.9935$

$y = -0.077x + 0.4896$
$R^2 = 0.9875$

$y = -0.21x - 0.6936$
$R^2 = 0.9998$

(see legend) / time, h

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 [sucrose]$_0$ = 100% and [sucrose]$_t$ = 25% in the first-order integrated rate law equation:

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

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

$$t = 6.6014 \text{ h} = \mathbf{6.6 \ h}$$

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.

14.99   Plan: To find concentration of reactant at a later time, given the initial concentration and the rate constant k, use an integrated rate law expression. Since the units on k are s^{-1}, this is a first-order reaction. Use the first-order integrated rate law. Since the time unit in k is seconds, time t must also be expressed in units of seconds. To find the fraction of reactant that has decomposed, divide that amount of reactant that has decomposed ($[N_2O_5]_0 - [N_2O_5]_t$) by the initial concentration.
Solution:

a) Converting t in min to s: $(5.00\ \text{min})\left(\dfrac{60\ \text{s}}{1\ \text{min}}\right) = 300.\ \text{s}$

$$\ln\dfrac{\left[N_2O_5\right]_t}{\left[N_2O_5\right]_0} = -kt \quad \text{or}$$

$\ln [N_2O_5]_t = \ln [N_2O_5]_0 - kt$
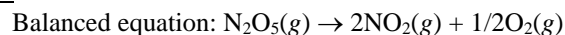$\ln [N_2O_5]_t = \ln [1.58\ \text{mol/L}] - (2.8 \times 10^{-3}\ \text{s}^{-1})(300.\ \text{s})$
$\ln [N_2O_5]_t = -0.382575$
$[N_2O_5]_t = 0.68210\ \text{mol/L} = \mathbf{0.68\ mol/L}$

b) Fraction decomposed $= \dfrac{[N_2O_5]_0 - [N_2O_5]_t}{[N_2O_5]_0} = \dfrac{1.58 - 0.68210\ \text{mol/L}}{1.58\ \text{mol/L}} = 0.56829 = \mathbf{0.57}$

14.102 Plan: To solve this problem, a clear picture of what is happening is useful. Initially only N_2O_5 is present at a pressure of 125 kPa. Then a reaction takes place that consumes the gas N_2O_5 and produces the gases NO_2 and O_2. The balanced equation gives the change in the number of moles of gas as N_2O_5 decomposes. Since the number of moles of gas is proportional to the pressure, this change mirrors the change in pressure. The total pressure at the end, 178 kPa, equals the sum of the partial pressures of the three gases.
Solution:
        Balanced equation: $N_2O_5(g) \rightarrow 2NO_2(g) + 1/2O_2(g)$
        Therefore, for each mole of dinitrogen pentaoxide that is consumed, 2.5 moles of gas are produced.

$N_2O_5(g) \rightarrow 2NO_2(g) + 1/2O_2(g)$				
Initial P (kPa)	125	0	0	total $P_{\text{initial}} = 125$ kPa
Final P (kPa)	125 − x	2x	1/2x	total $P_{\text{final}} = 178$ kPa

        Solve for x:

$$P_{N_2O_5} + P_{NO_2} + P_{O_2} = (125 - x) + 2x + 1/2x = 178$$

        x = 35.3333 kPa (unrounded)
        Partial pressure of NO_2 equals 2x = 2(35.3333 kPa) = 70.667 kPa = **71 kPa**.
Check: Substitute values for all partial pressures to find total final pressure:
        (125 − 35.3333)kPa + (2 x 35.3333 kPa) + ((1/2) x 35.3333 kPa) = 178 kPa
        The result agrees with the given total final pressure.

