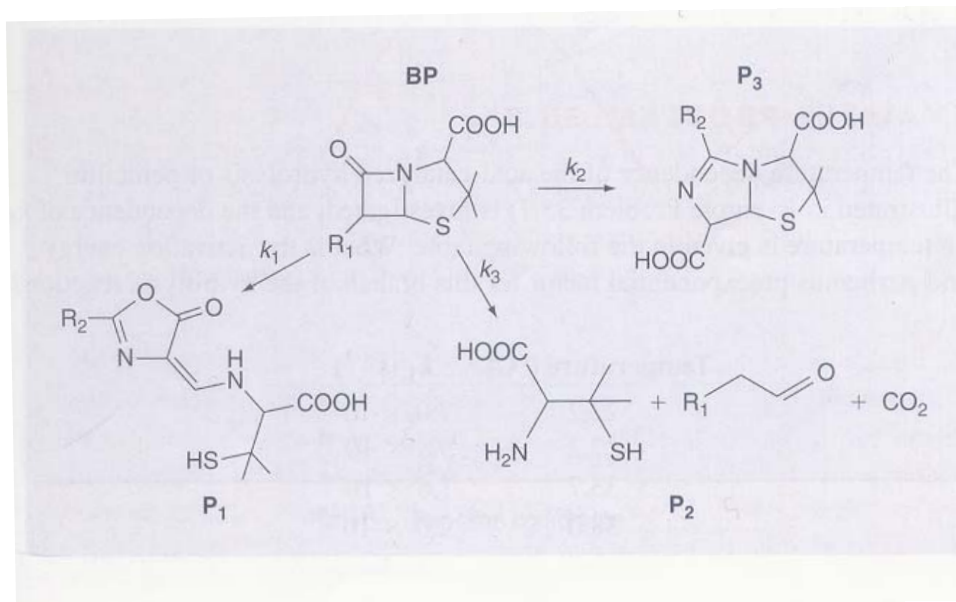FIGURE 35.12

Concentrations for a parallel reaction where $k_B = 2k_C = 0.1\ s^{-1}$.

Scan Figure 12 here

EXAMPLE 35.7

In acidic conditions, benzyl penicillin (BP) undergoes the following parellal reaction;

In the molecular structures, R1 and R2 indicate alkyl substituents. In a solution where PH=3, the rate constants for the processes at 22℃ are $k_1 = 7.0\times10^{-4}s^{-1}$, $k_2 = 4.1\times10^{-3}s^{-1}$, and $k_3 = 5.7\times10^{-3}s^{-1}$.

What is the yield for P1 formation?

Solution

Using Eq(35.79)

$$\Phi_{P_1} = \frac{k_1}{k_1 + k_2 + k_3} = \frac{7.0 \times 10^{-4}}{7,0 \times 10^{-4} + 4.1 \times 10^{-3} + 5.7 \times 10^{-3}} = 0.067$$

Of the BP that undergoes acid-catarlyzed dissiciation, 6.7% will result in the formation of P1.

35.9 Temperature Dependence of Rate Constant

$$k = Ae^{-E_a/RT} \quad \text{(Arrhenius eq)} \qquad (82)$$

$$\ln(k) = \ln(A) - \frac{E_a}{R}\frac{1}{T} \qquad (83)$$

A=Frequency factor or preexponential factor
E_a=Activation energy of reaction

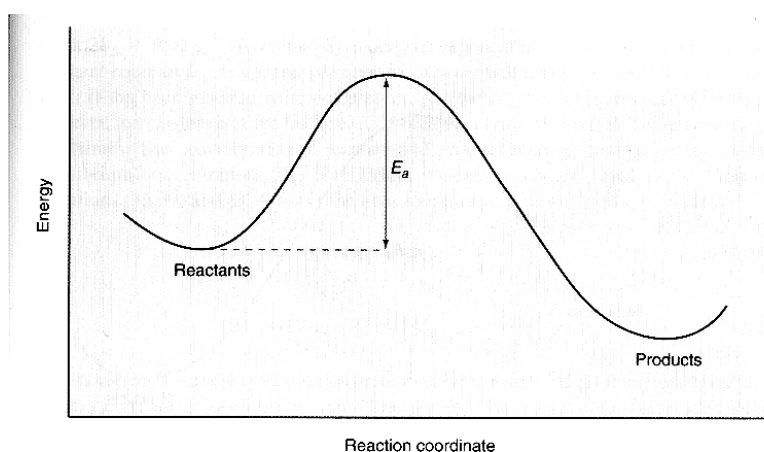Reaction proceeds as the energy is greater than the activation energy (See Figure 13).

