CHAPTER 13
CHEMICAL KINETICS

13.5   In general for a reaction aA + bB $\rightarrow$ cC + dD

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

(a) $\text{rate} = -\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[I_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$

(b) $\text{rate} = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t}$

Note that because the reaction is carried out in the aqueous phase, we do not monitor the concentration of water.

13.6   **(a)** $\text{rate} = -\frac{1}{2}\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}$

(b) $\text{rate} = -\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$

13.7 $\text{Rate} = -\frac{1}{2}\frac{\Delta[NO]}{\Delta t}$ $\frac{\Delta[NO]}{\Delta t} = -0.066 \; M/s$

$$-\frac{1}{2}\frac{\Delta[NO]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t}$$

(a) $\frac{\Delta[NO_2]}{\Delta t} = \textbf{0.066 } \textbf{\textit{M}/s}$

(b) $-\frac{1}{2}\frac{\Delta[NO]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t}$

$$\frac{\Delta[O_2]}{\Delta t} = \frac{-0.066 \; M/s}{2} = \textbf{-0.033 } \textbf{\textit{M}/s}$$

13.8   **Strategy:** The rate is defined as the change in concentration of a reactant or product with time. Each "change in concentration" term is divided by the corresponding stoichiometric coefficient. Terms involving reactants are preceded by a minus sign.

$$\text{rate} = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

Solution:
(a)   If hydrogen is reacting at the rate of −0.074 M/s, the rate at which ammonia is being formed is

$$\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t}$$

or

$$\frac{\Delta[NH_3]}{\Delta t} = -\frac{2}{3}\frac{\Delta[H_2]}{\Delta t}$$

$$\frac{\Delta[NH_3]}{\Delta t} = -\frac{2}{3}(-0.074 \ M/s) = \textbf{0.049} \ \textbf{\textit{M}/s}$$

(b) The rate at which nitrogen is reacting must be:

$$\frac{\Delta[N_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{3}(-0.074 \ M/s) = \textbf{−0.025} \ \textbf{\textit{M}/s}$$

Will the rate at which ammonia forms always be twice the rate of reaction of nitrogen, or is this true only at the instant described in this problem?

13.15 $\textbf{rate} = k[NH_4^+][NO_2^-] = (3.0 \times 10^{-4} \ /M \cdot s)(0.26 \ M)(0.080 \ M) = \textbf{6.2} \times \textbf{10}^{\textbf{−6}} \ \textbf{\textit{M}/s}$

13.16   Assume the rate law has the form:

$$rate = k[F_2]^x[ClO_2]^y$$

To determine the order of the reaction with respect to F_2, find two experiments in which the $[ClO_2]$ is held constant. Compare the data from experiments 1 and 3. When the concentration of F_2 is doubled, the reaction rate doubles. Thus, the reaction is *first-order* in F_2.

To determine the order with respect to ClO_2, compare experiments 1 and 2. When the ClO_2 concentration is quadrupled, the reaction rate quadruples. Thus, the reaction is *first-order* in ClO_2.

The rate law is:

$$rate = k[F_2][ClO_2]$$

The value of k can be found using the data from any of the experiments. If we take the numbers from the second experiment we have:

$$k = \frac{rate}{[F_2][ClO_2]} = \frac{4.8 \times 10^{-3} \ M/s}{(0.10 \ M)(0.040 \ M)} = 1.2 \ M^{-1}s^{-1}$$

Verify that the same value of k can be obtained from the other sets of data.

Since we now know the rate law and the value of the rate constant, we can calculate the rate at any concentration of reactants.

$$\textbf{rate} = k[F_2][ClO_2] = (1.2 \ M^{-1}s^{-1})(0.010 \ M)(0.020 \ M) = \textbf{2.4} \times \textbf{10}^{\textbf{−4}} \ \textbf{\textit{M}/s}$$

13.17   By comparing the first and second sets of data, we see that changing [B] does not affect the rate of the reaction. Therefore, the reaction is zero order in B. By comparing the first and third sets of data, we see that doubling [A] doubles the rate of the reaction. This shows that the reaction is first order in A.

$$rate = k[A]$$

From the first set of data:

$$3.20 \times 10^{-1} \ M/s = k(1.50 \ M)$$

$$k = 0.213 \ s^{-1}$$

What would be the value of k if you had used the second or third set of data? Should k be constant?

13.18 **Strategy:** We are given a set of concentrations and rate data and asked to determine the order of the reaction and the initial rate for specific concentrations of X and Y. To determine the order of the reaction, we need to find the rate law for the reaction. We assume that the rate law takes the form

$$rate = k[X]^x[Y]^y$$

How do we use the data to determine x and y? Once the orders of the reactants are known, we can calculate k for any set of rate and concentrations. Finally, the rate law enables us to calculate the rate at any concentrations of X and Y.

Solution:

(a) Experiments 2 and 5 show that when we double the concentration of X at constant concentration of Y, the rate quadruples. Taking the ratio of the rates from these two experiments

$$\frac{rate_5}{rate_2} = \frac{0.509 \ M/s}{0.127 \ M/s} \approx 4 = \frac{k(0.40)^x(0.30)^y}{k(0.20)^x(0.30)^y}$$

Therefore,

$$\frac{(0.40)^x}{(0.20)^x} = 2^x = 4$$

or, $x = 2$. That is, the reaction is second order in X. Experiments 2 and 4 indicate that doubling [Y] at constant [X] doubles the rate. Here we write the ratio as

$$\frac{rate_4}{rate_2} = \frac{0.254 \ M/s}{0.127 \ M/s} = 2 = \frac{k(0.20)^x(0.60)^y}{k(0.20)^x(0.30)^y}$$

Therefore,

$$\frac{(0.60)^y}{(0.30)^y} = 2^y = 2$$

or, $y = 1$. That is, the reaction is first order in Y. Hence, the rate law is given by:

$$rate = k[X]^2[Y]$$

The order of the reaction is $(2 + 1) = $ **3**. The reaction is *3rd-order*.

(b) The rate constant k can be calculated using the data from any one of the experiments. Rearranging the rate law and using the first set of data, we find:

$$k = \frac{rate}{[X]^2[Y]} = \frac{0.053 \ M/s}{(0.10 \ M)^2(0.50 \ M)} = 10.6 \ M^{-2}s^{-1}$$

Next, using the known rate constant and substituting the concentrations of X and Y into the rate law, we can calculate the initial rate of disappearance of X.

$$\textbf{rate} = (10.6 \ M^{-2}s^{-1})(0.30 \ M)^2(0.40 \ M) = \textbf{0.38 \textit{M/s}}$$

13.19 **(a)** second order,   **(b)** zero order,   **(c)** 1.5 order,   **(d)** third order

13.20 **(a)** For a reaction first-order in A,

$$Rate = k[A]$$

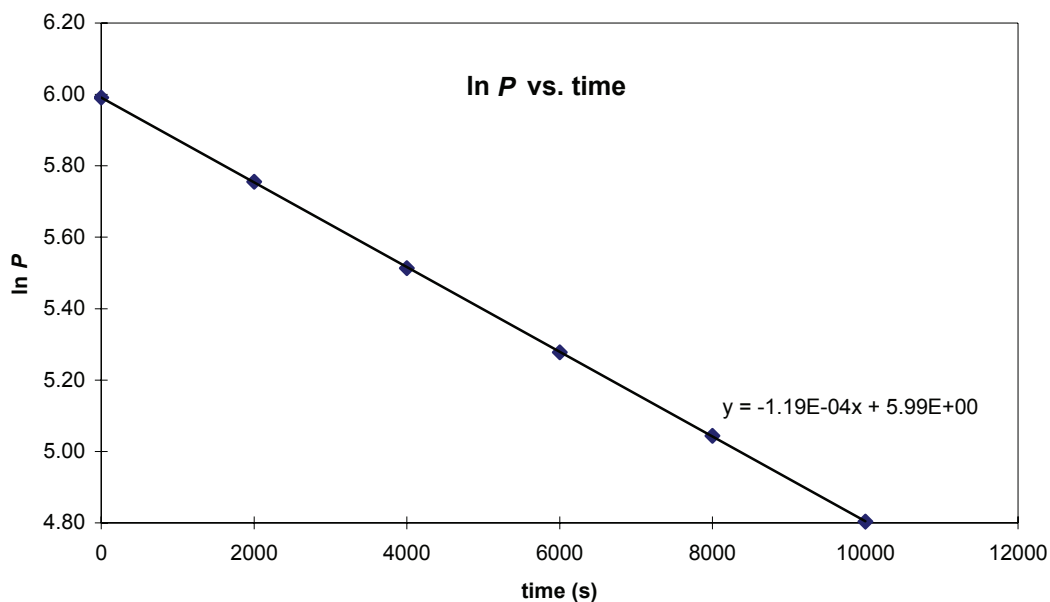$$1.6 \times 10^{-2} \text{ M/s} = k(0.35 \text{ M})$$

$$k = 0.046 \text{ s}^{-1}$$

(b) For a reaction second-order in A,

$$Rate = k[A]^2$$

$$1.6 \times 10^{-2} \text{ M/s} = k(0.35 \text{ M})^2$$

$$k = 0.13 \text{ /M·s}$$

**13.21** The graph below is a plot of ln P vs. time. Since the plot is linear, the reaction is 1st order.

Slope $= -k$

$$k = 1.19 \times 10^{-4} \text{ s}^{-1}$$

13.22 Let P_0 be the pressure of ClCO$_2$CCl$_3$ at $t = 0$, and let x be the decrease in pressure after time t. Note that from the coefficients in the balanced equation that the loss of 1 atmosphere of ClCO$_2$CCl$_3$ results in the formation of two atmospheres of COCl$_2$. We write:
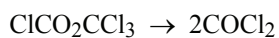
$$ClCO_2CCl_3 \rightarrow 2COCl_2$$

Time	[ClCO$_2$CCl$_3$]	[COCl$_2$]
$t = 0$	P_0	0
$t = t$	$P_0 - x$	$2x$

Thus the change (increase) in pressure (ΔP) is $2x - x = x$. We have:

t(s)	P (mmHg)	$\Delta P = x$	$P_{ClCO_2CCl_3}$	$\ln P_{ClCO_2CCl_3}$	$\dfrac{1}{P_{ClCO_2CCl_3}}$
0	15.76	0.00	15.76	2.757	0.0635
181	18.88	3.12	12.64	2.537	0.0791
513	22.79	7.03	8.73	2.167	0.115
1164	27.08	11.32	4.44	1.491	0.225

