Chapter 18

Kinetics—The Course of Chemical Reactions

We move from static structure and equilibrium to the time-dependent dynamics of chemical reaction: kinetics and mechanism. The accompanying exercises offer a chance both to work with the key equations and to strengthen the conceptual links between macroscopic rate laws and microscopic pathways. Large blocks of problems are devoted to first-order kinetics, second-order kinetics, the Arrhenius law, and assorted mechanistic considerations (including the principle of detailed balance).

The first 16 exercises provide a mostly qualitative recapitulation of the entire chapter, treating such topics as activation (Sections 18-2, 18-4, and 18-5), rates and rate laws (Section 18-3), elementary reactions (Section 18-6), and the difference between kinetic transformation and thermodynamic equilibrium (Section 18-5). Quantitative issues are addressed in earnest beginning with Exercise 17.

1. A transition state is an unstable species. It exists at a local maximum of potential energy. An intermediate is a stable species, although often short-lived. It exists at a local minimum of potential energy (but at a level still higher than the final products). See Figure 18.1 (overleaf).

2. The energy of reaction, ΔE_r, pertains to the fixed thermodynamic difference between reactants and products. The activation energy, E_a, pertains to the difference between the reactants (or some other stable species) and a particular transition state. Its value depends on the specific mechanism of reaction. See Figure 18.2.
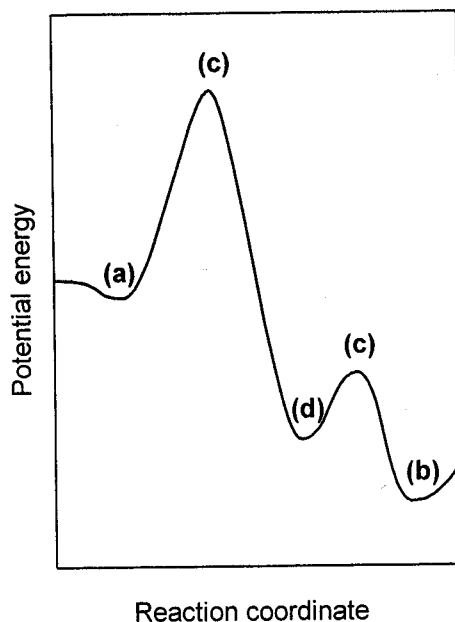
FIGURE 18.1 Labeled energy-of-reaction diagram for the hypothetical process considered in Exercises 1 and 2. (a) Reactants. (b) Products. (c) Transition states. (d) Intermediates. See also Figures 18-8, 18-11, and 18-13 in *PoC*.
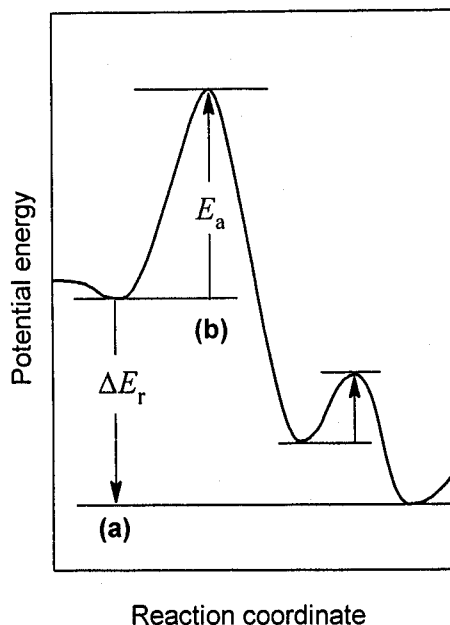

FIGURE 18.2 Energy diagram for the hypothetical process considered in Exercises 1 and 2. (a) Reaction energy, ΔE_r. The transformation is exothermic, yielding products lower in energy than the reactants. (b) Activation energy E_a for the slow step, equal in this system to the difference between the reactants and the first transition state (the tall peak on the left). In the second step, the difference between the intermediates and the corresponding transition state (the small peak on the right) is not as great. See also Figures 18-8, 18-11, and 18-13 in *PoC*.

3. We are given the standard change in free energy for two hypothetical reactions:

$$\Delta G°(1) = -100 \text{ kJ mol}^{-1}$$

$$\Delta G°(2) = -1000 \text{ kJ mol}^{-1}$$

These values correspond to fixed thermodynamic differences between reactants and products, independent of any particular route of reaction.

(a) $\Delta G°$ determines the value of K, the equilibrium constant, through the relationship

$$\Delta G° = -RT \ln K \qquad\qquad K = \exp\left(-\frac{\Delta G°}{RT}\right)$$

Reaction 2 has the more negative value of $\Delta G°$ and hence the larger equilibrium constant. It will produce the greater proportion of products at equilibrium. See Section 14-8 in *PoC*.

(b) We have insufficient information to determine the rate of reaction. To do so, we need to know the difference in energy between reactants and a transition state—not between reactants and the final products.

4. We continue with the processes of Exercise 3, this time taking into account the activation energies as well:

$$\Delta G°(1) = -100 \text{ kJ mol}^{-1} \qquad\qquad E_a(1) = 10 \text{ kJ mol}^{-1}$$

$$\Delta G°(2) = -1000 \text{ kJ mol}^{-1} \qquad\qquad E_a(2) = 50 \text{ kJ mol}^{-1}$$

(a) The reasoning is the same as before: Reaction 2 has the more negative value of $\Delta G°$ and thus the larger equilibrium constant. It yields the greater proportion of products at equilibrium.

      Note that $\Delta G°$, a fixed thermodynamic separation between reactants and products, remains the same regardless of kinetic pathway. The *rate* of reaction (as determined by the activation energy) has no effect on the composition of the equilibrium state.
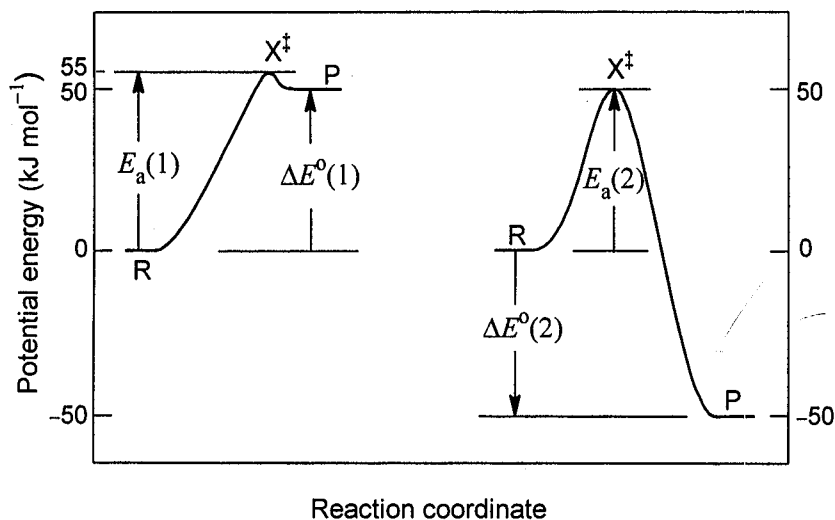
(b) Reaction 1 has the smaller activation energy and therefore the higher rate. It comes to equilibrium faster than reaction 2.

5. Again, two hypothetical reactions:

$$\Delta E°(1) = 50 \text{ kJ mol}^{-1} \qquad\qquad E_a(1) = 55 \text{ kJ mol}^{-1}$$

$$\Delta E°(2) = -50 \text{ kJ mol}^{-1} \qquad\qquad E_a(2) = 50 \text{ kJ mol}^{-1}$$

(a) The symbols R, $X^{\ddagger}$, and P denote reactants, transition state, and products, respectively. Reaction 1 is represented on the left of the diagram. Reaction 2 is represented on the right:

Reaction coordinate

Note that all differences in energy are relative, not absolute. The zero of the energy scale is arbitrary.

(b) Reaction 2 has the smaller activation energy. It runs faster than reaction 1 at a given temperature.

Realize, though, that the kinetic advantage of reaction 2 does not derive from its exothermicity relative to reaction 1. Rate of reaction is determined by the *activation energy*, not by the net difference in energy between reactants and products.

(c) The endothermic process (reaction 1) will yield more product at a higher temperature—once equilibrium is attained. According to Le Châtelier's principle, heat functions as a reactant in an endothermic reaction. A nonequilibrium system at high temperature, ridding itself of excess heat, moves to the right and comes to equilibrium with a larger proportion of products. Its equilibrium constant increases with temperature. See Section 12-6 as well as Examples 12-15 and 15-9 in *PoC*.

