
14. RATES OF REACTION

■ Solutions to Exercises

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

- 14.1 Rate of formation of $\text{NO}_2\text{F} = \Delta[\text{NO}_2\text{F}]/\Delta t$. Rate of reaction of $\text{NO}_2 = -\Delta[\text{NO}_2]/\Delta t$. Divide each rate by the coefficient of the corresponding substance in the equation:

$$\frac{1}{2} \frac{\Delta[\text{NO}_2\text{F}]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t}; \text{ or } \frac{\Delta[\text{NO}_2\text{F}]}{\Delta t} = - \frac{\Delta[\text{NO}_2]}{\Delta t}$$

14.2 $\text{Rate} = - \frac{\Delta[\text{I}^-]}{\Delta t} = - \frac{\Delta[0.00101 \text{ M} - 0.00169 \text{ M}]}{8.00 \text{ s} - 2.00 \text{ s}} = 1.\underline{1}3 \times 10^{-4} = 1.1 \times 10^{-4} \text{ M/s}$

- 14.3 The order with respect to CO is zero, and with respect to NO_2 is two. The overall order is two, the sum of the exponents in the rate law.

- 14.4 By comparing experiments 1 and 2, you see the rate is quadrupled when the $[\text{NO}_2]$ is doubled. Thus, the reaction is second order in NO_2 , and the rate law is

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

(continued)

The rate constant may be found by substituting experimental values into the rate-law expression. Based on values from Experiment 1,

$$k = \frac{\text{rate}}{[\text{NO}_2]^2} = \frac{7.1 \times 10 \text{ mol}/(\text{L} \cdot \text{s})}{(0.010 \text{ mol/L})^2} = 0.710 = 0.71 \text{ L}/(\text{mol} \cdot \text{s})$$

- 14.5 a. For $[\text{N}_2\text{O}_5]$ after $6.00 \times 10^2 \text{ s}$, use the first-order rate law, and solve for the concentration at time t :

$$\ln \frac{[\text{N}_2\text{O}_5]_t}{[1.65 \times 10^{-2} \text{ M}]} = -(4.80 \times 10^{-4} \text{ /s})(6.00 \times 10^2 \text{ s}) = -0.2880$$

Take the antilog of both sides to get

$$\frac{[\text{N}_2\text{O}_5]_t}{[1.65 \times 10^{-2} \text{ M}]} = e^{-0.2880} = 0.74976$$

Hence,

$$[\text{N}_2\text{O}_5]_t = 1.65 \times 10^{-2} \text{ M} \times 0.74976 = 0.01237 = 0.0124 \text{ mol/L}$$

- b. Substitute the values into the rate equation to get

$$\ln \frac{10.0\%}{100.0\%} = -(4.80 \times 10^{-4} \text{ /s}) \times t$$

Taking the log on the left side gives $\ln(0.100) = -2.30258$. Hence,

$$-2.30258 = -(4.80 \times 10^{-4} \text{ /s}) \times t$$

Or,

$$t = \frac{2.30258}{4.80 \times 10^{-4} \text{ /s}} = 4797 = 4.80 \times 10^3 \text{ s (80.0 min)}$$

- 14.6 Substitute $k = 9.2/\text{s}$ into the equation relating K and $t_{1/2}$.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{9.2/\text{s}} = 0.0753 = 0.075 \text{ s}$$

By definition, the half-life is the amount of time it takes to decrease the amount of substance present by one-half. Thus, it takes 0.0753 s for concentration to decrease by 50 percent and another 0.0753 s for the concentration to decrease by 50 percent of the remaining 50 percent (to 25 percent left), for a total of 0.1506, or 0.151, s.

- 14.7 Solve for E_a by substituting the given values into the two-temperature Arrhenius equation:

$$\ln \frac{2.14 \times 10^{-2}}{1.05 \times 10^{-3}} = \frac{E_a}{8.31 \text{ J/(mol} \cdot \text{K)}} \left(\frac{1}{759 \text{ K}} - \frac{1}{836 \text{ K}} \right)$$

$$3.0146 = \frac{E_a}{8.31 \text{ J/(mol} \cdot \text{K)}} (1.2135 \times 10^{-4} / \text{K})$$

$$E_a = \frac{3.0146 \times 8.31 \text{ J/mol}}{1.2135 \times 10^{-4}} = 2.064 \times 10^5 = 2.06 \times 10^5 \text{ J/mol}$$

Solve for the rate constant, k_2 , at 865 K by using the same equation and using $E_a = 2.064 \times 10^5 \text{ J/mol}$:

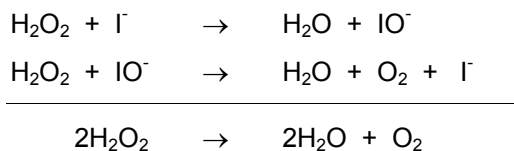
$$\ln \frac{k_2}{2.14 \times 10^{-2} / (\text{M}^{1/2} \cdot \text{s})} = \frac{2.064 \times 10^5 \text{ J/mol}}{8.31 \text{ J/(mol} \cdot \text{K)}} \left(\frac{1}{836 \text{ K}} - \frac{1}{865 \text{ K}} \right) = 0.99623$$

Taking antilogarithms,

$$\frac{k_2}{2.14 \times 10^{-2} / (\text{M}^{1/2} \cdot \text{s})} = e^{0.99623} = 2.7080$$

$$k_2 = 2.7080 \times (2.14 \times 10^{-2}) / (\text{M}^{1/2} \cdot \text{s}) = 5.7952 \times 10^{-2} = 5.80 \times 10^{-2} (\text{M}^{1/2} \cdot \text{s})$$

- 14.8 The net chemical equation is the overall sum of the two elementary reactions:



The IO^- is an intermediate; I^- is a catalyst. Neither appears in the net equation.

- 14.9 The reaction is bimolecular because it is an elementary reaction that involves two molecules.

- 14.10 For $\text{NO}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$, the rate law is

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

(The rate must be proportional to the concentration of both reactant molecules.)

- 14.11 The first step is the slow, rate-determining step. Therefore, the rate law predicted by the mechanism given is

$$\text{Rate} = k_1 [\text{H}_2\text{O}_2][\text{I}^-]$$

- 14.12 According to the rate-determining (slow) step, the rate law is

$$\text{Rate} = k_2[\text{NO}_3][\text{NO}]$$

Eliminate NO_3 from the rate law by looking at the first step, which is fast and reaches equilibrium. At equilibrium, the forward rate and the reverse rate are equal.

$$k_1[\text{NO}][\text{O}_2] = k_{-1}[\text{NO}_3]$$

Therefore, $[\text{NO}_3] = (k_1/k_{-1})[\text{NO}][\text{O}_2]$, so

$$\text{Rate} = \frac{k_2 k_1}{k_{-1}} [\text{NO}]^2 [\text{O}_2] = k [\text{NO}]^2 [\text{O}_2]$$

Where $k_2(k_1/k_{-1})$ has been replaced by k , which represents the experimentally observed rate constant.

■ Answers to Concept Checks

- 14.1 a. Since the slope is steeper at point A, point A must be a faster instantaneous rate.
 b. Since the curve is not a flat line, the rate of reaction must be constantly changing over time. Therefore, the rate for the reaction cannot be constant at all points in time.
- 14.2 a. Keeping in mind that all reactant species must be present in some concentration for a reaction to occur, the reaction with $[\text{Q}] = 0$ is the slowest since no reaction occurs. The other two reactions are equal in rate because the reaction is zero order with respect to $[\text{Q}]$; as long as there is some amount of Q present, the reaction rate depends on the $[\text{R}]$, which is constant in this case.
 b. Since $[\text{Q}]^0 = 1$, you can rewrite the rate law as follows: $\text{Rate} = k[\text{R}]^2$.
- 14.3 a. A possible rate law is: $\text{Rate of aging} = (\text{diet})^w(\text{exercise})^x(\text{sex})^y(\text{occupation})^z$. Your rate law probably will be different; however, the general form should be the same.

- b. You will need a sample of people who have all the factors the same except one. For example, using the equation given in part a, you could determine the effect of diet if you had a sample of people that were the same sex, exercised the same amount, and had the same occupation. You would need to isolate each factor in this fashion to determine the exponent on each factor.
- c. The exponent on the smoking factor would be two since you see a fourfold rate increase: $[2]^2 = 4$.
- 14.4 The half-life of a first-order reaction is constant over the course of the reaction. The half-life of a second-order reaction depends on the initial concentration and becomes longer as time elapses. Thus, the reaction must be second order because the half-life increases from 20 s to 40 s after time has elapsed.
- 14.5 a. Since the “hump” is larger, the A + B reaction has a higher activation energy.
- b. Since the activation energy is lower, the E + F reaction would have the larger rate constant. Keep in mind the inverse relationship between the activation energy, E_a , and the rate constant, k .
- c. Since, in both cases, energy per mole of the reactants is greater than that of the products, both reactions are exothermic.
- 14.6 a. Her finding should increase the rate since the activation energy, E_a , is inversely related to the rate constant, k ; a decrease in E_a results in an increase in the value of k .
- b. This is possible because the rate law does not have to reflect the overall stoichiometry of the reaction.
- c. No. Since the rate law is based on the slow step of the mechanism, it should be $\text{Rate} = k[Y]^2$.

■ Answers to Review Questions

- 14.1 The four variables that can affect rate are (1) the concentrations of the reactants, although in some cases a particular reactant's concentration does not affect the rate; (2) the presence and concentration of a catalyst; (3) the temperature of the reaction; and (4) the surface area of any solid reactant or solid catalyst.
- 14.2 The rate of reaction of HBr can be defined as the decrease in HBr concentration (or the increase in Br_2 product formed) over the time interval, Δt :

$$\text{Rate} = -1/4 \frac{\Delta[\text{HBr}]}{\Delta t} = 1/2 \frac{\Delta[\text{Br}_2]}{\Delta t} \quad \text{or} \quad -\frac{\Delta[\text{HBr}]}{\Delta t} = 2 \frac{\Delta[\text{Br}_2]}{\Delta t}$$

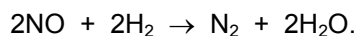
- 14.3 Two physical properties used to determine the rate are color, or absorption of electromagnetic radiation, and pressure. If a reactant or product is colored, or absorbs a different type of electromagnetic radiation than the other species, then measurement of the change in color (change in absorption of electromagnetic radiation) may be used to determine the rate. If a gas reaction involves a change in the number of gaseous molecules, measurement of the pressure change may be used to determine the rate.

- 14.4 Use the general example of a rate law in Section 14.3, where A and B react to give D and E with C as a catalyst:

$$\text{Rate} = k [A]^m [B]^n [C]^p$$

Note that the exponents m , n , and p are the orders of the individual reactants and catalyst. Assuming that m and n are positive numbers, the rate law predicts that increasing the concentrations of A and/or B will increase the rate. In addition, the rate will be increased by increasing the surface of the solid catalyst (making it as finely divided as possible, etc.). Finally, increasing the temperature will increase the rate constant, k , and increase the rate.

- 14.5 An example that illustrates that exponents have no relationship to coefficients is the reaction of nitric oxide and hydrogen from Example 14.12 in the text.



The experimental rate law given there is

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

Thus, the exponent for hydrogen is one, not two like the coefficient, and the overall order is three, not four like the sum of the coefficients.

- 14.6 The rate law for this reaction of iodide ion, arsenic acid, and hydrogen ion is

$$\text{Rate} = k[\text{I}^-][\text{H}_3\text{AsO}_4][\text{H}^+]$$

The overall order is $1 + 1 + 1 = 3$ (third order).

