is 1.26×10^{-15} $\text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1}$. Determine the value of the rate constant in units of $\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$.

28-6. The definition of the rate of reaction in terms of molar concentration (Equation 28.5) assumes that the volume remains constant during the course of the reaction. Derive an expression for the rate of reaction in terms of the molar concentration of a reactant A for the case in which the volume changes during the course of the reaction.

28-7. Derive the integrated rate law for a reaction that is zero order in reactant concentration.

28-8. Determine the rate law for the reaction described by

$$NO(g) + H_2(g) \longrightarrow \text{products}$$

from the initial rate data tabulated below.

$P_0(H_2)$/torr	$P_0(NO)$/torr	v_0/torr·s^{-1}
400	159	34
400	300	125
289	400	160
205	400	110
147	400	79

Calculate the rate constant for this reaction.

28-9. Sulfuryl chloride decomposes according to the equation

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Determine the order of the reaction with respect to $SO_2Cl_2(g)$ from the following initial-rate data collected at 298.15 K

$[SO_2Cl_2]_0$/mol·dm^{-3}	0.10	0.37	0.76	1.22
v_0/mol·dm^{-3}·s^{-1}	2.24×10^{-6}	8.29×10^{-6}	1.71×10^{-5}	2.75×10^{-5}

Calculate the rate constant for this reaction at 298.15 K.

28-10. Consider the reaction described by

$$Cr(H_2O)_6^{3+}(aq) + SCN^-(aq) \longrightarrow Cr(H_2O)_5(SCN)^{2+}(aq) + H_2O(l)$$

for which the following initial rate data were obtained at 298.15 K.

$[Cr(H_2O)_6^{3+}]_0$/mol·dm^{-3}	$[SCN^-]_0$/mol·dm^{-3}	v_0/mol·dm^{-3}·s^{-1}
1.21×10^{-4}	1.05×10^{-5}	2.11×10^{-11}
1.46×10^{-4}	2.28×10^{-5}	5.53×10^{-11}
1.66×10^{-4}	1.02×10^{-5}	2.82×10^{-11}
1.83×10^{-4}	3.11×10^{-5}	9.44×10^{-11}

Determine the rate law for the reaction and the rate constant at 298.15 K. Assume the orders are integers.

28-11. Consider the base-catalyzed reaction

$$OCl^-(aq) + I^-(aq) \longrightarrow OI^-(aq) + Cl^-(aq)$$

Use the following initial-rate data to determine the rate law and the corresponding rate constant for the reaction.

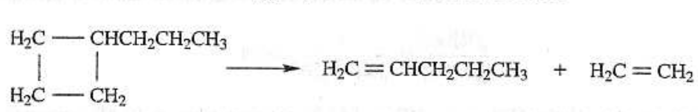
$[OCl^-]$/mol·dm^{-3}	$[I^-]$/mol·dm^{-3}	$[OH^-]$/mol·dm^{-3}	v_0/mol·dm^{-3}·s^{-1}
1.62×10^{-3}	1.62×10^{-3}	0.52	3.06×10^{-4}
1.62×10^{-3}	2.88×10^{-3}	0.52	5.44×10^{-4}
2.71×10^{-3}	1.62×10^{-3}	0.84	3.16×10^{-4}
1.62×10^{-3}	2.88×10^{-3}	0.91	3.11×10^{-4}

28-12. The reaction

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

is first order and has a rate constant of 2.24×10^{-5} s^{-1} at 320°C. Calculate the half-life of the reaction. What fraction of a sample of $SO_2Cl_2(g)$ remains after being heated for 5.00 hours at 320°C? How long will a sample of $SO_2Cl_2(g)$ need to be maintained at 320°C to decompose 92.0% of the initial amount present?

28-13. The half-life for the following gas-phase decomposition reaction



is found to be independent of the initial concentration of the reactant. Determine the rate law and integrated rate law for this reaction.

28-14. Hydrogen peroxide, H_2O_2, decomposes in water by a first-order kinetic process. A 0.156-mol·dm^{-3} solution of H_2O_2 in water has an initial rate of 1.14×10^{-5} mol·dm^{-3}·s^{-1}. Calculate the rate constant for the decomposition reaction and the half-life of the decomposition reaction.

28-15. A first-order reaction is 24.0% complete in 19.7 minutes. How long will the reaction take to be 85.5% complete? Calculate the rate constant for the reaction.

28-16. The nucleophilic substitution reaction

$$PhSO_2SO_2Ph(sln) + N_2H_4(sln) \longrightarrow PhSO_2NHNH_2(sln) + PhSO_2H(sln)$$

was studied in cyclohexane solution at 300 K. The rate law was found to be first order in $PhSO_2SO_2Ph$. For an initial concentration of $[PhSO_2SO_2Ph]_0 = 3.15 \times 10^{-5}$ mol·dm^{-3}, the following rate data were observed. Determine the rate law and the rate constant for this reaction.

$[N_2H_4]_0/10^{-2}$ mol·dm^{-3}	0.5	1.0	2.4	5.6
v/mol·dm^{-3}·s^{-1}	0.085	0.17	0.41	0.95

28-28. The following data are obtained for the reaction

$$N_2O(g) \longrightarrow N_2(g) + \tfrac{1}{2}O_2(g)$$

at 900 K.

t/s	0	3146	6494	13 933
$[N_2O]$/mol·dm^{-3}	0.521	0.416	0.343	0.246

The rate law for this reaction is second order in N_2O concentration. Calculate the rate constant for this decomposition reaction.

28-29. Consider a chemical reaction

$$A \longrightarrow \text{products}$$

that obeys the rate law

$$-\frac{d[A]}{dt} = k[A]^n$$

where n, the reaction order, can be any number except $n = 1$. Separate the concentration and time variables and then integrate the resulting expression assuming the concentration of A is $[A]_0$ at time $t = 0$ and is [A] at time t to show that

$$kt = \frac{1}{n-1}\left(\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}}\right) \qquad n \neq 1 \tag{1}$$

Use Equation 1 to show that the half-life of a reaction of order n is

$$kt_{1/2} = \frac{1}{n-1}\,\frac{2^{n-1}-1}{[A]_0^{n-1}} \qquad n \neq 1 \tag{2}$$

Show that this result reduces to Equation 28.29 when $n = 2$.

