26-8. Determine the rate law for the reaction described by

\[ \text{NO(g)} + \text{H}_2(g) \rightarrow \text{products} \]

from the initial rate data tabulated below.

<table>
<thead>
<tr>
<th>( P_0(\text{H}_2)/\text{torr} )</th>
<th>( P_0(\text{NO})/\text{torr} )</th>
<th>( v_0/\text{torr} \cdot \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>159</td>
<td>34</td>
</tr>
<tr>
<td>400</td>
<td>300</td>
<td>125</td>
</tr>
<tr>
<td>289</td>
<td>400</td>
<td>160</td>
</tr>
<tr>
<td>205</td>
<td>400</td>
<td>110</td>
</tr>
<tr>
<td>147</td>
<td>400</td>
<td>79</td>
</tr>
</tbody>
</table>

Calculate the rate constant for this reaction.

26-17. Show that if \( A \) reacts to form either \( B \) or \( C \) according to

\[ A \stackrel{k_1}{\rightarrow} B \quad \text{or} \quad A \stackrel{k_2}{\rightarrow} C \]

\[ [A] = [A]_0 e^{-\left(k_1 + k_2\right)t} \]

Now show that \( t_{1/2} \), the half-life of \( A \), is given by

\[ t_{1/2} = \frac{0.693}{k_1 + k_2} \]

Show that \( [B]/[C] = k_1/k_2 \) for all times \( t \). For the set of initial conditions \( [A] = [A]_0 \), \( [B]_0 = [C]_0 = 0 \), and \( k_2 = 4k_1 \), plot \( [A], [B], \) and \( [C] \) as a function of time on the same graph.
26-29. Consider a chemical reaction

\[ A \rightarrow \text{products} \]

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

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

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

\[ k_{t/2} = \frac{1}{n-1} \frac{2^{n-1} - 1}{[A]_0^{n-1}} \quad n \neq 1 \quad (2) \]

Show that this result reduces to Equation 26.29 when \( n = 2 \).

Equation 26.29 is the half-life expression for a second order reaction:

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

26-42. The Arrhenius parameters for the reaction described by

\[ \text{HO}_2(g) + \text{OH}(g) \rightarrow \text{H}_2\text{O}(g) + \text{O}_3(g) \]

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

26-45. The rate constant for the chemical reaction

\[ 2\text{N}_2\text{O}_3(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g) \]

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.
26-47. 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 $\Delta^\ddagger H^\circ = 31.38 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta^\ddagger S^\circ = 16.74 \text{ J} \cdot \text{K}^{-1}$. Calculate the standard Gibbs energy of activation and the rate constant for this reaction at 325 K.
27-35. 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-Menten mechanism for enzyme catalysis.

\[
\begin{align*}
E + S & \xrightarrow{k_1} ES \\
& \xrightleftharpoons[k_{-1}]{k_2} E + I
\end{align*}
\]

(1)

(2)

\[
ES \xrightarrow{k_3} E + P
\]

(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

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

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

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

where \(K_1 = [EI]/[E][I]\) 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

\[
v = \frac{d[P]}{dt} = \frac{k_3[E]_0[S]}{K_m + [S] + K_m'K_1[I]} \approx \frac{k_3[E]_0[S]_0}{K_m + [S]_0}
\]

(4)

where \(K_m' = K_m(1 + K_1[I])\). Note that the second expression in Equation 4 has the same functional form as the Michaelis-Menten equation. Does Equation 4 reduce to the expected result when \([I] \rightarrow 0\)?

27-36. 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?
Special Problem #1: It takes longer to cook foods at high altitude because water boils at a lower temperature. For example, at 8000 ft (2438 m) elevation, water boils at 92 °C. The major reaction when eggs are boiled is the denaturization of the protein, which has an activation energy of about 40 kJ/mol. If a “three minute egg” refers to a consistency obtained by boiling an egg for three minutes at sea level, how long would it take to make a three minute egg at 8000 ft?