CHAPTER

SIX

REACTION ENERGETICS AND CHEMICAL KINETICS

There are a number of fronts on which considerations of kinetics and thermodynamics merge, most notably in the analysis of a rate constant in terms of the energetics of the activation process. The aspects of the interrelations considered in the present chapter are these: (1) the temperature dependence of the rate constant, (2) the relations between forward and reverse reaction rates, and (3) the principle of microscopic reversibility, especially its implications for reaction mechanisms.

6-1 THE VARIATION OF RATE CONSTANT WITH TEMPERATURE

The temperature dependence of the rate constant for an elementary reaction is almost always expressed by a relation of the form given by Eq. (6-1). The quantity U has the

$$k = CT^n \exp\left(-\frac{U}{RT}\right) \tag{6-1}$$

dimensions of energy, and the exponent n is usually assigned a value of 0, $\frac{1}{2}$, or 1 depending upon the theoretical model chosen. Once n is chosen, a plot of the data as $\ln kT^{-n}$ against T^{-1} should be linear with a slope of $-U/R$ as seen by the relation

$$\ln \frac{k}{T^n} = \ln C - \frac{U}{R} T^{-1} \tag{6-2}$$

The value of C is then easily calculated by substitution. Or perhaps more simply, the data may be fit to Eq. (6-1) directly by the method of least squares. By such methods one obtains the values of the two adjustable parameters C and U. The three variants of Eq. (6-1) most commonly encountered are these:

(*a*) The Arrhenius relation, Eq. (6-3), in which the two parameters are A, the

$$k = A \exp\left(-\frac{E_a}{RT}\right) \tag{6-3}$$

preexponential factor (or frequency factor, the latter being a poor name because only in the case of a unimolecular reaction does A have frequency dimensions of s^{-1}), and E_a, termed the Arrhenius activation energy or sometimes simply the activation energy. The preexponential factor A is taken as independent of temperature.

(*b*) The collision theory relation for bimolecular reactions in the gas phase is given by Eq. (6-4), in which p symbolizes the so-called steric factor, E^* is the critical

$$k = pZ \exp\left(-\frac{E^*}{RT}\right) \tag{6-4}$$

collision energy, and Z is the collision frequency at unit concentration of reactants. The value of Z is obtained from the kinetic molecular theory of gases; it depends on the collision distance d_{AB} and on the masses of the reactants A and B (Sec. 8-1) according to Eq. (6-5). The preexponential value is thus proportional to $T^{1/2}$.

$$Z_{\mathrm{AB}} = \left[\frac{8\pi kT}{m_{\mathrm{A}} m_{\mathrm{B}}}(m_{\mathrm{A}} + m_{\mathrm{B}})\right]^{1/2} d_{\mathrm{AB}}{}^2 \tag{6-5}$$

(*c*) The Eyring or activated complex or absolute rate theory relation employs, as do the other formulations, two adjustable parameters. In this case they are $\Delta H^\ddagger$ the activation enthalpy and $\Delta S^\ddagger$ the activation entropy. The preexponential shows a first-power temperature dependence, Eq. (6-6), in which transmission coefficient κ is usually taken as unity

$$k = \kappa \frac{RT}{Nh} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \tag{6-6}$$

The theories will be considered in their own right in Secs. 8-2 and 8-3. For the present, the mathematical statements in Eqs. (6-5) and (6-6) will simply be taken as relations which can be used to correlate experimental values of a rate constant k as a function of temperature.

It may prove difficult to see at the outset why it is that the appropriate power of T in the preexponential term cannot be decided by accurate measurements. The difficulty is that the exponential energy term is usually so dominant that the differences in taking $n = 0, \frac{1}{2}$, or 1 are negligible. That is to say, for any reaction in which a plot of $\ln k$ versus T^{-1} is linear as required by the Arrhenius relation, plots of $\ln (k/T^{1/2})$ and of $\ln (k/T)$ versus T^{-1} are also linear within the usual experimental error of the kinetic data. To illustrate, consider the supposedly typical reaction whose rate at 300 K roughly doubles over a 10° temperature increase. Such a reaction has $U \sim 50$ kJ mol^{-1}.† The ratio of rate constants for the 10° increase is

$$\frac{k_{310}}{k_{300}} = \left(\frac{310}{300}\right)^n \exp\left[\frac{U}{R}\left(\frac{1}{300} - \frac{1}{310}\right)\right] \tag{6-7}$$

With the values specified above, k_{310}/k_{300} is 1.91 ($n = 0$), 1.94 ($n = \frac{1}{2}$), or 1.97 ($n = 1$). Clearly the exponential term is dominant, and once the choice of n has been made, only a slightly different value of U is required to correlate the data.