28-30. Show that Equation 1 of Problem 28–29 can be written in the form

$$\frac{\left(\frac{[A]_0}{[A]}\right)^x - 1}{x} = k[A]_0^x t$$

where $x = n - 1$. Now use L'Hopital's rule to show that

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

for $n = 1$. (Remember that $da^x/dx = a^x \ln a$.)

28-31. The following data were obtained for the reaction

$$N_2O(g) \longrightarrow N_2(g) + \tfrac{1}{2}O_2(g)$$

$[N_2O]_0$/mol·dm^{-3}	1.674×10^{-3}	4.458×10^{-3}	9.300×10^{-3}	1.155×10^{-2}
$t_{1/2}$/s	1200	470	230	190

Assume the rate law for this reaction is

$$-\frac{d[N_2O]}{dt} = k[N_2O]^n$$

and use Equation 2 of Problem 28–29 to determine the reaction order of N_2O by plotting $\ln t_{1/2}$ against $\ln[A]_0$. Calculate the rate constant for this decomposition reaction.

28-32. We will derive Equation 28.39 from Equation 28.38 in this problem. Rearrange Equation 28.38 to become

$$\frac{d[A]}{(k_1 + k_{-1})[A] - k_{-1}[A]_0} = -dt$$

and integrate to obtain

$$\ln\{(k_1 + k_{-1})[A] - k_{-1}[A]_0\} = -(k_1 + k_{-1})t + \text{constant}$$

or

$$(k_1 + k_{-1})[A] - k_{-1}[A]_0 = ce^{-(k_1+k_{-1})t}$$

where c is a constant. Show that $c = k_1[A]_0$ and that

$$(k_1 + k_{-1})[A] - k_{-1}[A]_0 = k_1[A]_0 e^{-(k_1+k_{-1})t} \tag{1}$$

Now let $t \to \infty$ and show that

$$[A]_0 = \frac{(k_1 + k_{-1})[A]_{eq}}{k_{-1}}$$

and

$$[A]_0 - [A]_{eq} = \frac{k_1[A]_{eq}}{k_{-1}} = \frac{k_1[A]_0}{k_1 + k_{-1}}$$

Use these results in Equation 1 to obtain Equation 28.39.

28-33. Consider the general chemical reaction

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P$$

If we assume that both the forward and reverse reactions are first order in their respective reactants, the rate law is given by (Equation 28.52)

$$\frac{d[P]}{dt} = k_1[A][B] - k_{-1}[P] \tag{1}$$

Now consider the response of this chemical reaction to a temperature jump. Let $[A] = [A]_{2,eq} + \Delta[A]$, $[B] = [B]_{2,eq} + \Delta[B]$, and $[P] = [P]_{2,eq} + \Delta[P]$, where the subscript "2,eq" refers to the new equilibrium state. Now use the fact that $\Delta[A] = \Delta[B] = -\Delta[P]$ to show that Equation 1 becomes

$$\frac{d\Delta[P]}{dt} = k_1[A]_{2,eq}[B]_{2,eq} - k_{-1}[P]_{2,eq}$$
$$- \{k_1([A]_{2,eq} + [B]_{2,eq}) + k_{-1}\}\Delta[P] + O(\Delta[P]^2)$$

Show that the first terms on the right side of this equation cancel and that Equations 28.53 and 28.54 result.

28-34. The equilibrium constant for the reaction

$$\mathrm{H^+(aq) + OH^-(aq)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{H_2O(l)}$$

at 25°C is $K_c = [\mathrm{H_2O}]/[\mathrm{H^+}][\mathrm{OH^-}] = 5.49 \times 10^{15}\ \mathrm{mol^{-1}\cdot dm^3}$. The time-dependent conductivity of the solution following a temperature jump to a final temperature of 25°C shows a relaxation time of $\tau = 3.7 \times 10^{-5}$ s. Determine the values of the rate constants k_1 and k_{-1}. At 25°C, the density of water is $\rho = 0.997\ \mathrm{g\cdot cm^{-3}}$.

28-35. The equilibrium constant for the reaction

$$\mathrm{D^+(aq) + OD^-(aq)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{D_2O(l)}$$

at 25°C is $K_c = 4.08 \times 10^{16}\ \mathrm{mol^{-1}\cdot dm^3}$. The rate constant k_{-1} is independently found to be $2.52 \times 10^{-6}\ \mathrm{s^{-1}}$. What do you predict for the observed relaxation time for a temperature-jump experiment to a final temperature of 25°C? The density of $\mathrm{D_2O}$ is $\rho = 1.104\ \mathrm{g\cdot cm^{-3}}$ at 25°C.

28-36. Consider the chemcial reaction described by

$$2\,\mathrm{A(aq)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{D(aq)}$$

If we assume the forward reaction is second order and the reverse reaction is first order, the rate law is given by

$$\frac{d[\mathrm{D}]}{dt} = k_1[\mathrm{A}]^2 - k_{-1}[\mathrm{D}] \qquad (1)$$

Now consider the response of this chemical reaction to a temperature jump. Let $[\mathrm{A}] = [\mathrm{A}]_{2,\mathrm{eq}} + \Delta[\mathrm{A}]$ and $[\mathrm{D}] = [\mathrm{D}]_{2,\mathrm{eq}} + \Delta[\mathrm{D}]$, where the subscript "2,eq" refers to the new equilibrium state. Now use the fact that $\Delta[\mathrm{A}] = -2\Delta[\mathrm{D}]$ to show that Equation 1 becomes

$$\frac{d\Delta[\mathrm{D}]}{dt} = -(4k_1[\mathrm{A}]_{2,\mathrm{eq}} + k_{-1})\Delta[\mathrm{D}] + O(\Delta[\mathrm{D}]^2)$$

Show that if we ignore the $O(\Delta[\mathrm{D}]^2)$ term, then

$$\Delta[\mathrm{D}] = \Delta[\mathrm{D}]_0 e^{-t/\tau}$$

where $\tau = 1/(4k_1[\mathrm{A}]_{2,\mathrm{eq}} + k_{-1})$.