FIGURE 35.13

A schematic drawing of the energy profile for a chemical reaction. Reactants must acquire sufficient energy to overcome the activation energy, E_a, for the reaction. The reaction coordinate represents the bonding and geometry changes that occur in the transformation of reactants into products.

Scan Figure 13 here.

EXAMPLE 35.8

The temperature dependence of the acid-catalyzed hydrolysis of penicillin (illustrated in Example problem 35.7) is invetigated, and the

dependence of k_1 on temperature is given in the following table. What is the activation energy and Arrhenius preexponential factor for this branch of the hydrolysis reaction?

Temperature (℃)	$k_1(s^{-1})$
22.2	7.0×10^{-4}
27.2	9.8×10^{-4}
33.7	1.6×10^{-3}
38.0	2.0×10^{-3}

Solution

A plot of ln(k1) versus 1/T is shown here;
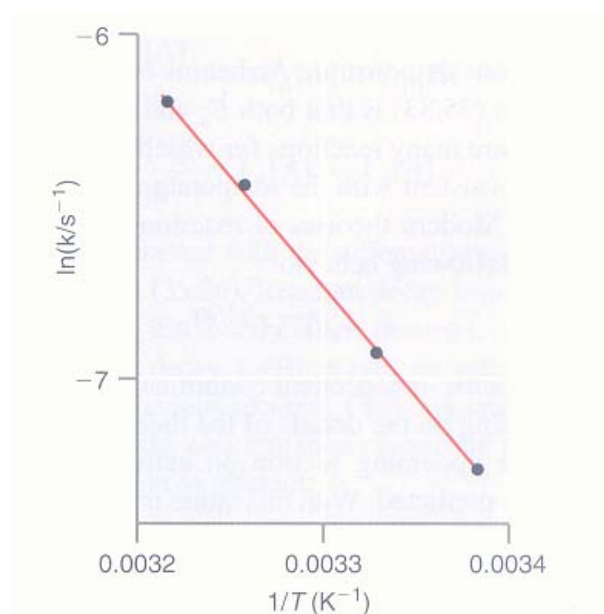
The data are indicated the points, and the solid line corresponds to the linear least-squares fit to the data. The equation for the line is

$$\ln(k) = (-6306.3K)\frac{1}{T} + 14.1$$

As shown in Eq (83), the slope of the line is equal to $-E_a/R$ such that

$$6306.3K = \frac{E_a}{R} \Rightarrow E_a = 52,400\,Jmol^{-1} = 52.4\,kJmol^{-1}$$

The y intercept is equal to ln(A) such that

$$A = e^{14.1} = 1.33 \times 10^6 s^{-1}$$

35.10 Reversible Reactions and Equilibrium

So far for irreversible reactions.

However, reversible reaction is also possible depending on the energies of the reaction (See Figure 14).
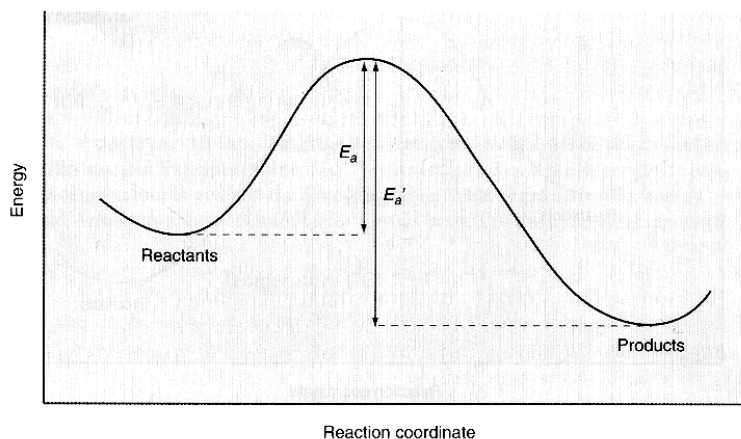

FIGURE 35.14

Reaction coordinate demonstrating the activation energy for reactants to form products, E_a, and the back reaction in which products form reactants, E_a'.