- 14.7 Use m to symbolize the reaction order as is done in the text. Then from the table for m and the change in rate in the text, m is two when the rate is quadrupled (increased fourfold). Using the equation in the text gives the same result:

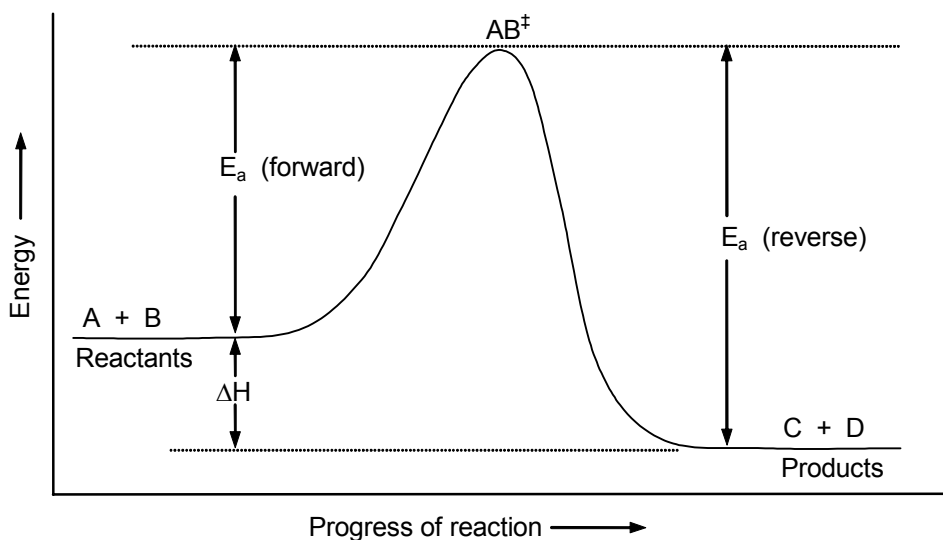
$$2^m = \text{new rate/old rate} = 4/1; \text{ thus, } m = 2$$

- 14.8 Use m to symbolize the reaction order as is done in the text. The table for m and the change in rate in the text cannot be used in this case. When $m = 0.5$, the new rate should be found using the equation in the text:

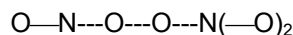
$$2^{0.50} = \sqrt{2} = 1.41 = \text{new rate/old rate}$$

Thus, the new rate is 1.41 times the old rate.

- 14.9 Use the half-life concept to answer the question without an equation. If the half-life for the reaction of $A(g)$ is 25 s, then the time for $A(g)$ to decrease to $1/4$ the initial value is two half-lives or $2 \times 25 = 50$ s. The time for $A(g)$ to decrease to $1/8$ the initial value is three half-lives, or $3 \times 25 = 75$ s.
- 14.10 The half-life equation for a first order reaction is $t_{1/2} = 0.693/k$. The half-life for the reaction is constant, independent of the reactant concentration. For a second order reaction, the half-life equation is $t_{1/2} = 1/(k[A]_0)$, and it depends on the initial reactant concentration.
- 14.11 According to transition-state theory, the two factors that determine whether a collision results in reaction or not are (1) the molecules must collide with the proper orientation to form the activated complex, and (2) the activated complex formed must have a kinetic energy greater than the activation energy.
- 14.12 The potential-energy diagram for the exothermic reaction of A and B to give activated complex AB^\ddagger and products C and D is given below.



- 14.13 The activated complex for the reaction of NO_2 with NO_3 to give NO , NO_2 , and O_2 has the structure below (dashed lines = bonds about to form or break):

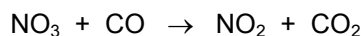
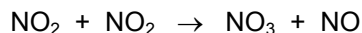


- 14.14 The Arrhenius equation expressed with the base e is

$$k = A e^{-E_a/RT}$$

The A term is the frequency factor and is equal to the product of p and Z from collision theory. The term p is the fraction of collisions with properly oriented reactant molecules, and Z is the frequency of collisions. Thus, A is the number of collisions with the molecules properly oriented. The E_a term is the activation energy, the minimum energy of collision required for two molecules to react. The R term is the gas constant, and T is the absolute temperature.

- 14.15 In the reaction of $\text{NO}_2(\text{g})$ with $\text{CO}(\text{g})$, an example of an intermediate is the temporary formation of NO_3 from the reaction of two NO_2 molecules in the first step:



- 14.16 It is generally impossible to predict the rate law from the equation alone because most reactions consist of several elementary steps whose combined result is summarized in the rate law. If these elementary steps are unknown, the rate law cannot be predicted.
- 14.17 The mechanism cannot be $2\text{NO}_2\text{Cl} \rightarrow 2\text{NO}_2 + \text{Cl}_2$ because the reaction is first order in NO_2Cl . The order in NO_2Cl would have to reflect the total number of molecules (two) for the proposed mechanism, but it does not.
- 14.18 The characteristic of the rate-determining step in a mechanism is that it is, relatively speaking, the slowest step of all the elementary steps (even though it may occur in seconds). Thus, the rate of disappearance of reactant(s) is limited by the rate of this step.
- 14.19 For the rate of decomposition of N_2O_4 ,

$$\text{Rate} = k_1[\text{N}_2\text{O}_4]$$

For the rate of formation of N_2O_4 ,

$$\text{Rate} = k_{-1}[\text{NO}_2]^2$$

(continued)

At equilibrium the rates are equal, so

$$k_1[\text{N}_2\text{O}_4] = k_{-1}[\text{NO}_2]^2$$

$$[\text{N}_2\text{O}_4] = (k_{-1}/k_1) [\text{NO}_2]^2$$

- 14.20 A catalyst operates by providing a pathway (mechanism) that occurs faster than the uncatalyzed pathway (mechanism) of the reaction. The catalyst is not consumed because after reacting in an early step, it is regenerated in a later step.
- 14.21 In physical adsorption, molecules adhere to a surface through *weak* intermediate forces, whereas in chemisorption the molecules adhere to the surface by *stronger* chemical bonding.
- 14.22 In the first step of catalytic hydrogenation of ethylene, the ethylene and hydrogen molecules diffuse to the catalyst surface and undergo chemisorption. Then the *pi* electrons of ethylene form temporary bonds to the metal catalyst, and the hydrogen molecule breaks into two hydrogen atoms. The hydrogen atoms next migrate to an ethylene held in position on the metal catalyst surface, forming ethane. Finally, because it cannot bond to the catalyst, the ethane diffuses away from the surface.

■ Answers to Conceptual Problems

- 14.23 a. You can write the rate expression in terms of the depletion of A:

$$\text{Rate of depletion of A} = - \frac{\Delta[\text{A}]}{\Delta t}$$

Or, you can write the rate expression in terms of the formation of B:

$$\text{Rate of formation of B} = + \frac{\Delta[\text{B}]}{\Delta t}$$

- b. No. Consider the stoichiometry of the reaction, which indicates that the rate of depletion of A would be faster than the rate of formation of B; for every three moles of A that are consumed, two moles of B would be formed.
- c. Taking into account the stoichiometry of the reaction, the two rate expressions that would give an equal rate when calculated over the same time interval are

$$\text{Rate} = - \frac{\Delta[\text{A}]}{3\Delta t} = \frac{\Delta[\text{B}]}{2\Delta t}$$

14.24 You cannot write the rate law for this reaction from the information given. The rate law can only be determined by experiment, not by the stoichiometry of the reaction.

14.25 a. The rate law for a second-order reaction is $\text{Rate} = k[A]^2$.

- b. The faster reaction rate will correspond to the container with the higher concentration of A. Both containers contain the same number of A particles, but the volume of container B is only one-half the volume of container A. Therefore, the initial concentration of A in container B is double the initial concentration of A in container A. Thus, the reaction will be faster in container B.
- c. For a second-order reaction, the relationship between the half-life, rate constant, and initial concentration of A is

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

Since the half-life is inversely proportional to the initial concentration, the shorter half-life will correspond to the higher initial concentration of A, which is container B.

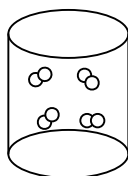
- d. The relative rates of the reactions can be determined as follows. Since the initial concentration of A in container B is double the initial concentration of A in container A, the ratio of the rate in container B to that in container A is

$$\frac{\text{Rate}_B}{\text{Rate}_A} = \frac{k[A]_{0,B}^2}{k[A]_{0,A}^2} = \left(\frac{[A]_{0,B}}{[A]_{0,A}} \right)^2 = \left(\frac{2[A]_{0,A}}{[A]_{0,A}} \right)^2 = 2^2 = 4$$

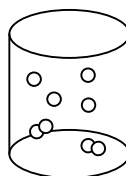
Thus, the reaction rate in container B is four times the reaction rate in container A.

- e. Since both containers start with the same number of A particles, and the reaction rate is faster in container B, more A particles will have reacted in container B than in container A, so container B will contain fewer atoms.

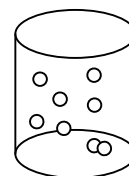
14.26 a. The reaction is first-order with a half-life of 10 seconds. Starting with four particles in the container, after 10 seconds (one half-life), two of the particles will have reacted and two will remain unreacted. After 20 seconds (two half-lives), three of the particles will have reacted and one will remain unreacted. The pictures are



$t = 0 \text{ s}$



$t = 10 \text{ s}$



$t = 20 \text{ s}$

(continued)

- b. If the half-life is the same for the second-order reaction, the pictures will be the same.
- c. After 10 seconds (one half-life), the concentration of the particles is one-half their initial value. If we call the particles A, then for the first-order case the relative reaction rates at the start and after 10 seconds are

$$\frac{\text{Rate}_0}{\text{Rate}_{10}} = \frac{k[A]_{0,0}}{k[A]_{0,10}} = \frac{[A]_{0,0}}{[A]_{0,10}} = \frac{[A]_0}{1/2[A]_0} = 2$$

Thus, for the first-order case, after 10 seconds, the rate is one-half the initial rate.

- d. After 10 seconds (one half-life), the concentration of the particles is one-half their initial value. If we call the particles A, then for the second-order case the relative reaction rates at the start and after 10 seconds are

$$\frac{\text{Rate}_0}{\text{Rate}_{10}} = \frac{k[A]_{0,0}^2}{k[A]_{0,10}^2} = \left(\frac{[A]_{0,0}}{[A]_{0,10}} \right)^2 = \left(\frac{[A]_0}{1/2[A]_0} \right)^2 = 2^2 = 4$$

Thus, for the second-order case, after 10 seconds, the rate is four times the initial rate.

- 14.27 a. If the concentration is tripled but there is no effect on the rate, the order of the reaction must be zero. Thus, $x = 0$.
- b. If the concentration is doubled, and the rate doubles, it is a first-order reaction. Thus, $x = 1$.
- c. If the concentration is tripled, and the rate goes up by a factor of 27, it is a third-order reaction. Thus, $x = 3$.
- 14.28 a. E must be a product since its concentration increases with time. If E were a reactant, you would expect the concentration to decrease over time.
- b. The average rate is faster between points A and B because the slope of the curve is steeper in this region. Remember, the steeper the curve, the greater the rate of change.
- 14.29 a. The rate has a constant value in region C because the slope of the curve is constant (flat) in this region.
- b. The rate is the fastest in region A because the slope of the curve is steepest in this region.
- 14.30 Since NO_2 is a product in the reaction, its concentration must increase with time. The only graph that has $[\text{NO}_2]$ increasing with time is curve C.

14.31 A number of answers will work as long as you match one of the existing concentrations of A or B. For example: $[A] = 2.0 \text{ M}$ with $[B] = 2.0 \text{ M}$, or $[A] = 1.0 \text{ M}$ with $[B] = 2.0 \text{ M}$.

14.32 The Arrhenius equation is

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

- When the temperature is decreased, the rate constant, k , will also decrease. When k decreases, the rate also decreases.
- When the activation energy is increased, the rate constant, k , also decreases. When k decreases, the rate also decreases.
- Since the activation energy is in the numerator, and the temperature is in the denominator, you cannot predict the effect without knowing the magnitude of the changes.