14.106 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 $T_1 = 90.0°C + 273.2 = 363.2$ K
$k_2 = 1$ egg/4.5 min $T_2 = 100.0°C + 273.2 = 373.2$ K
$E_a = ?$

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

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

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

$E_a = 7.2730 \times 10^3$ J/mol = **7.3x10³ J/mol**

14.108 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, [NO₂], and [O₂].
Solution:

a) Rate₁ = k_1[NO₂]   Rate₂ = k_2[O][O₂]}
    Rate₁ = rate₂
    k_1[NO₂] = k_2[O][O₂]

$$[O] = \frac{k_1[NO_2]}{k_2[O_2]} = \frac{\left(6.0 \times 10^{-3}\ s^{-1}\right)\left[4.0 \times 10^{-9}\ mol\ /\ L\right]}{\left(1.0 \times 10^6\ L/mol\bullet s\right)\left[1.0 \times 10^{-2}\ mol\ /\ L\right]} = \textbf{2.4x10}^{-15}\ mol\ /\ L$$

b) Since the rate of the two steps is equal, either can be used to determine rate of formation of ozone.
    Rate₂ = k_2[O][O₂] = (1.0x10⁶ L/mol•s)(2.4x10⁻¹⁵ mol/L)(1.0x10⁻² mol/L) = **2.4x10⁻¹¹ mol/L·s**

14.111 Plan: This problem involves the first-order integrated rate law (ln [A]$_t$/[A]$_0$ = –kt). The temperature must be part of the calculation of the rate constant. The concentration of the ammonium ion is directly related to the ammonia concentration. Use the given values of [NH₃]₀ and [NH₃]$_t$ and the calculated values of k to find time, t.
Solution:
a) [NH₃]₀ = 3.0 mol/m³   [NH₃]$_t$ = 0.35 mol/m³ T = 20°C
$k_1 = 0.47e^{0.095(T - 15°C)} = 0.47e^{0.095(20 - 15°C)} = 0.75576667$ d⁻¹

$$\ln\frac{[NH_3]_t}{[NH_3]_0} = -kt$$

$$t = -\frac{\ln\dfrac{[NH_3]_t}{[NH_3]_0}}{k}$$

$$t = -\frac{\ln\dfrac{\left[0.35\ mol/m^3\right]_t}{\left[3.0\ mol/m^3\right]_0}}{0.75576667\ d^{-1}} = 2.84272\ d = \textbf{2.8 d}$$

b) Repeating the calculation at the different temperature:
[NH₃]₀ = 3.0 mol/m³   [NH₃]$_t$ = 0.35 mol/m³ T = 10°C
$k_1 = 0.47e^{0.095(T - 15°C)} = 0.47e^{0.095(10 - 15°C)} = 0.292285976$ d⁻¹

$$t = -\frac{\ln\dfrac{[NH_3]_t}{[NH_3]_0}}{k}$$

$$t = -\frac{\ln\dfrac{\left[0.35\ mol/m^3\right]_t}{\left[3.0\ mol/m^3\right]_0}}{0.292285976\ d^{-1}}$$

$t = 7.35045$ d = **7.4 d**
c) For NH₄⁺ the rate = k_1[NH₄⁺]
        From the balanced chemical equation:

$$-\frac{\Delta\left[NH_4^+\right]}{\Delta t} = -\frac{1}{2}\frac{\Delta[O_2]}{\Delta t}$$

Thus, for O_2: Rate = $2 k_1[NH_4^+]$

$$\text{Rate} = (2)(0.75576667)\left[3.0 \text{ mol/m}^3\right] = 4.5346 = \textbf{4.5 mol/m}^3$$

14.114 Plan: Rate is the change in concentration divided by change in time. To find the average rate for each trial in part a), the change in concentration of $S_2O_3^{2-}$ is divided by the time required to produce the colour. The rate law is rate = $k[I^-]^m[S_2O_8^{2-}]^n$ 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, any experiment can be used to find the rate constant k. Since several solutions are mixed, final concentrations of each solution must be found with dilution calculations using $c_iV_i = c_fV_f$ in the form: $c_f = c_iV_i/V_f$.