Scan Figure 14 here.

Consider reverse reaction (84).

Forward reaction: 1st order in A

Backward reaction: 1st order in B

$$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B \qquad\qquad (84)$$

Differential rate equations for the reactant and product are

$$\frac{d[A]}{dt} = -k_A[A] + k_B[B] \qquad\qquad (85)$$

$$\frac{d[B]}{dt} = k_A[A] - k_B[B] \tag{86}$$

IC's;
@ t=0, [A]=[A]o, [B]=0 and
for t>0,

$$[A]_0 = [A] + [B] \tag{87}$$

Using the two IC's, (85) is integrated as

$$\frac{d[A]}{dt} = -k_A[A] + k_B[B] \tag{88}$$

$$= -k_A[A] + k_B([A]_0 - [A])$$

$$= -[A](k_A + k_B) + k_B[A]_0$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A](k_A + k_B) - k_B[A]_0} = -\int_0^t dt$$

To evaluate the integral (88), Use the following integration formula;

$$\int \frac{dx}{(a+bx)} = \frac{1}{b}\ln(a+bx)$$

Then

$$[A] = [A]_0 \frac{k_B + k_A e^{-(k_A + k_B)t}}{k_A + k_B} \tag{89}$$

$$[B] = [A]_0 (1 - \frac{k_B + k_A e^{-(k_A + k_B)t}}{k_A + k_B}) \tag{90}$$

[A] decays exponentially with an apparent rate constant, $(k_A + k_B)$.

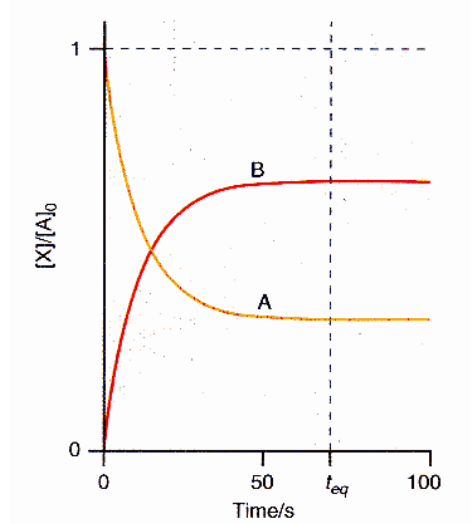Eqs (89) and (90) are plotted in Figure 15 with $k_A=2k_B=0.06s^{-1}$.

FIGURE 35.15

Time-dependent concentrations in which both forward and back reactions exist between reactant A and product B. In this example, $k_A = 2k_B = 0.06 \text{ s}^{-1}$. Note that the concentrations reach a constant value at longer times $(t \geq t_{eq})$ at which point the reaction reaches equilibrium.

Scan Figure 15

If the backward reaction were not present, [A] would decay to 0. Equilibrium concentrations of A and B are obtained as t→∞.

$$[A]_{eq} = \lim_{t \to \infty} [A] = [A]_0 \frac{k_B}{k_A + k_B} \tag{91}$$

$$[B]_{eq} = \lim_{t \to \infty} [B] = [A]_0 (1 - \frac{k_B}{k_A + k_B}) \tag{92}$$

Note the two equilibrium concentrations depend on the forward and backward rate constants.

For $t \geq t_{eq}$ reactant and product concentrations are no longer changed;

$$\frac{d[A]_{eq}}{dt} = \frac{d[B]_{eq}}{dt} = 0 \qquad\qquad (93)$$

Note the rates are not zero but are the same.

Subing differential rate equation into (93) gives

$$\frac{d[A]_{eq}}{dt} = \frac{d[B]_{eq}}{dt} = 0 = -k_A[A]_{eq} + k_B[B]_{eq}$$

$$\frac{k_A}{k_B} = \frac{[B]_{eq}}{[A]_{eq}} = K_c \qquad\qquad (94)$$

where Kc is the equilibrium constant in terms of concentration.