■ Solutions to Practice Problems

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

14.33 For the reaction $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$, the rate of decomposition of NO_2 and the rate of formation of O_2 are, respectively,

$$\text{Rate} = -\Delta[\text{NO}_2]/\Delta t$$

$$\text{Rate} = \Delta[\text{O}_2]/\Delta t$$

To relate the two rates, divide each rate by the coefficient of the corresponding substance in the chemical equation and equate them.

$$-1/2 \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

- 14.34 For the reaction $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$, the rate of formation of HI and the rate of decomposition of H_2 are, respectively,

$$\text{Rate} = \Delta[\text{HI}]/\Delta t$$

$$\text{Rate} = -\Delta[\text{H}_2]/\Delta t$$

To relate the two rates, divide each rate by the coefficient of the corresponding substance in the chemical equation and equate them.

$$-\frac{\Delta[\text{H}_2]}{\Delta t} = 1/2 \frac{\Delta[\text{HI}]}{\Delta t}$$

- 14.35 For the reaction $5\text{Br}^- + \text{BrO}_3^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$, the rate of decomposition of Br^- and the rate of decomposition of BrO_3^- are, respectively,

$$\text{Rate} = -\Delta[\text{Br}^-]/\Delta t$$

$$\text{Rate} = -\Delta[\text{BrO}_3^-]/\Delta t$$

To relate the two rates, divide each rate by the coefficient of the corresponding substance in the chemical equation and equate them.

$$1/5 \frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{\Delta[\text{BrO}_3^-]}{\Delta t}$$

- 14.36 For the reaction $3\text{I}^- + \text{H}_3\text{AsO}_4 + 2\text{H}^+ \rightarrow \text{I}_3^- + \text{H}_3\text{AsO}_3 + \text{H}_2\text{O}$, the rate of decomposition of I^- and the rate of formation of I_3^- are, respectively,

$$\text{Rate} = -\Delta[\text{I}^-]/\Delta t$$

$$\text{Rate} = \Delta[\text{I}_3^-]/\Delta t$$

To relate the two rates, divide each rate by the coefficient of the corresponding substance in the chemical equation and equate them.

$$-1/3 \frac{\Delta[\text{I}^-]}{\Delta t} = \frac{\Delta[\text{I}_3^-]}{\Delta t}$$

- 14.37
$$\text{Rate} = -\frac{\Delta[\text{NH}_4\text{NO}_2]}{\Delta t} = -\frac{[0.0432 \text{ M} - 0.500 \text{ M}]}{[3.00 \text{ hr} - 0.00 \text{ hr}]} = 2.27 \times 10^{-2} = 2.3 \times 10^{-2} \text{ M/hr}$$

$$14.38 \quad \text{Rate} = -\frac{\Delta[\text{FeCl}_3]}{\Delta t} = -\frac{[0.02638 \text{ M} - 0.3586 \text{ M}]}{[4.00 \text{ min} - 0.00 \text{ min}]} = 0.0023\text{70} = 0.00237 \text{ M/min}$$

$$14.39 \quad \text{Rate} = -\frac{\Delta[\text{Azo.}]}{\Delta t} = -\frac{[0.0101 \text{ M} - 0.0150 \text{ M}]}{7.00 \text{ min} - 0.00 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ sec}} = 1.\text{16} \times 10^{-5} \\ = 1.2 \times 10^{-5} \text{ M/s}$$

$$14.40 \quad \text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = -\frac{[0.1076 \text{ M} - 0.1103 \text{ M}]}{60.0 \text{ s} - 0.0 \text{ s}} = 4.\text{50} \times 10^{-5} = 4.5 \times 10^{-5} \text{ M/s}$$

14.41 If the rate law is $\text{rate} = k[\text{H}_2\text{S}][\text{Cl}_2]$, the order with respect to H_2S is 1 (first-order), and the order with respect to Cl_2 is also one (first-order). The overall order is $1 + 1 = 2$, second-order.

14.42 If the rate law is $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$, the order with respect to NO is two (second-order), and the order with respect to Cl_2 is one (first-order). The overall order is $2 + 1 = 3$, third-order.

14.43 If the rate law is $\text{rate} = k[\text{MnO}_4^-][\text{H}_2\text{C}_2\text{O}_4]$, the order with respect to MnO_4^- is one (first-order), the order with respect to $\text{H}_2\text{C}_2\text{O}_4$ is one (first-order), and the order with respect to H^+ is zero. The overall order is two, second-order.

14.44 If the rate law is $\text{rate} = k[\text{H}_2\text{O}_2][\text{Fe}^{2+}]$, the order with respect to H_2O_2 is one (first-order), the order with respect to Fe^{2+} is one (first-order), and the order with respect to H^+ is zero. The overall order is two, second-order.

14.45 The reaction rate doubles when the concentration of CH_3NNCH_3 is doubled, so the reaction is first-order in azomethane. The rate equation should have the form

$$\text{Rate} = k[\text{CH}_3\text{NNCH}_3]$$

Substituting values for the rate and concentration yields a value for k :

$$k = \frac{\text{rate}}{[\text{Azo.}]} = \frac{2.8 \times 10^{-6} \text{ M/s}}{1.13 \times 10^{-2} \text{ M}} = 2.\text{47} \times 10^{-4} = 2.5 \times 10^{-4} / \text{s}$$

- 14.46 The reaction rate doubles when the concentration of ethylene oxide is doubled, so the reaction is first-order in ethylene oxide. The rate equation should have the form

$$\text{Rate} = k[\text{C}_2\text{H}_4\text{O}]$$

Substituting values for the rate and concentration yields a value for k :

$$k = \frac{\text{rate}}{[\text{Et. Ox.}]} = \frac{5.57 \times 10^{-7} \text{ M/s}}{2.72 \times 10^{-3} \text{ M}} = 2.047 \times 10^{-4} = 2.05 \times 10^{-4}/\text{s}$$

- 14.47 Doubling $[\text{NO}]$ quadruples the rate, so the reaction is second-order in NO. Doubling $[\text{H}_2]$ doubles the rate, so the reaction is first-order in H_2 . The rate law should have the form

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

Substituting values for the rate and concentrations yields a value for k :

$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{H}_2]} = \frac{2.6 \times 10^{-5} \text{ M/s}}{[6.4 \times 10^{-3} \text{ M}]^2[2.2 \times 10^{-3} \text{ M}]} = 2.88 \times 10^2 = 2.9 \times 10^2 \text{ M}^2\text{s}$$

- 14.48 Doubling $[\text{NO}]$ quadruples the rate, so the reaction is second-order in NO. Doubling $[\text{O}_2]$ doubles the rate, so the reaction is first-order in O_2 . The rate law should have the form

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

Substituting values for the rate and concentrations yields a value for k :

$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{O}_2]} = \frac{0.0281 \text{ M/s}}{[0.0125 \text{ M}]^2[0.0253 \text{ M}]} = 7.108 \times 10^3 = 7.11 \times 10^3/\text{M}^2\text{s}$$

- 14.49 By comparing experiments 1 and 2, you see that tripling $[\text{ClO}_2]$ increases the rate ninefold; that is, $3^m = 9$, so $m = 2$ (and the reaction is second-order in ClO_2). From experiments 2 and 3, you see that tripling $[\text{OH}^-]$ triples the rate, so the reaction is first-order in OH^- . The rate law is

$$\text{Rate} = k[\text{ClO}_2]^2[\text{OH}^-]$$

Substituting values for the rate and concentrations yields a value for k :

$$k = \frac{\text{rate}}{[\text{ClO}_2]^2[\text{OH}^-]} = \frac{0.0248 \text{ M/s}}{[0.060 \text{ M}]^2[0.030 \text{ M}]} = 2.29 \times 10^2 = 2.3 \times 10^2/\text{M}^2\text{s}$$

- 14.50 By comparing experiments 2 and 3, you see that doubling $[I^-]$ doubles the rate, so the reaction is first-order in I^- . From experiments 1 and 3, you see that doubling $[ClO^-]$ also doubles the rate, so the reaction is first-order in ClO^- . From experiments 3 and 4, you see that doubling $[OH^-]$ halves the rate; that is, $2^m = 1/2$. Hence, $m = -1$, and the rate is inversely proportional to the first power of OH^- . The rate law is

$$\text{Rate} = k[I^-][ClO^-]/[OH^-]$$

Substituting values for the rate and concentrations yields a value for k :

$$k = \frac{\text{rate } [OH^-]}{[ClO^-][I^-]} = \frac{6.1 \times 10^{-2} \text{ M/s} [0.010 \text{ M}]}{[0.010 \text{ M}] [0.010 \text{ M}]} = 6.1 = 6.1/\text{s}$$

- 14.51 Let $[SO_2Cl_2]_0 = 0.0248 \text{ M}$ and $[SO_2Cl_2]_t$ = the concentration after 2.0 hr. Substituting these and $k = 2.2 \times 10^{-5}/\text{s}$ into the first-order rate equation gives

$$\ln \frac{[SO_2Cl_2]_t}{[0.0248 \text{ M}]} = -(2.2 \times 10^{-5}/\text{s}) \left(2.0 \text{ hr} \times \frac{3600 \text{ s}}{1 \text{ hr}} \right) = -0.1584$$

Taking the antilog of both sides gives

$$\frac{[SO_2Cl_2]_t}{[0.0248 \text{ M}]} = e^{-0.1584} = 0.8535$$

Solving for $[SO_2Cl_2]_t$ gives

$$[SO_2Cl_2]_t = 0.8525 \times [0.0248 \text{ M}] = 0.02116 = 0.021 = 2.1 \times 10^{-2} \text{ M}$$

- 14.52 Let $[C_3H_6]_0 = 0.0226 \text{ M}$ and $[C_3H_6]_t$ = the concentration after 899 s. Substituting these concentrations and $k = 6.0 \times 10^{-4}/\text{s}$ into the first-order rate equation gives

$$\ln \frac{[C_3H_6]_t}{[0.0226 \text{ M}]} = -(6.0 \times 10^{-4}/\text{s})(899 \text{ s}) = -0.5394$$

Taking the antilog of both sides gives

$$\frac{[C_3H_6]_t}{[0.0226 \text{ M}]} = e^{-0.5394} = 0.5830$$

Solving for $[C_3H_6]_t$ gives

$$[C_3H_6]_t = 0.5830 \times [0.0226 \text{ M}] = 0.0131 = 0.013 \text{ M}$$

14.53 The second-order integrated rate law is

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

Using a rate constant value of 0.225 L/(mol·s) and an initial concentration of 0.293 mol/L, after 35.4 s the concentration of A is

$$\frac{1}{[A]_t} = 0.225 \text{ L/(mol}\cdot\text{s)} \times 35.4 \text{ s} + \frac{1}{0.293 \text{ mol/L}}$$

$$\frac{1}{[A]_t} = 7.965 \text{ L/mol} + 3.412 \text{ L/mol} = 11.377 \text{ L/mol}$$

$$[A]_t = \frac{1}{11.377 \text{ L/mol}} = 0.087889 = 0.08789 \text{ M}$$

14.54 The second-order integrated rate law is

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

Using a rate constant value of 0.169 L/(mol·s) and an initial concentration of 0.159 mol/L, the time it would take for [A] to decrease to 6.07×10^{-3} mol/L is

$$\frac{1}{6.07 \times 10^{-3} \text{ mol/L}} = 0.169 \text{ L/(mol}\cdot\text{s)} \times t + \frac{1}{0.159 \text{ mol/L}}$$

$$0.169 \text{ L/(mol}\cdot\text{s)} \times t = \frac{1}{6.07 \times 10^{-3} \text{ mol/L}} - \frac{1}{0.159 \text{ mol/L}} = 158.45 \text{ L/mol}$$

$$t = \frac{158.45 \text{ L/mol}}{0.169 \text{ L/(mol}\cdot\text{s)}} = 937.6 = 938 \text{ s}$$

14.55 First, find the rate constant, k, by substituting experimental values into the first-order rate equation. Let $[\text{Et. Cl.}]_0 = 0.00100 \text{ M}$, $[\text{Et. Cl.}]_t = 0.00067 \text{ M}$, and $t = 155 \text{ s}$. Solving for k yields

$$k = -\frac{\ln \frac{[0.00067 \text{ M}]_t}{[0.00100 \text{ M}]_0}}{155 \text{ s}} = 2.583 \times 10^{-3}/\text{s}$$

(continued)

Now let $[\text{Et. Cl.}]_t$ = the concentration after 256 s, $[\text{Et. Cl.}]_o$ again = 0.00100 M, and use the value of k of $1.564 \times 10^{-3}/\text{s}$ to calculate $[\text{Et. Cl.}]_t$.

$$\ln \frac{[\text{Et. Cl.}]_t}{[0.00100 \text{ M}]} = - (2.584 \times 10^{-3}/\text{s})(256 \text{ s}) = -0.6614$$

Converting both sides to antilogs gives

$$\frac{[\text{Et. Cl.}]_t}{[0.00100 \text{ M}]} = 0.5161$$

$$[\text{Et. Cl.}]_t = 0.5161 \times [0.00100 \text{ M}] = 5.16 \times 10^{-4} = 5.2 \times 10^{-4} \text{ M}$$

- 14.56 First, find the rate constant, k , by substituting experimental values into the first-order rate equation. Let $[\text{Cyb.}]_o = 0.00150 \text{ M}$, $[\text{Cyb.}]_t = 0.00119 \text{ M}$, and $t = 455 \text{ s}$.

$$-k(455 \text{ s}) = \ln \frac{[0.00119 \text{ M}]}{[0.00150 \text{ M}]} = -0.23151$$

Solving gives $k = 5.088 \times 10^{-4}/\text{s}$. Now let $[\text{Cyb.}]_t$ = the concentration after 750 s and $[\text{Cyb.}]_o = 0.00150 \text{ M}$, and calculate $[\text{Cyb.}]_t$.