If the reaction is first order, then a plot of $\ln P_{ClCO_2CCl_3}$ vs. t would be linear. If the reaction is second order, a plot of $1/P_{ClCO_2CCl_3}$ vs. t would be linear. The two plots are shown below.
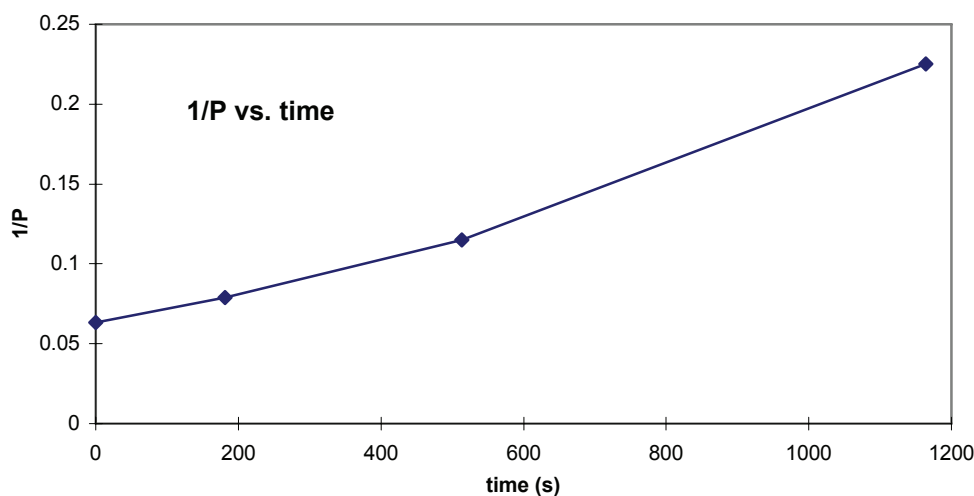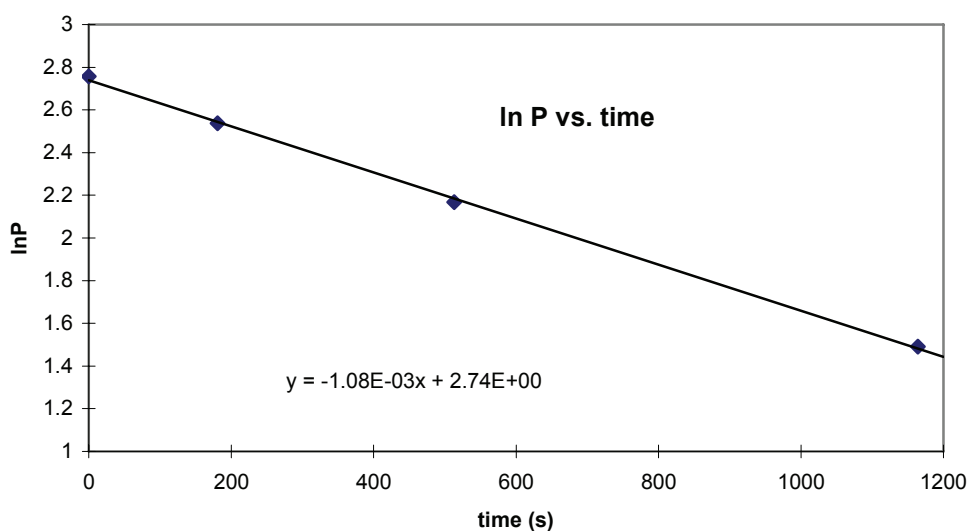
From the graphs we see that the reaction must be **first-order**. For a first-order reaction, the slope is equal to $-k$. The equation of the line is given on the graph. The rate constant is: $k = 1.08 \times 10^{-3} \text{ s}^{-1}$.

13.27   We know that half of the substance decomposes in a time equal to the half-life, $t_{1/2}$. This leaves half of the compound. Half of what is left decomposes in a time equal to another half-life, so that only one quarter of the original compound remains. We see that 75% of the original compound has decomposed after two half–lives. Thus two half-lives equal one hour, or the half-life of the decay is 30 min.

$$100\% \text{ starting compound } \xrightarrow{t_{1/2}} 50\% \text{ starting compound } \xrightarrow{t_{1/2}} 25\% \text{ starting compound}$$
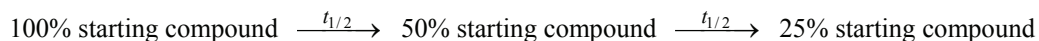
Using first order kinetics, we can solve for k using Equation (13.3) of the text, with $[A]_0 = 100$ and $[A] = 25$,

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

$$\ln \frac{25}{100} = -k(60 \text{ min})$$

$$k = -\frac{\ln(0.25)}{60 \text{ min}} = 0.023 \text{ min}^{-1}$$

Then, substituting k into Equation (13.6) of the text, you arrive at the same answer for $t_{1/2}$.

$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{0.023 \text{ min}^{-1}} = \textbf{30 min}$$

13.28   **(a)**
Strategy: To calculate the rate constant, k, from the half-life of a first-order reaction, we use Equation (13.6) of the text.

Solution: For a first-order reaction, we only need the half-life to calculate the rate constant. From Equation (13.6)

$$k = \frac{0.693}{t_{\frac{1}{2}}}$$

$$k = \frac{0.693}{35.0 \text{ s}} = \textbf{0.0198 s}^{-1}$$

(b)
Strategy: The relationship between the concentration of a reactant at different times in a first-order reaction is given by Equations (13.3) and (13.4) of the text. We are asked to determine the time required for 95% of the phosphine to decompose. If we initially have 100% of the compound and 95% has reacted, then what is left must be (100% − 95%), or 5%. Thus, the ratio of the percentages will be equal to the ratio of the actual concentrations; that is, $[A]_t/[A]_0 = 5\%/100\%$, or 0.05/1.00.

Solution: The time required for 95% of the phosphine to decompose can be found using Equation (13.3) of the text.

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

$$\ln \frac{(0.05)}{(1.00)} = -(0.0198 \text{ s}^{-1})t$$

$$t = -\frac{\ln(0.0500)}{0.0198 \text{ s}^{-1}} = \textbf{151 s}$$

13.29 **(a)** Since the reaction is known to be second-order, the relationship between reactant concentration and time is given by Equation (13.7) of the text. The problem supplies the rate constant and the initial (time = 0) concentration of NOBr. The concentration after 22s can be found easily.

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

$$\frac{1}{[\text{NOBr}]_t} = (0.80/M \cdot \text{s})(22\text{s}) + \frac{1}{0.086 \ M}$$

$$\frac{1}{[\text{NOBr}]_t} = 29 \ M^{-1}$$

[NOBr] = 0.034 M

If the reaction were first order with the same k and initial concentration, could you calculate the concentration after 22 s? If the reaction were first order and you were given the $t_{1/2}$, could you calculate the concentration after 22 s?

(b) The half-life for a second-order reaction *is* dependent on the initial concentration. The half-lives can be calculated using Equation (13.8) of the text.

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

$$t_{\frac{1}{2}} = \frac{1}{(0.80/M \cdot \text{s})(0.072 \ M)}$$
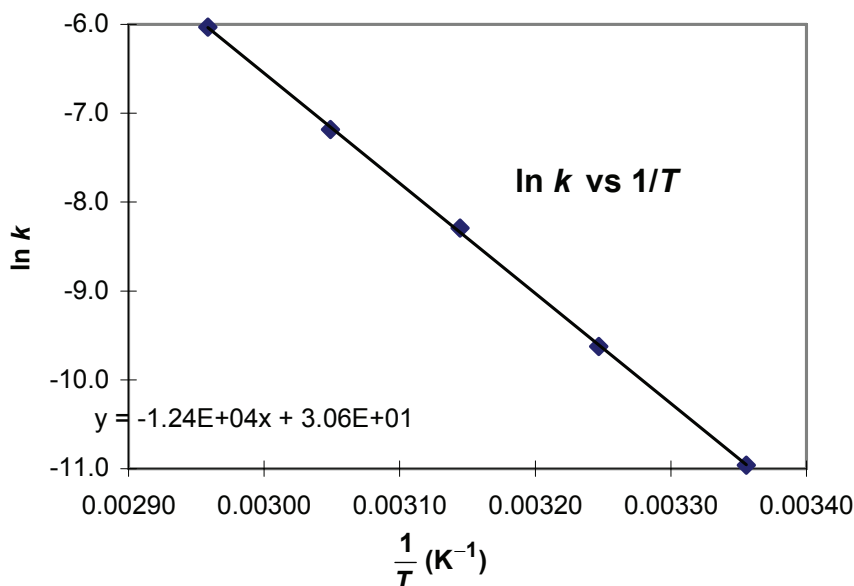
$$t_{\frac{1}{2}} = \textbf{17 s}$$

For an initial concentration of 0.054 M, you should find $t_{\frac{1}{2}} = \textbf{23 s}$. Note that the half-life of a second-order reaction is inversely proportional to the initial reactant concentration.

13.30 $$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt$$

$$\frac{1}{0.28} = \frac{1}{0.62} + 0.54t$$

$$t = \textbf{3.6 s}$$

13.37   Graphing Equation (13.13) of the text requires plotting ln k versus $1/T$. The graph is shown below.

The slope of the line is -1.24×10^4 K, which is $-E_a/R$. The activation energy is:

$$-E_a = \text{slope} \times R = (-1.24 \times 10^4 \text{ K}) \times (8.314 \text{ J/K·mol})$$

$$E_a = 1.03 \times 10^5 \text{ J/mol} = 103 \text{ kJ/mol}$$

Do you need to know the order of the reaction to find the activation energy? Is it possible to have a negative activation energy? What would a potential energy versus reaction coordinate diagram look like in such a case?

13.38   **Strategy:** A modified form of the Arrhenius equation relates two rate constants at two different temperatures [see Equation (13.14) of the text]. Make sure the units of R and E_a are consistent. Since the rate of the reaction at 250°C is 1.50×10^3 times faster than the rate at 150°C, the ratio of the rate constants, k, is also $1.50 \times 10^3 : 1$, because rate and rate constant are directly proportional.

Solution: The data are: $T_1 = 250°C = 523$ K, $T_2 = 150°C = 423$ K, and $k_1/k_2 = 1.50 \times 10^3$. Substituting into Equation (13.14) of the text,

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

$$\ln(1.50 \times 10^3) = \frac{E_a}{8.314 \text{ J/mol·K}}\left(\frac{523 \text{ K} - 423 \text{ K}}{(523 \text{ K})(423 \text{ K})}\right)$$

$$7.31 = \frac{E_a}{8.314 \dfrac{\text{J}}{\text{mol·K}}}\left(4.52 \times 10^{-4} \frac{1}{\text{K}}\right)$$

$$E_a = 1.35 \times 10^5 \text{ J/mol} = 135 \text{ kJ/mol}$$

13.39 The appropriate value of R is 8.314 J/K mol, not 0.0821 L·atm/mol·K. You must also use the activation energy value of 63000 J/mol (why?). Once the temperature has been converted to Kelvin, the rate constant is:

$$k = Ae^{-E_a/RT} = (8.7 \times 10^{12} \text{ s}^{-1})e^{-\left[\frac{63000 \text{ J/mol}}{(8.314 \text{ J/mol·K})(348 \text{ K})}\right]} = (8.7 \times 10^{12} \text{ s}^{-1})(3.5 \times 10^{-10})$$

$$k = 3.0 \times 10^3 \text{ s}^{-1}$$

Can you tell from the units of k what the order of the reaction is?

13.40 Use a modified form of the Arrhenius equation to calculate the temperature at which the rate constant is $8.80 \times 10^{-4} \text{ s}^{-1}$. We carry an extra significant figure throughout this calculation to minimize rounding errors.

