Dividing the first equation by the second gives

$$\frac{S(t) - S(\infty)}{S(0) - S(\infty)} = \frac{[A] - [A]_{2,eq}}{[A]_0 - [A]_{2,eq}}$$

or

$$[A] = [A]_{2,eq} + ([A]_0 - [A]_{2,eq})\frac{S(t) - S(\infty)}{S(0) - S(\infty)}$$

CHAPTER 29

Chemical Kinetics II: Reaction Mechanisms

PROBLEMS AND SOLUTIONS

29–1. Give the units of the rate constant for a unimolecular, bimolecular, and termolecular reaction.

Since v is in units of $mol \cdot dm^{-3} \cdot s^{-1}$, the units of k are

$$k_{unimolecular}: (mol \cdot dm^{-3} \cdot s^{-1})(dm^3 \cdot mol^{-1}) = s^{-1}$$
$$k_{bimolecular}: (mol \cdot dm^{-3} \cdot s^{-1})(dm^3 \cdot mol^{-1})^2 = dm^3 \cdot mol^{-1} \cdot s^{-1}$$
$$k_{termolecular}: (mol \cdot dm^{-3} \cdot s^{-1})(dm^3 \cdot mol^{-1})^3 = dm^6 \cdot mol^{-2} \cdot s^{-1}$$

29–2. Determine the rate law for the following reaction

$$F(g) + D_2(g) \xrightarrow{k} FD(g) + D(g)$$

Give the units of k. Determine the molecularity of this reaction.

Because this is an elementary reaction, the rate law is

$$v = k[F][D_2]$$

This is a bimolecular reaction, so the units of k are $dm^3 \cdot mol^{-1} \cdot s^{-1}$.

29–3. Determine the rate law for the reaction

$$I(g) + I(g) + M(g) \xrightarrow{k} I_2(g) + M(g)$$

where M is any molecule present in the reaction container. Give the units of k. Determine the molecularity of this reaction. Is this reaction identical to

$$I(g) + I(g) \xrightarrow{k} I_2(g)$$

Explain.

Because this is an elementary reaction, the rate law is

$$v = k[M][I]^2$$

This is a termolecular reaction, so the units of k are $dm^6 \cdot mol^{-2} \cdot s^{-1}$. There is a difference between the molecularity of the two reactions (the second one is bimolecular), so they are not identical.

29–4. For $T < 500$ K, the reaction

$$NO_2(g) + CO(g) \xrightarrow{k_{obs}} CO_2(g) + NO(g)$$

has the rate law

$$\frac{d[CO_2]}{dt} = k_{obs}[NO_2]^2$$

Show that the following mechanism is consistent with the observed rate law

$$NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g) \qquad \text{(rate determining)}$$

$$NO_3(g) + CO(g) \xrightarrow{k_2} CO_2(g) + NO_2(g)$$

Express k_{obs} in terms of k_1 and k_2.

If the first step of the mechanism is the rate-determining step, then the rate law is

$$\frac{d[CO_2]}{dt} = k_1[NO_2]^2$$

and $k_{obs} = k_1$. The rate constant k_2 does not affect k_{obs}.

29–5. Solve Equation 29.21 to obtain $[A] = [A]_0 e^{-k_1 t}$, and substitute this result into Equation 29.22 to obtain

$$\frac{d[I]}{dt} + k_2[I] = k_1[A]_0 e^{-k_1 t}$$

This equation is of the form (see the *CRC Handbook of Standard Mathematical Tables*, for example)

$$\frac{dy(x)}{dx} + p(x)y(x) = q(x)$$

a linear, first-order differential equation whose general solution is

$$y(x)e^{h(x)} = \int q(x)e^{h(x)}dx + c$$

where $h(x) = \int p(x)dx$ and c is a constant. Show that this solution leads to Equation 29.25.

The solution to Equation 29.21 (letting the concentration of [A] at $t = 0$ be $[A]_0$) is $[A] = [A]_0 e^{-k_1 t}$. Substituting into Equation 29.22 gives

$$\frac{d[I]}{dt} = k_1[A] - k_2[I]$$

$$= k_1[A]_0 e^{-k_1 t} - k_2[I]$$

$$\frac{d[I]}{dt} + k_2[I] = k_1[A]_0 e^{-k_1 t}$$

The solution to this differential equation is

$$[I]e^{k_2 t} = k_1[A]_0 \int e^{(k_2 - k_1)t}dt + c$$

$$[I] = \frac{k_1[A]_0}{k_2 - k_1}e^{-k_1 t} + ce^{-k_2 t}$$

At $t = 0$, $[I] = 0$, so

$$c = -\frac{k_1[A]_0}{k_2 - k_1}$$

and we obtain

$$[I] = \frac{k_1[A]_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \qquad (29.25)$$

29–6. Verify that Equation 29.32 is obtained if Equation 29.30 is substituted into Equation 29.23 and the resulting expression is integrated.

Start with Equations 29.23 and 29.30:

$$\frac{d[P]}{dt} = k_2[I] \qquad \text{and} \qquad [I] = \frac{k_1}{k_2}[A]_0 e^{-k_1 t}$$

Substituting Equation 29.30 into Equation 29.23 gives

$$\frac{d[P]}{dt} = k_1[A]_0 e^{-k_1 t}$$

and integrating gives

$$[P] = -[A]_0 e^{-k_1 t} + c$$

At $t = 0$, $[P] = 0$, and so $c = [A]_0$. Thus

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

which is Equation 29.32.

29–7. Consider the reaction mechanism

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

where $[A] = [A]_0$ and $[I]_0 = [P]_0 = 0$ at time $t = 0$. Use the exact solution to this kinetic scheme (Equations 29.24 through 29.26) to plot the time dependence of $[A]/[A]_0$, $[I]/[A]_0$, and $[P]/[A]_0$ versus $\log k_1 t$ for the case $k_2 = 2k_1$. On the same graph, plot the time dependence of $[A]/[A]_0$, $[I]/[A]_0$, and $[P]/[A]_0$ using the expressions for [A], [I], and [P] obtained assuming the steady-state approximation for [I]. Based on your results, can you use the steady-state approximation to model the kinetics of this reaction mechanism when $k_2 = 2k_1$?

Letting $x = k_1 t$ and $k_2 = 2k_1$, Equations 29.24 through 29.26 become

$$\frac{[A]}{[A]_0} = e^{-x}$$

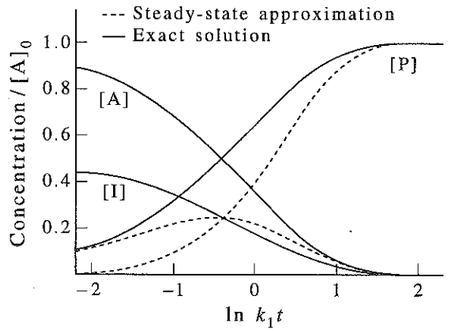
$$\frac{[I]}{[A]_0} = \frac{k_1}{2k_1 - k_1}(e^{-x} - e^{-2x}) = e^{-x} - e^{-2x}$$

$$\frac{[P]}{[A]_0} = 1 - \frac{[A]}{[A]_0} - \frac{[I]}{[I]_0} = 1 - 2e^{-x} - e^{-2x}$$

Likewise, letting $x = k_1 t$ and $k_2 = 2k_1$, the steady-state approximations for [A], [I], and [P] (Equations 29.24, 29.30, and 29.32) become

$$\frac{[A]}{[A]_0} = e^{-x} \qquad \frac{[I]}{[A]_0} = \frac{k_1}{2k_1} e^{-x} = \frac{e^{-x}}{2} \qquad \frac{[P]}{[A]_0} = 1 - e^{-x}$$

In the plot, the dashed lines represent the steady state approximations and the solid lines represent the exact values. Both give the same values for $[A]/[A]_0$, but the steady-state approximations of $[I]/[A]_0$ and $[P]/[A]_0$ differ significantly from the exact solutions. We can conclude that the steady-state approximation is not a good model for the kinetics of a reaction mechanism for which $k_2 = 2k_1$.



29–8. Consider the mechanism for the decomposition of ozone presented in Example 29–5. Explain why either (a) $v_{-1} \gg v_2$ and $v_{-1} \gg v_1$ or (b) $v_2 \gg v_{-1}$ and $v_2 \gg v_1$ must be true for the steady-state approximation to apply. The rate law for the decomposition reaction is found to be

$$\frac{d[O_3]}{dt} = -k_{obs}[O_3][M]$$

Is this rate law consistent with the conditions given by either (a) or (b) or both?

The mechanism presented in Example 29–5 is

$$M(g) + O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(g) + O(g) + M(g)$$

$$O(g) + O_3(g) \overset{k_2}{\Longrightarrow} 2O_2(g)$$

For the steady state approximation to apply, the concentration of O must be negligible. This means that the rates of reaction of [O] must be greater than the rates of formation of [O]. We examine each of the proposed conditions to determine whether this is true.

a. If $v_{-1} \gg v_2$ and $v_{-1} \gg v_1$, then very little O(g) can accumulate. When O(g) is generated, it reacts quickly back to reactants, and less often to the products.

b. If $v_2 \gg v_{-1}$ and $v_2 \gg v_1$, then when O(g) is formed it quickly goes to product, and (once again) very little is accumulated.