28-37. In Problem 28-36, you showed that the relaxation time for the dimerization reaction

$$2\,\mathrm{A(aq)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{D(aq)}$$

is given by $\tau = 1/(4k_1[\mathrm{A}]_{2,\mathrm{eq}} + k_{-1})$. Show that this equation can be rewritten as

$$\frac{1}{\tau^2} = k_{-1}^2 + 8k_1k_{-1}[\mathrm{S}]_0$$

where $[\mathrm{S}]_0 = 2[\mathrm{D}] + [\mathrm{A}] = 2[\mathrm{D}]_{2,\mathrm{eq}} + [\mathrm{A}]_{2,\mathrm{eq}}$.

28-38. The first step in the assembly of the protein yeast phosphoglycerate mutase is a reversible dimerization of a polypeptide,

$$2\,\mathrm{A(aq)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{D(aq)}$$

where A is the polypeptide and D is the dimer. Suppose that a $1.43 \times 10^{-5}\ \mathrm{mol\cdot dm^{-3}}$ solution of A is prepared and allowed to come to equilibrium at 280 K. Once equilibrium is achieved, the temperature of the solution is jumped to 293 K. The rate constants k_1 and k_{-1} for the dimerization reaction at 293 K are $6.25 \times 10^3\ \mathrm{dm^3\cdot mol^{-1}\cdot s^{-1}}$ and $6.00 \times 10^{-3}\ \mathrm{s^{-1}}$, respectively. Calculate the value of the relaxation time observed in the experiment. (*Hint:* See Problem 28–37.)

28-39. Does the Arrhenius A factor always have the same units as the reaction rate constant?

28-40. Use the results of Problems 28–26 and 28–27 to calculate the values of E_a and A for the decomposition of uranyl nitrate.

28-41. The experimental rate constants for the reaction described by

$$\mathrm{OH(g) + ClCH_2CH_2Cl(g) \longrightarrow H_2O(g) + ClCHCH_2Cl(g)}$$

at various temperatures are tabulated below.

T/K	292	296	321	333	343	363
$k/10^8\ \mathrm{dm^3\cdot mol^{-1}\cdot s^{-1}}$	1.24	1.32	1.81	2.08	2.29	2.75

Determine the values of the Arrhenius parameters A and E_a for this reaction.

28-42. The Arrhenius parameters for the reaction described by

$$\mathrm{HO_2(g) + OH(g) \longrightarrow H_2O(g) + O_2(g)}$$

are $A = 5.01 \times 10^{10}\ \mathrm{dm^3\cdot mol^{-1}\cdot s^{-1}}$ and $E_a = 4.18\ \mathrm{kJ\cdot mol^{-1}}$. Determine the value of the rate constant for this reaction at 298 K.

28-43. At what temperature will the reaction described in Problem 28–42 have a rate constant that is twice that at 298 K?

28-44. The rate constants for the reaction

$$\mathrm{CHCl_2(g) + Cl_2(g) \longrightarrow CHCl_3(g) + Cl(g)}$$

at different temperatures are tabulated below

T/K	357	400	458	524	533	615
$k/10^7\ \mathrm{dm^3\cdot mol^{-1}\cdot s^{-1}}$	1.72	2.53	3.82	5.20	5.61	7.65

Calculate the values of the Arrhenius parameters A and E_a for this reaction.

28-45. The rate constant for the chemical reaction

$$2\,\mathrm{N_2O_5(g)} \longrightarrow 4\,\mathrm{NO_2(g)} + \mathrm{O_2(g)}$$

doubles from 22.50°C to 27.47°C. Determine the activation energy of the reaction. Assume the pre-exponential factor is independent of temperature.

28-46. Show that if A reacts to form either B or C according to

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \qquad \text{or} \qquad \mathrm{A} \xrightarrow{k_2} \mathrm{C}$$

then E_a, the observed activation energy for the disappearance of A, is given by

$$E_a = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$

where E_1 is the activation energy for the first reaction and E_2 is the activation energy for the second reaction.

28-47. Cyclohexane interconverts between a "chair" and a "boat" structure. The activation parameters for the reaction from the chair to the boat form of the molecule are $\Delta^{\ddagger}H^{\circ} = 31.38\ \mathrm{kJ\cdot mol^{-1}}$ and $\Delta^{\ddagger}S^{\circ} = 16.74\ \mathrm{J\cdot K^{-1}}$. Calculate the standard Gibbs energy of activation and the rate constant for this reaction at 325 K.

28-48. The gas-phase rearrangement reaction

$$\text{vinyl allyl ether} \longrightarrow \text{allyl acetone}$$

has a rate constant of $6.015 \times 10^{-5}\ \mathrm{s^{-1}}$ at 420 K and a rate constant of $2.971 \times 10^{-3}\ \mathrm{s^{-1}}$ at 470 K. Calculate the values of the Arrhenius parameters A and E_a. Calculate the values of $\Delta^{\ddagger}H^{\circ}$ and $\Delta^{\ddagger}S^{\circ}$ at 420 K. (Assume ideal-gas behavior.)

28-49. The kinetics of a chemical reaction can be followed by a variety of experimental techniques, including optical spectroscopy, NMR spectroscopy, conductivity, resistivity, pressure changes, and volume changes. When using these techniques, we do not measure the concentration itself but we know that the observed signal is proportional to the concentration; the exact proportionality constant depends on the experimental technique and the species present in the chemical system. Consider the general reaction given by

$$\nu_A \mathrm{A} + \nu_B \mathrm{B} \longrightarrow \nu_Y \mathrm{Y} + \nu_Z \mathrm{Z}$$

where we assume that A is the limiting reagent so that $[\mathrm{A}] \to 0$ as $t \to \infty$. Let p_i be the proportionality constant for the contribution of species i to S, the measured signal from the instrument. Explain why at any time t during the reaction, S is given by

$$S(t) = p_A[\mathrm{A}] + p_B[\mathrm{B}] + p_Y[\mathrm{Y}] + p_Z[\mathrm{Z}] \tag{1}$$