$$\ln \frac{[\text{Cyb.}]_t}{[0.00150 \text{ M}]} = - (5.088 \times 10^{-4} / \text{s})(750 \text{ s}) = -0.3816$$

Taking the antilog of both sides yields

$$\frac{[\text{Cyb.}]_t}{[0.00150 \text{ M}]} = 0.68275$$

Solving for $[\text{Cyb.}]_t$ gives

$$[\text{Cyb.}]_t = 0.68275 \times [0.00150 \text{ M}] = 1.024 \times 10^{-3} = 1.02 \times 10^{-3} \text{ M}$$

- 14.57 For a first-order reaction, divide 0.693 by the rate constant to find the half-life:

$$t_{1/2} = 0.693 / (6.3 \times 10^{-4} / \text{s}) = 1.10 \times 10^3 = 1.1 \times 10^3 \text{ s (18.3 min)}$$

Now, use the half-life to determine the concentrations. When the concentration decreases to 50.0 percent of its initial value, this is equal to the half-life.

$$t_{50.0\% \text{ left}} = t_{1/2} = 1.10 \times 10^3 \text{ s}$$

When the concentration decreases to 25.0 percent of its initial value, this is equal to two half-lives.

$$t_{25.0\% \text{ left}} = t_{1/4 \text{ left}} = 2 \times t_{1/2} = 2 \times (1.10 \times 10^3 \text{ s}) = 2.20 \times 10^3 \text{ s (37 min)}$$

14.58 For a first-order reaction, divide 0.693 by the rate constant to find the half-life:

$$t_{1/2} = 0.693 / (6.2 \times 10^{-4} / \text{min}) = 1.117 \times 10^3 = 1.1 \times 10^3 \text{ min (18.6 hr)}$$

$$\begin{aligned} t_{25.0\% \text{ left}} &= t_{1/4 \text{ left}} = 2 \times t_{1/2} = 2 \times (1.117 \times 10^3 \text{ min}) \\ &= 2.235 \times 10^3 = 2.2 \times 10^3 \text{ min} \end{aligned}$$

$$\begin{aligned} t_{12.5\% \text{ left}} &= t_{1/8 \text{ left}} = 3 \times t_{1/2} = 3 \times (1.117 \times 10^3 \text{ min}) \\ &= 3.353 \times 10^3 = 3.4 \times 10^3 \text{ min} \end{aligned}$$

14.59 For a first-order reaction, divide 0.693 by the rate constant to find the half-life:

$$t_{1/2} = 0.693 / (2.0 \times 10^{-6} / \text{s}) = 3.465 \times 10^5 \text{ s (96.25 or 96 hr)}$$

$$t_{25\% \text{ left}} = t_{1/4 \text{ left}} = 2 \times t_{1/2} = 2 \times 96.25 \text{ hr} = 192.5 = 1.9 \times 10^2 \text{ hr}$$

$$t_{12.5\% \text{ left}} = t_{1/8 \text{ left}} = 3 \times t_{1/2} = 3 \times 96.25 \text{ hr} = 288.75 = 2.9 \times 10^2 \text{ hr}$$

$$t_{6.25\% \text{ left}} = t_{1/16 \text{ left}} = 4 \times t_{1/2} = 4 \times 96.25 \text{ hr} = 385.0 = 3.9 \times 10^2 \text{ hr}$$

$$t_{3.125\% \text{ left}} = t_{1/32 \text{ left}} = 5 \times t_{1/2} = 5 \times 96.25 \text{ hr} = 481.25 = 4.8 \times 10^2 \text{ hr}$$

14.60 For a first-order reaction, divide 0.693 by the rate constant to find the half-life:

$$t_{1/2} = 0.693 / (1.27 / \text{s}) = 0.5456 \text{ s}$$

$$t_{25\% \text{ left}} = t_{1/4 \text{ left}} = 2 \times t_{1/2} = 2 \times 0.5456 \text{ s} = 1.091 = 1.09 \text{ s}$$

$$t_{12.5\% \text{ left}} = t_{1/8 \text{ left}} = 3 \times t_{1/2} = 3 \times 0.5456 \text{ s} = 1.636 = 1.64 \text{ s}$$

$$t_{6.25\% \text{ left}} = t_{1/16 \text{ left}} = 4 \times t_{1/2} = 4 \times 0.5456 \text{ s} = 2.182 = 2.18 \text{ s}$$

$$t_{3.125\% \text{ left}} = t_{1/32 \text{ left}} = 5 \times t_{1/2} = 5 \times 0.5456 \text{ s} = 2.728 = 2.73 \text{ s}$$

14.61 The half-life for a second-order reaction is

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

Using a rate constant of 0.413 L/(mol·s) and an initial A concentration of 5.25×10^{-3} mol/L, the half-life is

$$t_{1/2} = \frac{1}{(0.413 \text{ L/(mol} \cdot \text{s)})(5.25 \times 10^{-3} \text{ mol/L})} = 461.2 = 461 \text{ s}$$

- 14.62 The rate constant for a second-order reaction is related to the half-life by

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

Using a half-life of 413 s and an initial A concentration of 5.99×10^{-3} mol/L, the rate constant is

$$k = \frac{1}{(413 \text{ s})(5.99 \times 10^{-3} \text{ mol/L})} = 0.4042 = 0.404 \text{ L/(mol}\cdot\text{s)}$$

- 14.63 Use the first-order rate equation, and solve for time, t . Let $[\text{Cr}^{3+}]_0 = 100.0$ percent; then the concentration at time t , $[\text{Cr}^{3+}]_t = (100.0\% - 85.0\%, \text{ or } 15.0\%)$. Use $k = 2.0 \times 10^{-6}/\text{s}$.

$$\ln \frac{[15.0]}{[100.0]} = -(2.0 \times 10^{-6}/\text{s}) t$$

$$t = -\frac{\ln(0.150)}{2.0 \times 10^{-6}/\text{s}} = 9.48 \times 10^5 \text{ s, or } 2.6 \times 10^2 \text{ hr}$$

- 14.64 Use the first-order rate equation, and solve for time, t . Let $[\text{Fe}^{3+}]_0 = 100.0$ percent; then the concentration at time t , $[\text{Fe}^{3+}]_t = (100.0\% - 90.0\%, \text{ or } 10.0\%)$. Use $k = 1.27/\text{s}$.

$$\ln \frac{[10.0\%]}{[100.0\%]} = -(1.27/\text{s}) t$$

$$t = -\frac{\ln(0.100)}{1.27/\text{s}} = 1.813 = 1.81 \text{ s}$$

- 14.65 The rate law for a zero-order reaction is

$$[A] = -kt + [A]_0$$

Using a rate constant of 8.1×10^{-2} mol/(L·s) and an initial concentration of 0.10 M, the time it would take for the concentration to change to 1.0×10^{-2} M is

$$1.0 \times 10^{-2} \text{ M} = -8.1 \times 10^{-2} \text{ mol/(L}\cdot\text{s)} \times t + 0.10 \text{ M}$$

$$t = \frac{0.10 \text{ M} - 1.0 \times 10^{-2} \text{ M}}{8.1 \times 10^{-2} \text{ M/s}} = 1.11 = 1.1 \text{ s}$$

14.66 The rate law for a zero-order reaction is

$$[A] = -kt + [A]_0.$$

Using a time of 3.3×10^2 s to go from an initial concentration of 0.50 M to 0.25 M, the rate constant is

$$0.25 \text{ M} = -k \times 3.3 \times 10^2 \text{ s} + 0.50 \text{ M}$$

$$k = \frac{0.50 \text{ M} - 0.25 \text{ M}}{3.3 \times 10^2 \text{ s}} = 7.57 \times 10^{-4} = 7.6 \times 10^{-4} \text{ M/s}$$

14.67 For the first-order plot, follow Figure 14.9, and plot $\ln [\text{ClO}_2]$ versus the time in seconds. The data used for plotting are

t, sec	$[\text{ClO}_2]$, M	$\ln [\text{ClO}_2]$
0.00	4.77×10^{-4}	-7.647
1.00	4.31×10^{-4}	-7.749
2.00	3.91×10^{-4}	-7.846
3.00	3.53×10^{-4}	-7.949
5.00	2.89×10^{-4}	-8.149
10.00	1.76×10^{-4}	-8.645
30.00	2.4×10^{-5}	-10.63
50.00	3.2×10^{-5}	-12.65

The plot yields an approximate straight line, demonstrating the reaction is first order in $[\text{ClO}_2]$. The slope of the line may be calculated from the difference between the last point and the first point:

$$\text{Slope} = \frac{[(-12.65) - (-7.647)]}{[50.00 - 0.00]\text{s}} = -0.1001/\text{s}$$

Just as the slope, m , was obtained for the plot in Figure 14.9, you can also equate m to $-k$, and calculate k as follows:

$$k = -\text{slope} = 0.1001 = 0.100/\text{s}$$

- 14.68 For the first-order plot, follow Figure 14.9, and plot $\ln [\text{MA}]$, the methyl acetate concentration, versus time in minutes. This plot does not yield a straight line, so the reaction is not first order. For the second-order plot, follow Figure 14.10, and plot $1/[\text{MA}]$ versus time in minutes. The data used for plotting are

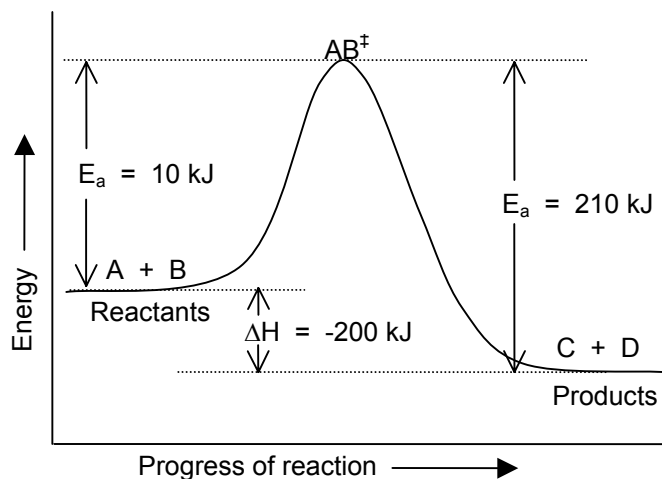
t, min	[MA], M	1/[MA]
0.00	0.01000	100.0
3.00	0.00740	135.1
4.00	0.00683	146.4
5.00	0.00634	157.7
10.00	0.00463	215.9
20.00	0.00304	328.9
30.00	0.00224	446.4

The plot requires a graph with too many lines to be reproduced here, but it yields a straight line, demonstrating that the reaction is second order in [MA]. The slope of the line may be calculated from the difference between the last point and the first point:

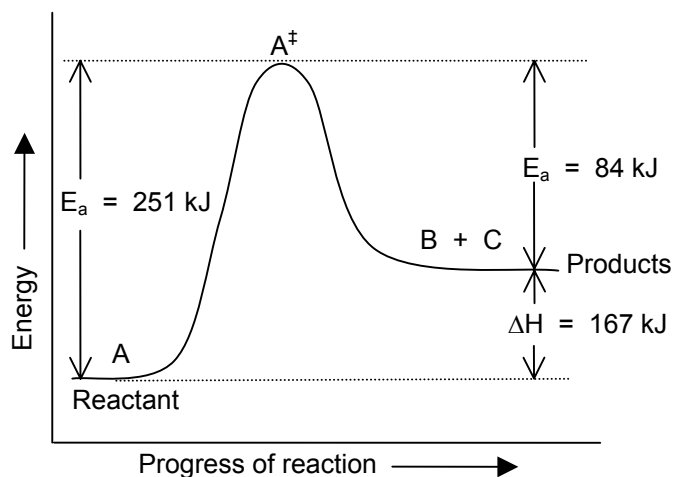
$$\text{Slope} = \frac{[446.4 - 100.0]/\text{M}}{[30.00 - 0.00]\text{min}} = \frac{11.54}{\text{M} \cdot \text{min}} = \frac{0.192}{\text{M} \cdot \text{s}}$$

In this case, the slope equals the rate constant, so $k = 11.5/(\text{M} \cdot \text{min})$, or $0.192/(\text{M} \cdot \text{s})$.

- 14.69 The potential-energy diagram is below. Because the activation energy for the forward reaction is +10 kJ, and $\Delta H^\circ = -200$ kJ, the activation energy for the reverse reaction is +210 kJ.