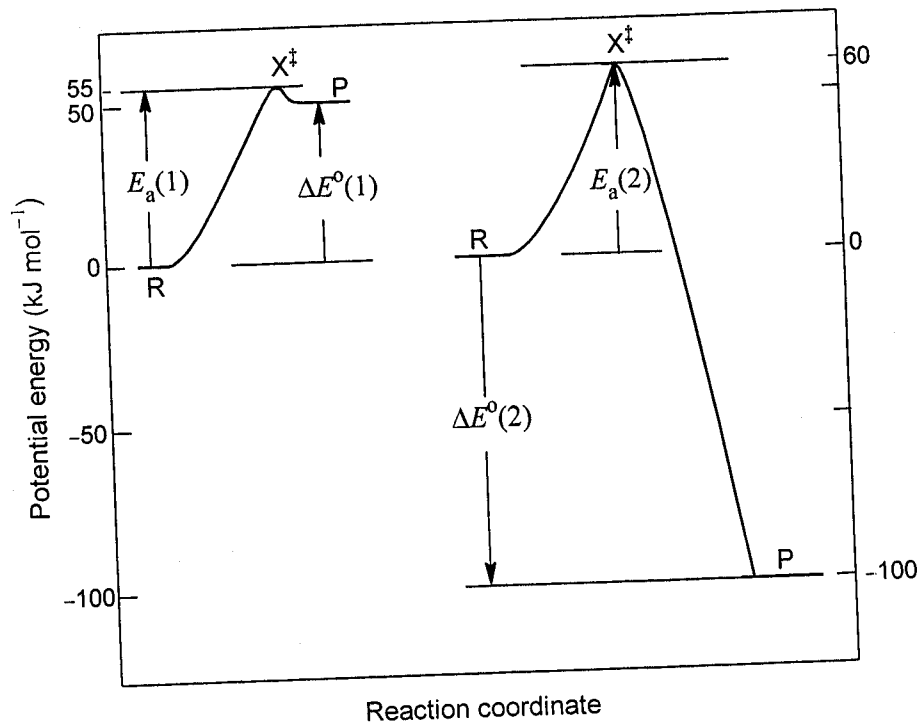**6.** Similar to the preceding exercise, but with a new set of energy parameters for reaction 2:

$$\Delta E^{\circ}(1) = 50 \text{ kJ mol}^{-1} \qquad E_a(1) = 55 \text{ kJ mol}^{-1}$$

$$\Delta E^{\circ}(2) = -100 \text{ kJ mol}^{-1} \qquad E_a(2) = 60 \text{ kJ mol}^{-1}$$

(a) The conventions are the same as in Exercise 5: R, X‡, and P denote reactants, transition state, and products, respectively. Reaction 1 is represented on the left; reaction 2 is represented on the right:

Reaction coordinate

(b) Reaction 1, with the lower activation energy, runs faster than reaction 2 at any given temperature. It makes no difference that reaction 1 is endothermic and reaction 2 is exothermic.

(c) The comparison is the same as in Exercise 5(c): Reaction 1, the endothermic process, yields more product at a higher temperature. The transformation is driven to the right, as predicted by Le Châtelier's principle. See the comments in the preceding exercise.

7. Start with the Arrhenius equation for the rate constant:

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

The ratio of k at two temperatures is independent of A,

$$\frac{k_2}{k_1} = \frac{A \exp\left(-\dfrac{E_a}{RT_2}\right)}{A \exp\left(-\dfrac{E_a}{RT_1}\right)} = \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

and thus we have an expression for k_2 in terms of k_1, E_a, T_1, and T_2:

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

Given $k_1 = 1$ when $T_1 = 273.15$ K (0°C), we then calculate a numerical value for k_2:

$$k_2 = \exp\left[-\frac{E_a}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}\left(\frac{1}{T_2} - \frac{1}{273.15 \text{ K}}\right)\right]$$

See pages 656–659 and Example 18-7 in *PoC*, as well as Exercises 36 through 43. One sample calculation (at 10°C, with $E_a = 1$ kJ mol^{-1}) should suffice:

$$T_2 = 283.15 \text{ K} \qquad E_a = 1000 \text{ J mol}^{-1}$$

$$k_2 = \exp\left[-\frac{E_a}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}\left(\frac{1}{T_2} - \frac{1}{273.15 \text{ K}}\right)\right]$$

$$= \exp\left[-\frac{1000 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}\left(\frac{1}{283.15 \text{ K}} - \frac{1}{273.15 \text{ K}}\right)\right]$$

$$= \exp(0.015551)$$

$$= 1.016$$

The others are all handled in the same way. Four-digit answers are given below.

RATE CONSTANT (arbitrary units)

|	E_a (kJ mol^{-1})	0°C	10°C	20°C	30°C	100°C
(a)	1	1.000	1.016	1.030	1.045	1.125
(b)	10	1.000	1.168	1.350	1.546	3.254
(c)	50	1.000	2.176	4.491	8.835	365.0
(d)	100	1.000	4.735	20.17	78.05	1.332×10^5

8. See Figures 18-12(a) and 3-2 in *PoC*.

(a) The catalyzed reaction, rendered in color both in the present exercise and in Figure 18-12(a), has the lower activation energy. Its transition state lies closer to the reactants.

(b) The difference in free energy between reactants and products is the same for both reactions. Catalysis does not change the yield of products at equilibrium.

9. Everyday experience enables us to make some rough estimates.

(a) The time needed for complete evaporation depends on volume and temperature. A few drops of water may evaporate within seconds on a hot day. A somewhat larger volume may take minutes or more.

(b) An extraordinarily slow process, the conversion of graphite into diamond occurs naturally on a geological time scale. Synthetic diamonds, however, can be manufactured in a matter of hours.

(c) The dissolution of sodium chloride in water requires only a few seconds.

10. The standard free energy of reaction and corresponding equilibrium constant are calculated as described in Chapter 14 of *PoC* (see Sections 14-7 and 14-8, together with Examples 14-7 and 14-8). For processes at 25°C, we may use the free energies of formation collected in Table C-16 of Appendix C (pages A85–A92):

$$aA + bB \rightarrow cC + dD$$
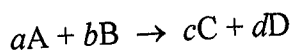
$$\Delta G° = c \, \Delta G_f°(C) + d \, \Delta G_f°(D) - a \, \Delta G_f°(A) - b \, \Delta G_f°(B)$$

$$K = \exp\left(-\frac{\Delta G°}{RT}\right)$$

See Section 13-4 and Examples 13-9 through 13-11 for a more detailed treatment of Hess's law, which justifies the summation of state functions such as enthalpy, entropy, and free energy.

(a) The evaporation of water at 25°C is nonspontaneous. The change in standard free energy is positive, and consequently the equilibrium constant is less than 1.

Free energy:

$$H_2O(\ell) \rightarrow H_2O(g)$$
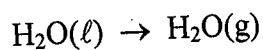
$$\Delta G° = \Delta G_f°\left[H_2O(g)\right] - \Delta G_f°\left[H_2O(\ell)\right]$$

$$= \left(-228.6 \text{ kJ mol}^{-1}\right) - \left(-237.2 \text{ kJ mol}^{-1}\right)$$

$$= 8.6 \text{ kJ mol}^{-1} \quad (\text{nonspontaneous, } \Delta G° > 0)$$
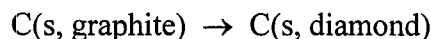
Equilibrium constant:

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left[-\frac{8.6 \times 10^3 \text{ J mol}^{-1}}{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)\left(298.15 \text{ K}\right)}\right] = 0.031$$

Both ΔG° and K are derived from fixed thermodynamic differences between reactants and products. They provide no insight into the kinetics of a process, which depends on activation energy and mechanism.