Figure 16: Method to determine forward and backward rate constants.
i) Measure the apparent decay constant for the reactant: $(k_A + k_B)$
ii) Measure Kc
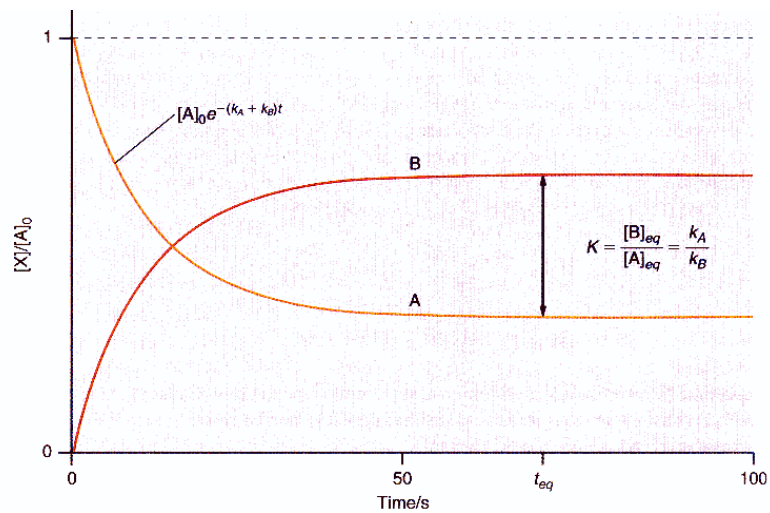 $\rightarrow$ 2 Eqs and 2 unknown; Solved

FIGURE 35.16

Methodology for determining forward and back rate constants. The apparent rate constant for reactant decay is equal to the sum of forward, k_A, and back, k_B, rate constants. The equilibrium constant is equal to k_A/k_B. These two measurements provide a system of two equations and two unknowns that can be readily evaluated to produce k_A and k_B.

Scan Figure 16 here.

Scan Example 35.9 here.

EXAMPLE PROBLEM 35.9

Consider the interconversion of the "boat" and "chair" conformations of cyclohexane:
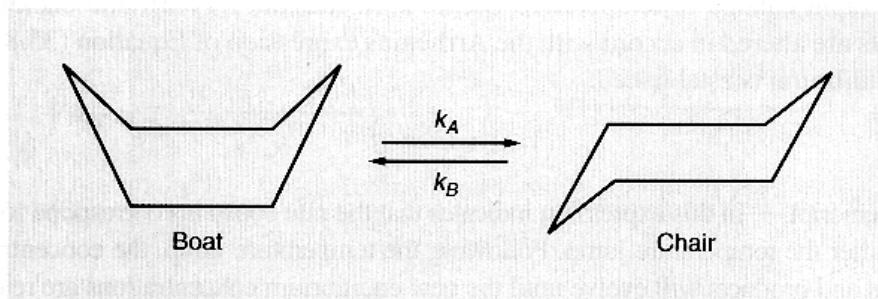
Boat   Chair

The reaction is first order in each direction, with an equilibrium constant of 10^4. The activation energy for the conversion of the chair conformer to the boat conformer is 42 kJ/mol. Assuming an Arrhenius preexponential factor of 10^{12} s^{-1}, what is the expected observed reaction rate constant at 298 K if one were to initiate this reaction starting with only the boat conformer?

Solution

Using the Arrhenius expression of Equation (35.82), k_B is given by

$$k_B = Ae^{-E_a/RT} = 10^{12}\ s^{-1} \exp\left[\frac{-42,000\ J\ mol^{-1}}{(8.314\ J\ mol^{-1}\ K^{-1})(298\ K)}\right]$$

$$= 4.34 \times 10^4\ s^{-1}$$

Using the equilibrium constant, k_A can be determined as follows:

$$K_c = 10^4 = \frac{k_A}{k_B}$$

$$k_A = 10^4\ k_B = 10^4(4.34 \times 10^4\ s^{-1}) = 4.34 \times 10^8\ s^{-1}$$

Finally, the apparent rate constant is simply the sum of k_A and k_B:

$$k_{app} = k_A + k_B = 4.34 \times 10^8\ s^{-1}$$

35.11 Perturbation-Relaxation Methods

$$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B \qquad (95)$$

$$A \underset{k_B^+}{\overset{k_A^+}{\rightleftharpoons}} B \qquad (96)$$

$$\frac{d[A]_{eq}}{dt} = 0 = -k_A^+[A]_{eq} + k_B^+[B]_{eq} \qquad (97)$$

$$k_A^+[A]_{eq} = k_B^+[B]_{eq}$$

$$[A] - \xi = [A]_{eq} \qquad (98)$$

$$[B] + \xi = [B]_{eq} \qquad (99)$$

$$\frac{d\xi}{dt} = -k_A^+[A] + k_B^+[B]$$

$$\frac{d\xi}{dt} = -k_A^+(\xi + [A]_{eq}) + k_B^+(-\xi + [B]_{eq}) \qquad (100)$$

$$= -k_A^+[A]_{eq} + k_B^+[B]_{eq} - \xi(k_A^+ + k_B^+)$$
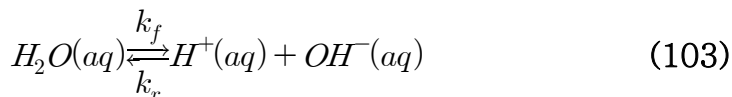
$$= -\xi(k_A^+ + k_B^+)$$

$$\tau = (k_A^+ + k_B^+)^{-1} \qquad (101)$$

$$\frac{d\xi}{dt} = -\frac{\xi}{\tau} \qquad (102)$$

$$\int_{\xi_0}^{\xi} \frac{d\xi'}{\xi'} = -\frac{1}{\tau} \int_0^t dt'$$

$$\xi = \xi_0 e^{-t/\tau}$$

35.12 The Autoioniation of Water: A T-Jump Example

$$H_2O(aq) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H^+(aq) + OH^-(aq) \qquad (103)$$

$$\frac{d[H_2O]}{dt} = -k_f[H_2O] + k_r[H^+][OH^-] \qquad (104)$$

$$\frac{d[H^+]}{dt} = k_f[H_2O] - k_r[H^+][OH^-] \qquad (105)$$

$$\frac{k_f^+}{k_r^+} = \frac{[H^+]_{eq}[OH^-]_{eq}}{[H_2O]_{eq}} = K_c \qquad (106)$$

$$\frac{d\xi}{dt} = -k_f^+[H_2O] + k_r^+[H^+][OH^-] \tag{107}$$

$$= -k_f^+(\xi + [H_2O]_{eq}) + k_r^+(\xi - [H^+]_{eq})(\xi - [OH^-]_{eq})$$

$$= -k_f^+\left(\xi + \frac{k_r^+}{k_f^+}[H^+]_{eq}[OH^-]_{eq}\right) + k_r^+(\xi - [H^+]_{eq})(\xi - [OH^-]_{eq})$$

$$= -k_f^+\xi - k_r^+\xi([H^+]_{eq} + [OH^-]_{eq}) + O(\xi^2)$$

$$\frac{d\xi}{dt} = -\xi(k_f^+ + k_r^+([H^+]_{eq} + [OH^-]_{eq})) \tag{108}$$

$$\frac{1}{\tau} = (k_f^+ + k_r^+([H^+]_{eq} + [OH^-]_{eq})) \tag{109}$$

$$\frac{1}{3.7 \times 10^{-5}s} = (k_f^+ + k_r^+([H^+]_{eq} + [OH^-]_{eq})) \tag{110}$$

$$\frac{k_f^+}{k_r^+} = \frac{[H^+]_{eq}[OH^-]_{eq}}{[H_2O]_{eq}} = \frac{(1 \times 10^{-7}M)(1 \times 10^{-7}M)}{55.4M} = 1.81 \times 10^{-16}M \tag{111}$$