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

$$\ln\left(\frac{4.60 \times 10^{-4} \text{ s}^{-1}}{8.80 \times 10^{-4} \text{ s}^{-1}}\right) = \frac{1.04 \times 10^5 \text{ J/mol}}{8.314 \text{ J/mol·K}}\left(\frac{1}{T_2} - \frac{1}{623 \text{ K}}\right)$$

$$\ln(0.5227) = (1.251 \times 10^4 \text{ K})\left(\frac{1}{T_2} - \frac{1}{623 \text{ K}}\right)$$

$$-0.6487 + 20.08 = \frac{1.251 \times 10^4 \text{ K}}{T_2}$$

$$19.43 T_2 = 1.251 \times 10^4 \text{ K}$$

$$T_2 = 644 \text{ K} = 371°C$$

13.41 Let k_1 be the rate constant at 295 K and $2k_1$ the rate constant at 305 K. We write:

$$\ln\frac{k_1}{2k_1} = \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

$$-0.693 = \frac{E_a}{8.314 \text{ J/K·mol}}\left(\frac{295 \text{ K} - 305 \text{ K}}{(295 \text{ K})(305 \text{ K})}\right)$$

$$E_a = 5.18 \times 10^4 \text{ J/mol} = 51.8 \text{ kJ/mol}$$

13.42 Since the ratio of rates is equal to the ratio of rate constants, we can write:

$$\ln\frac{\text{rate}_1}{\text{rate}_2} = \ln\frac{k_1}{k_2}$$

$$\ln\frac{k_1}{k_2} = \ln\left(\frac{2.0 \times 10^2}{39.6}\right) = \frac{E_a}{8.314 \text{ J/K·mol}}\left(\frac{(300 \text{ K} - 278 \text{ K})}{(300 \text{ K})(278 \text{ K})}\right)$$

$$E_a = 5.10 \times 10^4 \text{ J/mol} = 51.0 \text{ kJ/mol}$$

13.51   **(a)**   The order of the reaction is simply the sum of the exponents in the rate law (Section 13.2 of the text). The order of this reaction is 2.

(b)   The rate law reveals the identity of the substances participating in the slow or rate-determining step of a reaction mechanism. This rate law implies that the slow step involves the reaction of a molecule of NO with a molecule of Cl_2. If this is the case, then the first reaction shown must be the rate-determining (slow) step, and the second reaction must be much faster.

13.52   **(a)**   **Strategy:** We are given information as to how the concentrations of X_2, Y, and Z affect the rate of the reaction and are asked to determine the rate law. We assume that the rate law takes the form

$$rate = k[X_2]^x[Y]^y[Z]^z$$

How do we use the information to determine x, y, and z?

Solution: Since the reaction rate doubles when the X_2 concentration is doubled, the reaction is first-order in X. The reaction rate triples when the concentration of Y is tripled, so the reaction is also first-order in Y. The concentration of Z has no effect on the rate, so the reaction is zero-order in Z.

The rate law is:
$$\mathbf{rate = \mathit{k}[X_2][Y]}$$

(b)   If a change in the concentration of Z has no effect on the rate, the concentration of Z is not a term in the rate law. This implies that Z does not participate in the rate-determining step of the reaction mechanism.

(c)   **Strategy:** The rate law, determined in part (a), shows that the slow step involves reaction of a molecule of X_2 with a molecule of Y. Since Z is not present in the rate law, it does not take part in the slow step and must appear in a fast step at a later time. (If the fast step involving Z happened before the rate-determining step, the rate law would involve Z in a more complex way.)

Solution: A mechanism that is consistent with the rate law could be:

$$X_2 + Y \longrightarrow XY + X \qquad \text{(slow)}$$

$$X + Z \longrightarrow XZ \qquad \text{(fast)}$$

The rate law only tells us about the slow step. Other mechanisms with different subsequent fast steps are possible. Try to invent one.

Check: The rate law written from the rate-determining step in the proposed mechanism matches the rate law determined in part (a). Also, the two elementary steps add to the overall balanced equation given in the problem.

13.53   The first step involves forward and reverse reactions that are much faster than the second step. The rates of the reaction in the first step are given by:

$$\text{forward rate} = k_1[O_3]$$

$$\text{reverse rate} = k_{-1}[O][O_2]$$

It is assumed that these two processes rapidly reach a state of dynamic equilibrium in which the rates of the forward and reverse reactions are equal:

$$k_1[O_3] = k_{-1}[O][O_2]$$

If we solve this equality for [O] we have:

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2]}$$

The equation for the rate of the second step is:

$$\text{rate} = k_2[O][O_3]$$

If we substitute the expression for [O] derived from the first step, we have the experimentally verified rate law.

$$\text{overall rate} = \frac{k_1 k_2}{k_{-1}} \frac{[O_3]^2}{[O_2]} = k\frac{[O_3]^2}{[O_2]}$$

The above rate law predicts that higher concentrations of O_2 will decrease the rate. This is because of the reverse reaction in the first step of the mechanism. Notice that if more O_2 molecules are present, they will serve to scavenge free O atoms and thus slow the disappearance of O_3.

13.54 The experimentally determined rate law is first order in H_2 and second order in NO. In Mechanism I the slow step is bimolecular and the rate law would be:

$$\text{rate} = k[H_2][NO]$$

Mechanism I can be discarded.

The rate-determining step in Mechanism II involves the simultaneous collision of two NO molecules with one H_2 molecule. The rate law would be:

$$\text{rate} = k[H_2][NO]^2$$

Mechanism II is a possibility.

In Mechanism III we assume the forward and reverse reactions in the first fast step are in dynamic equilibrium, so their rates are equal:

$$k_f[NO]^2 = k_r[N_2O_2]$$

The slow step is bimolecular and involves collision of a hydrogen molecule with a molecule of N_2O_2. The rate would be:

$$\text{rate} = k_2[H_2][N_2O_2]$$

If we solve the dynamic equilibrium equation of the first step for $[N_2O_2]$ and substitute into the above equation, we have the rate law:

$$\text{rate} = \frac{k_2 k_f}{k_r}[H_2][NO]^2 = k[H_2][NO]^2$$

Mechanism III is also a possibility. Can you suggest an experiment that might help to decide between the two mechanisms?

13.61 Higher temperatures may disrupt the intricate three dimensional structure of the enzyme, thereby reducing or totally destroying its catalytic activity.

13.62   The rate-determining step involves the breakdown of ES to E and P. The rate law for this step is:

$$rate = k_2[ES]$$

In the first elementary step, the intermediate ES is in equilibrium with E and S. The equilibrium relationship is:

$$\frac{[ES]}{[E][S]} = \frac{k_1}{k_{-1}}$$

or

$$[ES] = \frac{k_1}{k_{-1}}[E][S]$$

Substitute [ES] into the rate law expression.

$$\textbf{rate} = k_2[ES] = \frac{k_1 k_2}{k_{-1}}[E][S]$$

13.63   In each case the gas pressure will either increase or decrease. The pressure can be related to the progress of the reaction through the balanced equation. In (d), an electrical conductance measurement could also be used.

13.64   Temperature, energy of activation, concentration of reactants, and a catalyst.

13.65   Strictly, the temperature must be given whenever the rate or rate constant of a reaction is quoted.

13.66   First, calculate the radius of the 10.0 cm^3 sphere.

$$V = \frac{4}{3}\pi r^3$$

$$10.0 \text{ cm}^3 = \frac{4}{3}\pi r^3$$

$$r = 1.34 \text{ cm}$$

The surface area of the sphere is:

$$\textbf{area} = 4\pi r^2 = 4\pi(1.34 \text{ cm})^2 = \textbf{22.6 cm}^2$$

Next, calculate the radius of the 1.25 cm^3 sphere.

$$V = \frac{4}{3}\pi r^3$$

$$1.25 \text{ cm}^3 = \frac{4}{3}\pi r^3$$

$$r = 0.668 \text{ cm}$$

The surface area of one sphere is:

$$area = 4\pi r^2 = 4\pi(0.668 \text{ cm})^2 = 5.61 \text{ cm}^2$$

$$\textbf{The total area of 8 spheres} = 5.61 \text{ cm}^2 \times 8 = \textbf{44.9 cm}^2$$

Obviously, the surface area of the eight spheres (44.9 cm^2) is greater than that of one larger sphere (22.6 cm^2). A greater surface area promotes the catalyzed reaction more effectively.

It can be dangerous to work in grain elevators, because the large surface area of the grain dust can result in a violent explosion.

13.67

P vs. time

$P = 270$ mmHg
$t = 13$ s

$P = 135$ mmHg
$t = 283$ s
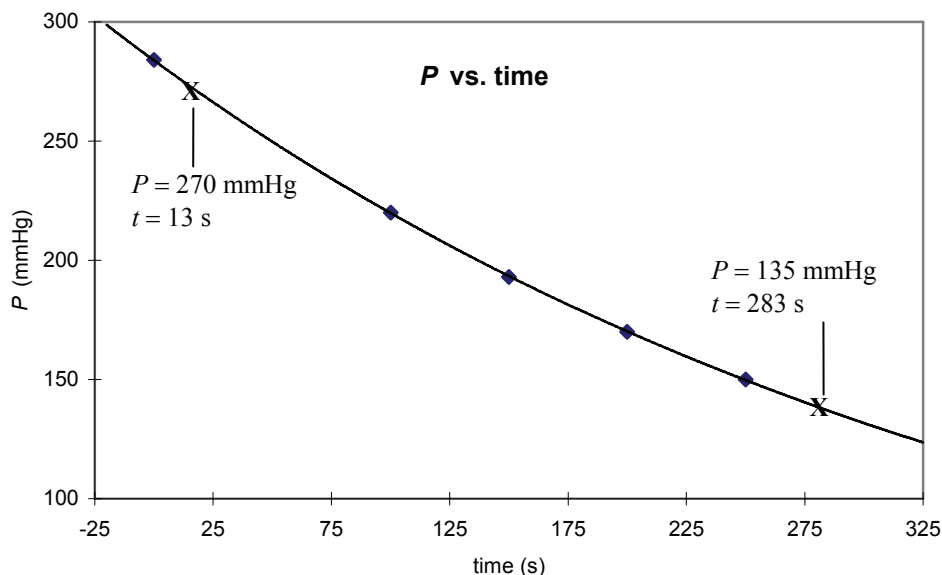
$$t_{1/2} = (283 - 13)\text{s} = 270 \text{ s}$$

13.68   The overall rate law is of the general form: rate $= k[H_2]^x[NO]^y$

(**a**)   Comparing Experiment #1 and Experiment #2, we see that the concentration of NO is constant and the concentration of H$_2$ has decreased by one-half. The initial rate has also decreased by one-half. Therefore, the initial rate is directly proportional to the concentration of H$_2$; $x = 1$.

Comparing Experiment #1 and Experiment #3, we see that the concentration of H$_2$ is constant and the concentration of NO has decreased by one-half. The initial rate has decreased by one-fourth. Therefore, the initial rate is proportional to the squared concentration of NO; $y = 2$.