For the steady state in O, we have (Example 29–5)

$$\frac{d[O_3]}{dt} = -\frac{2k_1 k_2 [O_3]^2[M]}{k_{-1}[O_2][M] + k_2[O_3]}$$

Because all these reactions are elementary, we can write

$$v_2 = k_2[O][O_3] \qquad v_1 = k_1[M][O_3] \quad \text{and} \quad v_{-1} = k_{-1}[O_2][O][M]$$

Under the conditions given by (a),

$$k_{-1}[O_2][O][M] \gg k_2[O][O_3]$$

$$k_{-1}[O_2][M] \gg k_2[O_3]$$

Then

$$\frac{d[O_3]}{dt} = -\frac{2k_1 k_2 [O_3]^2[M]}{k_{-1}[O_2][M] + k_2[O_3]} \approx -\frac{2k_1 k_2 [O_3]^2[M]}{k_{-1}[O_2][M]} = \frac{2k_1 k_2}{k_{-1}} \frac{[O_3]^2}{[O_2]}$$

which is not consistent with the observed rate law. Under the conditions given by (b),

$$k_2[O][O_3] \gg k_{-1}[O_2][O][M]$$

$$k_2[O_3] \gg k_{-1}[O_2][M]$$

Then

$$\frac{d[O_3]}{dt} = -\frac{2k_1 k_2 [O_3]^2[M]}{k_{-1}[O_2][M] + k_2[O_3]} \approx -\frac{2k_1 k_2 [O_3]^2[M]}{k_2[O_3]} = 2k_1[O_3][M]$$

which is consistent with the observed rate law.

29–9. Consider the reaction mechanism

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \qquad (1)$$

$$C \overset{k_2}{\Longrightarrow} P \qquad (2)$$

Write the expression for $d[P]/dt$, the rate of product formation. Assume equilibrium is established in the first reaction before any appreciable amount of product is formed, and thereby show that

$$\frac{d[P]}{dt} = k_2 K_c [A][B]$$

where K_c is the equilibrium constant for step (1) of the reaction mechanism. This assumption is called the *fast-equilibrium approximation*.

Product is formed only in step (2) of the reaction mechanism, so the rate of product formation can be written as

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{C}]$$

If equilibrium is established in the first reaction before any appreciable amount of product is formed, then

$$K_c = \frac{k_1}{k_{-1}} = \frac{[\mathrm{C}]}{[\mathrm{A}][\mathrm{B}]}$$

Solving for [C] and substituting gives

$$\frac{d[\mathrm{P}]}{dt} = k_2 K_c[\mathrm{A}][\mathrm{B}]$$

29–10. The rate law for the reaction of *para*-hydrogen to *ortho*-hydrogen

$$\textit{para}\text{-}\mathrm{H_2(g)} \xrightarrow{k_{obs}} \textit{ortho}\text{-}\mathrm{H_2(g)}$$

is

$$\frac{d[\textit{ortho}\text{-}\mathrm{H_2}]}{dt} = k_{obs}[\textit{para}\text{-}\mathrm{H_2}]^{3/2}$$

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

$$\textit{para}\text{-}\mathrm{H_2(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,\mathrm{H(g)} \qquad \text{(fast equilibrium)} \qquad (1)$$

$$\mathrm{H(g)} + \textit{para}\text{-}\mathrm{H_2(g)} \xrightarrow{k_2} \textit{ortho}\text{-}\mathrm{H_2(g)} + \mathrm{H(g)} \qquad (2)$$

Express k_{obs} in terms of the rate constants for the individual steps of the reaction mechanism.

The rate law is

$$\frac{d[\textit{ortho}\text{-}\mathrm{H_2}]}{dt} = k_2[\textit{para}\text{-}\mathrm{H_2}][\mathrm{H}]$$

Because the first step achieves a fast equilibrium,we can write

$$K_c = \frac{[\mathrm{H}]^2}{[\textit{para}\text{-}\mathrm{H_2}]}$$

where K_c is the equilibrium constant for step (1) of the reaction mechanism. Solving this equation for [H] gives

$$[\mathrm{H}] = K_c^{1/2}[\textit{para}\text{-}\mathrm{H_2}]^{1/2}$$

Substituting into the observed rate law,

$$\frac{d[\textit{ortho}\text{-}\mathrm{H_2}]}{dt} = k_2 K_c^{1/2}[\textit{para}\text{-}\mathrm{H_2}]^{3/2}$$

and therefore

$$k_{obs} = k_2 K_c^{1/2} = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}$$

29–11. Consider the decomposition reaction of $N_2O_5(g)$

$$2\,\mathrm{N_2O_5(g)} \xrightarrow{k_{obs}} 4\,\mathrm{NO_2(g)} + \mathrm{O_2(g)}$$

A proposed mechanism for this reaction is

$$\mathrm{N_2O_5(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NO_2(g)} + \mathrm{NO_3(g)}$$

$$\mathrm{NO_2(g)} + \mathrm{NO_3(g)} \xrightarrow{k_2} \mathrm{NO(g)} + \mathrm{NO_2(g)} + \mathrm{O_2(g)}$$

$$\mathrm{NO_3(g)} + \mathrm{NO(g)} \xrightarrow{k_3} 2\,\mathrm{NO_2(g)}$$

Assume that the steady-state approximation applies to both the NO(g) and $NO_3(g)$ reaction intermediates to show that this mechanism is consistent with the experimentally observed rate law

$$\frac{d[\mathrm{O_2}]}{dt} = k_{obs}[\mathrm{N_2O_5}]$$

Express k_{obs} in terms of the rate constants for the individual steps of the reaction mechanism.

Under the steady state approximation for NO, we can write

$$\frac{d[\mathrm{NO}]}{dt} = k_2[\mathrm{NO_2}][\mathrm{NO_3}] - k_3[\mathrm{NO}][\mathrm{NO_3}] = 0$$

Solving this equation for [NO] gives

$$[\mathrm{NO}] = \frac{k_2[\mathrm{NO_2}]}{k_3} \qquad (1)$$

Using the steady state approximation for NO_3, we can also write

$$\frac{d[\mathrm{NO_3}]}{dt} = k_1[\mathrm{N_2O_5}] - k_{-1}[\mathrm{NO_2}][\mathrm{NO_3}] - k_2[\mathrm{NO_2}][\mathrm{NO_3}] - k_3[\mathrm{NO_3}][\mathrm{NO}] = 0$$

Solving this equation for $[NO_3]$ gives

$$[\mathrm{NO_3}](k_{-1}[\mathrm{NO_2}] + k_2[\mathrm{NO_2}] + k_3[\mathrm{NO}]) = k_1[\mathrm{N_2O_5}]$$

or

$$[\mathrm{NO_3}] = \frac{k_1[\mathrm{N_2O_5}]}{k_{-1}[\mathrm{NO_2}] + k_2[\mathrm{NO_2}] + k_3[\mathrm{NO}]}$$

Substituting for [NO] from Equation 1, we find

$$[\mathrm{NO_3}] = \frac{k_1[\mathrm{N_2O_5}]}{k_{-1}[\mathrm{NO_2}] + k_2[\mathrm{NO_2}] + k_2[\mathrm{NO_2}]} \qquad (2)$$

Now, from step (2) of the reaction mechanism, we can express $d[O_2]/dt$ as

$$\frac{d[\mathrm{O_2}]}{dt} = k_2[\mathrm{NO_2}][\mathrm{NO_3}]$$

Substituting for $[NO_3]$ from Equation 2, we find

$$\frac{d[\mathrm{O_2}]}{dt} = k_2[\mathrm{NO_2}]\frac{k_1[\mathrm{N_2O_5}]}{k_2[\mathrm{NO_2}] + k_2[\mathrm{NO_2}] + k_{-1}[\mathrm{NO_2}]}$$

$$= \frac{k_1 k_2}{2k_2 + k_{-1}}[\mathrm{N_2O_5}]$$

and $k_{obs} = k_1 k_2/(2k_2 + k_{-1})$.

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.

For the first two steps, the fast equilibrium allows us to write

$$K_{c,1} = \frac{[M][Cl]^2}{[Cl_2][M]} = \frac{[Cl]^2}{[Cl_2]}$$

and

$$K_{c,2} = \frac{[ClCO][M]}{[Cl][CO][M]} = \frac{[ClCO]}{[Cl][CO]}$$

From these equations, we can write

$$[Cl] = K_{c,1}^{1/2}[Cl_2]^{1/2} \tag{1}$$

and

$$[ClCO] = K_{c,2}[Cl][CO] \tag{2}$$

Using the third step of the reaction mechanism to write $d[Cl_2CO]/dt$ and Equations 1 and 2, we have

$$\begin{aligned}\frac{d[Cl_2CO]}{dt} &= k_3[ClCO][Cl_2] \\ &= k_3 K_{c,2}[Cl][CO][Cl_2] \\ &= k_3 K_{c,2} K_{c,1}^{1/2}[Cl_2]^{3/2}[CO]\end{aligned}$$

Using the principle of detailed balance (Equation 29.6), we find that

$$k_{obs} = \frac{k_3 k_2 k_1^{1/2}}{k_{-2} k_{-1}^{1/2}}$$

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?

From step (1) of the reaction mechanism, the fast equilibrium allows us to write

$$K_c = \frac{[O_2NNH^-][H^+]}{[O_2NNH_2]}$$

and so the rate equation for the second step of the reaction mechanism becomes

$$\frac{d[N_2O]}{dt} = k_2[O_2NNH^-] = k_2 K_c \frac{[O_2NNH_2]}{[H^+]}$$

This is consistent with the observed rate law, and

$$k_{obs} = k_2 K_c = \frac{k_2 k_1}{k_{-1}}$$

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?