(b) The nonspontaneous conversion of graphite into diamond requires a small, but positive, change in standard free energy.
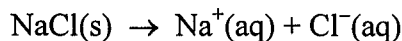
Free energy:

$$C(s, \text{ graphite}) \rightarrow C(s, \text{ diamond})$$

$$\Delta G^\circ = \Delta G_f^\circ \left[C(s, \text{ diamond})\right] - \Delta G_f^\circ \left[C(s, \text{ graphite})\right]$$

$$= \left(2.9 \text{ kJ mol}^{-1}\right) - \left(0 \text{ kJ mol}^{-1}\right)$$

$$= 2.9 \text{ kJ mol}^{-1} \quad (\text{nonspontaneous, } \Delta G^\circ > 0)$$

Equilibrium constant:

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left[-\frac{2.9 \times 10^3 \text{ J mol}^{-1}}{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)\left(298.15 \text{ K}\right)}\right] = 0.31$$

(c) The dissolution of NaCl is spontaneous at 25°C. The products (aqueous Na^+ and Cl^-) stand lower in free energy than the reactant (solid NaCl):

Free energy:

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$

$$\Delta G^\circ = \Delta G_f^\circ \left[Na^+(aq)\right] + \Delta G_f^\circ \left[Cl^-(aq)\right] - \Delta G_f^\circ \left[NaCl(s)\right]$$

$$= \left(-261.9 \text{ kJ mol}^{-1}\right) + \left(-131.2 \text{ kJ mol}^{-1}\right) - \left(-384.2 \text{ kJ mol}^{-1}\right)$$

$$= -8.9 \text{ kJ mol}^{-1} \quad (\text{spontaneous, } \Delta G^\circ < 0)$$

Equilibrium constant:

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left[-\frac{\left(-8.9 \times 10^3 \text{ J mol}^{-1}\right)}{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)\left(298.15 \text{ K}\right)}\right] = 36$$

11. We are told only that a certain hypothetical process is first order in A, first order in B, and second order in C:

$$A + 2B + C \rightarrow D + 3E$$

(a) The rate law is implicit in the statement of the problem:

first order in B

first order in A   second order in C

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

See pages 650–653 in *PoC*.

(b) A reaction rate has the units $M \text{ s}^{-1}$, where $M = \text{mol L}^{-1}$. Each factor of concentration in the rate law has the units M, and thus with four powers of concentration the units of k (the rate constant) are $M^{-3} \text{ s}^{-1}$:

$$k = \frac{\text{rate}}{[A][B][C]^2} \sim \frac{M \text{ s}^{-1}}{M \times M \times M^2} \sim M^{-3} \text{ s}^{-1}$$

(c) Given the rate, rate law, and concentrations, we calculate the numerical value of the rate constant k:

$$k = \frac{\text{rate}}{[A][B][C]^2} = \frac{1 \, M \text{ s}^{-1}}{\left(1 \, M\right)\left(1 \, M\right)\left(1 \, M\right)^2} = 1 \, M^{-3} \text{ s}^{-1}$$

(d) Substitute $k = 1 \, M^{-3} \text{ s}^{-1}$ and $[A] = [B] = [C] = 2 \, M$ into the rate equation:

$$\text{Rate} = k[A][B][C]^2 = (1 \, M^{-3} \text{ s}^{-1})(2 \, M)(2 \, M)(2 \, M)^2 = 16 \, M \text{ s}^{-1}$$

(e) The process does not occur in a single, elementary step. If it did, the exponents in the rate expression would match the stoichiometric coefficients in the chemical equation. We would have
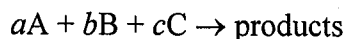
$$\text{Rate} = k[A][B]^2[C]$$

rather than

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

The result is not surprising, of course, since a simultaneous collision of four molecules is unlikely almost to the point of impossibility.

12. If a reaction proceeds in a single step, then its initial rate law matches the stoichiometry of the reactants:

$$a\text{A} + b\text{B} + c\text{C} \rightarrow \text{products}$$

$$\text{Rate} = k[A]^a[B]^b[C]^c$$

$$\text{Order} = a + b + c$$

See pages 675–678 and Examples 18-10 and 18-11 in *PoC*.

	MOLECULARITY	CHEMICAL EQUATION	RATE LAW	ORDER
(a)	bimolecular	$A + B \rightarrow 2C + D + E$	$k[A][B]$	2
(b)	unimolecular	$A \rightarrow 3B + C$	$k[A]$	1
(c)	bimolecular	$2A \rightarrow B$	$k[A]^2$	2
(d)	termolecular	$A + B + C \rightarrow D$	$k[A][B][C]$	3
(e)	termolecular	$A + 2B \rightarrow C$	$k[A][B]^2$	3

13. The reasoning is the same as in the preceding exercise (and is valid only if the reaction occurs in a single, elementary step):

$$\text{Rate} = k[A]^a[B]^b[C]^c$$

$$a\text{A} + b\text{B} + c\text{C} \rightarrow \text{products}$$

$$\text{Order} = a + b + c$$

The termolecular reactions, (d) and (e), are least likely to occur. See the table that follows.

	RATE LAW	CHEMICAL EQUATION	ORDER	MOLECULARITY
(a)	$k[A]$	$A \rightarrow$ products	1	unimolecular
(b)	$k[A]^2$	$2A \rightarrow$ products	2	bimolecular
(c)	$k[A][B]$	$A + B \rightarrow$ products	2	bimolecular
(d)	$k[A]^2[B]$	$2A + B \rightarrow$ products	3	termolecular
(e)	$k[A][B][C]$	$A + B + C \rightarrow$ products	3	termolecular

14. Maybe, maybe not. It is *possible* that the stated expression represents the rate law, but we cannot make any determination unless we know the mechanism. The initial rate law matches the stoichiometry of the reactants only if a transformation occurs in a single step. An experimental investigation must be undertaken to resolve the question.

15. False, for the same reasons given in the preceding exercise. Although each reaction has the same overall stoichiometry, the rate laws need not be the same—whether of the form $k[A]^2[B]$ or any other. The rate expressions depend on the activation energy and also the microscopic mechanism of reaction, a *sequence* of events not evident in the balanced equation.

16. Generalizing the arguments made in the text (pages 648–649), we define the average rate of any process as the change in some quantity $f(t)$ over a specified interval of time:

$$\text{Rate} = \frac{\Delta f}{\Delta t} = \frac{f(t_2) - f(t_1)}{t_2 - t_1}$$

(a) $\text{Rate} = \dfrac{\Delta(\text{distance})}{\Delta(\text{time})} = \dfrac{100 \text{ m}}{10.1 \text{ s}} = 9.90 \text{ m s}^{-1}$

(b) $\text{Rate} = \dfrac{\Delta(\text{leaves})}{\Delta(\text{time})} = \dfrac{1634 \text{ leaves}}{2 \text{ wk}} \times \left(\dfrac{1 \text{ wk}}{7 \text{ d}} \times \dfrac{1 \text{ d}}{86,400 \text{ s}} \right) = 0.001351 \text{ leaves s}^{-1}$

(c) $\text{Rate} = \dfrac{\Delta(\text{babies})}{\Delta(\text{time})} = \dfrac{2,993,00 \text{ babies}}{\text{y}} \times \left(\dfrac{1 \text{ y}}{365 \text{ d}} \times \dfrac{1 \text{ d}}{86,400 \text{ s}} \right) = 0.09491 \text{ babies s}^{-1}$

(d) $\text{Rate} = \dfrac{\Delta[\text{NOCl}]}{\Delta(\text{time})} = \dfrac{0.40 \text{ } M}{2.0 \text{ min}} \times \dfrac{1 \text{ min}}{60 \text{ s}} = 0.0033 \text{ } M \text{ s}^{-1}$

These rates are *average* quantities, computed over relatively long intervals of time. If we wish to predict a change over a short interval (between, say, midnight and one second after midnight), then we must record the data as a more closely spaced series in time.

Exercises 17 through 20 pertain to the formulation of macroscopic rate laws in general, as introduced on pages 647–653 and elaborated further in Examples 18-1 through 18-3.

**17.** The rate of reaction for the generic process

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$$
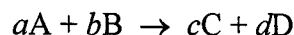
is defined equivalently as

$$\text{Rate} = -\frac{1}{a}\left(\frac{\Delta[\text{A}]}{\Delta t}\right) = -\frac{1}{b}\left(\frac{\Delta[\text{B}]}{\Delta t}\right) = \frac{1}{c}\left(\frac{\Delta[\text{C}]}{\Delta t}\right) = \frac{1}{d}\left(\frac{\Delta[\text{D}]}{\Delta t}\right)$$

By adopting this expression, we assume that the macroscopic rate is unaffected by the presence of intermediate species. If the assumption is valid, then reactants disappear and products appear at the same rate. See pages 648–650 and Examples 18-1 and 18-2 in *PoC*.