To dwell on this point but a bit longer, suppose one set out to decide the "correct" preexponential expression by using rate data of exceptionally high precision in a reaction of very small activation energy and thereby seeking to minimize the importance of the energy exponential. It is unlikely that would provide a definitive answer, because the equations as they are normally used take U as being temperature-independent. That is akin to taking a thermodynamic quantity ΔH° as temperature-independent, or $\Delta Cp^\circ = 0$, a good approximation but insufficient for high accuracy. The assumption of the temperature invariance of U introduces an assumption of the same magnitude as that contained in the question of the temperature exponent n. On the other hand, to explicitly include a temperature dependence, say a nonzero value of $\Delta C_p^\ddagger$, is to render the value of n indeterminate, owing to the one or more additional adjustable parameters contained in $\Delta C_p^\ddagger$.

6-2 ACTIVATION PARAMETERS

As an example of the calculations involved, consider data for the bimolecular reaction[1] of Eq. (6-8), for which rate constants at various temperatures are

$$NO + ClNO_2 \longrightarrow NO_2 + ClNO \tag{6-8}$$

T/K	300	311	323	334	344
$10^{-7}\ k/\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$	0.79	1.25	1.64	2.56	3.4

Values of ln k, ln $(k/T^{1/2})$, or ln (k/T) are plotted versus $1/T$; the slope, $-U/R$, is computed from a graphical or numerical analysis. These graphs are shown in Fig. 6-1. The numerical parameters from this treatment are incorporated into the following expressions:

Arrhenius:

$$k = 6.5 \times 10^{11} \exp\left(-\frac{28.2\ \text{kJ mol}^{-1}}{RT}\right) \tag{6-9}$$

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†A note on SI units: Convert (if you must) from SI units as follows: kilojoules to kilocalories by division by 4.184; 50 kJ mol^{-1} ≅ 12 kcal mol^{-1}. The constant R = 1.987 cal mol^{-1} K^{-1} = 8.314 J mol^{-1} K^{-1}. Absolute temperatures are denoted as 300 K ("300 kelvins").

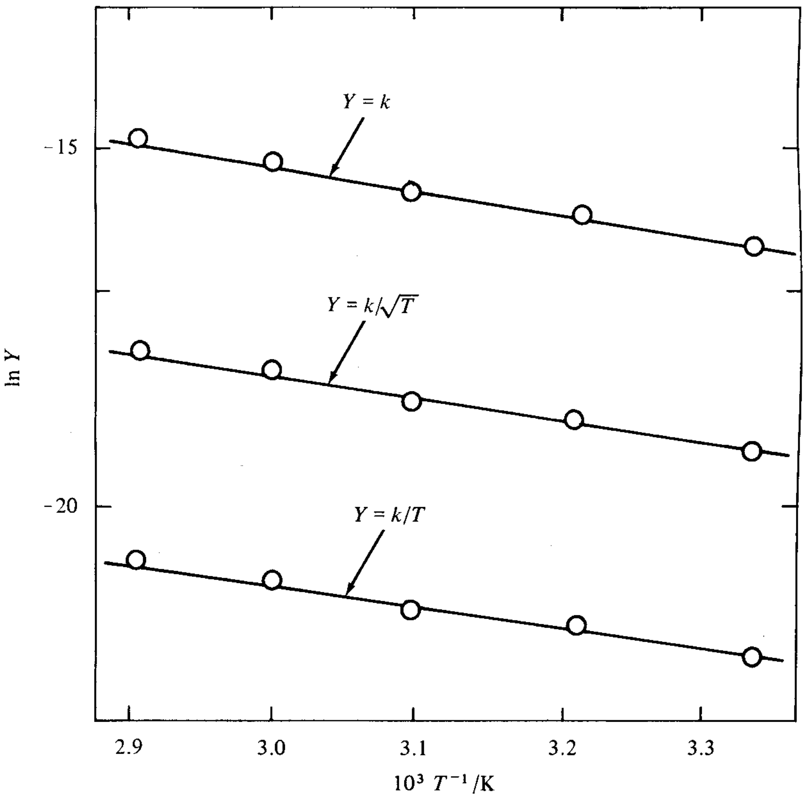

Figure 6-1 Plots indicating the temperature dependence of the rate constants. Upper line, Arrhenius relation, ln k versus $1/T$; middle line, collision theory, ln $(k/T^{1/2})$ versus $1/T$; lower line, activated complex theory, ln (k/T) versus $1/T$.