The rate equation for the second step of the reaction mechanism is still

$$\frac{d[N_2O]}{dt} = k_2[O_2NNH^-]$$

Applying the steady-state approximation to find $[O_2NNH^-]$, we find that

$$\frac{d[O_2NNH^-]}{dt} = 0 = k_1[O_2NNH_2] - k_{-1}[O_2NNH^-][H^+] - k_2[O_2NNH^-]$$

This gives

$$[O_2NNH^-](k_{-1}[H^+] + k_2) = k_1[O_2NNH_2]$$

$$[O_2NNH^-] = \frac{k_1[O_2NNH_2]}{k_{-1}[H^+] + k_2}$$

Then

$$\frac{d[N_2O]}{dt} = \frac{k_2 k_1 [O_2NNH_2]}{k_{-1}[H^+] + k_2}$$

which differs from the experimentally observed rate law. Note that if $k_2 \ll k_{-1}[H^+]$, the first step essentially achieves a fast equilibrium and we find the rate law given in the previous problem.

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.

From step (3) of the reaction mechanism, we can write

$$\frac{d[CH_3CH_2OH]}{dt} = k_3[CH_3CO_2H][CH_3CH_2O^-] \quad (1)$$

If we assume that equilibrium is quickly reached in step (1) of the reaction mechanism, we find that

$$K_{c,1} = \frac{k_1}{k_{-1}} = \frac{[CH_3CO^-(OH)OCH_2CH_3]}{[OH^-][CH_3COOCH_2CH_3]}$$

$$[CH_3CO^-(OH)OCH_2CH_3] = \frac{k_1}{k_{-1}}[OH^-][CH_3COOCH_2CH_3] \quad (2)$$

We now use the steady-state approximation for CH_3CO_2H to write

$$\frac{d[CH_3CO_2H]}{dt} = k_2[CH_3CO^-(OH)OCH_2CH_3] - k_3[CH_3CO_2H][CH_3CH_2O^-] = 0$$

Then

$$k_3[CH_3CO_2H][CH_3CH_2O^-] = k_2[CH_3CO^-(OH)OCH_2CH_3] \quad (3)$$

and the rate law becomes

$$\frac{d[CH_3CH_2OH]}{dt} = k_2[CH_3CO^-(OH)OCH_2CH_3]$$

$$= \frac{k_2 k_1}{k_{-1}}[OH^-][CH_3CHOOCH_2CH_3]$$

where we have substituted Equations 2 and 3 into Equation 1. This will give the observed rate law, with $k_{obs} = k_2 k_1 / k_{-1}$.

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 $[H^+]$.

From step (2) of the reaction mechanism, we write

$$\frac{d[O_2]}{dt} = k_2[C_6H_5CO_3H][C_6H_5CO_3^-]$$

Assuming that the first step reaches equilibrium rapidly, we have

$$K_c = \frac{k_1}{k_{-1}} = \frac{[H^+][C_6H_5CO_3^-]}{[C_6H_5CO_3H]}$$

$$[C_6H_5CO_3^-] = \frac{k_1}{k_{-1}}\frac{[C_6H_5CO_3H]}{[H^+]}$$

Substituting into the above rate law gives

$$\frac{d[O_2]}{dt} = \frac{k_2 k_1}{k_{-1}}\frac{[C_6H_5CO_3H]^2}{[H^+]}$$

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.

From step (2) of the reaction mechanism,

$$\frac{d[N_2]}{dt} = k_2[H_2][N_2O] \qquad (1)$$

We assume we can use the steady-state approximation for N_2O. Then

$$\frac{d[N_2O]}{dt} = k_1[H_2][NO]^2 - k_2[H_2][N_2O] = 0$$

or

$$[N_2O] = \frac{k_1}{k_2}[NO]^2$$

Substituting into Equation 1, we find that

$$\frac{d[N_2]}{dt} = k_1[H_2][NO]^2$$

If this mechanism is followed, then $k_{obs} = k_1$.

29–18. A second proposed mechanism for the reaction discussed in Problem 27-17 is

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

$$H_2(g) + N_2O_2(g) \xrightarrow{k_2} N_2O(g) + H_2O(g)$$

$$H_2(g) + N_2O(g) \xrightarrow{k_3} N_2(g) + H_2O(g)$$

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 27-17? Explain your reasoning.

From step (3) of the reaction mechanism, we can write (as in the previous problem)

$$\frac{d[N_2]}{dt} = k_3[H_2][N_2O] \qquad (1)$$

If we use the steady-state approximation for N_2O,

$$\frac{d[N_2O]}{dt} = 0 = k_2[H_2][N_2O_2] - k_3[H_2][N_2O]$$

$$[N_2O] = \frac{k_2}{k_3}[N_2O_2]$$

and Equation 1 becomes

$$\frac{d[N_2]}{dt} = k_2[H_2][N_2O_2] \qquad (2)$$

Now, if we assume that the first step establishes a fast equilibrium, we can write

$$K_{c,1} = \frac{k_1}{k_{-1}} = \frac{[N_2O_2]}{[NO]^2}$$

$$\frac{k_1}{k_{-1}}[NO]^2 = [N_2O_2]$$

Substituting into Equation 2 then gives

$$\frac{d[N_2]}{dt} = \frac{k_2k_1}{k_{-1}}[H_2][NO]^2$$

which would give an observed rate constant of k_2k_1/k_{-1}. It seems more probable that this mechanism is followed, because each step of this mechanism is a bimolecular reaction. The mechanism of Problem 29–17 requires a termolecular reaction to occur.

29–19. An alternative mechanism for the chemical reaction

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

(see Problem 29–12) is

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

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

$$Cl_3(g) + CO(g) \xrightarrow{k_3} Cl_2CO(g) + Cl(g)$$

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?

The observed rate law is (from Problem 29–12)

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

From step (3) of the reaction mechanism, we write

$$\frac{d[Cl_2CO]}{dt} = k_3[Cl_3][CO] \qquad (1)$$

Because steps (2) and (1) establish fast equilibria, we write

$$K_{c,2} = \frac{k_2}{k_{-2}} = \frac{[Cl_3]}{[Cl][Cl_2]}$$

which gives

$$[Cl_3] = \frac{k_2}{k_{-2}}[Cl][Cl_2] \qquad (2)$$

Also,

$$K_{c,1} = \frac{k_1}{k_{-1}} = \frac{[Cl]^2[M]}{[Cl_2][M]}$$

and so

$$[Cl] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_2]^{1/2}$$

Substituting this expression for [Cl] into Equation 2 gives

$$[Cl_3] = \frac{k_2}{k_{-2}}\left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_2]^{3/2}$$

and substituting this expression into Equation 1 gives

$$\frac{d[Cl_2CO]}{dt} = \frac{k_3 k_2 k_1^{1/2}}{k_{-2}k_{-1}^{1/2}}[Cl_2]^{3/2}[CO]$$

which corresponds to the observed rate law. To determine whether this mechanism occurs or that in Problem 29–12, we might check to see whether Cl_3 is produced during the reaction.

29–20. The Lindemann reaction mechanism for the isomerization reaction

$$CH_3NC(g) \longrightarrow CH_3CN(g)$$

is

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

$$CH_3NC^*(g) \xrightarrow{k_2} CH_3CN(g)$$

Under what conditions does the steady-state approximation apply to CH_3NC^*?

The steady-state approximation will apply if $d[CH_3NC^*]/dt \approx 0$. This will be true if $v_{-1} \gg v_1$, when $k_{-1}[CH_3NC^*] \gg k_1[CH_3NC]$, or if $v_2 \gg v_1$, when $k_2[CH_3NC^*] \gg k_1[CH_3NC][M]$. In both cases, the CH_3NC^* is slowly formed and quickly reacted, and the concentration of CH_3NC^* at any given time is very small.

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

$$CH_3NC(g) \Longrightarrow CH_3CN(g)$$

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

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

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

$$CH_3NC^*(g) \xrightarrow{k_3} CH_3CN$$

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

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

Show that this equation is equivalent to Equation 29.55 when [He] = 0.

Applying the steady-state approximation gives

$$\frac{d[CH_3NC^*]}{dt} = 0 = k_1[CH_3NC]^2 - k_{-1}[CH_3NC^*][CH_3NC] + k_2[CH_3NC][He] - k_{-2}[CH_3NC^*][He] - k_3[CH_3NC^*]$$

Then

$$(k_{-2}[He] + k_3 + k_{-1}[CH_3NC])[CH_3NC^*] = k_1[CH_3NC]^2 + k_2[CH_3NC][He]$$

and

$$[CH_3NC^*] = \frac{k_1[CH_3NC]^2 + k_2[CH_3NC][He]}{k_{-2}[He] + k_3 + k_{-1}[CH_3NC]}$$

From step (3), we have

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

If [He] = 0, then

$$\frac{d[CH_3CN]}{dt} = \frac{k_3 k_1[CH_3NC]^2}{k_3 + k_{-1}[CH_3NC]} = k_{obs}[CH_3NC]$$

which is Equation 29.55.