- 14.70 The potential-energy diagram is below. Because the activation energy for the forward reaction is +251 kJ, and ΔH° is +167 kJ, the activation energy for the reverse reaction is +84 kJ.



- 14.71 Solve the two-temperature Arrhenius equation for E_a by substituting $T_1 = 308$ K (from 35°C), $k_1 = 1.4 \times 10^{-4}$ /s, $T_2 = 318$ K (from 45 °C), and $k_2 = 5.0 \times 10^{-4}$ /s:

$$\ln \frac{5.0 \times 10^{-4}}{1.4 \times 10^{-4}} = \frac{E_a}{8.31 \text{ J/(mol} \cdot \text{K)}} \left(\frac{1}{308 \text{ K}} - \frac{1}{318 \text{ K}} \right)$$

Rearranging E_a to the left side and calculating $[1/308 - 1/318]$ gives

$$E_a = \frac{8.31 \text{ J/K} \times \ln(3.5714)}{1.0209 \times 10^{-4} \text{ /K}} = 1.037 \times 10^5 = 1.0 \times 10^5 \text{ J/mol}$$

To find the rate at 55 °C (328 K), use the first equation. Let k_2 in the numerator be the unknown and solve:

$$\ln \frac{k_2}{1.4 \times 10^{-4}} = \frac{1.037 \times 10^5 \text{ J/mol}}{8.31 \text{ J/(mol} \cdot \text{K)}} \left(\frac{1}{308 \text{ K}} - \frac{1}{328 \text{ K}} \right) = 2.468$$

$$\frac{k_2}{1.4 \times 10^{-4}} = 11.80$$

$$k_2 = 11.80 \times (1.4 \times 10^{-4} \text{ /s}) = 1.652 \times 10^{-3} = 1.7 \times 10^{-3} \text{ /s}$$

- 14.72 Solve the two-temperature Arrhenius equation for E_a by making these substitutions: $T_1 = 350 \text{ K}$, $k_1 = 9.3 \times 10^{-6}/\text{s}$, $T_2 = 400 \text{ K}$, and $k_2 = 6.9 \times 10^{-4}/\text{s}$.

$$\ln \frac{6.9 \times 10^{-4}/\text{s}}{9.3 \times 10^{-6}/\text{s}} = \frac{E_a}{8.31 \text{ J/(mol} \cdot \text{K)}} \left(\frac{1}{350 \text{ K}} - \frac{1}{400 \text{ K}} \right)$$

Rearranging and solving for E_a gives

$$\begin{aligned} E_a &= \frac{8.31 \text{ J/(mol} \cdot \text{K)} \times \ln \left(\frac{6.9 \times 10^{-4}}{9.3 \times 10^{-6}} \right)}{\left(\frac{1}{350 \text{ K}} - \frac{1}{400 \text{ K}} \right)} = 1.002 \times 10^5 \\ &= 1.00 \times 10^5 \text{ J/mol} \quad (100. \text{ kJ/mol}) \end{aligned}$$

To find the rate constant at 425 K, use the first equation with k_2 as the symbol for the rate constant at 475 K and $E_a = 1.002 \times 10^5 \text{ J/mol}$:

$$\ln \frac{k_2}{9.3 \times 10^{-6} / \text{s}} = \frac{1.002 \times 10^5 \text{ J/mol}}{8.31 \text{ J/(mol} \cdot \text{K)}} \left(\frac{1}{350 \text{ K}} - \frac{1}{425 \text{ K}} \right) = 6.080$$

Taking the antilog of both sides gives

$$\frac{k_2}{9.3 \times 10^{-6} / \text{s}} = e^{6.080} = 437.03$$

Solving for k_2 gives

$$k_2 = 437.03 \times (9.3 \times 10^{-6} / \text{s}) = 0.00406 = 0.0041 / \text{s}$$

- 14.73 Because the rate constant is proportional to the rate of a reaction, tripling the rate at 25°C also means that the rate constant at 25°C is tripled. Thus, $k_{35} = 3k_{25}$, and the latter can be substituted for k_{25} in the Arrhenius equation:

$$\ln \frac{3 k_{25}}{k_{25}} = \frac{E_a}{8.31 \text{ J/(mol} \cdot \text{K)}} \left(\frac{1}{298 \text{ K}} - \frac{1}{308 \text{ K}} \right)$$

$$1.0986 = (1.311 \times 10^{-5} \text{ mol/J}) E_a$$

$$E_a = \frac{1.0986}{1.311 \times 10^{-5} \text{ mol/J}} = 8.379 \times 10^4 \text{ J/mol} = 83.8 \text{ kJ/mol}$$

- 14.74 Because the rate constant is proportional to the rate of a reaction, quadrupling the rate at 25 °C also means that the rate constant at 25 °C is quadrupled. Thus, $k_{35} = 4k_{25}$, and the latter can be substituted for k_{35} in the Arrhenius equation:

$$\ln \frac{4 k_{25}}{k_{25}} = \frac{E_a}{8.31 \text{ J/(mol} \cdot \text{K)}} \left(\frac{1}{298 \text{ K}} - \frac{1}{308 \text{ K}} \right)$$

$$1.3862 = (1.311 \times 10^{-5} \text{ mol/J}) E_a$$

$$E_a = \frac{1.3862}{1.311 \times 10^{-5} \text{ mol/J}} = 1.0572 \times 10^5 \text{ J/mol} = 106 \text{ kJ/mol}$$

- 14.75 For plotting $\ln k$ versus $1/T$, the data below are used:

k	$\ln k$	$1/T$ (1/K)
0.527	-0.64055	1.686×10^{-3}
0.776	-0.25360	1.658×10^{-3}
1.121	0.11422	1.631×10^{-3}
1.607	0.47436	1.605×10^{-3}

The plot yields an approximate straight line. The slope of the line is calculated from the difference between the last and the first points:

$$\text{Slope} = \frac{(0.47436) - (-0.64055)}{[1.605 \times 10^{-3} - 1.686 \times 10^{-3}]/\text{K}} = -13764 \text{ K}$$

Because the slope = $-E_a/R$, you can solve for E_a using $R = 8.31 \text{ J/K}$:

$$\frac{-E_a}{8.31 \text{ J/(K} \cdot \text{mol)}} = -13764 \text{ K}$$

$$E_a = 5976 \text{ K} \times 8.31 \text{ J/K} = 1.143 \times 10^5 \text{ J/mol, or } 1.1 \times 10^2 \text{ kJ/mol}$$

- 14.76 For plotting $\ln k$ versus $1/T$, the data below are used:

k	$\ln k$	$1/T$ (K)
2.69×10^{-3}	-5.918	1.402×10^{-3}
6.21×10^{-3}	-5.081	1.364×10^{-3}
1.40×10^{-2}	-4.268	1.328×10^{-3}
3.93×10^{-2}	-3.236	1.294×10^{-3}

(continued)

The plot yields an approximate straight line. The slope of the line may be calculated from the difference between the last point and the first point:

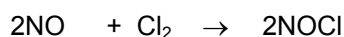
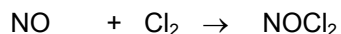
$$\text{Slope} = \frac{(-3.236) - (-5.918)}{[1.294 \times 10^{-3} - 1.402 \times 10^{-3}]/\text{K}} = -2.483 \times 10^4 \text{ K}$$

Because the slope = $-E_a/R$, you can solve for E_a using $R = 8.31 \text{ J/K}\cdot\text{mol}$:

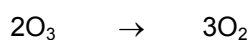
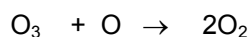
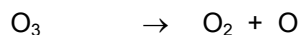
$$\frac{-E_a}{8.31 \text{ J/(K}\cdot\text{mol)}} = 2.483 \times 10^4 \text{ K}$$

$$E_a = 2.483 \times 10^4 \text{ K} \times 8.31 \text{ J/K}\cdot\text{mol} = 2.063 \times 10^5 \text{ J/mol} \quad (2.1 \times 10^2 \text{ kJ/mol})$$

- 14.77 The NOCl_2 is a reaction intermediate that is produced in the first reaction and consumed in the second. The overall reaction is the sum of the two elementary reactions:



- 14.78 The O atom is a reaction intermediate that is produced in the first reaction and consumed in the second. The overall reaction is the sum of the two elementary reactions:



- 14.79 a. Bimolecular b. Bimolecular c. Unimolecular d. Termolecular

- 14.80 a. Termolecular b. Bimolecular c. Bimolecular d. Unimolecular

- 14.81 a. Only O_3 occurs on the left side of the equation, so the rate law is

$$\text{Rate} = k[\text{O}_3]$$

- b. Both NOCl_2 and NO occur on the left side of the equation, so the rate law is

$$\text{Rate} = k[\text{NOCl}_2][\text{NO}]$$

14.82 a. Only CS_2 occurs on the left side of the equation, so the rate law is

$$\text{Rate} = k[\text{CS}_2]$$

b. Both CH_3Br and OH^- occur on the left side of the equation, so the rate law is

$$\text{Rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$$

14.83 Step 1 of the isomerization of cyclopropane, C_3H_6 , is slow, so the rate law for the overall reaction will be the rate law for this step, with $k_1 = k$, the overall rate constant:

$$\text{Rate} = k[\text{C}_3\text{H}_6]^2$$

14.84 Step 1 of the decomposition of NO_2Cl is slow, so the rate law for the overall reaction will be the rate law for this step, with $k_1 = k$, the overall rate constant:

$$\text{Rate} = k[\text{NO}_2\text{Cl}]$$

14.85 Step 2 of this reaction is slow, so the rate law for the overall reaction would appear to be the rate law for this step:

$$\text{Rate} = k_2[\text{I}]^2[\text{H}_2]$$

However, the rate law includes an intermediate, the I atom, and cannot be used unless the intermediate is eliminated. This can only be done using an equation for step 1. At equilibrium, you can write the following equality for step 1:

$$k_1[\text{I}_2] = k_{-1}[\text{I}]^2$$

Rearranging and then substituting for the $[\text{I}]^2$ term yields

$$[\text{I}]^2 = [\text{I}_2] \frac{k_1}{k_{-1}}$$

$$\text{Rate} = k_2(k_1/k_{-1})[\text{I}_2][\text{H}_2] = k[\text{I}_2][\text{H}_2] \quad (k = \text{the overall rate constant})$$

14.86 Step 2 of this reaction is slow, so the rate law for the overall reaction would appear to be the rate law for this step:

$$\text{Rate} = k_2[\text{O}_3][\text{O}]$$

However, the rate law includes an intermediate, the O atom, and cannot be used unless the intermediate is eliminated. This can only be done using an equation for step 1.

(continued)

At equilibrium, you can write the following equality for step 1:

$$k_1[\text{O}_3] = k_{-1}[\text{O}_2][\text{O}]$$

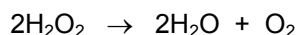
Rearranging and then substituting for the [O] term yields

$$[\text{O}] = \left[\frac{k_1}{k_{-1}} \right] \frac{[\text{O}_3]}{[\text{O}_2]}$$

$$\text{Rate} = k_2[\text{O}_3] \left[\frac{k_1}{k_{-1}} \right] \frac{[\text{O}_3]}{[\text{O}_2]}$$

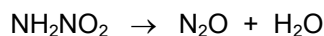
$$\text{Rate} = k_2 \left[\frac{k_1}{k_{-1}} \right] \frac{[\text{O}_3]^2}{[\text{O}_2]} = k \frac{[\text{O}_3]^2}{[\text{O}_2]} \quad (k = \text{overall rate constant})$$

- 14.87 The Br^- ion is the catalyst. It is consumed in the first step and regenerated in the second step. It speeds up the reaction by providing a pathway with a lower activation energy than that of a reaction pathway involving no Br^- . The overall reaction is obtained by adding the two steps together:



Bromide ion is added to the mixture to give the catalytic activity, and BrO^- is an intermediate.

- 14.88 The OH^- ion is the catalyst. It is consumed in the first step and regenerated in the second step. It speeds up the reaction by providing a pathway with a lower activation energy than that of a reaction pathway involving no OH^- ion. The overall reaction is obtained by adding the two steps together:



You could add NaOH to give the catalytic activity.

■ Solutions to General Problems

- 14.89 All rates of reaction are calculated by dividing the decrease in concentration by the difference in times; hence, only the setup for the first rate (after 10 minutes) is given below. This setup is

$$\begin{aligned}\text{Rate (10 min)} &= -\frac{(1.29 - 1.50) \times 10^{-2} \text{ M}}{(10 - 0) \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} \\ &= 3.5 \times 10^{-6} \text{ M/s}\end{aligned}$$

A summary of the times and rates is given in the table.