Show that the initial and final readings from the instrument are given by

$$S(0) = p_A[\mathrm{A}]_0 + p_B[\mathrm{B}]_0 + p_Y[\mathrm{Y}]_0 + p_Z[\mathrm{Z}]_0 \tag{2}$$

and

$$S(\infty) = p_B\left([\mathrm{B}]_0 - \frac{\nu_B}{\nu_A}[\mathrm{A}]_0\right) + p_Y\left([\mathrm{Y}]_0 + \frac{\nu_Y}{\nu_A}[\mathrm{A}]_0\right) + p_Z\left([\mathrm{Z}]_0 + \frac{\nu_Z}{\nu_A}[\mathrm{A}]_0\right) \tag{3}$$

Combine Equations 1 through 3 to show that

$$[\mathrm{A}] = [\mathrm{A}]_0 \frac{S(t) - S(\infty)}{S(0) - S(\infty)}$$

(*Hint*: Be sure to express [B], [Y], and [Z] in terms of their initial values, [A] and $[\mathrm{A}]_0$.)

28-50. Use the result of Problem 28–49 to show that for the first-order rate law, $v = k[\mathrm{A}]$, the time-dependent signal is given by

$$S(t) = S(\infty) + [S(0) - S(\infty)]e^{-kt}$$

28-51. Use the result of Problem 28–49 to show that for the second-order rate law, $v = k[\mathrm{A}]^2$, the time-dependent signal is given by

$$S(t) = S(\infty) + \frac{S(0) - S(\infty)}{1 + [\mathrm{A}]_0 kt}$$

28-52. Because there is a substantial increase in the volume of the solution as the reaction proceeds, the decomposition of diacetone alcohol can be followed by a dilatometer, a device that measures the volume of a sample as a function of time. The instrument readings at various times are tabulated below.

Time/s	0	24.4	35.0	48.0	64.8	75.8	133.4	∞
S/arbitrary units	8.0	20.0	24.0	28.0	32.0	34.0	40.0	43.3

Use the expressions derived in Problems 28–50 and 28–51 to determine if the decomposition reaction is a first- or second-order process.

28-53. In Problem 28–49, we assumed that A reacted completely so that $[\mathrm{A}] \to 0$ as $t \to \infty$. Show that if the reaction does not go to completion but establishes an equilibrium instead, then

$$[\mathrm{A}] = [\mathrm{A}]_{\mathrm{eq}} + \{[\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}}\} \frac{S(t) - S(\infty)}{S(0) - S(\infty)}$$

where $[\mathrm{A}]_{\mathrm{eq}}$ is the equilibrium concentration of A.

● **29-12.** The rate law for the reaction between CO(g) and Cl_2(g) to form phosgene (Cl_2CO)

$$Cl_2(g) + CO(g) \xrightarrow{k_{obs}} Cl_2CO(g)$$

is

$$\frac{d[Cl_2CO]}{dt} = k_{obs}[Cl_2]^{3/2}[CO]$$

Show that the following mechanism is consistent with this rate law.

$$Cl_2(g) + M(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Cl(g) + M(g) \qquad \text{(fast equilibrium)}$$

$$Cl(g) + CO(g) + M(g) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ClCO(g) + M(g) \qquad \text{(fast equilibrium)}$$

$$ClCO(g) + Cl_2(g) \xrightarrow{k_3} Cl_2CO(g) + Cl(g) \qquad \text{(slow)}$$

where M is any gas molecule present in the reaction container. Express k_{obs} in terms of the rate constants for the individual steps of the reaction mechanism.

29-13. Nitramide (O_2NNH_2) decomposes in water according to the chemical equation

$$O_2NNH_2(aq) \xrightarrow{k_{obs}} N_2O(g) + H_2O(l)$$

The experimentally determined rate law for this reaction is

$$\frac{d[N_2O]}{dt} = k_{obs}\frac{[O_2NNH_2]}{[H^+]}$$

A proposed mechanism for this reaction is

$$O_2NNH_2(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2NNH^-(aq) + H^+(aq) \qquad \text{(fast equilibrium)}$$

$$O_2NNH^-(aq) \xrightarrow{k_2} N_2O(g) + OH^-(aq) \qquad \text{(slow)}$$

$$H^+(aq) + OH^-(aq) \xrightarrow{k_3} H_2O(l) \qquad \text{(fast)}$$

Is this mechanism consistent with the observed rate law? If so, what is the relationship between k_{obs} and the rate constants for the individual steps of the mechanism?

29-14. What would you predict for the rate law for the reaction mechanism in Problem 29–13 if, instead of a fast equilibrium followed by a slow step, you assumed that the concentration of O_2NNH^-(aq) was such that the steady-state approximation could be applied to this reaction intermediate?

● **29-15.** The rate law for the hydrolysis of ethyl acetate by aqueous sodium hydroxide at 298 K

$$CH_3COOCH_2CH_3(aq) + OH^-(aq) \xrightarrow{k_{obs}} CH_3CO_2^-(aq) + CH_3CH_2OH(aq)$$

is

$$\frac{d[CH_3CH_2OH]}{dt} = k_{obs}[OH^-][CH_3COOCH_2CH_3]$$

Despite the form of this rate law, this reaction is not an elementary reaction but is believed to occur by the following mechanism

$$CH_3COOCH_2CH_3(aq) + OH^-(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3CO^-(OH)OCH_2CH_3(aq)$$

$$CH_3CO^-(OH)OCH_2CH_3(aq) \xrightarrow{k_2} CH_3CO_2H(aq) + CH_3CH_2O^-(aq)$$

$$CH_3CO_2H(aq) + CH_3CH_2O^-(aq) \xrightarrow{k_3} CH_3CO_2^-(aq) + CH_3CH_2OH(aq)$$

Under what conditions does this mechanism give the observed rate law? For those conditions, express k_{obs} in terms of the rate constants for the individual steps of the reaction mechanism.