29–22. Consider the reaction and mechanism given in Problem 29–10. The activation energy for the dissociation of $H_2(g)$ [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 $E_{a,obs}$, the experimentally determined activation energy, is given by

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

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

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

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

From Problem 29–10, $k_{obs} = k_2 k_1^{1/2}/k_{-1}^{1/2}$. If each step of the reaction mechanism shows Arrhenius behavior, we can write (as in Example 29–7)

$$k_1 = A_1 e^{-D_0/RT} \qquad k_{-1} = A_{-1} \qquad k_2 = A_2 e^{-E_2/RT}$$

(Note that the activation energy for the formation of H_2 is 0.) Substituting into an Arrhenius equation for the reaction rate constant gives

$$k_{obs} = \frac{k_2 k_1^{1/2}}{k_{-1}^{1/2}} = A_{obs}e^{-E_{a,obs}/RT}$$

$$\frac{A_2 A_1^{1/2}}{A_{-1}^{1/2}}e^{-E_2/RT}e^{-D_0/2RT} = A_{obs}e^{-E_{a,obs}/RT}$$

$$A_2\left(\frac{A_1}{A_{-1}}\right)^{1/2} e^{-(E_2+D_0/2)/RT} = A_{\text{obs}} e^{-E_{\text{a,obs}}/RT}$$

so

$$E_{\text{a,obs}} = E_2 + \frac{D_0}{2} \qquad \text{and} \qquad A_{\text{obs}} = A_2\left(\frac{A_1}{A_{-1}}\right)^{1/2}$$

29–23. The thermal decomposition of ethylene oxide occurs by the mechanism

$$H_2COCH_2(g) \overset{k_1}{\Longrightarrow} H_2COCH(g) + H(g)$$
$$H_2COCH(g) \overset{k_2}{\Longrightarrow} CH_3(g) + CO(g)$$
$$CH_3(g) + H_2COCH_2(g) \overset{k_3}{\Longrightarrow} H_2COCH(g) + CH_4(g)$$
$$CH_3(g) + H_2COCH(g) \overset{k_4}{\Longrightarrow} \text{products}$$

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

Initiation step: (1)
Propagation steps: (2), (3)
Termination step: (4)
From the termination step we have

$$\frac{d[\text{products}]}{dt} = k_4[CH_3][H_2COCH]$$

Treating CH_3 and H_2COCH by the steady-state approximation gives

$$\frac{d[CH_3]}{dt} = 0 = k_2[H_2COCH] - k_3[CH_3][H_2COCH_2] - k_4[CH_3][H_2COCH]$$

and

$$\frac{d[H_2COCH]}{dt} = 0 = -k_2[H_2COCH] + k_3[CH_3][H_2COCH_2] - k_4[CH_3][H_2COOH] + k_1[H_2COCH_2]$$

Adding these two expressions together gives

$$0 = -2k_4[CH_3][H_2COCH] + k_1[H_2COCH_2]$$
$$[CH_3][H_2COCH] = \frac{k_1}{2k_4}[H_2COCH_2]$$

so

$$\frac{d[\text{products}]}{dt} = \frac{k_1}{2}[H_2COCH_2]$$

which is first-order in $[H_2COCH_2]$.

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

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

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

is

$$CH_3CHO(g) \overset{k_1}{\Longrightarrow} CH_3(g) + CHO(g) \quad (1)$$
$$CH_3(g) + CH_3CHO(g) \overset{k_2}{\Longrightarrow} CH_4(g) + CH_3CO(g) \quad (2)$$
$$CH_3CO(g) \overset{k_3}{\Longrightarrow} CH_3(g) + CO(g) \quad (3)$$
$$2\,CH_3(g) \overset{k_4}{\Longrightarrow} C_2H_6 \quad (4)$$

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

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

This is a chain reaction.
Initiation step: (1)
Propagation steps: (2), (3)
Termination step: (4)
The rate laws for $CH_4(g)$, $CH_3(g)$, and $CH_3CO(g)$ are

$$\frac{d[CH_4]}{dt} = k_2[CH_3][CH_3CHO]$$
$$\frac{d[CH_3]}{dt} = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_3CO] - k_4[CH_3]^2$$
$$\frac{d[CH_3CO]}{dt} = k_2[CH_3][CH_3CHO] - k_3[CH_3CO]$$

Assuming the steady-state approximation for the appropriate intermediates, we find

$$\frac{d[CH_3CO]}{dt} = 0 = k_2[CH_3][CH_3CHO] - k_3[CH_3CO]$$
$$[CH_3CO] = \frac{k_2}{k_3}[CH_3][CH_3CHO] \quad (1)$$

and (using Equation 1 to express $[CH_3CO]$)

$$\frac{d[CH_3]}{dt} = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_3CO] - k_4[CH_3]^2$$
$$0 = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_2[CH_3][CH_3CHO] - k_4[CH_3]^2$$
$$[CH_3] = \left(\frac{k_1}{k_4}\right)^{1/2}[CH_3CHO]^{1/2}$$

Substituting this expression into the rate law for methane gives

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

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

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

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

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

The rate laws are

$$\frac{d[CO]}{dt} = k_3[CH_3CO]$$

$$\frac{d[CH_3]}{dt} = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_3CO]$$

$$\frac{d[CH_3CO]}{dt} = k_2[CH_3][CH_3CHO] - k_3[CH_3CO] - k_4[CH_3CHO]^2$$

Using the steady-state approximation gives

$$\begin{aligned} 0 &= k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_3CO] \\ +\,0 &= \qquad + k_2[CH_3][CH_3CHO] - k_3[CH_3CO] - k_4[CH_3CHO]^2 \\ \hline 0 &= k_1[CH_3CHO] \qquad\qquad\qquad\qquad - k_4[CH_3CHO]^2 \end{aligned}$$

We can then write

$$k_4[CH_3CHO]^2 = k_1[CH_3CHO]$$

$$[CH_3CHO] = \left(\frac{k_1}{k_4}\right)^{1/2} [CH_3CHO]^{1/2}$$

Finally, substituting into the rate law for CO gives

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

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

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

The chain length γ is the average number of times the propagation steps are repeated before a termination step occurs. For a decomposition reaction, it is the number of molecules decomposed by a single carrier molecule. (A carrier molecule is an intermediate responsible for chain propagation.) For the reaction mechanism given in Problem 29–25,

$$\gamma = \frac{\left(\frac{k_1}{k_4}\right)^{1/2} k_3[CH_3CHO]^{1/2}}{k_1[CH_3CHO]} = \left(\frac{1}{k_1k_4}\right)^{1/2} k_3[CH_3CHO]^{-1/2}$$

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

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

For the reaction mechanism given in Problem 29–24,

$$\gamma = \frac{\left(\frac{k_1}{k_4}\right)^{1/2} k_2[CH_3CHO]^{3/2}}{k_1[CH_3CHO]} = \left(\frac{1}{k_1k_4}\right)^{1/2} k_2[CH_3CHO]^{1/2}$$

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

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

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?

The rate law is

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

so

$$k_{obs} = \left(\frac{k_1}{k_4}\right)^{1/2} k_2$$

Using the Arrhenius equation, we can write

$$k_1 = A_1e^{-E_1/RT} \qquad k_4 = A_4e^{-E_4/RT} \qquad k_2 = A_2e^{-E_2/RT}$$

Then

$$A_{obs}e^{-E_{obs}/RT} = k_{obs} = \left(\frac{k_1}{k_4}\right)^{1/2} k_2 = A_2\left(\frac{A_1}{A_4}\right)^{1/2} e^{-(E_1-E_4)/2RT-E_2/RT}$$

From this, we find

$$A_{obs} = A_2\left(\frac{A_1}{A_4}\right)^{1/2} \qquad \text{and} \qquad E_{obs} = E_2 + \frac{1}{2}(E_1 - E_4)$$

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

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

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?

The rate law is

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

so

$$k_{obs} = \left(\frac{k_1}{k_4}\right)^{1/2} k_3$$

This is identical to k_{obs} in the previous problem, except that k_2 has been replaced by k_3. Thus

$$A_{obs} = A_3\left(\frac{A_1}{A_4}\right)^{1/2} \quad \text{and} \quad E_{obs} = E_3 + \frac{1}{2}(E_1 - E_4)$$

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.

The bond strength of the H_2 bond is much greater than that of the Br_2 bond. From Table 18.2, we can see that D_0 for H_2 is 432 kJ·mol^{-1}, while D_0 for Br_2 is only 190 kJ·mol^{-1}. It is therefore more likely that the Br_2 bond will dissociate than that the H_2 bond will dissociate.

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 $Cl_2(g)$.

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

The mechanism for this reaction is

$$Cl_2(g) + M(g) \overset{k_1}{\rightleftharpoons} 2\,Cl(g) + M(g) \quad (1)$$

$$Cl(g) + H_2(g) \overset{k_2}{\rightleftharpoons} HCl(g) + H(g) \quad (2)$$

$$H(g) + Cl_2(g) \overset{k_3}{\rightleftharpoons} HCl(g) + Cl(g) \quad (3)$$

$$2\,Cl(g) + M(g) \overset{k_4}{\rightleftharpoons} Cl_2(g) + M(g) \quad (4)$$

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

Initiation step: (1)
Propagation steps: (2), (3)
Termination step: (4)
The inhibition steps for the chain reaction between $H_2(g)$ and $Br_2(g)$ are (Section 29–7)

$$HBr(g) + H(g) \overset{k_{-2}}{\rightleftharpoons} Br(g) + H_2(g) \quad (4a)$$

$$HBr(g) + Br(g) \overset{k_3}{\rightleftharpoons} H(g) + Br_2(g) \quad (5a)$$

These reaction steps have molar enthalpies of

$$\Delta_{r,4a}\overline{H} = -D_0(H_2) + D_0(HBr) = -69\ kJ\cdot mol^{-1}$$

$$\Delta_{r,5a}\overline{H} = -D_0(Br_2) + D_0(HBr) = 173\ kJ\cdot mol^{-1}$$

We neglected the contribution of step (5a) because this reaction is so much more endothermic than Reaction 4a. The corresponding inhibition steps for the chain reaction between $H_2(g)$ and $Cl_2(g)$ would be

$$HCl(g) + H(g) \overset{k_{-2}}{\rightleftharpoons} Cl(g) + H_2(g) \quad (i)$$

$$HCl(g) + Br(g) \overset{k_3}{\rightleftharpoons} H(g) + Cl_2(g) \quad (ii)$$

with corresponding molar enthalpies

$$\Delta_{r,i}\overline{H} = -D_0(H_2) + D_0(HCl) = -4\ kJ\cdot mol^{-1}$$

$$\Delta_{r,ii}\overline{H} = -D_0(Cl_2) + D_0(HCl) = 189\ kJ\cdot mol^{-1}$$

Again, the contribution of the second step shown here is highly endothermic, and so we disregard this reaction. We also see that the first step shown is only slightly exothermic (in contrast with the corresponding step in the bromine reaction), so we can also neglect this step when describing the chain reaction involving Cl_2.