Solution:

a) $c_f S_2O_3^{2-}$ = [(10.0 mL)(0.0050 mol/L)]/50.0 mL = 0.0010 mol/L $S_2O_3^{2-}$

$$-\frac{\Delta[I_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta\left[S_2O_3^{2-}\right]}{\Delta t} = [1/2(0.0010 \text{ mol/L})]/\text{time} = [0.00050 \text{ mol/L}]/\text{time} = \text{rate}$$

Average rates:

Rate$_1$ = (0.00050 mol/L)/29.0 s = 1.724x10^{-5} mol/L•s= **1.7x10^{-5} mol/L•s**

Rate$_2$ = (0.00050 mol/L)/14.5 s = 3.448x10^{-5} mol/L•s = **3.4x10^{-5} mol/L•s**

Rate$_3$ = (0.00050 mol/L)/14.5 s = 3.448x10^{-5} mol/L•s = **3.4x10^{-5} mol/L•s**

b) c_f KI = $c_f I^-$ = [(10.0 mL)(0.200 mol/L)]/50.0 mL = 0.0400 mol/L I^- (Experiment 1)

$c_f I^-$ = [(20.0 mL)(0.200 mol/L)]/50.0 mL = 0.0800 mol/L I^- (Experiments 2 and 3)

c_f Na$_2$S$_2$O$_8$ = c_f S$_2$O$_8^{2-}$ = [(20.0 mL)(0.100 mol/L)]/50.0 mL

= 0.0400 mol/L $S_2O_8^{2-}$ (Experiments 1 and 2)

c_f S$_2$O$_8^{2-}$ = [(10.0 mL)(0.100 mol/L)]/50.0 mL = 0.0200 mol/L $S_2O_8^{2-}$ (Experiment 3)

Generic rate law equation: Rate = $k [I^-]^m[S_2O_8^{2-}]^n$

To find the order for I^-, use experiments 1 and 2 in which $[S_2O_8^{2-}]$ is constant while $[I^-]$ changes. 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 $[I^-]$.

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k_2\left[I^-\right]^m\left[S_2O_8^{2-}\right]^n}{k_1\left[I^-\right]^m\left[S_2O_8^{2-}\right]^n} \qquad \text{Concentration (mol/L) of } S_2O_8^{2-}\text{is constant.}$$

$$\frac{3.4\times10^{-5} \text{ mol}/\text{L•s}}{1.7\times10^{-5} \text{ mol}/\text{L•s}} = \frac{[0.0800]^m}{[0.0400]^m}$$

$2.0 = (2.00)^m$

$m = 1$

The reaction is **first order with respect to I^-**.

To find the order for $S_2O_8^{2-}$, use experiments 2 and 3 in which $[I^-]$ is constant while $[S_2O_8^{2-}]$ changes. 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 $[S_2O_8^{2-}]$.

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{k_3\left[I^-\right]^m\left[S_2O_8^{2-}\right]^n}{k_2\left[I^-\right]^m\left[S_2O_8^{2-}\right]^n} \qquad \text{Concentration (mol/L) of } I^- \text{ is constant.}$$

$$\frac{3.4\text{x}10^{-5} \text{ mol}/\text{L•s}}{3.4\text{x}10^{-5} \text{ mol}/\text{L•s}} = \frac{[0.0200]^n}{[0.0400]^n}$$

$1.0 = (0.500)^n$

$n = 0$

The reaction is **zero order with respect to $S_2O_8^{2-}$**.

c) Rate = $k[I^-]$

k = rate•/$[I^-]$

Using experiment 2 (unrounded rate value)

$$k = (3.448\text{x}10^{-5} \text{ mol/L}\bullet\text{s})/(0.0800 \text{ mol/L}) = 4.31\text{x}10^{-4} \text{ s}^{-1} = \mathbf{4.3\text{x}10^{-4} \text{ s}^{-1}}$$

d) **Rate = $(4.3\text{x}10^{-4} \text{ s}^{-1})[\text{I}^-]$**

14.117 Plan: This is a first-order process so use the first-order integrated rate law. The increasing cell density changes the integrated rate law from $-kt$ to $+kt$. In part a), we know t(2 h), k, and $[A]_0$ so $[A]_t$ can be found. Treat the concentration of the cells as you would molarity. Since the rate constant is expressed in units of min^{-1}, the time interval of 2 h must be converted to a time in minutes. In part b), $[A]_0$, $[A]_t$, and k are known and time t is calculated.