29-16. The decomposition of perbenzoic acid in water

$$2\,C_6H_5CO_3H(aq) \rightleftharpoons 2\,C_6H_5CO_2H(aq) + O_2(g)$$

is proposed to occur by the following mechanism

$$C_6H_5CO_3H(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_6H_5CO_3^-(aq) + H^+(aq)$$

$$C_6H_5CO_3H(aq) + C_6H_5CO_3^-(aq) \xrightarrow{k_2} C_6H_5CO_2H(aq) + C_6H_5CO_2^-(aq) + O_2(g)$$

$$C_6H_5CO_2^-(aq) + H^+(aq) \xrightarrow{k_3} C_6H_5CO_2H(aq)$$

Derive an expression for the rate of formation of O_2 in terms of the reactant concentration and $[H^+]$.

● **29-17.** The rate law for the reaction described by

$$2\,H_2(g) + 2\,NO(g) \xrightarrow{k_{obs}} N_2(g) + 2\,H_2O(g)$$

is

$$\frac{d[N_2]}{dt} = k_{obs}[H_2][NO]^2$$

Below is a proposed mechanism for this reaction

$$H_2(g) + NO(g) + NO(g) \xrightarrow{k_1} N_2O + H_2O(g)$$

$$H_2(g) + N_2O(g) \xrightarrow{k_2} N_2(g) + H_2O(g)$$

Under what conditions does this mechanism give the observed rate law? Express k_{obs} in terms of the rate constants for the individual steps of the mechanism.

29-18. A second proposed mechanism for the reaction discussed in Problem 29–17 is

$$\mathrm{NO(g) + NO(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{N_2O_2(g)}$$

$$\mathrm{H_2(g) + N_2O_2(g)} \overset{k_2}{\Longrightarrow} \mathrm{N_2O(g) + H_2O(g)}$$

$$\mathrm{H_2(g) + N_2O(g)} \overset{k_3}{\Longrightarrow} \mathrm{N_2(g) + H_2O(g)}$$

Under what conditions does this mechanism give the observed rate law? Express k_{obs} in terms of the rate constants for the individual steps of the mechanism. Do you favor this mechanism or that given in Problem 29–17? Explain your reasoning.

29-19. An alternative mechanism for the chemical reaction

$$\mathrm{Cl_2(g) + CO(g)} \xrightarrow{k_{\text{obs}}} \mathrm{Cl_2CO(g)}$$

(see Problem 29–12) is

$$\mathrm{Cl_2(g) + M(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{2\,Cl(g) + M(g)} \qquad \text{(fast equilibrium)}$$

$$\mathrm{Cl(g) + Cl_2(g)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Cl_3(g)} \qquad \text{(fast equilibrium)}$$

$$\mathrm{Cl_3(g) + CO(g)} \overset{k_3}{\Longrightarrow} \mathrm{Cl_2CO(g) + Cl(g)}$$

where M is any molecule present in the reaction chamber. Show that this mechanism also gives the observed rate law. How would you go about determining whether this mechanism or the one given in Problem 29–12 is correct?

● **29-20.** The Lindemann reaction mechanism for the isomerization reaction

$$\mathrm{CH_3NC(g)} \longrightarrow \mathrm{CH_3CN(g)}$$

is

$$\mathrm{CH_3NC(g) + M(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CH_3NC^*(g) + M(g)}$$

$$\mathrm{CH_3NC^*(g)} \overset{k_2}{\Longrightarrow} \mathrm{CH_3CN(g)}$$

Under what conditions does the steady-state approximation apply to $\mathrm{CH_3NC^*}$?

29-21. In Section 29–6 we examined the unimolecular reaction

$$\mathrm{CH_3NC(g)} \Longrightarrow \mathrm{CH_3CN(g)}$$

Consider this reaction carried out in the presence of a helium buffer gas. The collision of a $\mathrm{CH_3NC}$ molecule with either another $\mathrm{CH_3NC}$ molecule or a helium atom can energize the molecule, thereby leading to reaction. If the energizing reactions involving a $\mathrm{CH_3NC}$ molecule and a He atom occur with different rates, the reaction mechanism would be given by

$$\mathrm{CH_3NC(g) + CH_3NC(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CH_3NC^*(g) + CH_3NC(g)}$$

$$\mathrm{CH_3NC(g) + He(g)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{CH_3NC^*(g) + He(g)}$$

$$\mathrm{CH_3NC^*(g)} \overset{k_3}{\Longrightarrow} \mathrm{CH_3CN}$$

Apply the steady-state approximation to the intermediate species, $\mathrm{CH_3NC^*(g)}$, to show that

$$\frac{d[\mathrm{CH_3CN}]}{dt} = \frac{k_3(k_1[\mathrm{CH_3NC}]^2 + k_2[\mathrm{CH_3NC}][\mathrm{He}])}{k_{-1}[\mathrm{CH_3NC}] + k_{-2}[\mathrm{He}] + k_3}$$

Show that this equation is equivalent to Equation 29.55 when $[\mathrm{He}] = 0$.

29-22. Consider the reaction and mechanism given in Problem 29–10. The activation energy for the dissociation of $\mathrm{H_2(g)}$ [step (1)] is given by D_0, the dissociation energy. If the activation energy of step (2) of the mechanism is E_2, show that $E_{\text{a,obs}}$, the experimentally determined activation energy, is given by

$$E_{\text{a,obs}} = E_2 + \frac{D_0}{2}$$

Also show that A_{obs}, the experimentally determined Arrhenius pre-exponential factor, is given by

$$A_{\text{obs}} = A_2\left(\frac{A_1}{A_{-1}}\right)^{1/2}$$

where A_i is the Arrhenius pre-exponential factor corresponding to the rate constant k_i.

● **29-23.** The thermal decomposition of ethylene oxide occurs by the mechanism

$$\mathrm{H_2COCH_2(g)} \overset{k_1}{\Longrightarrow} \mathrm{H_2COCH(g) + H(g)}$$

$$\mathrm{H_2COCH(g)} \overset{k_2}{\Longrightarrow} \mathrm{CH_3(g) + CO(g)}$$

$$\mathrm{CH_3(g) + H_2COCH_2(g)} \overset{k_3}{\Longrightarrow} \mathrm{H_2COCH(g) + CH_4(g)}$$

$$\mathrm{CH_3(g) + H_2COCH(g)} \overset{k_4}{\Longrightarrow} \text{products}$$

Which of these reaction(s) are the initiation, propagation, and termination step(s) of the reaction mechanism? Show that if the intermediates $\mathrm{CH_3}$ and $\mathrm{H_2COCH}$ are treated by the steady-state approximation, the rate law, $d[\text{products}]/dt$, is first order in ethylene oxide concentration.