29–32. Derive the rate law for $v = (1/2)(d[HCl]/dt)$ for the mechanism of the

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

reaction given in Problem 29–31.

From steps (2) and (3), we write

$$\frac{d[HCl]}{dt} = k_2[Cl][H_2] + k_3[H][Cl_2] \quad (1)$$

Applying the steady-state approximation to Cl and H gives

$$\frac{d[Cl]}{dt} = 0 = 2k_1[Cl_2][M] - 2k_4[Cl]^2[M] - k_2[Cl][H_2] + k_3[H][Cl_2]$$

$$+\ \frac{d[H]}{dt} = 0 = \qquad\qquad + k_2[Cl][H_2] - k_3[H][Cl_2]$$

$$0 = 2k_1[Cl_2][M] - 2k_4[Cl]^2[M]$$

so

$$[Cl] = \left(\frac{k_1}{k_4}\right)^{1/2}[Cl_2]^{1/2}$$

Substituting this back into the steady-state approximation for H gives

$$[H] = \frac{k_2}{k_3}\frac{[Cl][H_2]}{[Cl_2]} = \frac{k_2}{k_3}\left(\frac{k_1}{k_4}\right)^{1/2}\frac{[Cl_2]^{1/2}[H_2]}{[Cl_2]} = \frac{k_2}{k_3}\left(\frac{k_1}{k_4}\right)^{1/2}\frac{[H_2]}{[Cl_2]^{1/2}}$$

Then Equation 1 becomes

$$\begin{aligned}\frac{d[HCl]}{dt} &= k_2[Cl][H_2] + k_3[H][Cl_2] \\ &= k_2\left(\frac{k_1}{k_4}\right)^{1/2}[Cl_2]^{1/2}[H_2] + k_2\left(\frac{k_1}{k_4}\right)^{1/2}[H_2][Cl_2]^{1/2} \\ &= 2k_2\left(\frac{k_1}{k_4}\right)^{1/2}[H_2][Cl_2]^{1/2}\end{aligned}$$

or

$$\frac{1}{2}\frac{d[HCl]}{dt} = k_2\left(\frac{k_1}{k_4}\right)^{1/2}[H_2][Cl_2]^{1/2}$$

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

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

we could have the photochemical initiation reaction

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

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 $d[Br]/dt$, 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 $d[HBr]/dt$ depend on I_{abs}?

The quantum yield is the number of Br_2 molecules that react for each photon absorbed. The quantity $I_{abs}t$ is the concentration of photons available, so

$$\frac{d[Br_2]}{dt} = \frac{d(I_{abs}\Phi t)}{dt} = I_{abs}$$

The rate of formation of Br in this step would be twice the rate of dissociation of Br_2, so

$$\frac{d[Br]}{dt} = 2I_{abs}$$

The expressions for $d[HBr]/dt$ and $d[H]/dt$ that were found in Section 29–7 (Equations 29.61 and 29.62) still apply, but now applying the steady-state approximation to Br and H gives

$$\begin{aligned}\frac{d[Br]}{dt} = 0 = 2I_{abs} &- k_2[Br][H_2] + k_{-2}[HBr][H] - k_{-1}[Br]^2 + k_3[H][Br_2] \\ + \frac{d[H]}{dt} = 0 = &\quad k_2[Br][H_2] - k_{-2}[HBr][H] \qquad - k_3[H][Br_2] \\ \hline 0 = 2I_{abs} &\qquad\qquad - k_{-1}[Br]^2\end{aligned}$$

so

$$[Br] = \left(\frac{2I_{abs}}{k_{-1}}\right)^{1/2}$$

Substituting this back into the steady-state approximation for H gives

$$[H] = \frac{k_2[Br][H_2]}{k_{-2}[HBr] + k_3[Br_2]} = \left(\frac{2I_{abs}}{k_{-1}}\right)^{1/2}\frac{k_2[H_2]}{k_{-2}[HBr] + k_3[Br_2]}$$

Then Equation 29.61 becomes

$$\begin{aligned}\frac{d[HBr]}{dt} &= k_2[Br][H_2] - k_{-2}[HBr][H] + k_3[H][Br_2] \\ &= k_2\left(\frac{2I_{abs}}{k_{-1}}\right)^{1/2}[H_2] - (k_{-2}[HBr] - k_3[Br_2])\left(\frac{2I_{abs}}{k_{-1}}\right)^{1/2}\frac{k_2[H_2]}{k_{-2}[HBr] + k_3[Br_2]} \\ &= k_2\left(\frac{2I_{abs}}{k_{-1}}\right)^{1/2}[H_2]\left[1 + \frac{k_3[Br_2] - k_{-2}[HBr]}{k_{-2}[HBr] + k_3[Br_2]}\right] \\ &= k_2\left(\frac{2I_{abs}}{k_{-1}}\right)^{1/2}\left[\frac{2[H_2]}{(k_{-2}/k_3)[HBr]/[Br_2] + 1}\right]\end{aligned}$$

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 $[S] = [S]_0$ and $[P] = 0$. We will now determine the Michaelis-Menton rate law by a different approach. Recall that the Michaelis-Menton mechanism is

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

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

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

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

where K_m is the Michaelis constant. Now show that

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

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

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

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

Applying the steady-state approximation to the rate law for ES gives

$$\frac{d[\mathrm{ES}]}{dt} = 0 = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}] - k_2[\mathrm{ES}]$$

$$[\mathrm{ES}] = \frac{k_1[\mathrm{E}][\mathrm{S}]}{k_{-1} + k_2} = \frac{[\mathrm{E}][\mathrm{S}]}{K_m}$$

Now using Equation 29.74 gives

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

$$= [\mathrm{E}]\left(1 + \frac{[\mathrm{S}]}{K_m}\right)$$

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

Substituting into Equation 1 gives

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

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

If $[\mathrm{S}] = [\mathrm{S}]_0$, this reduces to 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.

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

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

$$\mathrm{ES} \xrightarrow{k_3} \mathrm{E} + \mathrm{P} \qquad (3)$$

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 $K_1 = [\mathrm{EI}]/[\mathrm{E}][\mathrm{I}]$ 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

$$v = \frac{d[\mathrm{P}]}{dt} = \frac{k_3[\mathrm{E}]_0[\mathrm{S}]}{K_m + [\mathrm{S}] + K_m K_1[\mathrm{I}]} \approx \frac{k_3[\mathrm{E}]_0[\mathrm{S}]_0}{K_m' + [\mathrm{S}]_0} \qquad (4)$$

where $K_m' = K_m(1 + K_1[\mathrm{I}])$. 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 $[\mathrm{I}] \to 0$?

$$\frac{d[\mathrm{S}]}{dt} = -k_1[\mathrm{E}][\mathrm{S}] + k_{-1}[\mathrm{ES}]$$

$$\frac{d[\mathrm{ES}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}] - k_3[\mathrm{ES}]$$

$$\frac{d[\mathrm{EI}]}{dt} = k_2[\mathrm{E}][\mathrm{I}] - k_{-2}[\mathrm{EI}]$$

$$\frac{d[\mathrm{P}]}{dt} = k_3[\mathrm{ES}]$$

Applying the steady-state assumption to ES gives

$$0 = k_1[\mathrm{E}][\mathrm{S}] - (k_{-1} + k_3)[\mathrm{ES}]$$

$$[\mathrm{ES}] = \frac{k_1}{k_{-1} + k_3}[\mathrm{E}][\mathrm{S}] = \frac{[\mathrm{E}][\mathrm{S}]}{K_m}$$

Summing the concentrations of all components containing E gives

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

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

$$= [\mathrm{E}]\left(\frac{K_m + [\mathrm{S}] + [\mathrm{I}]K_m K_\mathrm{I}}{K_m}\right)$$

and so

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

The rate of formation of product (the reaction rate) is given by $v = k_3[\mathrm{ES}]$, so

$$v = \frac{d[\mathrm{P}]}{dt} = k_3[\mathrm{ES}] = k_3\frac{[\mathrm{E}][\mathrm{S}]}{K_m}$$

$$= k_3\frac{[\mathrm{E}]_0[\mathrm{S}]}{K_m + [\mathrm{S}] + K_m K_1[\mathrm{I}]}$$

$$\approx \frac{k_3[\mathrm{E}]_0[\mathrm{S}]_0}{K_m(1 + K_1[\mathrm{I}]) + [\mathrm{S}]_0} \approx \frac{k_3[\mathrm{E}]_0[\mathrm{S}]_0}{K_{m'} + [\mathrm{S}]_0}$$

If $[\mathrm{I}] \to 0$, then $K_{m'} \to K_m$ and so

$$v \to \frac{k_3[\mathrm{E}]_0[\mathrm{S}]_0}{K_m + [\mathrm{S}]_0}$$

as we would expect.