The overall rate law is: rate $= k[H_2][NO]^2$, and the order of the reaction is $1 + 2 = $ **3.**

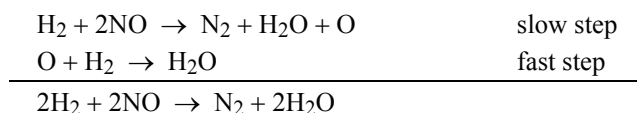(**b**)   Using Experiment #1 to calculate the rate constant,

$$\text{rate} = k[H_2][NO]^2$$

$$k = \frac{\text{rate}}{[H_2][NO]^2}$$

$$k = \frac{2.4 \times 10^{-6} \, M/\text{s}}{(0.010 \, M)(0.025 \, M)^2} = \mathbf{0.38 \, /M^2 \cdot s}$$

(c)   Consulting the rate law, we assume that the slow step in the reaction mechanism will probably involve one H_2 molecule and two NO molecules. Additionally the hint tells us that O atoms are an intermediate.

$$H_2 + 2NO \rightarrow N_2 + H_2O + O \qquad \text{slow step}$$
$$\underline{O + H_2 \rightarrow H_2O \qquad\qquad\qquad\quad \text{fast step}}$$
$$2H_2 + 2NO \rightarrow N_2 + 2H_2O$$

13.69   Since the methanol contains no oxygen–18, the oxygen atom must come from the phosphate group and not the water. The mechanism must involve a bond–breaking process like:

$$CH_3 - O \lll P \begin{matrix} O \\ \| \\ \end{matrix} - O - H$$
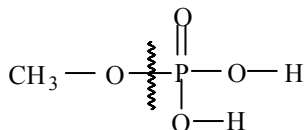
13.70   If water is also the solvent in this reaction, it is present in vast excess over the other reactants and products. Throughout the course of the reaction, the concentration of the water will not change by a measurable amount. As a result, the reaction rate will not appear to depend on the concentration of water.

13.71   Most transition metals have several stable oxidation states. This allows the metal atoms to act as either a source or a receptor of electrons in a broad range of reactions.

13.72   Since the reaction is first order in both A and B, then we can write the rate law expression:

$$\text{rate} = k[A][B]$$

Substituting in the values for the rate, [A], and [B]:

$$4.1 \times 10^{-4} \ M/s = k(1.6 \times 10^{-2})(2.4 \times 10^{-3})$$

$$\mathbf{k = 10.7 \ /M \cdot s}$$

Knowing that the overall reaction was second order, could you have predicted the units for k?

13.73   **(a)**   To determine the rate law, we must determine the exponents in the equation

$$\text{rate} = k[CH_3COCH_3]^x[Br_2]^y[H^+]^z$$

To determine the order of the reaction with respect to CH_3COCH_3, find two experiments in which the $[Br_2]$ and $[H^+]$ are held constant. Compare the data from experiments (1) and (5). When the concentration of CH_3COCH_3 is increased by a factor of 1.33, the reaction rate increases by a factor of 1.33. Thus, the reaction is first-order in CH_3COCH_3.

To determine the order with respect to Br_2, compare experiments (1) and (2). When the Br_2 concentration is doubled, the reaction rate does not change. Thus, the reaction is zero-order in Br_2.

To determine the order with respect to H^+, compare experiments (1) and (3). When the H^+ concentration is doubled, the reaction rate doubles. Thus, the reaction is first-order in H^+.

The rate law is:

$$\text{rate} = k[CH_3COCH_3][H^+]$$

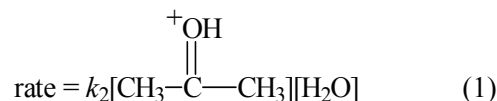**(b)**   Rearrange the rate law from part (a), solving for k.

$$k = \frac{\text{rate}}{[CH_3COCH_3][H^+]}$$
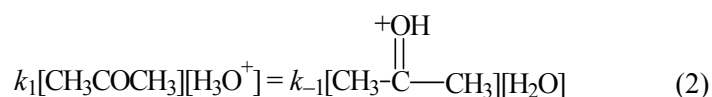
Substitute the data from any one of the experiments to calculate k. Using the data from Experiment (1),

$$k = \frac{5.7 \times 10^{-5} \ M/s}{(0.30 \ M)(0.050 \ M)} = 3.8 \times 10^{-3} \ /M \cdot s$$

(c)   Let k_2 be the rate constant for the slow step:

$$\begin{array}{c} ^{+}OH \\ \| \\ \text{rate} = k_2[CH_3-C-CH_3][H_2O] \end{array} \qquad (1)$$

Let k_1 and k_{-1} be the rate constants for the forward and reverse steps in the fast equilibrium.

$$\begin{array}{c} +OH \\ \| \\ k_1[CH_3COCH_3][H_3O^+] = k_{-1}[CH_3-C-CH_3][H_2O] \end{array} \qquad (2)$$

Therefore, Equation (1) becomes
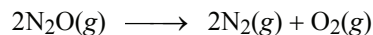
$$\text{rate} = \frac{k_1 k_2}{k_{-1}}[CH_3COCH_3][H_3O^+]]$$

which is the same as (a), where $k = k_1 k_2 / k_{-1}$.

13.74   Recall that the pressure of a gas is directly proportional to the number of moles of gas. This comes from the ideal gas equation.
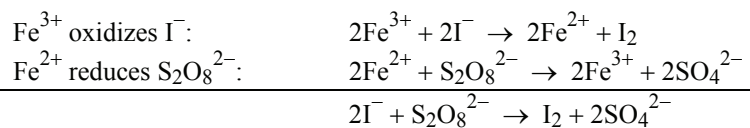
$$P = \frac{nRT}{V}$$

The balanced equation is:

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$$

From the stoichiometry of the balanced equation, for every one mole of N_2O that decomposes, one mole of N_2 and 0.5 moles of O_2 will be formed. Let's assume that we had 2 moles of N_2O at $t = 0$. After one half-life there will be one mole of N_2O remaining and one mole of N_2 and 0.5 moles of O_2 will be formed. The total number of moles of gas after one half-life will be:

$$n_T = n_{N_2O} + n_{N_2} + n_{O_2} = 1 \text{ mol} + 1 \text{ mol} + 0.5 \text{ mol} = 2.5 \text{ mol}$$

At $t = 0$, there were 2 mol of gas. Now, at $t_{\frac{1}{2}}$, there are 2.5 mol of gas. Since the pressure of a gas is directly proportional to the number of moles of gas, we can write:

$$\frac{2.10 \text{ atm}}{2 \text{ mol gas } (t = 0)} \times 2.5 \text{ mol gas}\left(\text{at } t_{\frac{1}{2}}\right) = \textbf{2.63 atm after one half-life}$$

13.75 Fe^{3+} undergoes a redox cycle: $Fe^{3+} \rightarrow Fe^{2+} \rightarrow Fe^{3+}$

Fe^{3+} oxidizes I^-: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

Fe^{2+} reduces $S_2O_8^{2-}$: $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

The uncatalyzed reaction is slow because both I^- and $S_2O_8^{2-}$ are negatively charged which makes their mutual approach unfavorable.

13.76   The rate expression for a third order reaction is:

$$rate = -\frac{\Delta[A]}{\Delta t} = k[A]^3$$

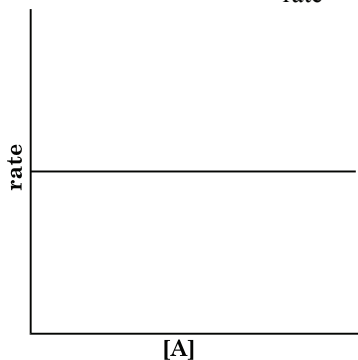The units for the rate law are:
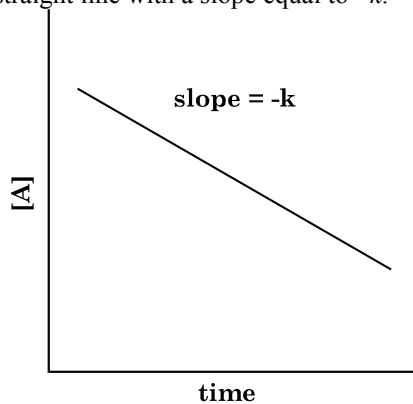
$$\frac{M}{s} = kM^3$$

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

13.77   For a rate law, *zero order* means that the exponent is zero. In other words, the reaction rate is just equal to a constant; it doesn't change as time passes.

(a)   The rate law would be:

$$rate = k[A]^0 = k$$

The integrated zero-order rate law is: $[A] = -kt + [A]_0$. Therefore, a plot of [A] versus time should be a straight line with a slope equal to $-k$.

(b) $[A] = [A]_0 - kt$

At $t_{\frac{1}{2}}$, $[A] = \dfrac{[A]_0}{2}$. Substituting into the above equation:

$$\frac{[A]_0}{2} = [A]_0 - kt_{\frac{1}{2}}$$

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

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

(c)   When $[A] = 0$,

$$[A]_0 = kt$$

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

Substituting for k,

$$t = \frac{[A]_0}{\dfrac{[A]_0}{2t_{\frac{1}{2}}}}$$

$$\boldsymbol{t = 2t_{\frac{1}{2}}}$$

This indicates that the integrated rate law is no longer valid after **two** half-lives.

13.78   Both compounds, A and B, decompose by first-order kinetics. Therefore, we can write a first-order rate equation for A and also one for B.

$$\ln\frac{[A]_t}{[A]_0} = -k_A t \qquad\qquad\qquad \ln\frac{[B]_t}{[B]_0} = -k_B t$$

$$\frac{[A]_t}{[A]_0} = e^{-k_A t} \qquad\qquad\qquad \frac{[B]_t}{[B]_0} = e^{-k_B t}$$

$$[A]_t = [A]_0 e^{-k_A t} \qquad\qquad\qquad [B]_t = [B]_0 e^{-k_B t}$$

We can calculate each of the rate constants, k_A and k_B, from their respective half-lives.

$$k_A = \frac{0.693}{50.0 \text{ min}} = 0.0139 \text{ min}^{-1} \qquad\qquad k_B = \frac{0.693}{18.0 \text{ min}} = 0.0385 \text{ min}^{-1}$$

The initial concentration of A and B are equal. $[A]_0 = [B]_0$. Therefore, from the first-order rate equations, we can write:

$$\frac{[A]_t}{[B]_t} = 4 = \frac{[A]_0 e^{-k_A t}}{[B]_0 e^{-k_B t}} = \frac{e^{-k_A t}}{e^{-k_B t}} = e^{(k_B - k_A)t} = e^{(0.0385 - 0.0139)t}$$

$$4 = e^{0.0246t}$$

$$\ln 4 \; = \; 0.0246t$$

$$t \; = \; \textbf{56.4 min}$$

13.79   There are three gases present and we can measure only the total pressure of the gases. To measure the partial pressure of azomethane at a particular time, we must withdraw a sample of the mixture, analyze and determine the mole fractions. Then,

$$P_{\text{azomethane}} \; = \; P_{\text{T}}X_{\text{azomethane}}$$

This is a rather tedious process if many measurements are required. A mass spectrometer will help (see Section 3.4 of the text).

13.80   **(a)**   Changing the concentration of a reactant has no effect on k.

(b)   If a reaction is run in a solvent other than in the gas phase, then the reaction mechanism will probably change and will thus change k.

(c)   Doubling the pressure simply changes the concentration. No effect on k, as in (a).

(d)   The rate constant k changes with temperature.