(a) Under the conditions as stated, chlorine gas disappears with an initial rate of $0.0030\ M\,\text{s}^{-1}$ when reacting with nitric oxide:

$$2\text{NO(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{NOCl(g)}$$
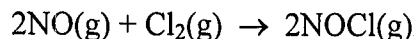
$$\frac{\Delta[\text{Cl}_2]}{\Delta t} = -0.0030\ M\ \text{s}^{-1}$$

The concentration of NO, another reactant, is stoichiometrically coupled to the concentration of Cl_2:

$$-\frac{1}{2}\left(\frac{\Delta[\text{NO}]}{\Delta t}\right) = -\frac{1}{1}\left(\frac{\Delta[\text{Cl}_2]}{\Delta t}\right) = -\left(-0.0030\ M\ \text{s}^{-1}\right)$$

$$\frac{\Delta[\text{NO}]}{\Delta t} = 2 \times \left(\frac{\Delta[\text{Cl}_2]}{\Delta t}\right) = 2 \times \left(-0.0030\ M\ \text{s}^{-1}\right) = -0.0060\ M\ \text{s}^{-1}$$

A minus sign attached to any value $\Delta[\text{R}]/\Delta t$ indicates that the reactant R is being consumed. The stoichiometric scaling factors ensure that the rate for each species is consistent with an overall common rate of magnitude $0.0030\ M\,\text{s}^{-1}$:

$$\text{Rate} = -\frac{1}{2}\left(\frac{\Delta[\text{NO}]}{\Delta t}\right) = -\frac{1}{2}\left(-0.0060\ M\ \text{s}^{-1}\right) = 0.0030\ M\ \text{s}^{-1}$$

$$\text{Rate} = -\frac{1}{1}\left(\frac{\Delta[\text{Cl}_2]}{\Delta t}\right) = -\left(-0.0030\ M\ \text{s}^{-1}\right) = 0.0030\ M\ \text{s}^{-1}$$

(b) The concentration of NOCl, a product, increases with time. It varies in the same way as the concentration of NO, but with a positive sign to reflect the appearance rather than disappearance of the species:

$$\frac{1}{2}\left(\frac{\Delta[NOCl]}{\Delta t}\right) = -\frac{1}{2}\left(\frac{\Delta[NO]}{\Delta t}\right)$$

$$\frac{\Delta[NOCl]}{\Delta t} = -\frac{\Delta[NO]}{\Delta t} = -\left(-0.0060\ M\ s^{-1}\right) = 0.0060\ M\ s^{-1}$$

Again, the value is consistent with an overall rate of reaction equal to $0.0030\ M\ s^{-1}$:

$$Rate = \frac{1}{2}\left(\frac{\Delta[NOCl]}{\Delta t}\right) = \frac{1}{2}\left(0.0060\ M\ s^{-1}\right) = 0.0030\ M\ s^{-1}$$

(c) We assume that the relationship between concentration and time is linear over the interval considered ($t = 5.0$ s):

$$[NOCl]_t = [NOCl]_0 + \frac{\Delta[NOCl]}{\Delta t}\Delta t$$

$$= 0 + \left(0.0060\ M\ s^{-1}\right)\left(5.0\ s\right)$$

$$= 0.030\ M$$

18. Substitute the stated values of $[NO]_0$ and $[Cl_2]_0$ into the experimentally determined rate law:

$$Rate = k[NO]^2[Cl_2] \qquad k(263\ K) = 3.0\ M^{-2}\ s^{-1}$$

For example, the initial rate (at $t = 0$) proves to be $3.8 \times 10^{-4}\ M\ s^{-1}$ under the conditions specified in (a):

$$[NO]_0 = 0.050\ M \qquad [Cl_2]_0 = 0.050\ M$$

$$Initial\ rate = k[NO]_0^2[Cl_2]_0$$

$$= \left(3.0\ M^{-2}\ s^{-1}\right)\left(0.050\ M\right)^2\left(0.050\ M\right) = 3.75 \times 10^{-4}\ M\ s^{-1}$$

$$= 3.8 \times 10^{-4}\ M\ s^{-1} \quad (2\ sig\ fig)$$

The remaining calculations are all done in the same way.

	$[NO]_0$ (M)	$[Cl_2]_0$ (M)	Rate ($M\,s^{-1}$)
(a)	0.050	0.050	3.8×10^{-4}
(b)	0.050	0.100	7.5×10^{-4}
(c)	0.100	0.050	1.5×10^{-3}
(d)	0.100	0.100	3.0×10^{-3}

19. Inspecting the data, we make the following observations:

1. The rate doubles when $[O_2]_0$ is doubled and $[NO]_0$ is held constant (trial 2 versus trial 1):

$$\frac{1.42 \times 10^{-2}\ M\,s^{-1}}{7.11 \times 10^{-3}\ M\,s^{-1}} = 2.00$$

2. The rate triples when $[O_2]_0$ is tripled and $[NO]_0$ is held constant (trial 3 versus trial 1):

$$\frac{2.13 \times 10^{-2}\ M\,s^{-1}}{7.11 \times 10^{-3}\ M\,s^{-1}} = 3.00$$

3. The rate quadruples when $[NO]_0$ is doubled and $[O_2]_0$ is held constant (trial 4 versus trial 1):

$$\frac{2.84 \times 10^{-2}\ M\,s^{-1}}{7.11 \times 10^{-3}\ M\,s^{-1}} = 3.99$$

4. The rate increases ninefold when $[NO]_0$ is tripled and $[O_2]_0$ is held constant (trial 5 versus trial 1):

$$\frac{6.40 \times 10^{-2}\ M\,s^{-1}}{7.11 \times 10^{-3}\ M\,s^{-1}} = 9.00$$

From observations 1 and 2 we find a first-order dependence on $[O_2]$,

$$\text{Rate} \propto [O_2]$$

and from observations 3 and 4 we find a second-order dependence on $[NO]$:

$$\text{Rate} \propto [NO]^2$$

Overall, the reaction is third order:

$$\text{Rate} = k[NO]^2[O_2]$$

To establish the value of k, we substitute the rate corresponding to each pair of initial concentrations. The procedure is demonstrated below for trial 1:

$$k = \frac{\text{rate}}{[NO]^2[O_2]}$$

$$= \frac{7.11 \times 10^{-3} \ M \ s^{-1}}{\left(1.00 \times 10^{-2} \ M\right)^2 \left(1.00 \times 10^{-2} \ M\right)}$$

$$= 7.11 \times 10^3 \ M^{-2} \ s^{-1} \quad \text{(trial 1)}$$

Averaging over the five trials yields $k = 7.10 \times 10^3 \ M^{-2} \ s^{-1}$.

20. Carry over the rate constant derived in the preceding exercise,

$$k = 7.10 \times 10^3 \ M^{-2} \ s^{-1}$$

and insert the specified initial concentrations into the rate law:

$$\text{Rate} = k[NO]^2[O_2]$$

Trial 1, for example, shows an initial rate of $8.9 \times 10^{-4} \ M \, s^{-1}$:

$$[NO]_0 = 0.0050 \ M \qquad [O_2]_0 = 0.0050 \ M$$

$$\text{Initial rate} = k[NO]_0^2[O_2]_0$$

$$= \left(7.10 \times 10^3 \ M^{-2} \ s^{-1}\right)\left(0.0050 \ M\right)^2 \left(0.0050 \ M\right)$$

$$= 8.9 \times 10^{-4} \ M \, s^{-1} \quad \text{(trial 1)}$$

The procedure is the same for all four trials:

TRIAL	$[NO]_0$ (M)	$[O_2]_0$ (M)	RATE ($M \, s^{-1}$)
1	0.0050	0.0050	8.9×10^{-4}
2	0.0050	0.0100	1.8×10^{-3}
3	0.0200	0.0300	8.52×10^{-2}
4	0.0300	0.0300	1.92×10^{-1}

First-order reactions are covered on pages 653–656 of PoC *and explored further in Examples 18-4 and 18-5.*

21. The rate approximately doubles when the initial concentration of SO_2Cl_2 is doubled. It approximately triples when $[SO_2Cl_2]_0$ is tripled, and it approximately quadruples when $[SO_2Cl_2]_0$ is quadrupled. These observations are consistent with a rate law of the form $k[SO_2Cl_2]$.

(a) We can extract the rate constant observed in each trial by rearranging the first-order equation

$$\text{Rate} = k[SO_2Cl_2]$$

to solve for k at $t = 0$:

$$k = \frac{\text{initial rate}}{[SO_2Cl_2]_0}$$

$$= \frac{2.21 \times 10^{-6}\ M\ s^{-1}}{0.100\ M} = 2.21 \times 10^{-5}\ s^{-1} \qquad \text{(trial 1)}$$

$$= \frac{4.39 \times 10^{-6}\ M\ s^{-1}}{0.200\ M} = 2.195 \times 10^{-5}\ s^{-1} \qquad \text{(trial 2)}$$

$$= \frac{6.60 \times 10^{-6}\ M\ s^{-1}}{0.300\ M} = 2.20 \times 10^{-5}\ s^{-1} \qquad \text{(trial 3)}$$

$$= \frac{8.80 \times 10^{-6}\ M\ s^{-1}}{0.400\ M} = 2.20 \times 10^{-5}\ s^{-1} \qquad \text{(trial 4)}$$

The result, averaged over all four trials, is $k = 2.20 \times 10^{-5}\ s^{-1}$. The corresponding half-life is 3.15×10^4 s (equivalently, 8.75 h):

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{2.20 \times 10^{-5}\ s^{-1}} = 3.15 \times 10^4\ s$$

See Example 18-4, beginning on page R18.9 of *PoC*.