Collision theory:

$$k = 2.1 \times 10^{10}\, T^{1/2} \exp\left(-\frac{26.8 \text{ kJ mol}^{-1}}{RT}\right) \tag{6-10}$$

Activated complex theory:

$$k = 7.1 \times 10^{8}\, T \exp\left(-\frac{25.4 \text{ kJ mol}^{-1}}{RT}\right) \tag{6-11}$$

The numerical value 7.1×10^8 must be equal to the quantity $(R/Nh) \exp(\Delta S^{\ddagger}/R)$ of Eq. (6-6). With substitution of the values for the physical constants, the numerical value of $\Delta S^{\ddagger}$ is -28.1 J mol^{-1} K^{-1}, and the rate constant expressed in the form of Eq. (6-6) is

$$k = \frac{RT}{Nh} \exp\left(-\frac{28.1 \text{ J mol}^{-1} \text{ K}^{-1}}{R}\right) \times \exp\left(-\frac{25.4 \text{ kJ mol}^{-1}}{RT}\right) \tag{6-12}$$

If the rate constant values are first converted to the standard state[†] 1 mol dm^{-3}, the absolute rate theory expression becomes

$$k = \frac{RT}{Nh} \exp\left(-\frac{85.5\ \mathrm{J\ mol^{-1}\ K^{-1}}}{R}\right) \times \exp\left(-\frac{25.4\ \mathrm{kJ\ mol^{-1}}}{RT}\right) \tag{6-13}$$

The value of $\Delta S^{\ddagger}$ changes from -28.1 to -85.5 J $\mathrm{mol^{-1}\ K^{-1}}$. The magnitude of the change is that due solely to the "dilution" implied by the change in standard state.[§]

It is this author's view that nothing is to be gained by mixing the three expressions. A hybrid of the Arrhenius and activated complex theory expressions, for example, can be obtained by algebraic substitutions, but there is no apparent advantage in using such an equation to correlate kinetic data in terms of, say, E_a and $\Delta S^{\ddagger}$.

All of the expressions considered in this section are properly applied only to an authentic rate constant. Values of apparent rate constants which contain unaccounted for concentration dependences cannot correctly be used. The preexponential factor, in particular, would be erroneous if, say, a pseudo-first-order rate constant were correlated by any of the forms considered.

It should be evident that the numerical values of the activation parameters based on these different equations are related to each other. Consider one case, the relation between E_a of the Arrhenius equation and $\Delta H^{\ddagger}$ of activated complex theory. The defining relations from Eqs. (6-3) and (6-5) are

$$E_a = -R \frac{d \ln k}{d(1/T)}$$

$$\Delta H^{\ddagger} = -R \frac{d \ln (k/T)}{d(1/T)}$$

The latter can be rewritten as

$$\Delta H^{\ddagger} = -R \frac{d \ln k}{d(1/T)} - R \frac{d \ln (1/T)}{d(1/T)}$$

which transforms to

$$\Delta H^{\ddagger} = E_a - RT \tag{6-14}$$

Thus, near room temperature, E_a is roughly 2.5 kJ mol^{-1} larger than $\Delta H^{\ddagger}$. By similar methods the relation between A and $\Delta S^{\ddagger}$ can be obtained (see Prob. 6-8).

[†] The concentration unit for species in solution is almost invariably taken as 1 mol dm^{-3}. The situation for gas-phase reactions seems less uniform. The choice of the concentration unit is equivalent to the choice of a standard state for the activation parameters. It is important to note that the numerical value of $\Delta S^{\ddagger}$ (or of any other preexponential factor) varies with this choice, except for first-order reactions.

[§] The bimolecular rate constant corresponds to this process,

$$\mathrm{A} + \mathrm{B} \longrightarrow [\text{activated complex}]^{\ddagger}$$

The change in $\Delta S^{\ddagger}$ is identical with the changes in ΔS° for a gas-phase equilibrium of the same form, $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}$. One mole of an ideal gas expanded from 1 cm^3 to 1 dm^3 increases its entropy by $R \ln (10^3/1) = 57.4\ \mathrm{J\ mol^{-1}\ K^{-1}}$.

6-3 THE TEMPERATURE DEPENDENCE OF COMPOSITE RATE CONSTANTS

It is common to encounter rate expressions in which the experimental rate constant is a composite of the rate constants and/or equilibrium constants for several reactions. Depending on the particular mathematical form of a given expression, such an experimental rate constant may or may not depend on temperature in such a manner that ln (k/T^n) versus $1/T$ will be linear.

By way of example, consider three mechanisms for the net reaction A = C.