**(e)**   A catalyst changes the reaction mechanism and therefore changes k.

13.81
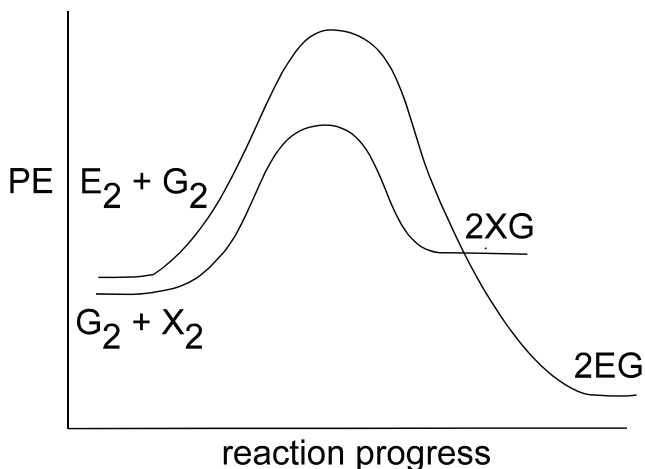
13.82   Mathematically, the amount left after ten half–lives is:

$$\left(\frac{1}{2}\right)^{10} \; = \; \textbf{9.8} \times \textbf{10}^{-4}$$

13.83   **(a)**   A catalyst works by changing the reaction mechanism, thus lowering the activation energy.
(b)   A catalyst changes the reaction mechanism.
(c)   A catalyst does not change the enthalpy of reaction.
(d)   A catalyst increases the forward rate of reaction.
(e)   A catalyst increases the reverse rate of reaction.

13.84   The net ionic equation is:

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$
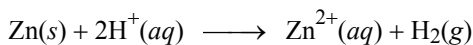
(a)   Changing from the same mass of granulated zinc to powdered zinc **increases** the rate because the surface area of the zinc (and thus its concentration) has increased.

(b)   Decreasing the mass of zinc (in the same granulated form) will **decrease** the rate because the total surface area of zinc has decreased.

(c)   The concentration of protons has decreased in changing from the strong acid (hydrochloric) to the weak acid (acetic); the rate will **decrease**.

(d)   An increase in temperature will **increase** the rate constant k; therefore, the rate of reaction increases.

13.85   At very high $[H_2]$,

$$k_2[H_2] \gg 1$$

$$\textbf{rate} = \frac{k_1[NO]^2[H_2]}{k_2[H_2]} = \frac{k_1}{k_2}[NO]^2$$

At very low $[H_2]$,

$$k_2[H_2] \ll 1$$

$$\textbf{rate} = \frac{k_1[NO]^2[H_2]}{1} = k_1[NO]^2[H_2]$$

The result from Problem 13.68 agrees with the rate law determined for low $[H_2]$.

13.86   If the reaction is 35.5% complete, the amount of A remaining is 64.5%. The ratio of $[A]_t/[A]_0$ is 64.5%/100% or 0.645/1.00. Using the first-order integrated rate law, Equation (13.3) of the text, we have
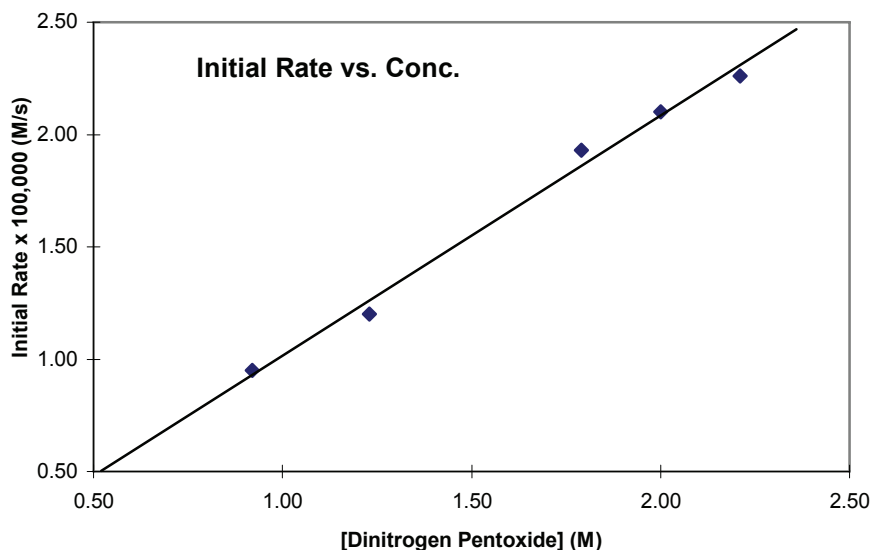
$$\ln\frac{[A]_t}{[A]_0} = -kt$$

$$\ln\frac{0.645}{1.00} = -k(4.90 \text{ min})$$

$$-0.439 = -k(4.90 \text{ min})$$

$$k = \textbf{0.0896 min}^{-1}$$

13.87   First we plot the data for the reaction: $2N_2O_5 \rightarrow 4NO_2 + O_2$

The data in linear, what means that the initial rate is directly proportional to the concentration of N_2O_5.

Thus, the rate law is:

$$\textbf{Rate} \; = \; \textbf{\textit{k}}[\textbf{N}_2\textbf{O}_5]$$

The rate constant k can be determined from the slope of the graph $\left(\dfrac{\Delta(\text{Initial Rate})}{\Delta[N_2O_5]} \right)$ or by using any set of

data.

$$k \; = \; 1.0 \times 10^{-5}\,\text{s}^{-1}$$

Note that the rate law is **not** Rate $= k[N_2O_5]^2$, as we might expect from the balanced equation. In general, the order of a reaction must be determined by experiment; it cannot be deduced from the coefficients in the balanced equation.

13.88   The first-order rate equation can be arranged to take the form of a straight line.

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

If a reaction obeys first-order kinetics, a plot of $\ln[A]$ vs. t will be a straight line with a slope of $-k$.

The slope of a plot of $\ln[N_2O_5]$ vs. t is $-6.18 \times 10^{-4}\,\text{min}^{-1}$. Thus,
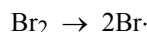
$$k \; = \; 6.18 \times 10^{-4}\,\text{min}^{-1}$$

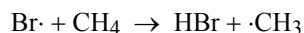The equation for the half-life of a first-order reaction is:

$$t_{\frac{1}{2}} \; = \; \frac{0.693}{k}$$

$$t_{\frac{1}{2}} \; = \; \frac{0.693}{6.18 \times 10^{-4}\,\text{min}^{-1}} \; = \; \textbf{1.12} \times \textbf{10}^{\textbf{3}}\,\textbf{min}$$

13.89 The red bromine vapor absorbs photons of blue light and dissociates to form bromine atoms.

$$Br_2 \rightarrow 2Br\cdot$$

The bromine atoms collide with methane molecules and abstract hydrogen atoms.

$$Br\cdot + CH_4 \rightarrow HBr + \cdot CH_3$$

The methyl radical then reacts with Br_2, giving the observed product and regenerating a bromine atom to start the process over again:

$$\cdot CH_3 + Br_2 \rightarrow CH_3Br + Br\cdot$$

$$Br\cdot + CH_4 \rightarrow HBr + \cdot CH_3 \qquad \text{and so on...}$$
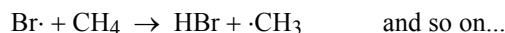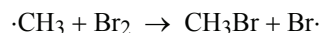
13.90 (a) In the two-step mechanism the rate-determining step is the collision of a hydrogen molecule with two iodine atoms. If visible light increases the concentration of iodine atoms, then the rate must increase. If the true rate-determining step were the collision of a hydrogen molecule with an iodine molecule (the one-step mechanism), then the visible light would have no effect (it might even slow the reaction by depleting the number of available iodine molecules).

(b) To split hydrogen molecules into atoms, one needs ultraviolet light of much higher energy.

13.91 For a first order reaction: $\ln\left(\dfrac{\text{decay rate at } t = t}{\text{decay rate at } t = 0}\right) = -kt$

$$\ln\left(\frac{0.186}{0.260}\right) = -(1.21 \times 10^{-4} \text{ yr}^{-1})t$$

$$t = \mathbf{2.77 \times 10^3 \text{ yr}}$$

13.92 (a) We can write the rate law for an elementary step directly from the stoichiometry of the balanced reaction. In this rate-determining elementary step three molecules must collide simultaneously (one X and two Y's). This makes the reaction termolecular, and consequently the rate law must be third order: first order in X and second order in Y.

The rate law is:
$$\text{rate} = k[X][Y]^2$$

(b) The value of the rate constant can be found by solving algebraically for k.

$$k = \frac{\text{rate}}{[X][Y]^2} = \frac{3.8 \times 10^{-3} \text{ } M/\text{s}}{(0.26 \text{ } M)(0.88 \text{ } M)^2} = \mathbf{1.9 \times 10^{-2} \text{ } M^{-2}\text{s}^{-1}}$$

Could you write the rate law if the reaction shown were the overall balanced equation and not an elementary step?

13.93 (a) $O + O_3 \rightarrow 2O_2$
(b) Cl is a catalyst; ClO is an intermediate.
(c) The C–F bond is stronger than the C–Cl bond.
(d) Ethane will remove the Cl atoms:
$$Cl + C_2H_6 \rightarrow HCl + C_2H_5$$

(e)
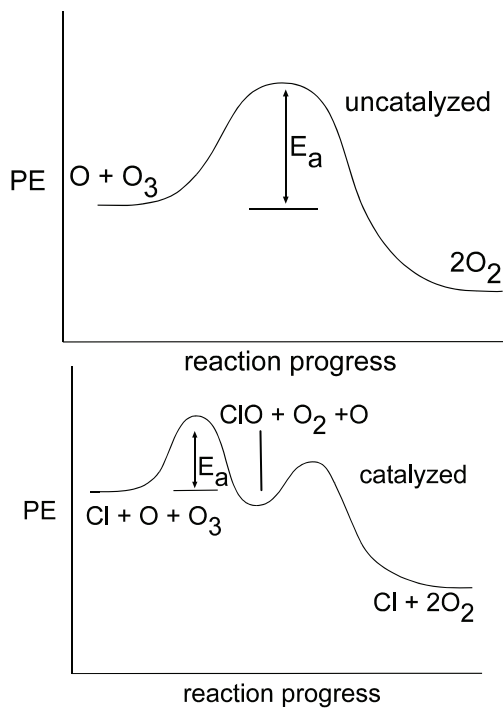
The overall reaction is: $O + O_3 \rightarrow 2O_2$.

$$\Delta H^\circ_{rxn} = 2\Delta H^\circ_f(O_2) - [\Delta H^\circ_f(O) + \Delta H^\circ_f(O_3)]$$

$$\Delta H^\circ_{rxn} = 2(0) - [(1)(249.4 \text{ kJ/mol}) + (1)(142.2 \text{ kJ/mol})]$$

$$\Delta H^\circ_{rxn} = -391.6 \text{ kJ/mol}$$

The reaction is exothermic.