The next six problems examine the kinetics of the thermal decomposition of acetaldehyde.

29-24. A proposed mechanism for the thermal decomposition of acetaldehyde

$$\mathrm{CH_3CHO(g)} \xrightarrow{k_{\text{obs}}} \mathrm{CH_4(g) + CO(g)}$$

is

$$\mathrm{CH_3CHO(g)} \overset{k_1}{\Longrightarrow} \mathrm{CH_3(g)} + \mathrm{CHO(g)} \tag{1}$$

$$\mathrm{CH_3(g)} + \mathrm{CH_3CHO(g)} \overset{k_2}{\Longrightarrow} \mathrm{CH_4(g)} + \mathrm{CH_3CO(g)} \tag{2}$$

$$\mathrm{CH_3CO(g)} \overset{k_3}{\Longrightarrow} \mathrm{CH_3(g)} + \mathrm{CO(g)} \tag{3}$$

$$2\,\mathrm{CH_3(g)} \overset{k_4}{\Longrightarrow} \mathrm{C_2H_6} \tag{4}$$

Is this reaction a chain reaction? If so, identify the initiation, propagation, inhibition, and termination step(s). Determine the rate laws for $CH_4(g)$, $CH_3(g)$, and $CH_3CO(g)$. Show that if you assume the steady-state approximation for the intermediate species, $CH_3(g)$ and $CH_3CO(g)$, the rate law for methane formation is given by

$$\frac{d[\mathrm{CH_4}]}{dt} = \left(\frac{k_1}{2k_4}\right)^{1/2} k_2[\mathrm{CH_3CHO}]^{3/2}$$

29-25. Suppose that we replace the termination step (Equation 4) of the mechanism in Problem 29–24 with the termination reaction

$$2\,\mathrm{CH_3CO(g)} \overset{k_4}{\Longrightarrow} \mathrm{CH_3COCOCH_3}$$

Determine the rate laws for CO(g), $CH_3(g)$, and $CH_3CO(g)$. Once again, assume that the steady-state approximation can be applied to the intermediates $CH_3(g)$ and $CH_3CO(g)$, and show that in this case the rate of formation of CO is given by

$$\frac{d[\mathrm{CO}]}{dt} = \left(\frac{k_1}{k_4}\right)^{1/2} k_3[\mathrm{CH_3CHO}]^{1/2}$$

29-26. The chain length γ of a chain reaction is defined as the rate of the overall reaction divided by the rate of the initiation step. Give a physical interpretation of the chain length. Show that γ for the reaction mechanism and rate law given in Problem 29–25 is

$$\gamma = k_3\left(\frac{1}{k_1k_4}\right)^{1/2} [\mathrm{CH_3CHO}]^{-1/2}$$

29-27. Show that the chain length γ (see Problem 29–26) for the reaction mechanism and the rate law given in Problem 29–24 is

$$\gamma = k_2\left(\frac{1}{k_1k_4}\right)^{1/2} [\mathrm{CH_3CHO}]^{1/2}$$

29-28. Consider the mechanism for the thermal decomposition of acetaldehyde given in Problem 29–24. Show that E_{obs}, the measured Arrhenius activation energy for the overall reaction, is given by

$$E_{\text{obs}} = E_2 + \tfrac{1}{2}(E_1 - E_4)$$

where E_i is the activation energy of the ith step of the reaction mechanism. How is A_{obs}, the measured Arrhenius pre-exponential factor for the overall reaction, related to the Arrhenius pre-exponential factors for the individual steps of the reaction mechanism?

29-29. Consider the mechanism for the thermal decomposition of acetaldehyde given in Problem 29–25. Show that E_{obs}, the measured Arrhenius activation energy for the overall reaction, is given by

$$E_{\text{obs}} = E_3 + \tfrac{1}{2}(E_1 - E_4)$$

where E_i is the activation energy of the ith step of the reaction mechanism. How is A_{obs}, the measured Arrhenius pre-exponential factor for the overall reaction, related to the Arrhenius pre-exponential factors for the individual steps of the reaction mechanism?

29-30. Consider the reaction between $H_2(g)$ and $Br_2(g)$ discussed in Section 29–7. Justify why we ignored the $H_2(g)$ dissociation reaction in favor of the $Br_2(g)$ dissociation reaction as being the initiating step of the reaction mechanism.

29-31. In Section 29–7, we considered the chain reaction between $H_2(g)$ and $Br_2(g)$. Consider the related chain reaction between $H_2(g)$ and $Cl_2(g)$.

$$\mathrm{Cl_2(g)} + \mathrm{H_2(g)} \longrightarrow 2\,\mathrm{HCl(g)}$$

The mechanism for this reaction is

$$\mathrm{Cl_2(g)} + \mathrm{M(g)} \overset{k_1}{\Longrightarrow} 2\,\mathrm{Cl(g)} + \mathrm{M(g)} \tag{1}$$

$$\mathrm{Cl(g)} + \mathrm{H_2(g)} \overset{k_2}{\Longrightarrow} \mathrm{HCl(g)} + \mathrm{H(g)} \tag{2}$$

$$\mathrm{H(g)} + \mathrm{Cl_2(g)} \overset{k_3}{\Longrightarrow} \mathrm{HCl(g)} + \mathrm{Cl(g)} \tag{3}$$

$$2\,\mathrm{Cl(g)} + \mathrm{M(g)} \overset{k_4}{\Longrightarrow} \mathrm{Cl_2(g)} + \mathrm{M(g)} \tag{4}$$

Label the initiation, propagation, and termination step(s). Use the following bond dissociation data to explain why it is reasonable not to include the analogous inhibition steps in this mechanism that are included in the mechanism for the chain reaction involving $Br_2(g)$

Molecule	D_0/kJ·mol^{-1}
H_2	432
HBr	363
HCl	428
Br_2	190
Cl_2	239

29-32. Derive the rate law for $v = (1/2)(d[\mathrm{HCl}]/dt)$ for the mechanism of the

$$\mathrm{Cl_2(g)} + \mathrm{H_2(g)} \longrightarrow 2\,\mathrm{HCl(g)}$$

reaction given in Problem 29–31.