29–36. Antibiotic-resistant bacteria have an enzyme, penicillinase, that catalyzes the decomposition of the antibiotic. The molecular mass of penicillinase is 30 000 g·mol^{-1}. The turnover number of the enzyme at 28°C is 2000 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 g·mol^{-1}, in 20 seconds at 28°C, how many active sites does the enzyme have?

$$\frac{6.4 \times 10^{-6}\ \text{g}}{30\,000\ \text{g·mol}^{-1}} = 2.13 \times 10^{-10}\ \text{mol penicillinase}$$

$$\frac{3.11 \times 10^{-3}\ \text{g}}{364\ \text{g·mol}^{-1}} = 8.54 \times 10^{-6}\ \text{mol amoxicillin}$$

This is the amount of amoxicillin catalyzed in twenty seconds. Since the catalyst is not destroyed in the reaction, the same amount of penicillinase will destroy 2.56×10^{-5} mol of amoxicillin in one minute. Now

$$\text{turnover number} \times \#\ \text{active sites} = \frac{2.56 \times 10^{-5}\ \text{mol·min}^{-1}}{2.13 \times 10^{-10}\ \text{mol}}$$

$$2000\ \text{s}^{-1} \times \#\ \text{active sites} = 1.20 \times 10^{5}\ \text{min}^{-1}$$

$$\#\ \text{active sites} = \frac{2.00 \times 10^{3}\ \text{s}^{-1}}{2000\ \text{s}^{-1}} = 1$$

29–37. Show that the inverse of Equation 29.78 is

$$\frac{1}{v} = \frac{1}{v_{max}} + \frac{K_m}{v_{max}}\frac{1}{[S]_0} \qquad (1)$$

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} mol·dm^{-3}, the following data were obtained.

v/mol·dm^{-3}·s^{-1}	$[CO_2]_0/10^{-3}$ mol·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

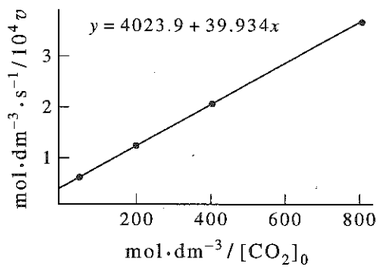
Plot these data according to Equation 1, and determine the values of K_m, the Michaelis constant, and k_2, the rate constant for product formation from the enzyme-substrate complex from the slope and intercept of the best-fit line to the plotted data.

Recall that $v_{max} = k_2[E]_0$, so we find

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

$$\frac{1}{v} = \frac{K_m}{k_2[S]_0[E]_0} + \frac{1}{k_2[E]_0}$$

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



We can now solve for v_{max} and K_m:

$$\frac{1}{v_{max}} = 4020\ \text{dm}^3\text{·s·mol}^{-1}$$

$$v_{max} = 2.49 \times 10^{-4}\ \text{mol·dm}^{-3}\text{·s}^{-1}$$

$$\frac{K_m}{v_{max}} = 39.9\ \text{s}$$

$$K_m = 9.94 \times 10^{-3}\ \text{mol·dm}^{-3}$$

Because we are given that $[E]_0 = 2.32 \times 10^{-9}$ mol·dm^{-3}, we find

$$k_2 = \frac{v_{max}}{[E]_0} = \frac{2.49 \times 10^{-4}\ \text{mol·dm}^{-3}\text{·s}^{-1}}{2.32 \times 10^{-9}\ \text{mol·dm}^{-3}} = 1.07 \times 10^{5}\ \text{s}^{-1}$$

29–38. Carbonic anhydrase catalyzes the reaction

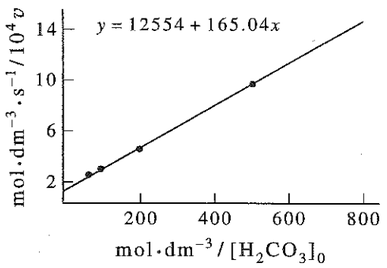
$$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq)$$

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.

We use the method developed in Problem 29–37, and plot $1/v$ versus $1/[H_2CO_3]_0$:



As before,

$$\frac{1}{v_{max}} = 12\,600\ \text{dm}^3\cdot\text{s}\cdot\text{mol}^{-1}$$

$$v_{max} = 7.94 \times 10^{-5}\ \text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$$

$$\frac{K_m}{v_{max}} = 165\ \text{s}$$

$$K_m = 1.31 \times 10^{-2}\ \text{mol}\cdot\text{dm}^{-3}$$

Because we are given $[E]_0 = 2.32 \times 10^{-9}\ \text{mol}\cdot\text{dm}^{-3}$, we find

$$k_2 = \frac{v_2}{[E]_0} = 3.43 \times 10^4\ \text{s}^{-1}$$

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

The Michaelis-Menton mechanism gives the rate expression

$$v = \frac{k_2[S]_0[E]_0}{K_m + [S]_0} \tag{29.78}$$

If $[S]_0 = K_m$, then this becomes

$$v = \frac{k_2 K_m[E]_0}{2K_m} = \frac{k_2[E]_0}{2} = \frac{v_{max}}{2}$$

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

The Michaelis-Menton equation is

$$v = \frac{k_2[S]_0[E]_0}{K_m + [S]_0} = \frac{v_{max}[S]_0}{K_m + [S]_0} \tag{29.78}$$

The turnover number for a single active site catalyst is equal to $v_{max}/[E]_0$, so

$$v_{max} = (4.0 \times 10^7\ \text{s}^{-1})(0.016 \times 10^{-6}\ \text{mol}\cdot\text{dm}^{-3})$$
$$= 0.64\ \text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$$

and

$$v = \frac{(0.64\ \text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1})(4.32 \times 10^{-6}\ \text{mol}\cdot\text{dm}^{-3})}{(25 \times 10^{-3}\ \text{mol}\cdot\text{dm}^{-3}) + (4.32 \times 10^{-6}\ \text{mol}\cdot\text{dm}^{-3})} = 1.11 \times 10^{-4}\ \text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$$

29–41. The presence of $4.8 \times 10^{-6}\ \text{mol}\cdot\text{dm}^{-3}$ 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.)

The inital rate is now given by (from Problem 29–35)

$$v = \frac{k_3[E]_0[S]_0}{K_m(1 + K_I[I]) + [S]} = \frac{v_{max}[S]_0}{K_m(1 + K_I[I]) + [S]}$$

(recall that, in this case, $k_3[E]_0 = v_{max}$). The maximum rate is the same for this problem as the previous problem, and v can be found by dividing the initial rate found in Problem 29–40 by 3.6, so

$$3.08 \times 10^{-5} = \frac{(0.64)(4.32 \times 10^{-6})}{(25 \times 10^{-3})[1 + K_I(4.8 \times 10^{-6}\ \text{mol}\cdot\text{dm}^{-3})] + 4.32 \times 10^{-6}}$$

$$1 + K_I(4.8 \times 10^{-6}\ \text{mol}\cdot\text{dm}^{-3}) = \frac{(0.64)(4.32 \times 10^{-6}) - (4.32 \times 10^{-6})(3.08 \times 10^{-5})}{(3.08 \times 10^{-5})(25 \times 10^{-3})}$$

$$K_I = 5.4 \times 10^5\ \text{dm}^3\cdot\text{mol}^{-1}$$

29–42. The turnover number for acetylcholinesterase, an enzyme with a single active site that metabolizes acetylcholine, is $1.4 \times 10^4\ \text{s}^{-1}$. 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 $4.2 \times 10^4\ \text{g}\cdot\text{mol}^{-1}$; acetylcholine has the molecular formula $C_7NO_2H_{16}^+$.)

$$\frac{2.16 \times 10^{-6}\ \text{g}}{4.2 \times 10^4\ \text{g}\cdot\text{mol}^{-1}} = 5.1 \times 10^{-11}\ \text{mol acetocholinesterase}$$

The enzyme has a single active site, so

$$v_{max} = (\text{turnover number})(\text{mol acetocholinesterase})$$
$$= (1.4 \times 10^4\ \text{s}^{-1})(5.1 \times 10^{-11}\ \text{mol})\left(\frac{3600\ \text{hr}^{-1}}{1\ \text{s}^{-1}}\right) = 2.6 \times 10^{-3}\ \text{mol}\cdot\text{hr}^{-1}$$

The molecular mass of acetylcholine is $146.21\ \text{g}\cdot\text{mol}^{-1}$, so 0.38 g of acetylcholine are metabolized in one hour.

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

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

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

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

We can write the rate laws for Br and Br_2^* as

$$\frac{d[\mathrm{Br}]}{dt} = -2k_1[\mathrm{Br}]^2 + 2k_{-1}[\mathrm{Br}_2^*]$$
$$\frac{d[\mathrm{Br}_2^*]}{dt} = k_1[\mathrm{Br}]^2 - k_{-1}[\mathrm{Br}_2^*] - k_2[\mathrm{Br}_2^*][\mathrm{M}]$$

Using the steady-state approximation for Br_2^* gives

$$[\mathrm{Br}_2^*] = \frac{k_1[\mathrm{Br}]^2}{k_{-1} + k_2[\mathrm{M}]}$$

Then

$$\frac{d[\mathrm{Br}]}{dt} = -2k_1[\mathrm{Br}]^2 + \frac{2k_1k_{-1}[\mathrm{Br}]^2}{k_{-1} + k_2[\mathrm{M}]}$$
$$= \frac{-2k_1k_{-1}[\mathrm{Br}]^2 - 2k_1[\mathrm{Br}]^2k_2[\mathrm{M}] + 2k_{-1}k_1[\mathrm{Br}]^2}{k_{-1} + k_2[\mathrm{M}]}$$
$$= \frac{-2k_1k_2[\mathrm{Br}]^2[\mathrm{M}]}{k_{-1} + k_2[\mathrm{M}]}$$

If $v_2 \gg v_{-1}$, then $k_2[\mathrm{Br}_2^*][\mathrm{M}] \gg k_{-1}[\mathrm{Br}_2^*]$ and so $k_2[\mathrm{M}] \gg k_{-1}$. The rate equation then becomes

$$\frac{d[\mathrm{Br}]}{dt} = -2k_1[\mathrm{Br}]^2$$

If $v_2 \ll v_{-1}$, then $k_2[\mathrm{M}] \ll k_{-1}$. The rate equation then becomes

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

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?