13.94
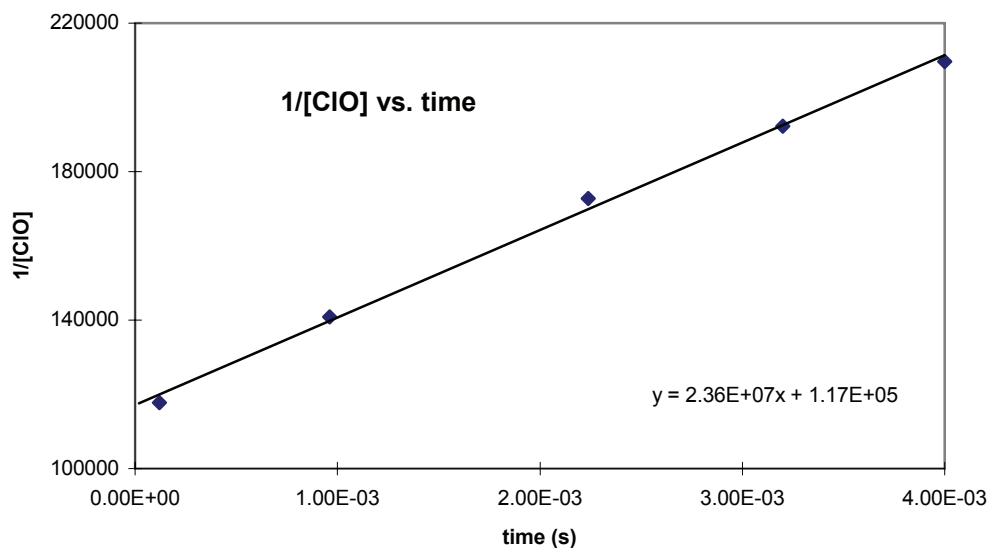
Reaction is **second-order** because a plot of 1/[ClO] vs. time is a straight line. The slope of the line equals the rate constant, k.

$$k = \text{Slope} = \mathbf{2.4 \times 10^7 \ /M \cdot s}$$

13.95   We can calculate the ratio of k_1/k_2 at 40°C using the Arrhenius equation.

$$\frac{k_1}{k_2} = \frac{Ae^{-E_{a_1}/RT}}{Ae^{-E_{a_2}/RT}} = e^{-(E_{a_1} - E_{a_2})/RT} = e^{-\Delta E_a/RT}$$

$$8.0 = e^{\dfrac{-\Delta E_a}{(8.314 \ \text{J/K·mol})(313 \ \text{K})}}$$

$$\ln(8.0) = \frac{-\Delta E_a}{(8.314 \ \text{J/K} \cdot \text{mol})(313 \ \text{K})}$$

$$\Delta E_a = -5.4 \times 10^3 \ \text{J/mol}$$

Having calculated ΔE_a, we can substitute back into the equation to calculate the ratio k_1/k_2 at 300°C (573 K).

$$\frac{k_1}{k_2} = e^{-\dfrac{-5.4 \times 10^3 \ \text{J/mol}}{(8.314 \ \text{J/K·mol})(573 \ \text{K})}} = \mathbf{3.1}$$

13.96   During the first five minutes or so the engine is relatively cold, so the exhaust gases will not fully react with the components of the catalytic converter. Remember, for almost all reactions, the rate of reaction increases with temperature.
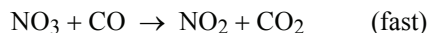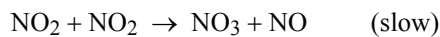
13.97
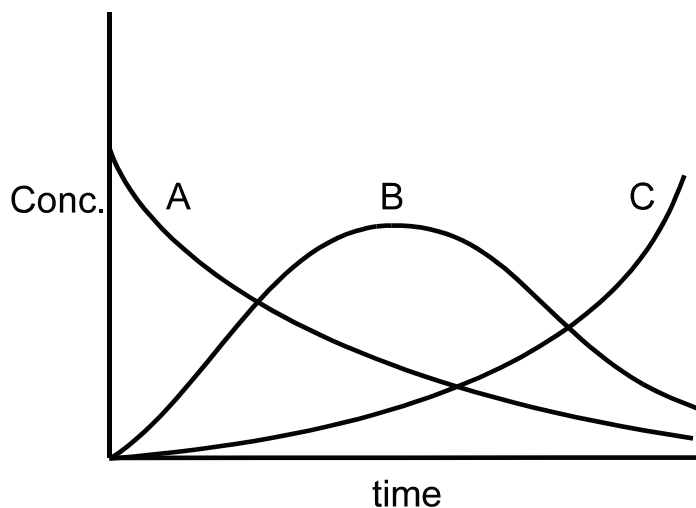
The actual appearance depends on the relative magnitudes of the rate constants for the two steps.

13.98   **(a)** E_a has a large value.

   (b) $E_a \approx 0$. Orientation factor is not important.

13.99   A plausible two-step mechanism is:

$$NO_2 + NO_2 \rightarrow NO_3 + NO \qquad \text{(slow)}$$

$$NO_3 + CO \rightarrow NO_2 + CO_2 \qquad \text{(fast)}$$

13.100   First, solve for the rate constant, k, from the half-life of the decay.

$$t_{\frac{1}{2}} = 2.44 \times 10^5 \text{ yr} = \frac{0.693}{k}$$

$$k = \frac{0.693}{2.44 \times 10^5 \text{ yr}} = 2.84 \times 10^{-6} \text{ yr}^{-1}$$

Now, we can calculate the time for the plutonium to decay from 5.0×10^2 g to 1.0×10^2 g using the equation for a first-order reaction relating concentration and time.

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

$$\ln \frac{1.0 \times 10^2}{5.0 \times 10^2} = -(2.84 \times 10^{-6} \text{ yr}^{-1})t$$

$$-1.61 = -(2.84 \times 10^{-6} \text{ yr}^{-1})t$$

$$t = 5.7 \times 10^5 \text{ yr}$$

13.101   At high pressure of PH_3, all the sites on W are occupied, so the rate is independent of $[PH_3]$.

**13.102** **(a)**   Catalyst: Mn^{2+}; intermediate: Mn^{3+}

First step is rate-determining.

(b)   Without the catalyst, the reaction would be a termolecular one involving 3 cations! (Tl^+ and two Ce^{4+}). The reaction would be slow.

(c)   The catalyst is a homogeneous catalyst because it has the same phase (aqueous) as the reactants.

13.103 (a) Since a plot of ln (sucrose) vs. time is linear, the reaction is 1st order.
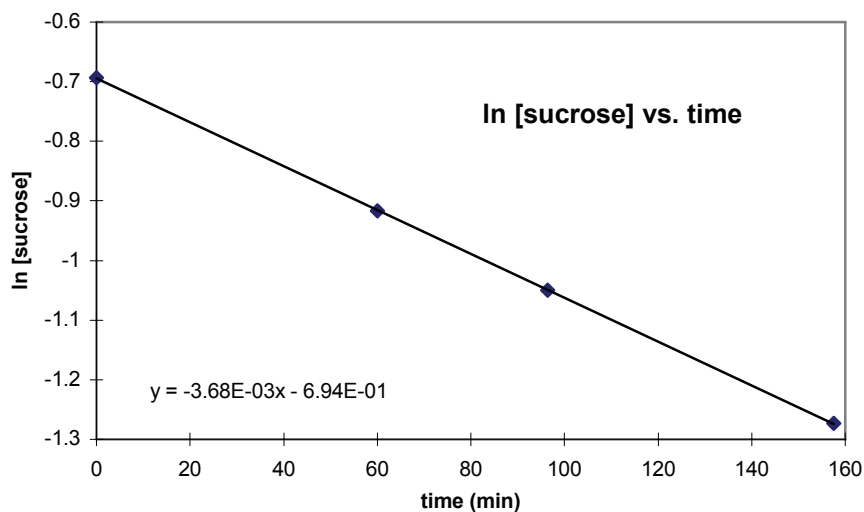
$$\text{Slope} = -3.68 \times 10^{-3} \text{ min}^{-1} = -k$$

$$k = 3.68 \times 10^{-3} \text{ min}^{-1}$$

(b) $\ln \dfrac{[A]_t}{[A]_0} = -kt$

$$\ln\left(\frac{0.05}{1}\right) = -(3.68 \times 10^{-3})t$$

$$t = 814 \text{ min}$$

(c) $[H_2O]$ is roughly unchanged. This is a pseudo-first-order reaction.

13.104 Initially, the number of moles of gas in terms of the volume is:

$$n = \frac{PV}{RT} = \frac{(0.350 \text{ atm})V}{\left(0.0821\dfrac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(450 + 273)\text{K}} = 5.90 \times 10^{-3} \, V$$

We can calculate the concentration of dimethyl ether from the following equation.

$$\ln \frac{[(CH_3)_2 O]_t}{[(CH_3)_2 O]_0} = -kt$$

$$\frac{[(CH_3)_2 O]_t}{[(CH_3)_2 O]_0} = e^{-kt}$$

Since, the volume is held constant, it will cancel out of the equation. The concentration of dimethyl ether after 8.0 minutes (480 s) is:

$$[(CH_3)_2 O]_t = \left(\frac{5.90 \times 10^{-3} \, V}{V}\right) e^{-\left(3.2 \times 10^{-4} \frac{1}{\text{s}}\right)(480 \text{ s})}$$

$$[(CH_3)_2 O]_t = 5.06 \times 10^{-3} \, M$$

After 8.0 min, the concentration of $(CH_3)_2O$ has decreased by $(5.90 \times 10^{-3} - 5.06 \times 10^{-3})M$ or 8.4×10^{-4} M. Since three moles of product form for each mole of dimethyl ether that reacts, the concentrations of the products are $(3)(8.4 \times 10^{-4}$ M$) = 2.5 \times 10^{-3}$ M.

The pressure of the system after 8.0 minutes is:

$$P = \frac{nRT}{V} = \left(\frac{n}{V}\right)RT = MRT$$

$$P = [(5.06 \times 10^{-3}) + (2.5 \times 10^{-3})]M \times (0.0821 \text{ L·atm/mol·K})(723 \text{ K})$$

$$\boldsymbol{P = 0.45 \text{ atm}}$$

13.105 This is a unit conversion problem. Recall that 1000 cm^3 = 1 L.

$$k = 7.9 \times 10^{-15} \frac{\text{cm}^3}{\text{molecule·s}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}}$$

$$\boldsymbol{k} = 4.8 \times 10^6 \text{ L/mol·s} = \boldsymbol{4.8 \times 10^6 \text{ /M·s}}$$

13.106 (a) $\dfrac{\Delta[B]}{\Delta t} = k_1[A] - k_2[B]$

(b)   If, $\dfrac{\Delta[B]}{\Delta t} = 0$

Then, from part (a) of this problem:

$$k_1[A] = k_2[B]$$

$$\boldsymbol{[B] = \frac{k_1}{k_2}[A]}$$

13.107 (a)   Drinking too much alcohol too fast means all the alcohol dehydrogenase (ADH) active sites are tied up and the excess alcohol will damage the central nervous system.

(b)   Both ethanol and methanol will compete for the same site at ADH. An excess of ethanol will replace methanol at the active site, leading to methanol's discharge from the body.

13.108 (a)   The first-order rate constant can be determined from the half-life.