Solution:

a) Converting time in h to min: $(2 \text{ h})\left(\dfrac{60 \text{ min}}{1 \text{ h}}\right) = 120 \text{ min}$

$\ln [A]_t = \ln [A]_0 + kt$

$\ln [A]_t = \ln [1.0\text{x}10^3] + (0.035 \text{ min}^{-1})(120 \text{ min})$

$\ln [A]_t = 11.107755$

$[A]_t = 6.6686\text{x}10^4 \text{ cells/L} = \mathbf{7\text{x}10^4 \text{ cells/L}}$

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

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

$\dfrac{\ln [2\times10^3 \text{ cells/L}] - \ln [1\times10^3 \text{ cells/L}]}{0.035 \text{ min}^{-1}} = t$

$t = 19.804 \text{ min} = \mathbf{2.0\text{x}10^1 \text{ min}}$

14.120 Plan: For part a), use the Monod equation to calculate μ for values of S between 0.0 and 1.0 kg/m^3 and then graph. For parts b) and c), use the Monod equation to calculate μ at the given conditions. The value of μ is the rate constant k in the first-order integrated rate law. The increasing population density changes the integrated rate law from $-kt$ to $+kt$. We know t(1 h), k, and $[A]_0$ so $[A]_t$ can be found. Treat the density of the cells as you would molarity.

Solution:
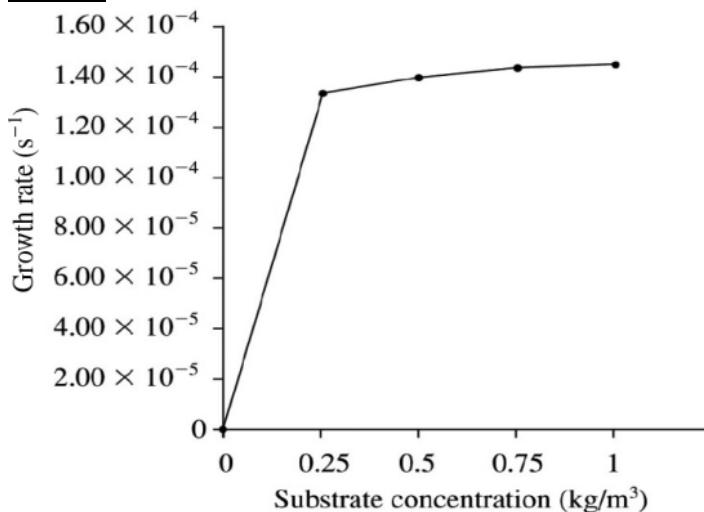
$\mu = \dfrac{\mu_{max} S}{K_s + S} = \dfrac{\left(1.5\text{x}10^{-4} \text{ s}^{-1}\right)\left(0.25 \text{ kg/m}^3\right)}{\left(0.03 \text{ kg/m}^3\right)+\left(0.25 \text{ kg/m}^3\right)} = 1.34\text{x}10^{-4} \text{ s}^{-1}$

$\mu = \dfrac{\mu_{max} S}{K_s + S} = \dfrac{\left(1.5\text{x}10^{-4} \text{ s}^{-1}\right)\left(0.50 \text{ kg/m}^3\right)}{\left(0.03 \text{ kg/m}^3\right)+\left(0.50 \text{ kg/m}^3\right)} = 1.42\text{x}10^{-4} \text{ s}^{-1}$