29-33. It is possible to initiate chain reactions using photochemical reactions. For example, in place of the thermal initiation reaction for the $Br_2(g) + H_2(g)$ chain reaction

$$\mathrm{Br_2(g)} + \mathrm{M} \overset{k_1}{\Longrightarrow} 2\,\mathrm{Br(g)} + \mathrm{M}$$

we could have the photochemical initiation reaction

$$\mathrm{Br_2(g)} + h\nu \Longrightarrow 2\,\mathrm{Br(g)}$$

If we assume that all the incident light is absorbed by the Br_2 molecules and that the quantum yield for photodissociation is 1.00, then how does the photochemical rate of dissociation of Br_2 depend on I_{abs}, the number of photons per unit time per unit volume? How does $d[\mathrm{Br}]/dt$, the rate of formation of Br, depend on I_{abs}? If you assume that the chain reaction is initiated only by the photochemical generation of Br, then how does $d[\mathrm{HBr}]/dt$ depend on I_{abs}?

29-34. In Section 29–9, we derived the Michaelis-Menton rate law for enzyme catalysis. The derivation presented there is limited to the case in which only the rate of the initial reaction is measured so that $[\mathrm{S}] = [\mathrm{S}]_0$ and $[\mathrm{P}] = 0$. We will now determine the Michaelis-Menton rate law by a different approach. Recall that the Michaelis-Menton mechanism is

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES}$$

$$\mathrm{ES} \overset{k_2}{\Longrightarrow} \mathrm{E} + \mathrm{P}$$

The rate law for this reaction is $v = k_2[\mathrm{ES}]$. Write the rate expression for [ES]. Show that if you apply the steady-state approximation to this intermediate, then

$$[\mathrm{ES}] = \frac{[\mathrm{E}][\mathrm{S}]}{K_m} \tag{1}$$

where K_m is the Michaelis constant. Now show that

$$[\mathrm{E}]_0 = [\mathrm{E}] + \frac{[\mathrm{E}][\mathrm{S}]}{K_m} \tag{2}$$

(*Hint*: The enzyme is not consumed.) Solve Equation 2 for [E] and substitute the result into Equation 1 and thereby show that

$$v = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{K_m + [\mathrm{S}]} \tag{3}$$

If the rate is measured during a time period when only a small amount of substrate is consumed, then $[\mathrm{S}] = [\mathrm{S}]_0$ and Equation 3 reduces to the Michaelis-Menton rate law given by Equation 29.78.

29-35. The ability of enzymes to catalyze reactions can be hindered by *inhibitor molecules*. One of the mechanisms by which an inhibitor molecule works is by competing with the substrate molecule for binding to the active site of the enzyme. We can include this inhibition reaction in a modified Michaelis-Menton mechanism for enzyme catalysis.

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES} \tag{1}$$

$$\mathrm{E} + \mathrm{I} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{EI} \tag{2}$$

$$\mathrm{ES} \overset{k_3}{\Longrightarrow} \mathrm{E} + \mathrm{P} \tag{3}$$

In Equation 2, I is the inhibitor molecule and EI is the enzyme-inhibitor complex. We will consider the case where reaction (2) is always in equilibrium. Determine the rate laws for [S], [ES], [EI], and [P]. Show that if the steady-state assumption is applied to ES, then

$$[\mathrm{ES}] = \frac{[\mathrm{E}][\mathrm{S}]}{K_m}$$

where K_m is the Michaelis constant, $K_m = (k_{-1} + k_3)/k_1$. Now show that material balance for the enzyme gives

$$[\mathrm{E}]_0 = [\mathrm{E}] + \frac{[\mathrm{E}][\mathrm{S}]}{K_m} + [\mathrm{E}][\mathrm{I}]K_{\mathrm{I}}$$

where $K_{\mathrm{I}} = [\mathrm{EI}]/[\mathrm{E}][\mathrm{I}]$ is the equilibrium constant for step (2) of the above reaction mechanism. Use this result to show that the initial reaction rate is given by

$$v = \frac{d[\mathrm{P}]}{dt} = \frac{k_3[\mathrm{E}]_0[\mathrm{S}]}{K_m + [\mathrm{S}] + K_m K_{\mathrm{I}}[\mathrm{I}]} \approx \frac{k_3[\mathrm{E}]_0[\mathrm{S}]_0}{K'_m + [\mathrm{S}]_0} \tag{4}$$

where $K'_m = K_m(1 + K_{\mathrm{I}}[\mathrm{I}])$. Note that the second expression in Equation 4 has the same functional form as the Michaelis-Menton equation. Does Equation 4 reduce to the expected result when $[\mathrm{I}] \rightarrow 0$?

29-36. Antibiotic-resistant bacteria have an enzyme, penicillinase, that catalyzes the decomposition of the antibiotic. The molecular mass of penicillinase is 30 000 $\mathrm{g \cdot mol^{-1}}$. The turnover number of the enzyme at 28°C is 2000 $\mathrm{s^{-1}}$. If 6.4 μg of penicillinase catalyzes the destruction of 3.11 mg of amoxicillin, an antibiotic with a molecular mass of 364 $\mathrm{g \cdot mol^{-1}}$, in 20 seconds at 28°C, how many active sites does the enzyme have?

● **29-37.** Show that the inverse of Equation 29.78 is

$$\frac{1}{v} = \frac{1}{v_{\max}} + \frac{K_m}{v_{\max}}\frac{1}{[\mathrm{S}]_0} \tag{1}$$

This equation is called the *Lineweaver-Burk equation*. In Example 29–9, we examined the reaction for the hydration of CO_2 that is catalyzed by the enzyme carbonic anhydrase. For a total enzyme concentration of 2.32×10^{-9} $\mathrm{mol \cdot dm^{-3}}$, the following data were obtained.