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$\boldsymbol{k} = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{28.1 \text{ yr}} = \boldsymbol{0.0247 \text{ yr}^{-1}}$$

(b)   See Problem 13.82. Mathematically, the amount left after ten half–lives is:

$$\left(\frac{1}{2}\right)^{10} = \boldsymbol{9.8 \times 10^{-4}}$$

(c)   If 99.0% has disappeared, then 1.0% remains. The ratio of $[A]_t/[A]_0$ is 1.0%/100% or 0.010/1.00. Substitute into the first-order integrated rate law, Equation (13.3) of the text, to determine the time.

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

$$\ln \frac{0.010}{1.0} = -(0.0247 \text{ yr}^{-1})t$$

$$-4.6 = -(0.0247 \text{ yr}^{-1})t$$

$$t = \textbf{186 yr}$$

13.109 **(1)**   Assuming the reactions have roughly the same frequency factors, the one with the largest activation energy will be the slowest, and the one with the smallest activation energy will be the fastest. The reactions ranked from slowest to fastest are:

(b) < (c) < (a)

(2)   Reaction (a): **$\Delta H = -40$ kJ/mol**

Reaction (b): **$\Delta H = 20$ kJ/mol**

Reaction (c): **$\Delta H = -20$ kJ/mol**

(a) and (c) are exothermic, and (b) is endothermic.

13.110 **(a)**   There are three elementary steps: A → B, B → C, and C → D.

(b)   There are two intermediates: B and C.

(c)   The third step, C → D, is rate determining because it has the largest activation energy.

(d)   The overall reaction is exothermic.

13.111   The fire should not be doused with water, because titanium acts as a catalyst to decompose steam as follows:

$$2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$$
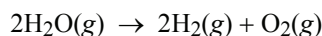
H_2 gas is flammable and forms an explosive mixture with O_2.

13.112   Let $k_{cat} = k_{uncat}$

Then,

$$Ae^{\frac{-E_a(\text{cat})}{RT_1}} = Ae^{\frac{-E_a(\text{uncat})}{RT_2}}$$

Since the frequency factor is the same, we can write:

$$e^{\frac{-E_a(\text{cat})}{RT_1}} = e^{\frac{-E_a(\text{uncat})}{RT_2}}$$

Taking the natural log (*ln*) of both sides of the equation gives:

$$\frac{-E_a(\text{cat})}{RT_1} = \frac{-E_a(\text{uncat})}{RT_2}$$

or,

$$\frac{E_a(\text{cat})}{T_1} = \frac{E_a(\text{uncat})}{T_2}$$

Substituting in the given values:

$$\frac{7.0 \text{ kJ/mol}}{293 \text{ K}} = \frac{42 \text{ kJ/mol}}{T_2}$$

$$\boldsymbol{T_2 = 1.8 \times 10^3 \text{ K}}$$

This temperature is much too high to be practical.

13.113 First, let's calculate the number of radium nuclei in 1.0 g.

$$1.0 \text{ g} \times \frac{1 \text{ mol Ra}}{226.03 \text{ g Ra}} \times \frac{6.022 \times 10^{23} \text{ Ra nuclei}}{1 \text{ mol Ra}} = 2.7 \times 10^{21} \text{ Ra nuclei}$$

We can now calculate the rate constant, k, from the activity and the number of nuclei, and then we can calculate the half-life from the rate contant.

activity $= kN$

$$\boldsymbol{k} = \frac{\text{activity}}{N} = \frac{3.70 \times 10^{10} \text{ nuclear disintegrations/s}}{2.7 \times 10^{21} \text{ nuclei}} = \boldsymbol{1.4 \times 10^{-11} \text{ /s}}$$

The half-life is:

$$\boldsymbol{t_{\frac{1}{2}}} = \frac{0.693}{k} = \frac{0.693}{1.4 \times 10^{-11} \text{ 1/s}} = \boldsymbol{5.0 \times 10^{10} \text{ s}}$$

Next, let's convert 500 years to seconds. Then we can calculate the number of nuclei remaining after 500 years.

$$500 \text{ yr} \times \frac{365 \text{ days}}{1 \text{ yr}} \times \frac{24 \text{ h}}{1 \text{ day}} \times \frac{3600 \text{ s}}{1 \text{ h}} = 1.58 \times 10^{10} \text{ s}$$

Use the first-order integrated rate law to determine the number of nuclei remaining after 500 years.

$$\ln\frac{N_t}{N_0} = -kt$$

$$\ln\left(\frac{N_t}{2.7 \times 10^{21}}\right) = -(1.4 \times 10^{-11} \text{ 1/s})(1.58 \times 10^{10} \text{ s})$$

$$\frac{N_t}{2.7 \times 10^{21}} = e^{-0.22}$$

$$N_t = 2.2 \times 10^{21} \text{ Ra nuclei}$$

Finally, from the number of nuclei remaining after 500 years and the rate constant, we can calculate the activity.

$$\text{activity} = kN$$

$$\textbf{activity} = (1.4 \times 10^{-11} \text{/s})(2.2 \times 10^{21} \text{ nuclei}) = \textbf{3.1} \times \textbf{10}^{\textbf{10}} \textbf{ nuclear disintegrations/s}$$

13.114 **(a)** The rate law for the reaction is:

$$\text{rate} = k[\text{Hb}][\text{O}_2]$$

We are given the rate constant and the concentration of Hb and O_2, so we can substitute in these quantities to solve for rate.

$$\text{rate} = (2.1 \times 10^6 \text{/M·s})(8.0 \times 10^{-6} \text{ M})(1.5 \times 10^{-6} \text{ M})$$

$$\textbf{rate} = \textbf{2.5} \times \textbf{10}^{-\textbf{5}} \textbf{ M/s}$$

(b) If HbO_2 is being formed at the rate of 2.5×10^{-5} M/s, then O_2 is being consumed at the same rate, $\textbf{2.5} \times \textbf{10}^{-\textbf{5}}$ **M/s**. Note the 1:1 mole ratio between O_2 and HbO_2.

(c) The rate of formation of HbO_2 increases, but the concentration of Hb remains the same. Assuming that temperature is constant, we can use the same rate constant as in part (a). We substitute rate, [Hb], and the rate constant into the rate law to solve for O_2 concentration.

$$\text{rate} = k[\text{Hb}][\text{O}_2]$$

$$1.4 \times 10^{-4} \text{ M/s} = (2.1 \times 10^6 \text{/M·s})(8.0 \times 10^{-6} \text{ M})[\text{O}_2]$$

$$[\textbf{O}_\textbf{2}] = \textbf{8.3} \times \textbf{10}^{-\textbf{6}} \textbf{ M}$$

13.115 Initially, the rate increases with increasing pressure (concentration) of NH_3. The straight-line relationship in the first half of the plot shows that the rate of reaction is directly proportional to the concentration of ammonia. Rate = $k[NH_3]$. The more ammonia that is adsorbed on the tungsten surface, the faster the reaction. At a certain pressure (concentration), the rate is no longer dependent on the concentration of ammonia (horizontal portion of plot). The reaction is now zero-order in NH_3 concentration. At a certain concentration of NH_3, all the reactive sites on the metal surface are occupied by NH_3 molecules, and the rate becomes constant. Increasing the concentration further has no effect on the rate.

13.116 $t_{\frac{1}{2}} \propto \dfrac{1}{[\text{A}]_0^{n-1}}$

$t_{\frac{1}{2}} = C\dfrac{1}{[\text{A}]_0^{n-1}}$, where C is a proportionality constant.

Substituting in for zero, first, and second-order reactions gives:

$n = 0 \qquad t_{\frac{1}{2}} = C\dfrac{1}{[\text{A}]_0^{-1}} = C[\text{A}]_0$

$n = 1 \qquad t_{\frac{1}{2}} = C\dfrac{1}{[\text{A}]_0^{0}} = C$

$$n = 2 \qquad t_{\frac{1}{2}} = C\frac{1}{[A]_0}$$

Compare these results with those in Table 13.3 of the text. What is C in each case?

13.117 (a) The relationship between half-life and rate constant is given in Equation (13.6) of the text.

$$k = \frac{0.693}{t_{\frac{1}{2}}}$$

$$k = \frac{0.693}{19.8 \text{ min}}$$

$$k = 0.0350 \text{ min}^{-1}$$

(b) Following the same procedure as in part (a), we find the rate constant at 70°C to be 1.58×10^{-3} min^{-1}. We now have two values of rate constants (k_1 and k_2) at two temperatures (T_1 and T_2). This information allows us to calculate the activation energy, E_a, using Equation (13.14) of the text.

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

$$\ln\left(\frac{0.0350 \text{ min}^{-1}}{1.58 \times 10^{-3} \text{ min}^{-1}}\right) = \frac{E_a}{(8.314 \text{ J/mol} \cdot \text{K})}\left(\frac{373 \text{ K} - 343 \text{ K}}{(373 \text{ K})(343 \text{ K})}\right)$$

$$E_a = 1.10 \times 10^5 \text{ J/mol} = 110 \text{ kJ/mol}$$

(c) Since all the above steps are elementary steps, we can deduce the rate law simply from the equations representing the steps. The rate laws are:

Initiation: rate $= k_i[R_2]$

Propagation: rate $= k_p[M][M_1]$

Termination: rate $= k_t[M'][M'']$

The reactant molecules are the ethylene monomers, and the product is polyethylene. Recalling that intermediates are species that are formed in an early elementary step and consumed in a later step, we see that they are the radicals M'·, M"·, and so on. (The R· species also qualifies as an intermediate.)

(d) The growth of long polymers would be favored by a high rate of propagations and a low rate of termination. Since the rate law of propagation depends on the concentration of monomer, an increase in the concentration of ethylene would increase the propagation (growth) rate. From the rate law for termination we see that a low concentration of the radical fragment M'· or M"· would lead to a slower rate of termination. This can be accomplished by using a low concentration of the initiator, R_2.