ALTERNATIVE METHOD: Equally valid would be to plot the initial rate versus the initial concentration, $[SO_2Cl_2]_0$, to obtain a straight line with slope equal to k. See Figure 18.3.

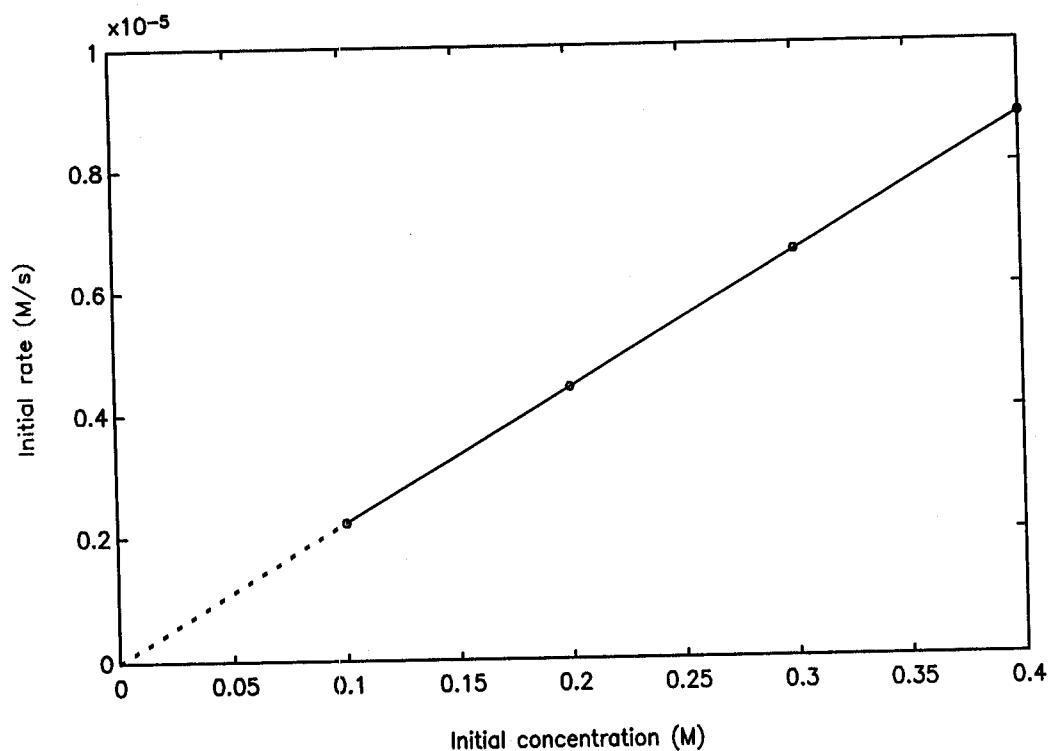The graphical technique is also illustrated in Example 18-4.

FIGURE 18.3   Plot of the data given in Exercise 21: initial rate of reaction versus the initial concentration of SO_2Cl_2. The slope of the line, $2.20 \times 10^{-5} \text{ s}^{-1}$, is equal to the rate constant k in the first-order rate law: Rate $= k[SO_2Cl_2]$.

(b) Insert the rate constant and initial concentration

$$k = 2.20 \times 10^{-5} \text{ s}^{-1} \qquad\qquad [SO_2Cl_2]_0 = 0.0150 \ M$$

into the exponentially decaying first-order profile:

$$[SO_2Cl_2]_t = [SO_2Cl_2]_0 \exp(-kt)$$

The calculation at $t = 3.00$ h is typical:

$$t = 3.00 \text{ h} \times \frac{3600 \text{ s}}{\text{h}} = 1.08 \times 10^4 \text{ s}$$

$$[SO_2Cl_2]_{t=3\,h} = (0.0150 \ M)\exp\left[-(2.20 \times 10^{-5} \text{ s}^{-1})(1.08 \times 10^4 \text{ s})\right] = 0.0118 \ M$$

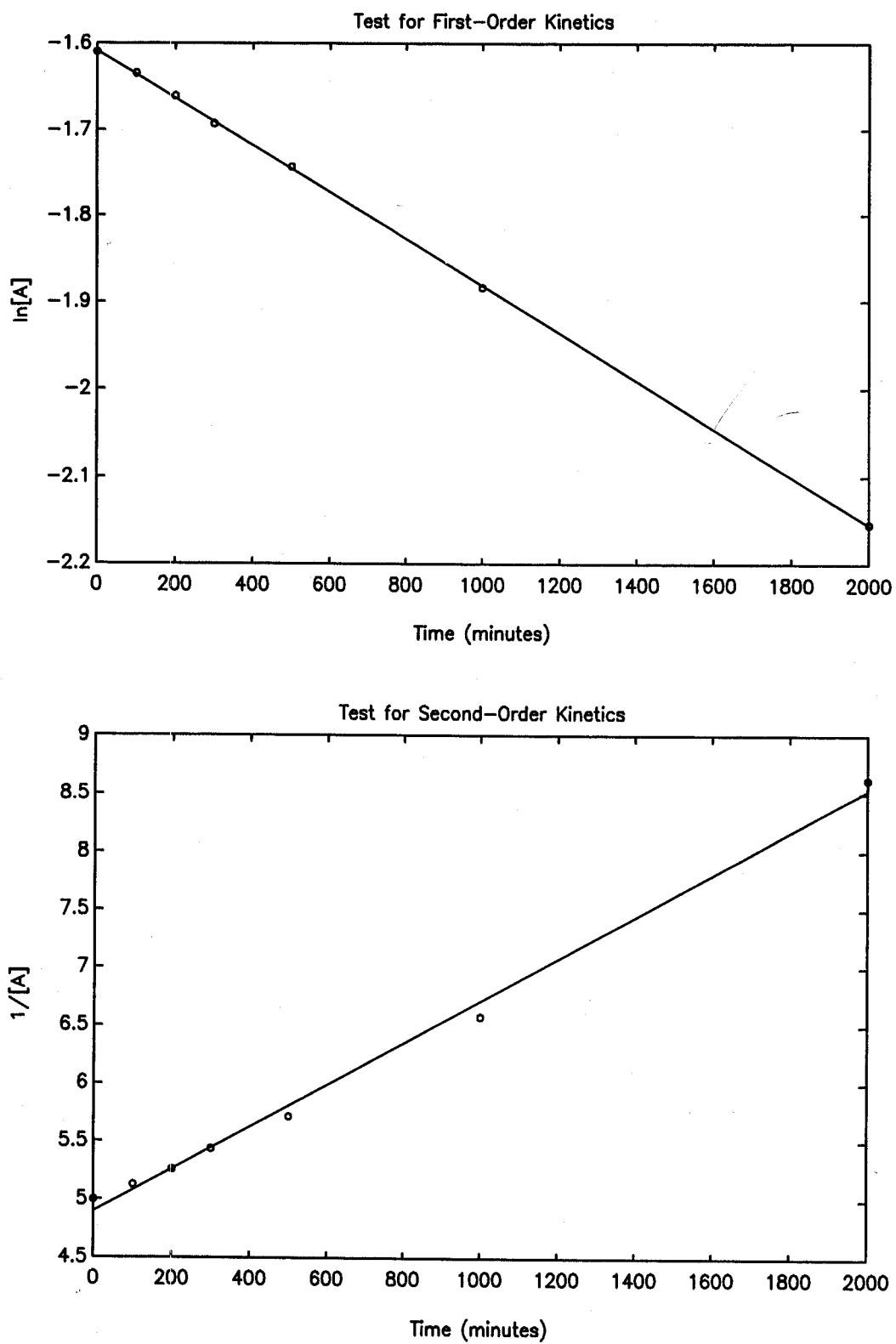Results for 3, 6, 9, 12, 15, and 18 hours are collected on the second page following.

Test for First-Order Kinetics

Test for Second-Order Kinetics

FIGURE 18.4   Plots of ln [A] versus t (top) and 1/[A] versus t (bottom) for the data given in Exercise 22. The semilog plot yields a straight line with a slope of -2.73×10^{-4} min^{-1}. The points in the lower plot do not fall on a straight line. (A = $C_6H_{12}O_6$, glucose)

Time (h)	$[SO_2Cl_2]_t$ (M)
0.00	1.50×10^{-2}
3.00	1.18×10^{-2}
6.00	9.33×10^{-3}
9.00	7.35×10^{-3}
12.00	5.80×10^{-3}
15.00	4.57×10^{-3}
18.00	3.61×10^{-3}

22. We continue to exploit the logarithmic/exponential time dependence of any first-order process:

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

$$[A]_t = [A]_0 \exp(-kt)$$

See pages 653–656 and Examples 18-4 and 18-5 in *PoC*. Second-order reactions are illustrated in Example 18-6.