Time, min	Rate
10	$3.50 \times 10^{-6} = 3.5 \times 10^{-6} \text{ M/s}$
20	$3.17 \times 10^{-6} = 3.2 \times 10^{-6} \text{ M/s}$
30	$2.50 \times 10^{-6} = 2.5 \times 10^{-6} \text{ M/s}$

- 14.90 All rates of reaction are calculated by dividing the decrease in concentration by the difference in times; only the setup for the first rate after 1.0 min is given below:

$$\begin{aligned}\text{Rate (1.0 min)} &= -\frac{(0.1076 - 0.1103) \text{ M}}{(1.0 - 0) \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 4.50 \times 10^{-5} \\ &= 4.5 \times 10^{-5} \text{ M/s}\end{aligned}$$

A summary of the times and rates is given in the table.

Time, min	Rate
1.0	$4.50 \times 10^{-5} = 4.5 \times 10^{-5} \text{ M/s}$
2.0	$4.33 \times 10^{-5} = 4.3 \times 10^{-5} \text{ M/s}$
3.0	$4.00 \times 10^{-5} = 4.0 \times 10^{-5} \text{ M/s}$

- 14.91 The calculation of the average concentration and the division of the rate by the average concentration are the same for all three time intervals. Thus, only the setup for the first interval is given:

$$k_{10 \text{ min}} = \frac{\text{rate}}{\text{avg. conc.}} = \frac{3.50 \times 10^{-6} \text{ M/s}}{\left[\frac{(1.50 + 1.29) \times 10^{-2} \text{ M}}{2} \right]} = 2.508 \times 10^{-4} / \text{s}$$

(continued)

A summary of the times, rate constants, and average rate constant is given in the table.

Time	Rate	k
10 min	$3.50 \times 10^{-6} \text{ M/s}$	$2.508 \times 10^{-4}/\text{s}$
20 min	$3.17 \times 10^{-6} \text{ M/s}$	$2.652 \times 10^{-4}/\text{s}$
30 min	$2.50 \times 10^{-6} \text{ M/s}$	$2.439 \times 10^{-4}/\text{s}$
----	---- average k	$2.533 \times 10^{-4} = 2.5 \times 10^{-4}/\text{s}$

- 14.92 The calculation of the average concentration and the division of the rate by the average concentration are the same for all three time intervals. Thus, only the setup for the first interval is given:

$$K_{1.0 \text{ min}} = \frac{\text{rate}}{\text{avg. conc.}} = \frac{4.50 \times 10^{-5} \text{ M/s}}{\left(\frac{0.1103 \text{ M} + 0.1076 \text{ M}}{2} \right)^2} = 3.79 \times 10^{-3}/(\text{M}\cdot\text{s})$$

A summary of the times, rate constants, and average rate constant is given in the table.

Time	Rate	k
1.0 min	$4.50 \times 10^{-5} \text{ M/s}$	$3.79 \times 10^{-3}/(\text{M}\cdot\text{s})$
2.0 min	$4.33 \times 10^{-5} \text{ M/s}$	$3.83 \times 10^{-3}/(\text{M}\cdot\text{s})$
3.0 min	$4.00 \times 10^{-5} \text{ M/s}$	$3.71 \times 10^{-3}/(\text{M}\cdot\text{s})$
----	---- average k	$= 3.78 \times 10^{-3} = 3.8 \times 10^{-3}/(\text{M}\cdot\text{s})$

- 14.93 Use the first-order rate equation $k = 1.26 \times 10^{-4}/\text{s}$, the initial methyl acetate $[\text{MA}]_0 = 100$ percent, and $[\text{MA}]_t = (100\% - 65\%, \text{ or } 35\%)$.

$$t = -\frac{\ln \frac{35\%}{100\%}}{1.26 \times 10^{-4}/\text{s}} = 8.3319 \times 10^3 = 8.33 \times 10^3 \text{ s}$$

- 14.94 Use the first-order rate equation; substitute $k = 4.3 \times 10^{-5}/\text{s}$, the initial benzene diazonium chloride $[\text{BC}]_0 = 100$ percent, and $[\text{BC}]_t = (100\% - 75\%, \text{ or } 25\%)$.

$$t = \frac{\ln \frac{25\%}{100\%}}{3.3 \times 10^{-5}/\text{s}} = 4.20 \times 10^4 = 4.2 \times 10^4 \text{ s}$$

14.95 Use $k = 1.26 \times 10^{-4}/\text{s}$, and substitute into the $t_{1/2}$ equation:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.26 \times 10^{-4}/\text{s}} = 5.500 \times 10^3 = 5.50 \times 10^3 \text{ s (1.53 hr)}$$

14.96 Use $k = 4.3 \times 10^{-5}/\text{s}$, and substitute into the $t_{1/2}$ equation:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.3 \times 10^{-5}/\text{s}} = 1.61 \times 10^4 = 1.6 \times 10^4 \text{ s (4.5 hr)}$$

14.97 First, find the rate constant from the first-order rate equation, substituting the initial concentration of $[\text{comp.}]_0 = 0.0350 \text{ M}$, and the $[\text{comp.}]_t = 0.0250 \text{ M}$.

$$\ln \frac{0.0250 \text{ M}}{0.0350 \text{ M}} = -k (65 \text{ s})$$

Rearranging and solving for k gives

$$k = \frac{\left(\ln \frac{0.0250 \text{ M}}{0.0350 \text{ M}} \right)}{65 \text{ s}} = 5.17 \times 10^{-3}/\text{s}$$

Now, arrange the first-order rate equation to solve for $[\text{comp.}]_t$; substitute the above value of k , again using $[\text{comp.}]_0 = 0.0350 \text{ M}$.

$$\ln \frac{[\text{comp.}]_t}{0.0350 \text{ M}} = -(5.18 \times 10^{-3}/\text{s})(88 \text{ s}) = -0.4558$$

Taking the antilog of both sides gives

$$\frac{[\text{comp.}]_t}{0.0350 \text{ M}} = e^{-0.4558} = 0.6339$$

$$[\text{comp}]_t = 0.6339 \times [0.0350 \text{ M}]_0 = 0.0221 = 0.022 \text{ M}$$

- 14.98 First, find the rate constant from the rearranged first-order rate equation substituting the initial concentration of $[\text{comp.}]_o = 0.1180 \text{ M}$ and the $[\text{comp.}]_t = 0.0950 \text{ M}$. Use k to find the fraction.

$$k = \frac{\left(\ln \frac{0.0950 \text{ M}}{0.1180 \text{ M}} \right)}{5.2 \text{ min}} = 4.169 \times 10^{-2} / \text{min}$$

$$\ln \frac{[\text{comp.}]_t}{0.1180 \text{ M}} = -(4.169 \times 10^{-3} / \text{s})(7.1 \text{ min}) = -0.2960$$

Taking the antilogarithm of both sides yields

$$\frac{[\text{comp.}]_t}{0.1180 \text{ M}} = 0.7437 = 0.74 \text{ (fraction remaining)}$$

- 14.99 a. The rate constant for a second-order reaction is related to the half-life by

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

Using a half-life of $5.92 \times 10^{-2} \text{ s}$ and an initial A concentration of 0.50 mol/L , the rate constant is

$$k = \frac{1}{(5.92 \times 10^{-2} \text{ s})(0.50 \text{ mol/L})} = 33.78 = 34 \text{ L/(mol}\cdot\text{s)}$$

- b. The second-order integrated rate law is

$$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_o}$$

Using an initial concentration of C_4H_8 (A) of 0.010 M , after $3.6 \times 10^2 \text{ s}$, the concentration will be

$$\frac{1}{[\text{A}]_t} = 33.78 \text{ L/(mol}\cdot\text{s)}(3.6 \times 10^2 \text{ s}) + \frac{1}{0.010 \text{ mol/L}}$$

$$\frac{1}{[\text{A}]_t} = 12,162 \text{ L/mol} + 100.0 \text{ L/mol} = 12,262 \text{ L/mol}$$

$$[\text{A}]_t = \frac{1}{12,262 \text{ L/mol}} = 8.155 \times 10^{-5} = 8.2 \times 10^{-5} \text{ M}$$

14.100a. A plot of $1/[A]$ versus time is a straight line for a second-order reaction.

b. The second-order integrated rate law is

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

After 57 s, the concentration of A dropped 40 percent of its initial value, so $[A]_t = 0.60[A]_0$, or $(0.60)(0.50 \text{ M}) = 0.30 \text{ M}$. Using these values gives

$$\frac{1}{0.30 \text{ mol/L}} = k \times (57 \text{ s}) + \frac{1}{0.50 \text{ mol/L}}$$

$$k \times (57 \text{ s}) = \frac{1}{0.30 \text{ mol/L}} - \frac{1}{0.50 \text{ mol/L}} = 1.333 \text{ L/mol}$$

$$k = \frac{1.333 \text{ L/mol}}{57 \text{ s}} = 0.0233 = 0.023 \text{ L/(mol}\cdot\text{s)}$$

14.101 The second-order integrated rate law is

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

The starting concentration of NO_2 (A) is 0.050 M . Using a rate constant of $0.775 \text{ L/(mol}\cdot\text{s)}$, after $2.5 \times 10^2 \text{ s}$ the concentration of NO_2 will be

$$\frac{1}{[A]_t} = 0.775 \text{ L/(mol}\cdot\text{s)}(2.5 \times 10^2 \text{ s}) + \frac{1}{0.050 \text{ mol/L}}$$

$$\frac{1}{[A]_t} = 193 \text{ L/mol} + 20.0 \text{ L/mol} = 213. \text{ L/mol}$$

$$[A]_t = \frac{1}{213 \text{ L/mol}} = 4.67 \times 10^{-3} = 4.7 \times 10^{-3} \text{ M}$$

The half life is

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

Using a rate constant of $0.775 \text{ L/(mol}\cdot\text{s)}$ and an initial A concentration of 0.10 mol/L , the half-life is

$$t_{1/2} = \frac{1}{(0.775 \text{ L/(mol}\cdot\text{s)})(0.050 \text{ mol/L})} = 25.80 = 26 \text{ s}$$

14.102 The second-order integrated rate law is

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

The starting concentration is 0.10 M. Using a rate constant of $3.1 \times 10^{-2} \text{ L}/(\text{mol}\cdot\text{s})$, after $1.0 \times 10^2 \text{ s}$, the concentration will be

$$\frac{1}{[A]_t} = 3.1 \times 10^{-2} \text{ L}/(\text{mol}\cdot\text{s})(1.0 \times 10^2 \text{ s}) + \frac{1}{0.10 \text{ mol/L}}$$

$$\frac{1}{[A]_t} = 3.1 \text{ L/mol} + 10.0 \text{ L/mol} = 13.1 \text{ L/mol}$$

$$[A]_t = \frac{1}{13.1 \text{ L/mol}} = 0.0763 = 0.076 \text{ M}$$

The half life is

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

Using a rate constant of $3.1 \times 10^{-2} \text{ L}/(\text{mol}\cdot\text{s})$ and an initial concentration of 0.10 mol/L, the half-life is

$$t_{1/2} = \frac{1}{(3.1 \times 10^{-2} \text{ L}/(\text{mol}\cdot\text{s}))(0.10 \text{ mol/L})} = 322.5 = 3.2 \times 10^2 \text{ s}$$

14.103 The $\ln [\text{CH}_3\text{NNCH}_3]$ and time data for the plot are tabulated below.

t. min	$\ln [\text{CH}_3\text{NNCH}_3]$
0	-4.1997
10	-4.3505
20	-4.5098
30	-4.6564

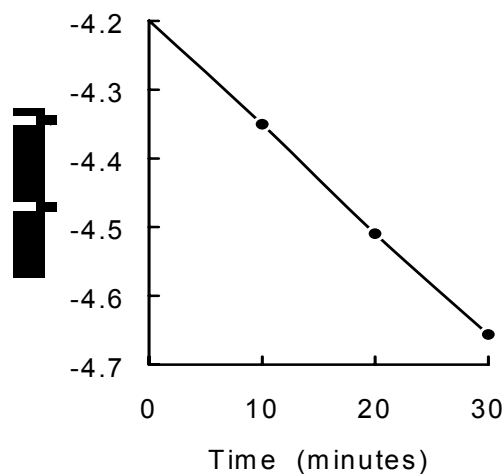
From the graph the slope, m , is calculated:

$$m = \frac{(-4.6564) - (-4.1997)}{(30 - 0) \text{ min}}$$

$$= -0.01522 / \text{min}$$

Because the slope also = $-k$, this gives

$$k = -(-0.01522/\text{min})(1 \text{ min}/60 \text{ s}) = 2.53 \times 10^{-4} = 2.5 \times 10^{-4}/\text{s}$$