CCl_4 is the better catalyst for this reaction. There is a difference in the catalytic behavior of the gases because CCl_4 has vibrational and rotational energy levels, which make it more effective in absorbing energy from the excited bromine molecule.

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

$$2\mathrm{H_2(g)} + \mathrm{O_2(g)} \longrightarrow 2\mathrm{H_2O(g)}$$

is −457.4 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?

Although the reaction is spontaneous, it has a very high energy of activation, and so it is very unlikely that the reactants will have enough energy to create water vapor. This mixture will be indefinitely stable as long as no external catalysts are present to lower the activation energy and facilitate the reaction. (It will eventually react even in the absence of catalysts, however, as the reaction is spontaneous).

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

$$\mathrm{H_2(g)} + \mathrm{F_2(g)} \longrightarrow 2\mathrm{HF(g)}$$

The mechanism for this reaction involves the elementary steps

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

Comment on why the reaction $H_2(g) + M(g) \rightarrow 2H(g) + M(g)$ 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 $d[\mathrm{HF}]/dt$ for the above mechanism assuming that the steady-state approximation can be applied to both intermediate species, F(g) and H(g).

The reaction $H_2(g) + M(g) \rightarrow 2H(g) + M(g)$ is not included in the mechanism of the laser because a very large energy would be needed to break the H_2 bond (≈ 432 kJ·mol^{-1}). Now we can write the rate laws for HF, F, and H:

$$\frac{d[\mathrm{HF}]}{dt} = k_2[\mathrm{F}][\mathrm{H_2}] - k_{-2}[\mathrm{HF}][\mathrm{H}] + k_3[\mathrm{H}][\mathrm{F_2}]$$
$$\frac{d[\mathrm{F}]}{dt} = 2k_1[\mathrm{F_2}][\mathrm{M}] - 2k_{-1}[\mathrm{F}]^2[\mathrm{M}] - k_2[\mathrm{F}][\mathrm{H_2}] + k_{-2}[\mathrm{HF}][\mathrm{H}] + k_3[\mathrm{H}][\mathrm{F_2}]$$
$$\frac{d[\mathrm{H}]}{dt} = k_2[\mathrm{F}][\mathrm{H_2}] - k_{-2}[\mathrm{HF}][\mathrm{H}] - k_3[\mathrm{H}][\mathrm{F_2}]$$

Applying the steady-state approximation gives

$$\begin{aligned} 0 &= 2k_1[F_2][M] - 2k_{-1}[F]^2[M] - k_2[F][H_2] + k_{-2}[HF][H] + k_3[H][F_2] \\ +\,0 &= \qquad\qquad + k_2[F][H_2] - k_{-2}[HF][H] - k_3[H][F_2] \\ \hline 0 &= 2k_1[F_2][M] - 2k_{-1}[F]^2[M] \end{aligned}$$

so

$$[F] = \frac{k_1^{1/2}[F_2]^{1/2}}{k_{-1}^{1/2}}$$

Substituting into the steady-state approximation for H gives

$$0 = k_2\frac{k_1^{1/2}[F_2]^{1/2}[H_2]}{k_{-1}^{1/2}} - k_{-2}[HF][H] - k_3[H][F_2]$$

$$[H] = \frac{k_2\left(\dfrac{k_1}{k_{-1}}\right)^{1/2}[F_2]^{1/2}[H_2]}{k_{-2}[HF] + k_3[F_2]}$$

Finally, substitute into the rate equation for HF to get

$$\frac{d[HF]}{dt} = k_2[F][H_2] - k_{-2}[HF][H] + k_3[H][F_2]$$

$$= \left(\frac{k_1}{k_{-1}}\right)^{1/2} k_2[F_2]^{1/2}[H_2] + (k_3[F_2] - k_{-2}[HF])\frac{k_2\left(\dfrac{k_1}{k_{-1}}\right)^{1/2}[F_2]^{1/2}[H_2]}{k_{-2}[HF] + k_3[F_2]}$$

$$= \left(\frac{k_1}{k_{-1}}\right)^{1/2} k_2[F_2]^{1/2}[H_2]\left(1 + \frac{k_3[F_2] - k_{-2}[HF]}{k_{-2}[HF] + k_3[F_2]}\right)$$

$$= \left(\frac{k_1}{k_{-1}}\right)^{1/2} k_2[F_2]^{1/2}[H_2]\frac{2k_3[F_2]}{k_{-2}[HF] + k_3[F_2]}$$

$$\frac{1}{2}\frac{d[HF]}{dt} = \left(\frac{k_1}{k_{-1}}\right)^{1/2} k_2[F_2]^{1/2}[H_2]\frac{1}{1 + (k_{-2}/k_3)[HF][F_2]^{-1}}$$

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

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

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

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

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

where we have used the symbol j to indicate that the rate constant is for a photochemical reaction. Determine the rate expressions for $d[O]/dt$ and $d[O_3]/dt$. Assume that both intermediate species, O(g) and O_3(g), can be treated by the steady-state approximation and thereby show that

$$[O] = \frac{2j_1[O_2] + j_3[O_3]}{k_2[O_2][M] + k_4[O_3]} \tag{1}$$

and

$$[O_3] = \frac{k_2[O][O_2][M]}{j_3 + k_4[O]} \tag{2}$$

Now substitute Equation 1 into Equation 2 and solve the resulting quadratic formula for $[O_3]$ to obtain

$$[O_3] = [O_2]\frac{j_1}{2j_3}\left\{\left(1 + 4\frac{j_3}{j_1}\frac{k_2}{k_4}[M]\right)^{1/2} - 1\right\}$$

Typical values for these parameters at an altitude of 30 km are $j_1 = 2.51 \times 10^{-12}$ s^{-1}, $j_3 = 3.16 \times 10^{-4}$ s^{-1}, $k_2 = 1.99 \times 10^{-33}$ $cm^6 \cdot molecule^{-2} \cdot s^{-1}$, $k_4 = 1.26 \times 10^{-15}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, $[O_2] = 3.16 \times 10^{17}$ $molecule \cdot cm^{-3}$, and $[M] = 3.98 \times 10^{17}$ $molecule \cdot cm^{-3}$. Find $[O_3]$ and [O] at an altitude of 30 km using Equations 1 and 2. Was the use of the steady-state assumption justified?

The rate expressions for the intermediate species O and O_3 are

$$\frac{d[O]}{dt} = 2j_1[O_2] + j_3[O_3] - k_2[O][O_2][M] - k_4[O][O_3]$$

$$\frac{d[O_3]}{dt} = k_2[O][O_2][M] - j_3[O_3] - k_4[O][O_3]$$

Applying the steady-state approximation gives (Equation 1)

$$k_4[O][O_3] + k_2[O][O_2][M] = 2j_1[O_2] + j_3[O_3]$$

$$[O] = \frac{2j_1[O_2] + j_3[O_3]}{k_4[O_3] + k_2[O_2][M]}$$

and (Equation 2)

$$j_3[O_3] + k_4[O][O_3] = k_2[O][O_2][M]$$

$$[O_3] = \frac{k_2[O][O_2][M]}{j_3 + k_4[O]}$$

Substituting Equation 1 into Equation 2 gives

$$[O_3]\left(j_3 + k_4[O]\right) = k_2[O][O_2][M]$$

$$j_3[O_3] + k_4[O_3]\frac{2j_1[O_2] + j_3[O_3]}{k_4[O_3] + k_2[O_2][M]} = k_2[O_2][M]\frac{2j_1[O_2] + j_3[O_3]}{k_4[O_3] + k_2[O_2][M]}$$

$$j_3k_2[O_3][O_2][M] + k_4j_3[O_3]^2 + 2j_1k_4[O_3][O_2] + k_4j_3[O_3]^2 = 2k_2j_1[O_2]^2[M] + j_3k_2[O_3][O_2][M]$$

This equation can be written as

$$0 = 2k_4j_3[O_3]^2 + 2j_1k_4[O_3][O_2] - 2k_2j_1[O_2]^2[M]$$

$$0 = [O_3]^2 + \frac{j_1}{j_3}[O_2][O_3] - \frac{k_2j_1}{k_4j_3}[O_2]^2[M]$$

$$[O_3] = -\frac{j_1}{2j_3}[O_2] \pm \frac{1}{2}\sqrt{\left(\frac{j_1}{j_3}\right)^2[O_2]^2 + 4\frac{k_2}{k_4}\frac{j_1}{j_3}[O_2]^2[M]}$$

$$= -\frac{j_1}{2j_3}[O_2] \pm \sqrt{\left(\frac{j_1}{2j_3}\right)^2[O_2]^2 + \frac{k_2}{k_4}\frac{j_1}{j_3}[O_2]^2[M]}$$

$$= -\frac{j_1}{2j_3}[O_2] \pm \frac{j_1}{2j_3}[O_2]\sqrt{1 + \frac{4k_2}{k_4}\frac{j_3}{j_1}[M]}$$

We must have a positive value of $[O_3]$, so we have

$$[O_3] = -\frac{j_1}{2j_3}[O_2] + \frac{j_1}{2j_3}[O_2]\sqrt{1 + \frac{4k_2}{k_4}\frac{j_3}{j_1}[M]}$$
$$= [O_2]\frac{j_1}{2j_3}\left[\left(1 + 4\frac{j_3}{j_1}\frac{k_2}{k_4}[M]\right)^{1/2} - 1\right]$$