(a) Plot $\ln [C_6H_{12}O_6]_t$ versus t to test for first-order dependence, and plot $1/[C_6H_{12}O_6]_t$ versus t to test for second-order dependence. The points corresponding to $\ln [C_6H_{12}O_6]_t$ cluster narrowly around a straight line. Those corresponding to $1/[C_6H_{12}O_6]_t$ do not. See Figure 18.4.

Hence the process is first order, not second order.

(b) Determine the slope of the line that best fits the points in the plot of $\ln [C_6H_{12}O_6]_t$ versus t. A linear regression analysis (available as a function on many scientific calculators) yields the value $k = 2.73 \times 10^{-4}$ min^{-1} for the rate constant:

$$\text{Slope} = -2.73 \times 10^{-4} \text{ min}^{-1} = -k$$

$$k = -\text{slope} = -(-2.73 \times 10^{-4} \text{ min}^{-1}) = 2.73 \times 10^{-4} \text{ min}^{-1}$$

The associated half-life is 2.54×10^3 min:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{2.73 \times 10^{-4} \text{ min}^{-1}} = 2.54 \times 10^3 \text{ min}$$
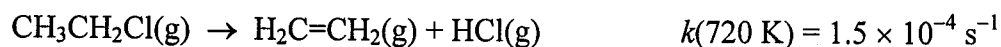
(c) Given the rate constant and initial concentration,

$$k = 2.73 \times 10^{-4} \text{ min}^{-1} \qquad [C_6H_{12}O_6]_0 = 0.200 \ M$$

we solve for the concentration of glucose after 24 hours of exponential decay:

$$t = 24.0 \text{ h} \times \frac{60 \text{ min}}{\text{h}} = 1.44 \times 10^3 \text{ min}$$

$$[C_6H_{12}O_6]_{t=24 \text{ h}} = [C_6H_{12}O_6]_0 \exp(-kt)$$

$$= (0.200 \text{ } M) \exp\left[-(2.73 \times 10^{-4} \text{ min}^{-1})(1.44 \times 10^3 \text{ min})\right] = 0.135 \text{ } M$$

23. We consider another first-order reaction, the gas-phase decomposition of chloroethane into ethene and hydrogen chloride:

$$CH_3CH_2Cl(g) \rightarrow H_2C{=}CH_2(g) + HCl(g) \qquad k(720 \text{ K}) = 1.5 \times 10^{-4} \text{ s}^{-1}$$

(a) The rate at any time t is directly proportional to the instantaneous concentration:

$$\text{Rate}(t) = k[CH_3CH_2Cl]_t$$

At $t = 0$, the concentration is specified as 0.100 M:

$$\text{Rate}(0) = k[CH_3CH_2Cl]_0 = (1.5 \times 10^{-4} \text{ s}^{-1})(0.100 \text{ } M) = 1.5 \times 10^{-5} \text{ } M\text{s}^{-1}$$

(b) The initial concentration decays exponentially with a rate constant equal to $1.5 \times 10^{-4} \text{ s}^{-1}$:

$$[CH_3CH_2Cl]_t = [CH_3CH_2Cl]_0 \exp(-kt)$$

$$[CH_3CH_2Cl]_{t=100 \text{ s}} = (0.100 \text{ } M) \exp\left[-(1.5 \times 10^{-4} \text{ s}^{-1})(100 \text{ s})\right] = 0.099 \text{ } M$$

$$[CH_3CH_2Cl]_{t=1000 \text{ s}} = (0.100 \text{ } M) \exp\left[-(1.5 \times 10^{-4} \text{ s}^{-1})(1000 \text{ s})\right] = 0.086 \text{ } M$$

$$[CH_3CH_2Cl]_{t=10,000 \text{ s}} = (0.100 \text{ } M) \exp\left[-(1.5 \times 10^{-4} \text{ s}^{-1})(10,000 \text{ s})\right] = 0.022 \text{ } M$$

24. Methyl radicals are produced from ethane in a first-order reaction:

$$C_2H_6(g) \rightarrow 2CH_3(g) \qquad k(700°C) = 5.36 \times 10^{-4} \text{ s}^{-1}$$

(a) The half-life is determined in the usual way:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{5.36 \times 10^{-4} \text{ s}^{-1}} = 1.29 \times 10^3 \text{ s}$$

See pages 653–656 and Example 18-4 in *PoC*.

(b) Write the first-order decay equation in the form

$$\ln\,[C_2H_6]_t = -kt + \ln\,[C_2H_6]_0$$

and solve for t:

$$t = -\frac{1}{k}\Big(\ln[C_2H_6]_t - \ln[C_2H_6]_0\Big) = -\frac{1}{k}\ln\frac{[C_2H_6]_t}{[C_2H_6]_0}$$

Inserting the specified concentrations,

$$[C_2H_6]_t = 0.680\;M \qquad [C_2H_6]_0 = 1.000\;M$$

we calculate an elapsed time of 720 s:

$$t = -\frac{1}{k}\ln\frac{[C_2H_6]_t}{[C_2H_6]_0} = -\frac{1}{5.36\times10^{-4}\;s^{-1}}\ln\!\left(\frac{0.680\;M}{1.000\;M}\right) = 7.20\times10^2\;s$$

See Example 18-5 (in particular, the QUESTION/ANSWER dialogue on page R18.13).

(c) The ratio of concentrations—and hence the elapsed time—is the same as in (b):

$$\frac{1.360\;M}{2.000\;M} = \frac{0.680\;M}{1.000\;M} = 0.680$$

$$t = 7.20\times10^2\;s$$

(d) Again, the same ratio and the same elapsed time:

$$\frac{1.856\;M}{2.730\;M} = \frac{1.360\;M}{2.000\;M} = \frac{0.680\;M}{1.000\;M} = 0.680$$

$$t = 7.20\times10^2\;s$$

25. The rate constant for a first-order process is inversely proportional to the half-life:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.6931}{22.7\;\text{min}} = 3.05\times10^{-2}\;\text{min}^{-1} \qquad (45°C)$$

Knowing both k and the initial concentration of N_2O_5 (given as 1.00 M), we can then calculate the rate of reaction at any time t:

$$\text{Rate}(t) = k[N_2O_5]_t = k \times \underbrace{[N_2O_5]_0 \exp(-kt)}_{[N_2O_5]_t}$$

The four computations are worked out explicitly below:

$$\text{Rate}(0) = \left(3.05 \times 10^{-2} \ \text{min}^{-1}\right) \times \left(1.00 \ M\right) \exp\left[-\left(3.05 \times 10^{-2} \ \text{min}^{-1}\right)\left(0 \ \text{min}\right)\right]$$

$$= 3.05 \times 10^{-2} \ M \ \text{min}^{-1}$$

$$\text{Rate}(10.0 \ \text{min}) = \left(3.05 \times 10^{-2} \ \text{min}^{-1}\right) \times \left(1.00 \ M\right) \exp\left[-\left(3.05 \times 10^{-2} \ \text{min}^{-1}\right)\left(10.0 \ \text{min}\right)\right]$$

$$= 2.25 \times 10^{-2} \ M \ \text{min}^{-1}$$

$$\text{Rate}(20.0 \ \text{min}) = \left(3.05 \times 10^{-2} \ \text{min}^{-1}\right) \times \left(1.00 \ M\right) \exp\left[-\left(3.05 \times 10^{-2} \ \text{min}^{-1}\right)\left(20.0 \ \text{min}\right)\right]$$

$$= 1.66 \times 10^{-2} \ M \ \text{min}^{-1}$$

$$\text{Rate}(30.0 \ \text{min}) = \left(3.05 \times 10^{-2} \ \text{min}^{-1}\right) \times \left(1.00 \ M\right) \exp\left[-\left(3.05 \times 10^{-2} \ \text{min}^{-1}\right)\left(30.0 \ \text{min}\right)\right]$$

$$= 1.22 \times 10^{-2} \ M \ \text{min}^{-1}$$

26. The calculations here are analogous to those in Exercise 24. See Example 18-5 in *PoC*.

(a) Write the first-order decay equation in the form

$$\ln [FClO_2]_t = -kt + \ln [FClO_2]_0$$

and solve for k:

$$k = -\frac{1}{t}\left(\ln[FClO_2]_t - \ln[FClO_2]_0\right) = -\frac{1}{t}\ln\frac{[FClO_2]_t}{[FClO_2]_0}$$