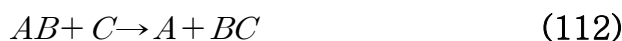Substitution of Equation (35.111) into Equation (35.110) yields the following value for the reverse rate constant:

$$\frac{1}{3.7 \times 10^{-5}s} = (k_f^+ + k_r^+([H^+]_{eq} + [OH^-]_{eq}))$$

$$= (1.81 \times 10^{-16}M(k_r^+) + k_r^+(2.00 \times 10^{-7}M))$$

$$\frac{1}{(3.7 \times 10^{-5}s)(2.0 \times 10^{-7}M)} = k_r^+$$

$$1.35 \times 10^{11}M^{-1}s^{-1} = k_r^+$$

Finally, the forward rate constant is

$$k_f^+ = (k_r^+)1.83 \times 10^{-16}M = (1.35 \times 10^{11}M^{-1}s^{-1})(1.83 \times 10^{-16}M)$$

$$= 2.47 \times 10^{-5}s^{-1}$$

35.13 Potential Energy Surfaces

$$AB + C \rightarrow A + BC \tag{112}$$

35.14 Diffusion Controlled Reactions

$$A + B \xrightarrow{k_d} AB \tag{113}$$

$$AB \xrightarrow{k_r} A + B \tag{114}$$

$$AB \xrightarrow{k_p} P \qquad (115)$$

$$R = k_p[AB] \qquad (116)$$

$$\frac{d[AB]}{dt} = 0 = k_d[A][B] - k_r[AB] - k_p[AB] \qquad (117)$$

$$[AB] = \frac{k_d[A][B]}{k_r + k_p}$$
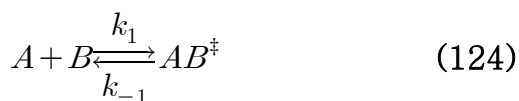
$$R = \frac{k_p k_d}{k_r + k_p}[A][B] \qquad (118)$$

$$R = k_d[A][B] \qquad (119)$$

$$k_d = 4\pi N_A(r_A + r_B)D_{AB} \qquad (120)$$

$$D = \frac{kT}{6\pi\eta r} \qquad (121)$$

$$R = \frac{k_p k_d}{k_r}[A][B] \qquad (122)$$

35.15 Activated Complex Theory

$$A + B \xrightarrow{k} P \qquad (123)$$

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB^{\ddagger} \qquad (124)$$

$$AB^{\ddagger} \xrightarrow{k_2} P \qquad (125)$$

$$\frac{d[A]}{dt} = 0 = -k_1[A][B] + k_{-1}[AB^{\ddagger}] \qquad (126)$$

$$[AB^{\ddagger}] = \frac{k_1}{k_{-1}}[A][B] = \frac{K_c^{\ddagger}}{c^{\circ}}[A][B]$$

$$K_c^{\ddagger} = \frac{[AB^{\ddagger}]/c^{\circ}}{([A]/c^{\circ})([B]/c^{\circ})} = \frac{[AB^{\ddagger}]c^{\circ}}{[A][B]}$$

$$R = \frac{d[P]}{dt} = k_2[AB^{\ddagger}] \qquad (127)$$

$$R = \frac{d[P]}{dt} = \frac{k_2 K_c^{\ddagger}}{c^{\circ}}[A][B] \qquad (128)$$

$$k_2 = \kappa\nu \qquad (129)$$

$$R = \frac{\kappa \nu K_c^{\ddagger}}{c^{\circ}}[A][B] \qquad (130)$$

$$K_c^{\ddagger} = q_{rc}\overline{K_c^{\ddagger}} = \frac{k_B T}{h\nu}\overline{K_c^{\ddagger}} \qquad (131)$$

$$k = \kappa \frac{k_B T}{hc^{\circ}}\overline{K_c^{\ddagger}} \qquad (132)$$

$$\Delta G^{\ddagger} = -RT \ln K_c^{\ddagger} \qquad (133)$$

$$k = \frac{k_B T}{hc^{\circ}}e^{-\Delta G^{\ddagger}/RT} \qquad (134)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad (135)$$

$$k = \frac{k_B T}{hc^{\circ}}e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT} \qquad (136)$$

$$E_a = RT^2(\frac{d\ln k}{dT}) \qquad (137)$$

$$E_a = RT^2(\frac{d}{dT}\ln(\frac{kT}{hc^{\circ}}\overline{K_c^{\ddagger}})) = RT + RT^2(\frac{d\ln\overline{K_c^{\ddagger}}}{dT})$$

$$E_a = RT + \Delta U^{\ddagger}$$

$$\Delta U^{\ddagger} = \Delta H^{\ddagger} - \Delta(PV)^{\ddagger} \qquad (138)$$