For the given parameters,

$$[O_3] = (3.16 \times 10^{17}\ \text{molecule}\cdot\text{cm}^{-3})\frac{2.51 \times 10^{-12}\ \text{s}^{-1}}{2(3.16 \times 10^{-4}\ \text{s}^{-1})}$$
$$\left\{\left[1 + 4\frac{(3.16 \times 10^{-4}\ \text{s}^{-1})(1.99 \times 10^{-33}\ \text{cm}^6\cdot\text{molecule}^{-2}\cdot\text{s}^{-1})}{(2.51 \times 10^{-12}\ \text{s}^{-1})(1.26 \times 10^{15}\ \text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1})}\right.\right.$$
$$\left.\left.\times(3.98 \times 10^{17}\ \text{molecule}\cdot\text{cm}^{-3})\right]^{1/2} - 1\right\}$$
$$= (1.25 \times 10^{9}\ \text{molecule}\cdot\text{cm}^{-3})\left(1.78 \times 10^{4}\right)$$
$$= 2.23 \times 10^{13}\ \text{molecule}\cdot\text{cm}^{-3}$$

This value is about 10^4 less than the value of [M]. Using this value for $[O_3]$ in Equation 1 gives (we drop the units for convenience)

$$[O] = \frac{2(2.51 \times 10^{-12})(3.16 \times 10^{17}) + (3.16 \times 10^{-4})(2.23 \times 10^{13})}{(1.99 \times 10^{-33})(3.16 \times 10^{17})(3.98 \times 10^{17}) + (1.26 \times 10^{-15})(2.23 \times 10^{13})}$$
$$= 2.82 \times 10^{7}\ \text{molecules}\cdot\text{cm}^{-3}$$

so the use of the steady-state approximation is justified.

In the next four problems we shall examine the explosive reaction

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

29–48. A simplified mechanism for this reaction is

$$\text{electric spark} + H_2(g) \longrightarrow 2\,H(g) \quad (1)$$
$$H(g) + O_2(g) \xrightarrow{k_1} OH(g) + O(g) \quad (2)$$
$$O(g) + H_2(g) \xrightarrow{k_2} OH(g) + H(g) \quad (3)$$
$$H_2(g) + OH(g) \xrightarrow{k_3} H_2O(g) + H(g) \quad (4)$$
$$H(g) + O_2(g) + M(g) \xrightarrow{k_4} HO_2(g) + M(g) \quad (5)$$

A reaction that produces more molecules that can participate in chain-propagation steps than it consumes is called a branching chain reaction. Label the branching chain reaction(s), inititation reaction(s), propagation reaction(s), and termination reaction(s) for this mechanism. Use the following bond dissociation energies to evaluate the energy change for steps (2) and (3).

Molecule	D_0/kJ·mol^{-1}
H_2	432
O_2	493
OH	424

Branching chain: (2), (3)
Initiation: (1)
Propagation: (4)
Termination: (5)

Using the bond dissocation energies, we find that

$$\Delta_2\text{Energy} = -D_0(OH) + D_0(O_2) = 69\ \text{kJ}\cdot\text{mol}^{-1}$$
$$\Delta_3\text{Energy} = -D_0(OH) + D_0(H_2) = 8\ \text{kJ}\cdot\text{mol}^{-1}$$

29–49. Using the mechanism given in Problem 29–48, determine the rate expression for [H] when the initiation step involves an electric spark that gives rise to a rate I_0 of the hydrogen atom production. Determine the rate expresions for [OH] and [O]. Assume that $[O] \approx [OH] \ll [H]$, so now we can apply the steady-state approximation to the intermediate species, O(g) and OH(g). Show that this use of the steady-state approximation gives

$$[O] = \frac{k_1[H][O_2]}{k_2[H_2]} \quad \text{and} \quad [OH] = \frac{2k_1[H][O_2]}{k_3[H_2]}$$

Use these results and your rate expression for [H] to show that

$$\frac{d[H]}{dt} = I_0 + (2k_1[O_2] - k_4[O_2][M])[H]$$

We must add the rate I_0 to the rate expression for [H] we would find without the electric spark, so

$$\frac{d[H]}{dt} = I_0 - k_1[H][O_2] + k_2[O][H_2] + k_3[OH][H_2] - k_4[H][O_2][M]$$
$$\frac{d[OH]}{dt} = k_1[H][O_2] + k_2[O][H_2] - k_3[OH][H_2]$$
$$\frac{d[O]}{dt} = k_1[H][O_2] - k_2[O][H_2]$$

Using the steady-state approximation for O and OH gives

$$0 = k_1[H][O_2] - k_2[O][H_2]$$
$$[O] = \frac{k_1[H][O_2]}{k_2[H_2]}$$

$$0 = k_1[H][O_2] + k_2[O][H_2] - k_3[OH][H_2]$$
$$[OH] = \frac{k_1[H][O_2] + k_2[O][H_2]}{k_3[H_2]}$$
$$= \frac{2k_1[H][O_2]}{k_3[H_2]}$$

Substituting into the rate expression for [H] gives

$$\frac{d[H]}{dt} = I_0 - k_1[H][O_2] + k_2[O][H_2] + k_3[OH][H_2] - k_4[H][O_2][M]$$
$$= I_0 - k_1[H][O_2] + \frac{k_1k_2[H][H_2][O_2]}{k_2[H_2]} + \frac{2k_1k_3[H_2][H][O_2]}{k_3[H_2]} - k_4[H][O_2][M]$$
$$= I_0 - k_1[H][O_2] + k_1[H][O_2] + 2k_1[H][O_2] - k_4[H][O_2][M]$$
$$= I_0(2k_1[O_2] - k_4[O_2][M])[H]$$

29–50. Consider the result of Problem 29–49. The rate of hydrogen atom production has a functional dependence of

$$\frac{d[\mathrm{H}]}{dt} = I_0 + (\alpha - \beta)[\mathrm{H}] \tag{1}$$

Which step(s) of the chemical reaction are responsible for the magnitudes of α and β? We can envision two solutions to this rate law, one for $\alpha > \beta$ and one for $\alpha < \beta$. For $\alpha < \beta$ show that the solution to Equation 1 becomes

$$[\mathrm{H}] = \frac{I_0}{\beta - \alpha}(1 - e^{-(\beta-\alpha)t})$$

Plot [H] as a function of time. Determine the slope of the plot at short times. Determine the final steady-state value of [H].

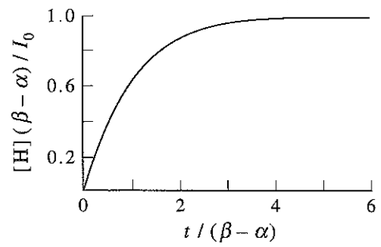
Write the rate expression for [H] as

$$\frac{d[\mathrm{H}]}{dt} + (\beta - \alpha)[\mathrm{H}] = I_0$$

This is of the form discussed in Problem 29–5, so

$$\begin{aligned}
[\mathrm{H}] &= e^{-\int(\beta-\alpha)dt}\left[\int e^{\int(\beta-\alpha)dt} I_0 dt\right] \\
&= e^{-(\beta-\alpha)t}\left[\int e^{(\beta-\alpha)t} I_0 dt\right] \\
&= e^{-(\beta-\alpha)t}\left[\frac{e^{(\beta-\alpha)t}}{\beta-\alpha} I_0 - \frac{I_0}{\beta-\alpha}\right] \\
&= \frac{I_0}{\beta-\alpha} - \frac{I_0}{\beta-\alpha} e^{-(\beta-\alpha)t} = \frac{I_0}{\beta-\alpha}\left[1 - e^{-(\beta-\alpha)t}\right]
\end{aligned}$$

We plot $[\mathrm{H}](\beta - \alpha)$ versus t below.



At short times the slope of the plot is $I_0 t$ and the final steady-state value of [H] is $I_0/(\beta - \alpha)$.

29–51. We now consider the solution to the equation (Problem 29–50)

$$\frac{d[\mathrm{H}]}{dt} = I_0 + (\alpha - \beta)[\mathrm{H}]$$

when $\alpha > \beta$. Show that the solution to this differential equation is given by

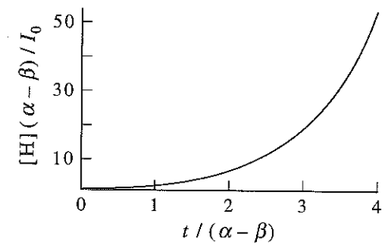
$$[\mathrm{H}] = \frac{I_0}{\alpha - \beta}(e^{(\alpha-\beta)t} - 1)$$

Plot [H] as a function of time. Describe the differences observed between this plot and that obtained in Problem 29–50. Which case do you think is characteristic of a chemical explosion?

The solution is the same as in the previous problem, since the relative magnitudes of α and β were not considered when solving the differential equation. However, since $\alpha > \beta$, to make their difference positive we can express the solution above in terms of $\alpha - \beta$, instead of $\beta - \alpha$. Then

$$\begin{aligned}
[\mathrm{H}] &= \frac{I_0}{\beta-\alpha}\left[1 - e^{-(\beta-\alpha)t}\right] \\
&= \frac{-I_0}{\alpha-\beta}\left[1 - e^{(\alpha-\beta)t}\right] \\
&= \frac{I_0}{\alpha-\beta}\left[e^{(\alpha-\beta)t} - 1\right]
\end{aligned}$$

We plot $[\mathrm{H}](\alpha - \beta)$ versus t:



In this case the concentration of H does not converge as $t \to \infty$, and so this case is characteristic of a chemical explosion.