Inserting the specified concentrations at $t = 1127$ s,

$$[FClO_2]_t = 0.0354 \ M \qquad [FClO_2]_0 = 0.0600 \ M$$

we calculate a first-order rate constant of $4.68 \times 10^{-4} \ \text{s}^{-1}$:

$$k = -\frac{1}{t}\ln\frac{[\text{FClO}_2]_t}{[\text{FClO}_2]_0} = -\frac{1}{1127 \text{ s}}\ln\frac{0.0354\ M}{0.0600\ M} = 4.68 \times 10^{-4}\ \text{s}^{-1}$$

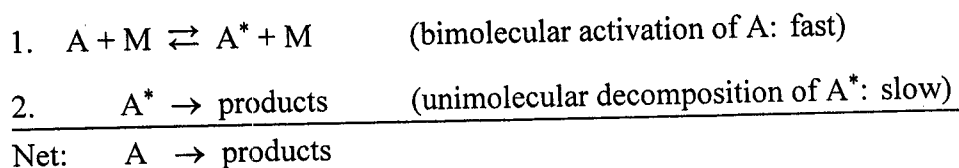The corresponding half-life is equal to $(\ln 2)/k$:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{4.68 \times 10^{-4}\ \text{s}^{-1}} = 1.48 \times 10^3\ \text{s}$$

(b) Similar. Given k (see above) and a pair of concentrations, solve for t:

$$[\text{FClO}_2]_t = 0.0200\ M \qquad\qquad [\text{FClO}_2]_0 = 0.0354\ M$$

$$t = -\frac{1}{k}\ln\frac{[\text{FClO}_2]_t}{[\text{FClO}_2]_0} = -\frac{1}{4.68 \times 10^{-4}\ \text{s}^{-1}}\ln\frac{0.0200\ M}{0.0354\ M} = 1.22 \times 10^3\ \text{s}$$

27. A first-order reaction need not occur in a single, unimolecular step. Unimolecular decomposition is often preceded by a bimolecular collision of reactant A with some other molecule M:

1.	$A + M \rightleftarrows A^* + M$	(bimolecular activation of A: fast)
2.	$A^* \rightarrow$ products	(unimolecular decomposition of A^*: slow)
Net:	$A \rightarrow$ products	

If the bimolecular step is fast, as suggested above, then the reaction order is set by the rate-determining unimolecular step—the slow, first-order transformation of the energized reactant (A^*) into products. Thus the overall reaction is first order, but more than one species is needed to bring it about. See pages 677–678 in *PoC*.

Second-order reactions are described on page 656 of PoC *and illustrated in Example 18-6 (beginning on page R18.13).*

28. We consider the gas-phase recombination of iodine radicals, a second-order process:

$$2I(g) \rightarrow I_2(g)$$
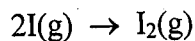
$$\text{Rate} = k[I]^2 \qquad k(25°\text{C}) = 7.0 \times 10^9\ M^{-1}\ \text{s}^{-1} \qquad [I]_0 = 1.0 \times 10^{-3}\ M$$

The reciprocal concentration, $1/[I]$, varies linearly with time:

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

(a) The half-life under second-order kinetics is dependent on the initial concentration:

$$[I]_{t_{1/2}} = \frac{[I]_0}{2}$$

$$\frac{1}{[I]_{t_{1/2}}} = \frac{2}{[I]_0} = kt_{1/2} + \frac{1}{[I]_0}$$

$$t_{1/2} = \frac{1}{k[I]_0} = \frac{1}{\left(7.0 \times 10^9 \ M^{-1} \ s^{-1}\right)\left(1.0 \times 10^{-3} \ M\right)} = 1.4 \times 10^{-7} \ s$$

(b) Rearrange the second-order concentration dependence

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

to solve for $[I]_t$, as demonstrated below for $t = 1.0 \times 10^{-8}$ s:

$$[I]_t = \frac{[I]_0}{kt[I]_0 + 1} = \frac{1.0 \times 10^{-3} \ M}{\left(7.0 \times 10^9 \ M^{-1} \ s^{-1}\right)\left(1.0 \times 10^{-8} \ s\right)\left(1.0 \times 10^{-3} \ M\right) + 1} = 9.3 \times 10^{-4} \ M$$

The other calculations in the series are all done in the same way:

TIME (s)	$[I]_t$ (M)
0	1.0×10^{-3}
1.0×10^{-8}	9.3×10^{-4}
5.0×10^{-8}	7.4×10^{-4}
1.0×10^{-7}	5.9×10^{-4}
5.0×10^{-7}	2.2×10^{-4}
1.0×10^{-6}	1.3×10^{-4}

After 1.0×10^{-6} s, the concentration of I has fallen to 13% of its original value:

$$\frac{[I]_t}{[I]_0} \times 100\% = \frac{1.3 \times 10^{-4} \ M}{1.0 \times 10^{-3} \ M} \times 100\% = 13\%$$

(c) From the stoichiometry of the reaction, we know that one mole of I_2 is produced for every two moles of I consumed:

$$2I(g) \rightarrow I_2(g)$$
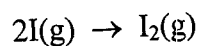
Thus if $[I]_t$ denotes the concentration of I remaining at time t, then the concentration of I *consumed* must be

$$[I]_0 - [I]_t$$

and the concentration of I_2 simultaneously present must be

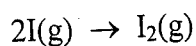$$[I_2]_t = \frac{1}{2}\left([I]_0 - [I]_t\right)$$

At $t = 1.0 \times 10^{-6}$ s, the value of $[I_2]_t$ is 4.4×10^{-4} M:

$$[I_2]_t = \frac{1}{2}\left(1.0 \times 10^{-3} \ M - 1.3 \times 10^{-4} \ M\right) = 4.4 \times 10^{-4} \ M$$

(d) Calculate ΔG° and then K, as described in Section 14-8 and Example 14-8 of *PoC*. The free energies of formation are listed in Table C-16 of Appendix C (*PoC*, pages A85–A92):

$$\Delta G_f^\circ[I(g)] = 70.2 \text{ kJ mol}^{-1} \qquad \Delta G_f^\circ[I_2(g)] = 19.3 \text{ kJ mol}^{-1}$$

Standard change in free energy:

$$2I(g) \rightarrow I_2(g)$$

$$\Delta G^\circ = \Delta G_f^\circ[I_2(g)] - 2\,\Delta G_f^\circ[I(g)]$$

$$= \left(\frac{19.3 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{70.2 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) = -121.1 \text{ kJ}$$

$$= -1.211 \times 10^5 \text{ J} \quad (\text{per mole of } I_2)$$

Equilibrium constant:

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left[-\frac{\left(-1.211 \times 10^5 \text{ J mol}^{-1}\right)}{\left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}\right)\left(298 \text{ K}\right)}\right] \approx 1.7 \times 10^{21}$$

The products are heavily favored thermodynamically. We expect all the I atoms to be recombined once the reaction comes to equilibrium.

29. Repeat the calculations of the preceding exercise, this time starting with a tenfold smaller initial concentration:

$$[I]_0 = 1.0 \times 10^{-4} \, M$$

(a) Inversely proportional to $[I]_0$, the first half-life increases by a factor of 10 relative to its value in Exercise 28:

$$t_{1/2} = \frac{1}{k[I]_0} = \frac{1}{\left(7.0 \times 10^9 \; M^{-1} \; s^{-1}\right)\left(1.0 \times 10^{-4} \; M\right)} = 1.4 \times 10^{-6} \text{ s}$$

(b) Substitute $[I]_0 = 1.0 \times 10^{-4} \, M$ into the equation

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

to obtain $[I]_t$ as a function of t:

TIME (s)	$[I]_t$ (M)
0	1.0×10^{-4}
1.0×10^{-8}	9.9×10^{-5}
5.0×10^{-8}	9.7×10^{-5}
1.0×10^{-7}	9.3×10^{-5}
5.0×10^{-7}	7.4×10^{-5}
1.0×10^{-6}	5.9×10^{-5}

After 1.0×10^{-6} s, the concentration of I has only fallen to 59% of its original value:

$$\frac{[I]_t}{[I]_0} \times 100\% = \frac{5.9 \times 10^{-5} \; M}{1.0 \times 10^{-4} \; M} \times 100\% = 59\%$$

Recall from the preceding exercise that this ratio is 13% when $[I]_0$ is $1.0 \times 10^{-3} \, M$. The reaction goes slower now that the initial concentration is smaller.