$$E_a = \Delta H^{\ddagger} + RT \, (solutions) \qquad (139)$$

$$A = \frac{ek_B T}{hc^{\circ}}e^{\Delta S^{\ddagger}/R} \, (solutions, bimolecular) \qquad (140)$$

$$A = \frac{ek_B T}{h}e^{\Delta S^{\ddagger}/R} \, (solutions, unimolecular) \qquad (141)$$

gas, uni $\qquad E_a = \Delta H^{\ddagger} + RT \qquad A = \frac{ek_B T}{h}e^{\Delta S^{\ddagger}/R} \qquad (142)$

gas, bi $\qquad E_a = \Delta H^{\ddagger} + 2RT \qquad A = \frac{e^2 k_B T}{hc^{\circ}}e^{\Delta S^{\ddagger}/R} \qquad (143)$

gas, tri $\qquad E_a = \Delta H^{\ddagger} + 3RT \qquad A = \frac{e^3 k_B T}{h(c^{\circ})^2}e^{\Delta S^{\ddagger}/R} \qquad (144)$

EXAMPLE PROBLEM 35.10

In aqueous solution at 25°C and pH 7.4 the diffusion coefficient for hemoglobin (radius $= 35\ \text{Å}$) is $7.6 \times 10^{-7}\ \text{cm}^2\ \text{s}^{-1}$, and the diffusion coefficient for O_2 (radius $= 2.0\ \text{Å}$) is $2.2 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}$. The rate constant for the binding of O_2 to hemoglobin is $4 \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}$. Is this a diffusion-controlled reaction?
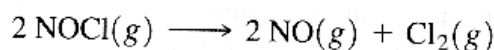
Solution

Assuming the reaction is diffusion controlled, the rate constant is expected to be

$$
\begin{aligned}
k_d &= 4\pi N_A (r_A + r_B) D_{AB} \\
&= 4\pi N_A (35 \times 10^{-8}\ \text{cm} + 2.0 \times 10^{-8}\ \text{cm}) \\
&\quad (7.6 \times 10^{-7}\ \text{cm}^2\ \text{s}^{-1} + 2.2 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}) \\
&= 6.4 \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}
\end{aligned}
$$

The diffusion-controlled rate constant is significantly greater than the experimentally measured rate constant; therefore, the binding of O_2 to hemoglobin is not diffusion controlled.

EXAMPLE PROBLEM 35.11

The thermal decomposition reaction of nitrosyl halides is important in tropo-spheric chemistry. For example, consider the decomposition of NOCl:

$$2\,NOCl(g) \longrightarrow 2\,NO(g) + Cl_2(g)$$

The Arrhenius parameters for this reaction are $A = 1.00 \times 10^{13}\,M^{-1}\,s^{-1}$ and $E_a = 104\,kJ\,mol^{-1}$. Calculate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for this reaction with $T = 300\,K$.

Solution

This is a bimolecular reaction such that

$$\Delta H^{\ddagger} = E_a - 2RT = 104\,kJ\,mol^{-1} - 2(8.314\,J\,mol^{-1}\,K^{-1})(300\,K)$$

$$= 104\,kJ\,mol^{-1} - (4.99 \times 10^3\,J\,mol^{-1})\left(\frac{1\,kJ}{1000\,J}\right) = 99.0\,kJ\,mol^{-1}$$

$$\Delta S^{\ddagger} = R\ln\left(\frac{Ahc^{\circ}}{e^2 kT}\right)$$

$$= (8.314\,J\,mol^{-1}\,K^{-1})\ln\left(\frac{(1.00 \times 10^{13}\,M^{-1}\,s^{-1})(6.626 \times 10^{-34}\,J\,s)(1\,M)}{e^2(1.38 \times 10^{-23}\,J\,K^{-1})(300\,K)}\right)$$

$$= -12.7\,J\,mol^{-1}\,K^{-1}$$

One of the utilities of this calculation is that the sign and magnitude of $\Delta S^{\ddagger}$ pro-vide information on the structure of the activated complex at the transition state relative to the reactants. The negative value in this example illustrates that the activated complex has a lower entropy (or is more ordered) than the reactants. This observation is consistent with a mechanism in which the two NOCl reac-tants form a complex that eventually decays to produce NO and Cl.