14.104 The $\ln [\text{H}_2\text{O}_2]$ and time data for the plot are tabulated below.

t. min	$\ln [\text{H}_2\text{O}_2]$
0.0	-2.3025
5.0	-2.5207
10.0	-2.7364
15.0	-2.9584

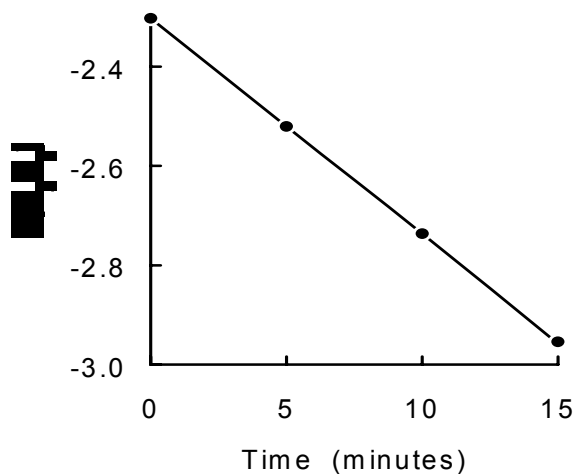
From the graph the slope, m , is calculated:

$$m = \frac{(-2.9584) - (-2.3025)}{(15.0 - 0) \text{ min}}$$

$$= -0.04372/\text{min}$$

Because the slope also = $-k$, this gives

$$k = -(-0.04372/\text{min})(1 \text{ min}/60 \text{ s}) = 7.287 \times 10^{-4} = 7.29 \times 10^{-4}/\text{s}$$



14.105 The rate law for a zero-order reaction is

$$[A] = -kt + [A]_0.$$

Using a rate constant of $3.7 \times 10^{-6} \text{ mol/(L}\cdot\text{s)}$ and an initial concentration of $5.0 \times 10^{-4} \text{ M}$, the time it would take for the concentration to drop to $5.0 \times 10^{-5} \text{ M}$ is

$$5.0 \times 10^{-5} \text{ M} = -8.1 \times 10^{-2} \text{ mol/(L}\cdot\text{s)} \times t + 5.0 \times 10^{-4} \text{ M}$$

$$t = \frac{(5.0 \times 10^{-4} \text{ M}) - (5.0 \times 10^{-5} \text{ M})}{3.7 \times 10^{-6} \text{ M/s}} = 121.6 = 1.2 \times 10^2 \text{ s}$$

The half-life for a zero-order reaction is

$$t_{1/2} = \frac{[A]_0}{2k} = \frac{5.0 \times 10^{-4} \text{ M}}{2(3.7 \times 10^{-6} \text{ M/s})} = 67.57 = 68 \text{ s}$$

14.106 The rate law for a zero-order reaction is

$$[A] = -kt + [A]_0.$$

If it takes $3.3 \times 10^2 \text{ s}$ for the initial concentration of B to go from 0.50 M to 0.20 M , the rate constant is

$$0.20 \text{ M} = -k \times 3.3 \times 10^2 \text{ s} + 0.50 \text{ M}$$

$$k = \frac{(0.50 \text{ M}) - (0.20 \text{ M})}{3.3 \times 10^2 \text{ s}} = 9.09 \times 10^{-4} = 9.1 \times 10^{-4} \text{ mol/(L}\cdot\text{s)}$$

The half-life for a zero-order reaction is

$$t_{1/2} = \frac{[A]_0}{2k} = \frac{0.50 \text{ M}}{2(9.09 \times 10^{-4} \text{ M/s})} = 275 = 2.8 \times 10^2 \text{ s}$$

14.107 Rearrange the two-temperature Arrhenius equation to solve for E_a in J, using $k_1 = 0.498 \text{ M/s}$ at $T_1 = 592 \text{ K}$ (319°C) and $k_2 = 1.81 \text{ M/s}$ at 627 K (354°C). Assume $(1/T_1 - 1/T_2)$ has three significant figures.

$$E_a = \frac{(8.31 \text{ J/mol}\cdot\text{K}) \ln\left(\frac{1.81}{0.498}\right)}{\left(\frac{1}{592 \text{ K}} - \frac{1}{627 \text{ K}}\right)} = 1.137 \times 10^5 \text{ J/mol} = 114 \text{ kJ/mol}$$

(continued)

To obtain A, rearrange the ln form of the one-temperature Arrhenius equation; substitute the value of E_a obtained above, and use $k_1 = 0.498 \text{ M/s}$ at $T_1 = 592 \text{ K}$.

$$\ln A = \ln 0.498 + \frac{1.137 \times 10^5 \text{ J/mol}}{8.31 \text{ J/(mol} \cdot \text{K)} \times 592 \text{ K}} = 22.420$$

$$A = 5.46 \times 10^9 = 5 \times 10^9$$

To obtain k at 420°C (693 K), also use the ln form of the one-temperature Arrhenius equation:

$$\ln k = 22.420 - \frac{1.137 \times 10^5 \text{ J/mol}}{8.31 \text{ J/(mol} \cdot \text{K)} \times 693 \text{ K}} = 2.671$$

$$k = e^{2.671} = 14.45 = 14 \text{ M/s}$$

- 14.108 Rearrange the two-temperature Arrhenius equation; solve for E_a using $k_1 = 8.7 \times 10^{-4} \text{ (M} \cdot \text{s)}$ at $T_1 = 303 \text{ K}$ (30°C) and $k_2 = 1.8 \times 10^{-3} \text{ (M} \cdot \text{s)}$ at 313 K (40°C).

$$E_a = \frac{8.31 \text{ J/(mol} \cdot \text{K)} \times \ln \left(\frac{1.8 \times 10^{-3} \text{ (M} \cdot \text{s)}}{8.7 \times 10^{-4} \text{ (M} \cdot \text{s)}} \right)}{\left(\frac{1}{303 \text{ K}} - \frac{1}{313 \text{ K}} \right)} = 5.729 \times 10^4 \text{ (57 kJ/mol)}$$

To obtain A, rearrange the ln form of the one-temperature Arrhenius equation; substitute the value of E_a obtained above and use $k_1 = 8.7 \times 10^{-4} \text{ (M} \cdot \text{s)}$ at $T_1 = 303 \text{ K}$.

$$\ln A = \ln[8.7 \times 10^{-4}] + \frac{5.729 \times 10^4 \text{ J/mol}}{8.31 \text{ J/(mol} \cdot \text{K)} \times 303 \text{ K}} = 15.70$$

$$A = e^{15.70} = 6.646 \times 10^6 \text{ (M} \cdot \text{s)}$$

To obtain k at 45°C (318 K), also use the ln form of the one-temperature Arrhenius equation:

$$\ln k = 15.70 - \frac{5.729 \times 10^4 \text{ J/mol}}{8.31 \text{ J/(mol} \cdot \text{K)} \times 318 \text{ K}} = -5.970$$

$$k = e^{-5.970} = 2.551 \times 10^{-3} = 3 \times 10^{-3} \text{ (M} \cdot \text{s)}$$

- 14.109 If the reaction occurs in one step, the coefficients of NO_2 and CO in this elementary reaction are each one, so the rate law should be

$$\text{Rate} = k[\text{NO}_2][\text{CO}]$$

- 14.110 If the reaction occurs in one step, the coefficients of CH_3Cl and OH^- in this elementary reaction are each one, so the rate law should be

$$\text{Rate} = k[\text{CH}_3\text{Cl}][\text{OH}^-]$$

- 14.111 The slow step determines the observed rate, so the overall rate constant, k , should be equal to the rate constant for the first step, and the rate law should be

$$\text{Rate} = k[\text{NO}_2\text{Br}]$$

- 14.112 The slow step determines the observed rate, so the overall rate constant, k , should be equal to the rate constant for the first step, and the rate law should be:

$$\text{Rate} = k[(\text{CH}_3)_3\text{CCl}]$$

- 14.113 The slow step determines the observed rate; assuming k_2 is the rate constant for the second step, the rate law would appear to be

$$\text{Rate} = k_2[\text{NH}_3][\text{HOCN}]$$

However, this rate law includes two intermediate substances that are neither reactants nor products. The rate law cannot be used unless both are eliminated. This can only be done using an equation from step 1. At equilibrium in step 1, you can write the following equality, assuming k_1 and k_{-1} are the rate constants for the forward and back reactions, respectively:

$$k_1[\text{NH}_4^+][\text{OCN}^-] = k_{-1}[\text{NH}_3][\text{HOCN}]$$

Rearranging and then substituting for the $[\text{NH}_3][\text{HOCN}]$ product gives

$$[\text{NH}_3][\text{HOCN}] = (k_1/k_{-1})[\text{NH}_4^+][\text{OCN}^-]$$

$$\text{Rate} = k_2(k_1/k_{-1})[\text{NH}_4^+][\text{OCN}^-] = k[\text{NH}_4^+][\text{OCN}^-] \quad (k = \text{overall rate constant})$$

- 14.114 The slow step determines the observed rate; assuming k_2 is the rate constant for the second step and using $[\text{HA}^+]$ for $[\text{CH}_3\text{C}(\text{OH}^+)\text{CH}_3]$, the rate law would appear to be

$$\text{Rate} = k_2[\text{HA}^+][\text{H}_2\text{O}]$$

However, this rate law includes the intermediates HA^+ and H_2O that are neither reactants nor products. The rate law cannot be used unless both are eliminated. This can only be done using an equation from step 1. At equilibrium in step 1, you can write the following equality, assuming k_1 and k_{-1} are the rate constants for the forward and back reactions, respectively:

$$k_1[\text{A}][\text{H}_3\text{O}^+] = k_{-1}[\text{HA}^+][\text{H}_2\text{O}]$$

Rearranging and then substituting for the $[\text{HA}^+][\text{H}_2\text{O}]$ product gives

$$\text{Rate} = k_2(k_1/k_{-1})[\text{A}][\text{H}_3\text{O}^+] = k[\text{A}][\text{H}_3\text{O}^+] \quad (k = \text{overall rate constant})$$

- 14.115a. The reaction is first order in O_2 because the rate doubled with a doubling of the oxygen concentration. The reaction is second order in NO because the rate increased by a factor of eight when both the NO and O_2 concentrations were doubled.

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

- b. The initial rate of the reaction for Experiment 4 can be determined by first calculating the value of the rate constant using Experiment 1 for the data.

$$0.80 \times 10^{-2} \text{ M/s} = k[4.5 \times 10^{-2} \text{ M}]^2[2.2 \times 10^{-2} \text{ M}]$$

Solving for the rate constant gives

$$k = 1.796 \times 10^2 \text{ M}^{-2}\text{s}^{-1}$$

Now, use the data in Experiment 4 and the rate constant to determine the initial rate of the reaction.

$$\text{Rate} = 1.796 \times 10^2 \text{ M}^{-2}\text{s}^{-1} [3.8 \times 10^{-1} \text{ M}]^2[4.6 \times 10^{-3} \text{ M}]$$

$$\text{Rate} = 0.119 = 0.12 \text{ mol/L}\cdot\text{s}$$

14.116a. From the information given, the rate law is

$$\text{Rate} = k[\text{CH}_3\text{Cl}][\text{H}_2\text{O}]^2$$

Using just the units for each term in the rate law will give the units for the rate constant.

$$\text{M/s} = k(\text{M})(\text{M})^2$$

Thus, the units for k must be

$$k = \text{M}^{-2}\text{s}^{-1}$$

b. Plugging into the rate equation gives

$$1.50 \text{ M/s} = k[0.40 \text{ M}][0.40 \text{ M}]^2$$

$$k = 23.43 = 23 \text{ M}^{-2}\text{s}^{-1}$$

14.117a.i) Rate will decrease because OH^- will react with H_3O^+ and lower its concentration.

ii) Rate will decrease because the dilution with water will decrease both the H_3O^+ and CH_3CSNH_2 concentrations.

b.i) The catalyst will provide another pathway, and k will increase because E_a will be smaller.

ii) The rate constant changes with temperature, and it will decrease with a decrease in temperature as fewer molecules will have enough energy to react.