$\mu = \dfrac{\mu_{max}S}{K_s + S} = \dfrac{\left(1.5 \times 10^{-4}\ s^{-1}\right)\left(0.75\ kg/m^3\right)}{\left(0.03\ kg/m^3\right)+\left(0.75\ kg/m^3\right)} = 1.44 \times 10^{-4}\ s^{-1}$

$\mu = \dfrac{\mu_{max}S}{K_s + S} = \dfrac{\left(1.5 \times 10^{-4}\ s^{-1}\right)\left(1.0\ kg/m^3\right)}{\left(0.03\ kg/m^3\right)+\left(1.0\ kg/m^3\right)} = 1.46 \times 10^{-4}\ s^{-1}$

b) $\mu = \dfrac{\mu_{max}S}{K_s + S} = \dfrac{\left(1.5 \times 10^{-4}\ s^{-1}\right)\left(0.30\ kg/m^3\right)}{\left(0.03\ kg/m^3\right)+\left(0.30\ kg/m^3\right)} = 1.3636 \times 10^{-4}\ s^{-1}$

Converting time in h to seconds: $(1\ h)\left(\dfrac{3600\ s}{1\ h}\right) = 3600\ s$

ln [A]$_t$ = ln [A]$_0$ + kt
ln [A]$_t$ = ln [5.0x10^3] + (1.3636x10^{-4} s^{-1})(3600 s)
ln [A]$_t$ = 9.00808919
[A]$_t$ = 8.1689x10^3 cells/m³= **8.2x10^3 cells/m³**

c) $\mu = \dfrac{\mu_{max}S}{K_s + S} = \dfrac{\left(1.5 \times 10^{-4}\ s^{-1}\right)\left(0.70\ kg/m^3\right)}{\left(0.03\ kg/m^3\right)+\left(0.70\ kg/m^3\right)} = 1.438356 \times 10^{-4}\ s^{-1}$

ln [A]$_t$ = ln [A]$_0$ + kt
ln [A]$_t$ = ln [5.0x10^3] + (1.438356x10^{-4} s^{-1})(3600 s)
ln [A]$_t$ = 9.03500135
[A]$_t$ = 8.39172x10^3 cells/m³= **8.4x10^3 cells/m³**

14.125   Plan: This is a first-order reaction so use the first-order integrated rate law. In part a), use the first-order half-life equation and the given value of k to find the half-life. In parts b) and c), solve the first-order integrated rate law to find the time necessary for 40.% and 90.% of the acetone to decompose. If 40.% of the acetone has decomposed, 100 – 40. = 60.% remains at time t. If 90.% of the acetone has decomposed, 100 – 90. = 10.% remains at time t.
Solution:

a) $t_{1/2} = \dfrac{\ln 2}{k} = \dfrac{\ln 2}{8.7 \times 10^{-3}\ s^{-1}} = 79.672\ s = $ **8.0x10^1 s**

b) ln [acetone]$_t$ = ln [acetone]$_0$ – kt

$\dfrac{\ln [acetone]_t\ -\ \ln [acetone]_0}{-k} = t$ $\qquad\qquad$ 40.% of acetone has decomposed; [acetone]$_t$ = 100 – 40. = 60.%

$\dfrac{\ln [60.]\ -\ \ln [100]}{-8.7 \times 10^{-3}\ s^{-1}} = t = 58.71558894 s = $ **59 s**

c) ln [acetone]$_t$ = ln [acetone]$_0$ – kt

$\dfrac{\ln [acetone]_t\ -\ \ln [acetone]_0}{-k} = t$ $\qquad\qquad$ 90.% of acetone has decomposed; [acetone]$_t$ = 100 – 90. = 10.%

$\dfrac{\ln [10.]\ -\ \ln [100]}{-8.7 \times 10^{-3}\ s^{-1}} = t = 264.66\ s = $ **2.6x10^2 s**