A slowdown of this sort, common to many kinds of reactions, is especially marked for a second-order process. The rate is proportional to the square of the concentration:

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

(c) One mole of I_2 is produced for every two moles of I consumed:

$$[I_2]_t = \frac{1}{2}\left([I]_0 - [I]_t\right) = \frac{1}{2}\left(1.0 \times 10^{-4}\ M - 5.9 \times 10^{-5}\ M\right) = 2.1 \times 10^{-5}\ M$$

(d) The reaction is slower (see part b above), but the value of the equilibrium constant remains the same. Thermodynamic properties of the equilibrium state are determined solely by fixed differences in state functions such as enthalpy, entropy, and free energy—not the variable kinetics or mechanism of reaction.

30. We are given kinetic information about the gas-phase decomposition of NOBr into NO and Br_2:

$$2NOBr(g) \rightarrow 2NO(g) + Br_2(g)$$
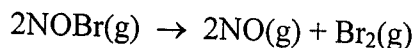
$$\text{Rate} = k[NOBr]^2 \qquad k(10°C) = 0.80\ M^{-1}\ s^{-1} \qquad [NOBr]_0 = 0.200\ M$$

(a) The half-life is inversely proportional to the initial concentration:

$$t_{1/2} = \frac{1}{k[NOBr]_0} = \frac{1}{\left(0.80\ M^{-1}\ s^{-1}\right)\left(0.200\ M\right)} = 6.25\ s = 6.3\ s \qquad \text{(2 sig fig)}$$

When $t = t_{1/2}$, the concentration of NOBr in the equation

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

falls to one-half its initial value. See also Exercise 28 and Example 18-6.

(b) See Figure 18.5 on the next page. A plot of $[NOBr]_t$ versus time,

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

does not conform to a first-order decay profile. The functional dependence of $[NOBr]_t$ on t is something other than purely exponential:

$$[NOBr]_t \neq [NOBr]_0 \exp(-kt)$$

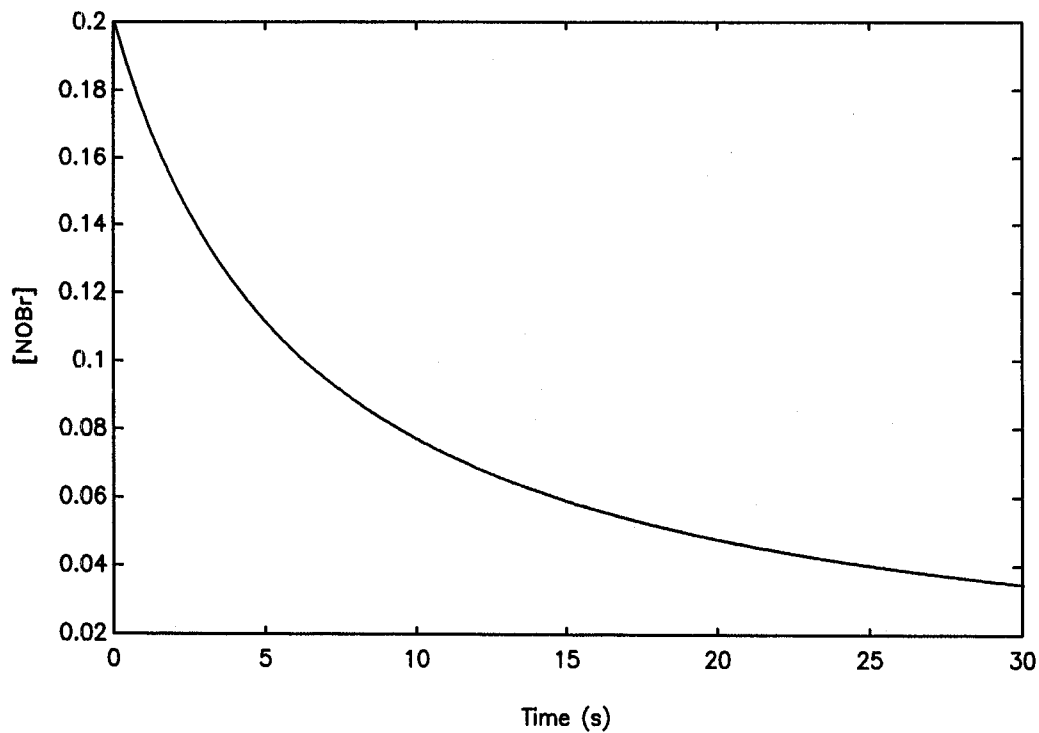FIGURE 18.5   A plot of [NOBr] versus time for the second-order reaction described in Exercise 30. The concentration is measured in moles per liter, M.
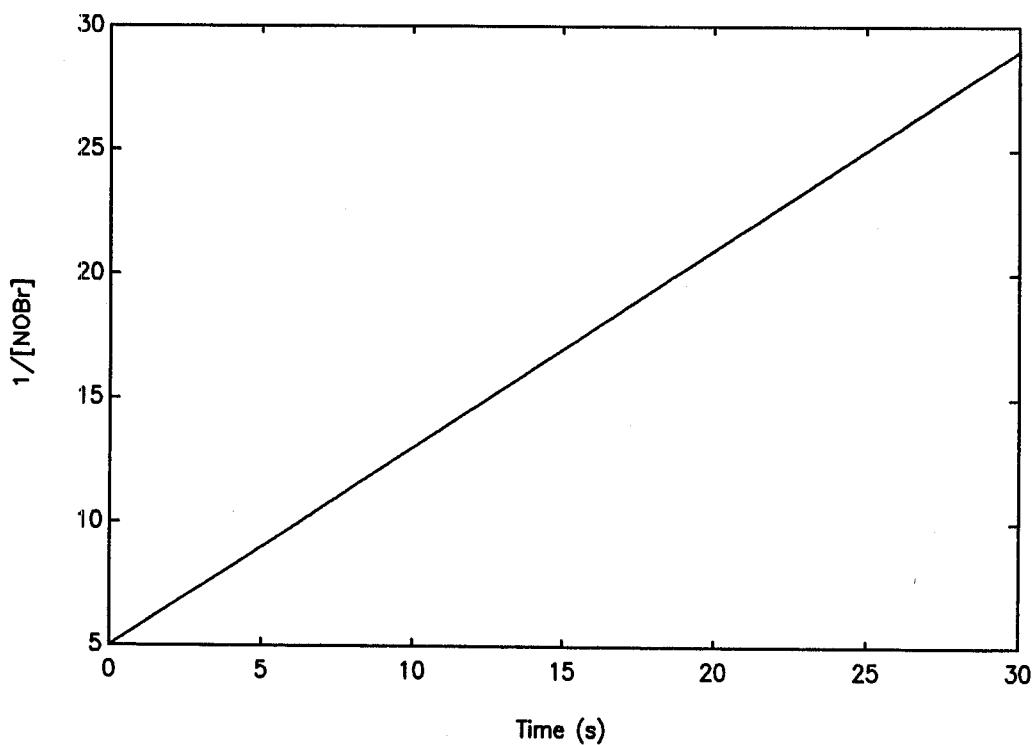

FIGURE 18.6   A plot of 1/[NOBr] versus time for the second-order reaction described in Exercise 30. The reciprocal concentration is measured in units of M^{-1}.

(c) See Figure 18.6. A plot of $1/[\text{NOBr}]_t$ versus time yields a straight line with slope k and vertical intercept $1/[\text{NOBr}]_0$:

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

(d) Substitute the instantaneous concentration

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

into the rate law

$$\text{Rate}(t) = k[\text{NOBr}]_t^2$$

to obtain the rate at any time t:

$$\text{Rate}(t) = k\left(\frac{[\text{NOBr}]_0}{kt[\text{NOBr}]_0 + 1}\right)^2$$

Results for 0 s, 15 s, and 30 s are worked out below:

$$\text{Rate}(0) = \left(0.80\ M^{-1}\ s^{-1}\right)\left[\frac{0.200\ M}{\left(0.80\ M^{-1}\ s^{-1}\right)\left(0\ s\right)\left(0.200\ M\right) + 1}\right]^2$$

$$= 3.2 \times 10^{-2}\ M\ s^{-1}$$

$$\text{Rate}(15\ s) = \left(0.80\ M^{-1}\ s^{-1}\right)\left[\frac{0.200\ M}{\left(0.80\ M^{-1}\ s^{-1}\right)\left(15\ s\right)\left(0.200\ M\right) + 1}\right]^2$$

$$= 2.8 \times 10^{-3}\ M\ s^{-1}$$

$$\text{Rate}(30\ s) = \left(0.80\ M^{-1}\ s^{-1}\right)\left[\frac{0.200\ M}{\left(0.80\ M^{-1}\ s^{-1}\right)\left(30\ s\right)\left(0.200\ M\right) + 1}\right]^2$$

$$= 9.5 \times 10^{-4}\ M\ s^{-1}$$