13.118 (a) The units of the rate constant show the reaction to be second-order, meaning the rate law is most likely:

Rate $= k[H_2][I_2]$

We can use the ideal gas equation to solve for the concentrations of H_2 and I_2. We can then solve for the initial rate in terms of H_2 and I_2 and then convert to the initial rate of formation of HI. We carry an extra significant figure throughout this calculation to minimize rounding errors.

$$n = \frac{PV}{RT}$$

$$\frac{n}{V} = M = \frac{P}{RT}$$

Since the total pressure is 1658 mmHg and there are equimolar amounts of H_2 and I_2 in the vessel, the partial pressure of each gas is 829 mmHg.

$$[H_2] = [I_2] = \frac{\left(829 \text{ mmHg} \times \dfrac{1 \text{ atm}}{760 \text{ mmHg}}\right)}{\left(0.0821 \dfrac{L \cdot atm}{mol \cdot K}\right)(400 + 273)\,K} = 0.01974 \; M$$

Let's convert the units of the rate constant to /M·min, and then we can substitute into the rate law to solve for rate.

$$k = 2.42 \times 10^{-2} \frac{1}{M \cdot s} \times \frac{60 \text{ s}}{1 \text{ min}} = 1.452 \frac{1}{M \cdot min}$$

$$\text{Rate} = k[H_2][I_2]$$

$$\text{Rate} = \left(1.452 \frac{1}{M \cdot min}\right)(0.01974 \; M)(0.01974 \; M) = 5.658 \times 10^{-4} \; M/min$$

We know that,

$$\text{Rate} = \frac{1}{2} \frac{\Delta[HI]}{\Delta t}$$

or

$$\frac{\Delta[HI]}{\Delta t} = 2 \times \text{Rate} = (2)(5.658 \times 10^{-4} \; M/min) = \mathbf{1.13 \times 10^{-3} \; \textbf{\textit{M}}/\textbf{min}}$$

(b) We can use the second-order integrated rate law to calculate the concentration of H_2 after 10.0 minutes. We can then substitute this concentration back into the rate law to solve for rate.

$$\frac{1}{[H_2]_t} = kt + \frac{1}{[H_2]_0}$$

$$\frac{1}{[H_2]_t} = \left(1.452 \frac{1}{M \cdot min}\right)(10.0 \text{ min}) + \frac{1}{0.01974 \; M}$$

$$[H_2]_t = 0.01534 \; M$$

We can now substitute this concentration back into the rate law to solve for rate. The concentration of I_2 after 10.0 minutes will also equal 0.01534 M.

$$\text{Rate} = k[H_2][I_2]$$

$$\text{Rate} = \left(1.452 \frac{1}{M \cdot min}\right)(0.01534 \; M)(0.01534 \; M) = 3.417 \times 10^{-4} \; M/min$$

We know that,

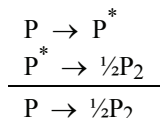$$\text{Rate} = \frac{1}{2} \frac{\Delta[HI]}{\Delta t}$$

or

$$\frac{\Delta[\text{HI}]}{\Delta t} = 2 \times \text{Rate} = (2)(3.417 \times 10^{-4} \text{ M/min}) = \textbf{6.83} \times \textbf{10}^{-4} \textbf{ M/min}$$

The concentration of HI after 10.0 minutes is:

$$[\text{HI}]_t = ([\text{H}_2]_0 - [\text{H}_2]_t) \times 2$$

$$\textbf{[HI]}_t = (0.01974 \text{ M} - 0.01534 \text{ M}) \times 2 = \textbf{8.8} \times \textbf{10}^{-3} \textbf{ M}$$

13.119 First, we write an overall balanced equation.

$$\text{P} \rightarrow \text{P}^*$$
$$\underline{\text{P}^* \rightarrow \text{½P}_2}$$
$$\text{P} \rightarrow \text{½P}_2$$

The average molar mass is given by:

$$\overline{\mathcal{M}} = \frac{\left([\text{P}]_t \mathcal{M} + 2[\text{P}_2]\mathcal{M}\right) \dfrac{\text{mol}}{\text{L}} \times \dfrac{\text{g}}{\text{mol}}}{\left([\text{P}]_t + [\text{P}_2]\right) \dfrac{\text{mol}}{\text{L}}} \qquad (1)$$

where $\mathcal{M}$ is the molar mass of P and $[\text{P}]_t$ is the concentration of P at a later time in the reaction. Note that in the numerator $[\text{P}_2]$ is multiplied by 2 because the molar mass of P_2 is double that of P. Also note that the units work out to give units of molar mass, g/mol.

Based on the stoichiometry of the reaction, the concentration of $[\text{P}_2]$ is:

$$[\text{P}_2] = \frac{[\text{P}]_0 - [\text{P}]_t}{2}$$

Substituting back into Equation (1) gives:

$$\overline{\mathcal{M}} = \frac{\left([\text{P}]_t \mathcal{M} + 2\dfrac{[\text{P}]_0 - [\text{P}]_t}{2}\mathcal{M}\right)}{\left([\text{P}]_t + \dfrac{[\text{P}]_0 - [\text{P}]_t}{2}\right)} = \frac{\left([\text{P}]_t \mathcal{M} + [\text{P}]_0 \mathcal{M} - [\text{P}]_t \mathcal{M}\right)}{\left([\text{P}]_t + \dfrac{1}{2}[\text{P}]_0 - \dfrac{1}{2}[\text{P}]_t\right)} = \frac{2\mathcal{M}[\text{P}]_0}{[\text{P}]_0 + [\text{P}]_t} \qquad (2)$$

In the proposed mechanism, the denaturation step is rate-determining. Thus,

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

Because we are looking at change in concentration over time, we need the first-order integrated rate law, Equation (13.3) of the text.

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

$$\frac{[\text{P}]_t}{[\text{P}]_0} = e^{-kt}$$

$$[\text{P}]_t = [\text{P}]_0 e^{-kt}$$

Substituting into Equation (2) gives:

$$\overline{\mathcal{M}} = \frac{2\mathcal{M}[P]_0}{[P]_0 + [P]_0\,e^{-kt}} = \frac{2\mathcal{M}}{1 + e^{-kt}}$$

or

$$\frac{2\mathcal{M} - \overline{\mathcal{M}}}{\overline{\mathcal{M}}} = e^{-kt}$$

$$\ln\left(\frac{2\mathcal{M} - \overline{\mathcal{M}}}{\overline{\mathcal{M}}}\right) = -kt$$

The rate constant, k, can be determined by plotting $\ln\left(\dfrac{2\mathcal{M} - \overline{\mathcal{M}}}{\overline{\mathcal{M}}}\right)$ versus t. The plot will give a straight line with a slope of $-k$.

13.120 The half-life is related to the initial concentration of A by

$$t_{\frac{1}{2}} \propto \frac{1}{[A]_0^{n-1}}$$

According to the data given, the half-life doubled when $[A]_0$ was halved. This is only possible if the half-life is inversely proportional to $[A]_0$. Substituting $n = 2$ into the above equation gives:

$$t_{\frac{1}{2}} \propto \frac{1}{[A]_0}$$

Looking at this equation, it is clear that if $[A]_0$ is halved, the half-life would double. The reaction is **second-order**.

We use Equation (13.8) of the text to calculate the rate constant.

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

$$\boldsymbol{k} = \frac{1}{[A]_0 t_{\frac{1}{2}}} = \frac{1}{(1.20\ M)(2.0\ \text{min})} = \boldsymbol{0.42\ /M \cdot min}$$

13.121 (a) The half-life of a reaction and the initial concentration are related by

$$t_{\frac{1}{2}} = C\frac{1}{[A]_0^{n-1}}$$

where C is a constant. Taking the common logarithm of both sides of the equation,
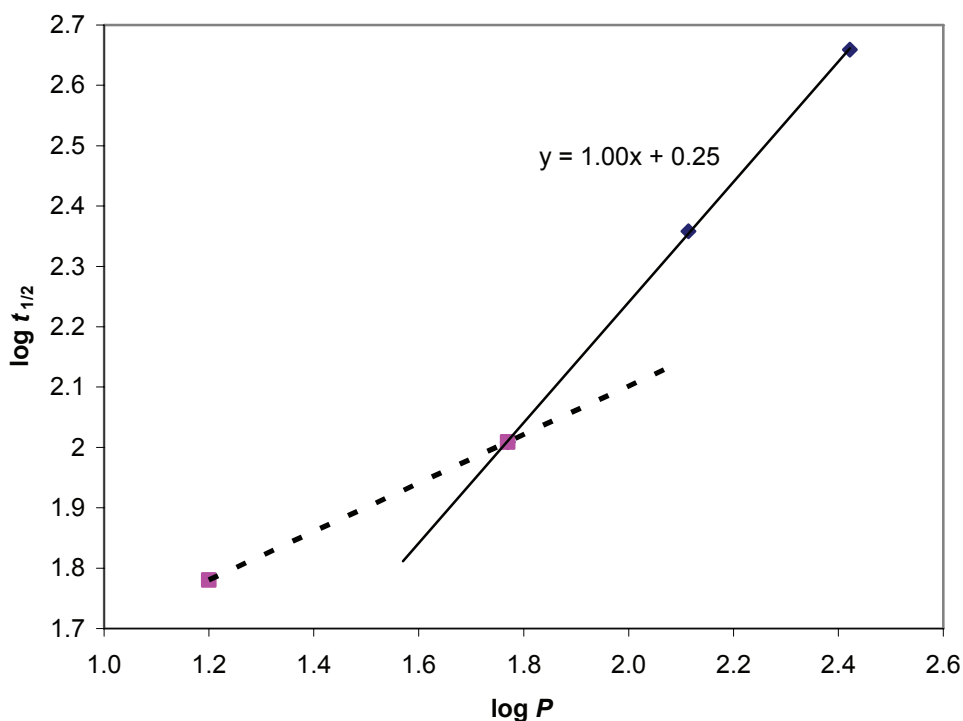
$$\log t_{\frac{1}{2}} = \log C - (n - 1)\log[A]_0$$

Because pressure is proportional to concentration at constant temperature, the above equation can also be written as

$$\log t_{\frac{1}{2}} = -(n - 1)\log P + \log C'$$

A plot of $\log t_{\frac{1}{2}}$ vs. $\log P$ gives a slope of $-(n-1)$. The data used for the plot are:

$\log P$	$\log t_{\frac{1}{2}}$
2.422	2.659
2.114	2.358
1.77	2.009
1.20	1.78

There are clearly two types of behavior exhibited in the graph. At pressures above 50 mmHg, the graph appears to be a straight line. Fitting these three points results in a best fit line with an equation of $y = 1.00x + 0.25$. The slope of the line is 1.00; therefore, $1.00 = -(n-1)$, or $n = 0$, and the reaction is zero-order.

Although the data are limited, it is clear that there is a change in slope below 50 mmHg, indicating a change in reaction order. It does appear that the limiting slope as pressure approaches zero is itself zero. Thus, $0 = -(n-1)$, or $n = 1$, and the limiting behavior is that of a first-order reaction.

(b) As discovered in part **(a)**, the reaction is first-order at low pressures and zero-order at pressures above 50 mmHg.

(c) The mechanism is actually the same at all pressures considered. At low pressures, the fraction of the tungsten surface covered is proportional to the pressure of NH_3, so the rate of decomposition will have a first-order dependence on ammonia pressure. At increased pressures, all the catalytic sites are occupied by NH_3 molecules, and the rate becomes independent of the ammonia pressure and hence zero-order in NH_3.

13.122   From Equation (13.14) of the text,

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

$$\ln \left(\frac{k_1}{k_2} \right) = \frac{2.4 \times 10^5 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{606 \text{ K}} - \frac{1}{600 \text{ K}} \right)$$

$$\ln \left(\frac{k_1}{k_2} \right) = -0.48$$

$$\frac{k_2}{k_1} = e^{0.48} = 1.6$$

The rate constant at 606 K is 1.6 times greater than that at 600 K. This is a **60%** increase in the rate constant for a 1% increase in temperature! The result shows the profound effect of an exponential dependence. In general, the larger the E_a, the greater the influence of T on k.

13.123 λ_1 (the absorbance of A) decreases with time. This would happen for all the mechanisms shown. Note that λ_2 (the absorbance of B) increases with time and then decreases. Therefore, B cannot be a product as shown in mechanisms (a) or (b). If B were a product its absorbance would increase with time and level off, but it would not decrease. Since the concentration of B increases and then after some time begins to decrease, it must mean that it is produced and then it reacts to produce product as in mechanisms (c) and (d). In mechanism (c), two products are C and D, so we would expect to see an increase in absorbance for two species. Since we see an increase in absorbance for only one species, then the mechanism that is consistent with the data must be **(d)**. λ_3 is the absorbance of C.