$v/\mathrm{mol \cdot dm^{-3} \cdot s^{-1}}$	$[\mathrm{CO_2}]_0/10^{-3}\ \mathrm{mol \cdot dm^{-3}}$
2.78×10^{-5}	1.25
5.00×10^{-5}	2.50
8.33×10^{-5}	5.00
1.66×10^{-4}	20.00

Plot these data according to Equation 1, and determine the values of K_m, the Michaelis constant, and k_2, the rate constant for product formation from the enzyme-substrate complex from the slope and intercept of the best-fit line to the plotted data.

29-38. Carbonic anhydrase catalyzes the reaction

$$\mathrm{H_2O(l)} + \mathrm{CO_2(g)} \rightleftharpoons \mathrm{H_2CO_3(aq)}$$

Data for the reverse dehydration reaction using a total enzyme concentration of 2.32×10^{-9} mol·dm^{-3} are given below

v/mol·dm^{-3}·s^{-1}	$[H_2CO_3]_0/10^{-3}$ mol·dm^{-3}
1.05×10^{-5}	2.00
2.22×10^{-5}	5.00
3.45×10^{-5}	10.00
4.17×10^{-5}	15.00

Use the approach discussed in Problem 29–37 to determine the values of K_m, the Michaelis constant, and k_2, the rate of product formation from the enzyme substrate complex.

29-39. Show that the Michaelis-Menton mechanism for enzyme catalysis gives $v = (1/2)v_{\max}$ when $[S]_0 = K_m$.

29-40. The protein catalase catalyzes the reaction

$$2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)$$

and has a Michaelis constant of $K_m = 25 \times 10^{-3}$ mol·dm^{-3} and a turnover number of 4.0×10^7 s^{-1}. Calculate the initial rate of this reaction if the total enzyme concentration is 0.016×10^{-6} mol·dm^{-3} and the initial substrate concentration is 4.32×10^{-6} mol·dm^{-3}. Calculate $v_{\max}$ for this enzyme. Catalase has a single active site.

29-41. The presence of 4.8×10^{-6} mol·dm^{-3} of a competitive inhibitor decreases the initial rate calculated in Problem 29–40 by a factor of 3.6. Calculate K_I, the equilibrium constant for the binding reaction between the enzyme and the inhibitor. (*Hint*: See Problem 29–35.)

29-42. The turnover number for acetylcholinesterase, an enzyme with a single active site that metabolizes acetylcholine, is 1.4×10^4 s^{-1}. How many grams of acetylcholine can 2.16×10^{-6} g of acetylcholinesterase metabolize in one hour? (Take the molecular mass of the enzyme to be 4.2×10^4 g·mol^{-1}; acetylcholine has the molecular formula $C_7NO_2H_{16}^+$.)

29-43. Consider the following mechanism for the recombination of bromine atoms to form molecular bromine

$$2\,Br(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Br_2^*(g)$$

$$Br_2^*(g) + M(g) \xrightarrow{k_2} Br_2(g) + M(g)$$

The first step results in formation of an energized bromine molecule. This excess energy is then removed by a collision with a molecule M in the sample. Show that if the steady-state approximation is applied to $Br_2^*(g)$, then

$$\frac{d[Br]}{dt} = -\frac{2k_1k_2[Br]^2[M]}{k_{-1} + k_2[M]}$$

Determine the limiting expression for $d[Br]/dt$ when $v_2 \gg v_{-1}$. Determine the limiting expression for $d[Br]/dt$ when $v_2 \ll v_{-1}$.

29-44. A mechanism for the recombination of bromine atoms to form molecular bromine is given in Problem 29–43. When this reaction occurs in the presence of a large excess of buffer gas, a negative activation energy is measured. Because M(g), the buffer gas molecule, is responsible for the deactivation of $Br_2^*(g)$ but is not consumed itself by the reaction, we can consider it to be a catalyst. Below are the measured rate constants for this reaction in the presence of the same concentration of excess Ne(g) and CCl_4(g) buffer gases at several temperatures. Which gas is the better catalyst for this reaction?

	Ne	CCl_4
T/K	k_{obs}/mol^{-2}·dm^6·s^{-1}	k_{obs}/mol^{-2}·dm^6·s^{-1}
367	1.07×10^9	1.01×10^{10}
349	1.15×10^9	1.21×10^{10}
322	1.31×10^9	1.64×10^{10}
297	1.50×10^9	2.28×10^{10}

Why do you think there is a difference in the "catalytic" behavior of these two buffer gases?

29-45. The standard Gibbs energy change of reaction for

$$2H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$$

is −457.2 kJ at 298 K. At room temperature, however, this reaction does not occur and mixtures of gaseous hydrogen and oxygen are stable. Explain why this is so. Is such a mixture indefinitely stable?

29-46. The HF(g) chemical laser is based on the reaction

$$H_2(g) + F_2(g) \longrightarrow 2\,HF(g)$$

The mechanism for this reaction involves the elementary steps

	$\Delta_r H°$/kJ·mol^{-1} at 298K
(1) $F_2(g) + M(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,F(g) + M(g)$	+159
(2) $F(g) + H_2(g) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HF(g) + H(g)$	−134
(3) $H(g) + F_2(g) \xrightarrow{k_3} HF(g) + F(g)$	−411

Comment on why the reaction $H_2(g) + M(g) \rightarrow 2\,H(g) + M(g)$ is not included in the mechanism of the HF(g) laser even though it produces a reactant that could participate in step (3) of the reaction mechanism. Derive the rate law for $d[HF]/dt$ for the above mechanism assuming that the steady-state approximation can be applied to both intermediate species, F(g) and H(g).

29-47. A mechanism for ozone creation and destruction in the stratosphere is

$$O_2(g) + h\nu \xrightarrow{j_1} O(g) + O(g)$$

$$O(g) + O_2(g) + M(g) \xrightarrow{k_2} O_3(g) + M(g)$$

$$O_3(g) + h\nu \xrightarrow{j_3} O_2(g) + O(g)$$

$$O(g) + O_3(g) \xrightarrow{k_4} O_2(g) + O_2(g)$$