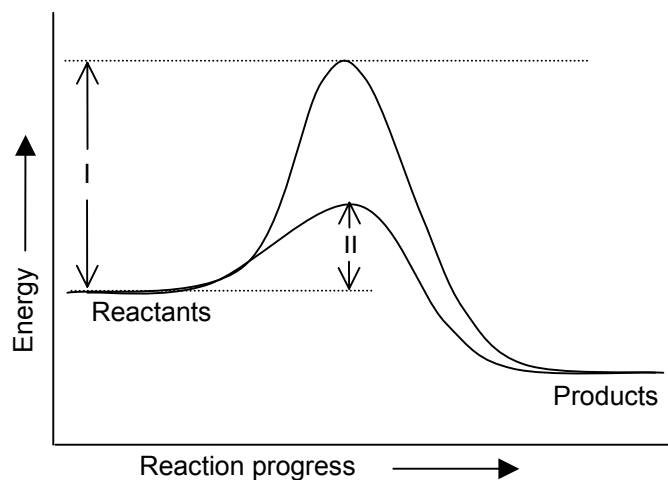
14.118a.i) The $[\text{H}_3\text{O}^+]$ is increased, so the rate will increase.

ii) The $[\text{H}_3\text{O}^+]$ and $[\text{CH}_3\text{COOCH}_3]$ concentrations will be decreased, so the rate of reaction will decrease.

b.i) The rate of reaction will increase, but the rate constant will remain the same.

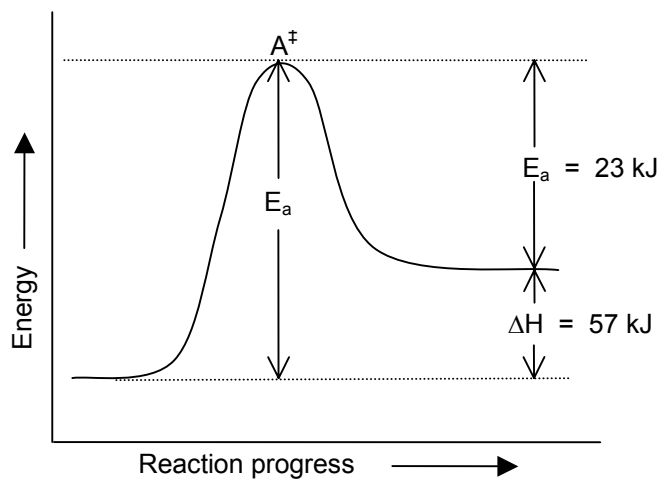
ii) The rate constant will increase as more molecules have enough energy to react.

14.119a. The diagram:



- b. In the diagram, I represents the activation energy for the uncatalyzed reaction, and II represents the activation energy for the catalyzed reaction. A catalyst provides another pathway for a chemical reaction and, with a lower activation energy, more molecules have enough energy to react, so the reaction will be faster.

14.120a. The diagram:



(continued)

b. $E_a = E_{ar} + \Delta H$

$$E_a = 23 + 57 = 80 \text{ kJ}$$

- c. The forward reaction will be more sensitive to a temperature change because it has the largest activation energy. When E_a is large, the ratio of the number of molecules that have enough energy to react is larger than when E_a is smaller.

- 14.121 a. The rate of a chemical reaction is the change in the concentration of a reactant or product with time. For a reactant,

$$-\Delta c/\Delta t \text{ or } -d[c]/dt.$$

- b. The rate changes because the concentration of the reactant has changed.

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

c. $\text{Rate} = k[A]^m[B]^n$

The rate will equal k when the reactants all have 1.00 M concentrations.

- 14.122. Factors which affect the rates of reactions:

- i) Concentrations of the reactants
- ii) Temperature
- iii) Catalysts

At higher concentrations, more molecules can undergo effective collisions and give more product per unit of time. The temperature affects the number of molecules that have enough energy to react. The higher the temperature, the larger the fraction of molecules that have enough energy to react. Catalysts provide another pathway for reaction that has a lower activation energy, so more molecules have the minimum energy to react.

The value of the rate constant for a particular reaction depends upon the temperature and the activation energy. The concentration of catalyst and the solvent, if the reaction occurs in solution, can affect E_a .

■ Solutions to Cumulative-Skills Problems

14.123 The balanced equation is:



Note that the moles of O_2 formed will be one-half that of the moles of N_2O_5 decomposed. Now use the integrated form of the first-order rate law to calculate the fraction of the 1.00 mol N_2O_5 decomposing in 20.0 hr, or 1200 min.

$$\ln \frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_0} = -kt = -(6.2 \times 10^{-4}/\text{min})(1200 \text{ min}) = -0.744$$

$$\frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_0} = e^{-0.744} = 0.4752$$

$$\text{Fraction of } \text{N}_2\text{O}_5 \text{ decomposed} = 1.000 - 0.4752 = 0.5248$$

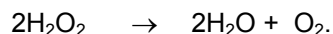
Since there is 1.00 mol of N_2O_5 present at the start, the moles of N_2O_5 decomposed is 0.5248 mol. Thus,

$$\text{Mol } \text{O}_2 \text{ formed} = (1 \text{ O}_2/2 \text{ N}_2\text{O}_5) \times 0.5248 \text{ mol } \text{N}_2\text{O}_5 = 0.26237 \text{ mol } \text{O}_2$$

Now, use the ideal gas law to calculate the volume of this number of moles of O_2 gas at 45 °C and 780 mmHg.

$$\begin{aligned} V &= \frac{nRT}{P} = \frac{(0.26237 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}))(318 \text{ K})}{(770/760) \text{ atm}} \\ &= 6.758 = 6.8 \text{ L} \end{aligned}$$

14.124 The balanced equation is:



Note that the moles of O_2 formed will be equal to the moles of H_2O_2 decomposed. Now, use the integrated form of the first-order rate law to calculate the fraction of the 1.00 mol H_2O_2 decomposing in 20.0 min or 1200 sec.

$$\ln \frac{[\text{H}_2\text{O}_2]_t}{[\text{H}_2\text{O}_2]_0} = -kt = -(7.40 \times 10^{-4}/\text{s})(1200 \text{ s}) = -0.8880$$

$$\frac{[\text{H}_2\text{O}_2]_t}{[\text{H}_2\text{O}_2]_0} = e^{-0.8880} = 0.41147$$

(continued)

$$\text{Fraction of H}_2\text{O}_2 \text{ decomposed} = 1.00 - 0.41147 = 0.58852$$

Since there is 1.00 mol of H_2O_2 present at the start, the moles of H_2O_2 decomposed are 0.58852 mol. Thus,

$$\text{Mol O}_2 \text{ formed} = (1 \text{ O}_2 / 1 \text{ H}_2\text{O}_2) \times 0.58852 \text{ mol H}_2\text{O}_2 = 0.58852 \text{ mol O}_2$$

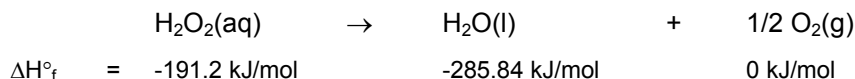
Now, use the ideal gas law to calculate the volume of this number of moles of O_2 gas at 25 °C and 740 mmHg.

$$\begin{aligned} V &= \frac{nRT}{P} = \frac{(0.58852 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}))(298 \text{ K})}{(740/760) \text{ atm}} \\ &= 14.7 = 15 \text{ L} \end{aligned}$$

14.125 Using the first-order rate law, the initial rate of decomposition is given by

$$\text{Rate} = k[\text{H}_2\text{O}_2] = (7.40 \times 10^{-4}/\text{s}) \times (1.50 \text{ M H}_2\text{O}_2) = 1.110 \times 10^{-3} \text{ M H}_2\text{O}_2/\text{s}$$

The heat liberated per second per mol of H_2O_2 can be found by first calculating the standard enthalpy of the decomposition of one mol of H_2O_2 :



For the reaction, the standard enthalpy change is

$$\Delta H^\circ = -285.84 \text{ kJ/mol} - (-191.2 \text{ kJ/mol}) = -94.64 \text{ kJ/mol H}_2\text{O}_2$$

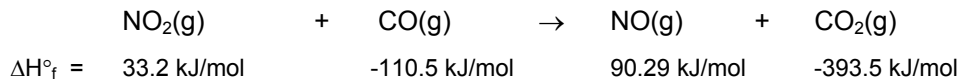
The heat liberated per second is:

$$\frac{94.64 \text{ kJ}}{\text{mol H}_2\text{O}_2} \times \frac{1.110 \times 10^{-3} \text{ mol H}_2\text{O}_2}{\text{L} \cdot \text{s}} \times 2.00 \text{ L} = 0.21010 = 0.210 \text{ kJ/s}$$

14.126 Using the second-order rate law, the initial rate of reaction of NO_2 is

$$\text{Rate} = k[\text{NO}_2]^2 = 0.515 \text{ L}/(\text{mol} \cdot \text{s}) \times [0.0250 \text{ M NO}_2]^2 = 3.218 \times 10^{-4} \text{ M NO}_2/\text{s}$$

The heat liberated per second per mol of NO_2 can be found by first calculating the standard enthalpy for the reaction of one mol of NO_2 :



(continued)

For the reaction, the change in standard enthalpy is

$$\Delta H^\circ = 90.29 - 393.5 - (33.2) - (-110.5) = -225.9 \text{ kJ/mol NO}_2$$

The heat liberated per second is

$$\frac{225.9 \text{ kJ}}{\text{mol NO}_2} \times \frac{3.218 \times 10^{-4} \text{ mol NO}_2}{\text{L} \cdot \text{s}} \times 3.50 \text{ L} = 0.2544 = 0.254 \text{ kJ/s}$$

14.127 Use the ideal gas law ($P/RT = n/V$) to calculate the mol/L of each gas:

$$[\text{O}_2] = \frac{(345/760) \text{ atm}}{0.082057 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 612 \text{ K}} = 0.009039 \text{ mol O}_2/\text{L}$$

$$[\text{NO}] = \frac{(155/760) \text{ atm}}{0.082057 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 612 \text{ K}} = 0.004061 \text{ mol NO/L}$$

The rate of decrease of NO is

$$\begin{aligned} \frac{1.16 \times 10^{-5} \text{ L}^2}{\text{mol}^2 \cdot \text{s}} \times \left(\frac{4.061 \times 10^{-3} \text{ mol}}{1 \text{ L}} \right)^2 \times \frac{9.039 \times 10^{-3} \text{ mol}}{1 \text{ L}} \\ = 1.729 \times 10^{-12} \text{ mol}/(\text{L} \cdot \text{s}) \end{aligned}$$

The rate of decrease in atm/s is found by multiplying by RT:

$$\frac{1.729 \times 10^{-12} \text{ mol}}{\text{L} \cdot \text{s}} \times \frac{0.082057 \text{ L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 612 \text{ K} = 8.682 \times 10^{-11} \text{ atm/s}$$

The rate of decrease in mmHg/s is

$$8.682 \times 10^{-11} \text{ atm/s} \times (760 \text{ mmHg/atm}) = 6.598 \times 10^{-8} = 6.60 \times 10^{-8} \text{ mmHg/s}$$

14.128 Use the ideal gas law ($P/RT = n/V$) to calculate the mol/L of each gas:

$$[\text{H}_2] = \frac{(324/760) \text{ atm}}{0.082057 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 1099 \text{ K}} = 0.004727 \text{ mol H}_2/\text{L}$$

$$[\text{NO}] = \frac{(144/760) \text{ atm}}{0.082057 \text{ L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 1099 \text{ K}} = 0.002101 \text{ mol NO/L}$$

(continued)

The rate of NO decrease is twice the rate of H₂ decrease, so

$$2 \times \frac{1.10 \times 10^{-7} \text{ L}^2}{\text{mol}^2 \cdot \text{s}} \times \left(\frac{2.101 \times 10^{-3} \text{ mol}}{1 \text{ L}} \right)^2 \times \frac{4.727 \times 10^{-3} \text{ mol}}{1 \text{ L}}$$

$$= 4.5905 \times 10^{-15} \text{ mol}/(\text{L} \cdot \text{s})$$

The rate of decrease in atm/s is found by multiplying by RT:

$$\frac{4.5905 \times 10^{-15} \text{ mol}}{\text{L} \cdot \text{s}} \times \frac{0.082057 \text{ L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 1099 \text{ K} = 4.139 \times 10^{-13} \text{ atm/s}$$

The rate of decrease in mmHg/s is

$$4.139 \times 10^{-13} \text{ atm/s} \times (760 \text{ mmHg/atm}) = 3.146 \times 10^{-10} = 3.15 \times 10^{-10} \text{ mmHg/s}$$

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