(*a*)

$$\mathrm{A} \rightleftharpoons \mathrm{B} \qquad \text{fast}, K_1 \ll 1 \tag{6-15}$$

$$\mathrm{B} \xrightarrow{2} \mathrm{C} \qquad \text{rate-limiting} \tag{6-16}$$

$$\frac{-d[\mathrm{A}]}{dt} = k_2 K_1 [\mathrm{A}] \tag{6-17}$$

The form of the temperature dependence is seen from the following formulation

$$k_{\text{app}} = k_2 K_1 = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S_2^\ddagger}{R}\right) \exp\left(-\frac{\Delta H_2^\ddagger}{RT}\right) \times \exp\left(\frac{\Delta S_1^\circ}{R}\right) \exp\left(-\frac{\Delta H_1^\circ}{RT}\right)$$

Combining terms gives

$$\frac{k_{\text{app}}}{T} = \frac{k_2 K_1}{T} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_1^\circ + \Delta S_2^\ddagger}{R}\right) \times \exp\left(-\frac{\Delta H_1^\circ + \Delta H_2^\ddagger}{RT}\right) \tag{6-18}$$

Clearly, a plot of ln (k_{app}/T) versus $1/T$ will be linear, and the apparent activation enthalpy, computed as $-R \times$ slope, is seen to be the sum of ΔH_1° and $\Delta H_2^\ddagger$. It should be noted that if ΔH_1° for the equilibrium step is negative, the observed activation enthalpy will be lower than the value of $\Delta H^\ddagger$ for the rate-limiting step. Indeed, occasionally a negative value of $\Delta H_{\text{obs}}^\ddagger$ may result, and the reaction rate actually decreases with increasing temperature.

(*b*) This mechanism consists of parallel pathways for the reaction of A:

$$\mathrm{A} \xrightarrow{3} \mathrm{C} \quad \text{and} \quad \begin{array}{l} \mathrm{A} \xrightarrow{4} \mathrm{B} \\ \mathrm{B} = \mathrm{C}\ (\text{fast}) \end{array}$$

$$\frac{-d[\mathrm{A}]}{dt} = (k_3 + k_4)[\mathrm{A}] \tag{6-19}$$

If we substitute for k_3 and k_4 of Eq. (6-19) an expression from activated complex theory [Eq. (6-6)], the resulting expression for the experimental composite $k_{(6\text{-}19)} = k_3 + k_4$ has the form

$$\frac{k_{(6\text{-}19)}}{T} = C_1 \exp\left(-\frac{\Delta H_3^\ddagger}{RT}\right) + C_2 \exp\left(-\frac{\Delta H_4^\ddagger}{RT}\right) \tag{6-20}$$

Based on this relation, try to construct the shape of the usual temperature plot, ln $(k_{(6\text{-}19)}/T)$ versus $1/T$. A pictorial way of doing so is to appreciate that the rate constant having the larger value of $\Delta H^{\ddagger}$ will rise more steeply with increasing temperature until, at some value of T, it will effectively dominate; by analogy, the rate constant having the lower value of $\Delta H^{\ddagger}$ will dominate at lower temperature. Since the slope of the plot under discussion is $-\Delta H^{\ddagger}/R$, such a plot will always curve *gradually* upward when a composite experimental rate constant is a *sum* of individual constants.

(*c*) This mechanism consists of successive steps:

$$\mathrm{A} \underset{-5}{\overset{5}{\rightleftharpoons}} \mathrm{B} \xrightarrow{6} \mathrm{C} \qquad \mathrm{B} = \text{steady-state intermediate} \tag{6-21}$$

$$\frac{-d[\mathrm{A}]}{dt} = \frac{k_5 k_6}{k_{-5} + k_6}[\mathrm{A}] \tag{6-22}$$

This situation also corresponds to a nonlinear plot of ln $(k_{(6\text{-}21)}/T)$ versus $1/T$ in the range where k_6 and k_{-5} are comparable. In this case, however, the plot will be curved downward (see Prob. 6-10).

In practice, curvature in plots of ln (k_{app}/T) versus $1/T$ may arise from causes other than a complex mechanism. That is particularly so for reactions in which the presumed temperature independence of E_a or $\Delta H^{\ddagger}$ (that is, $\Delta Cp^{\ddagger} = 0$) is not a good approximation. It may not be one in solution reactions, particularly with ionic reagents, as considered further in Sec. 6-6.

The enthalpy of activation $\Delta H^{\ddagger}$ is a measure of the height of the energy barrier, particularly bond strengths within and between the reactants, which must be overcome to attain the transition state. The larger the value of $\Delta H^{\ddagger}$, the slower the reaction, other factors being equal. An increase of 5.7 kJ mol^{-1} in $\Delta H^{\ddagger}$ corresponds to a factor of 10 in the rate constant at room temperature. If a reaction occurs with a value of $\Delta H^{\ddagger}$ less than the dissociation energy of a particular group in the molecule, one can conclude that the bond to this group has not broken during the activation process.†

The entropy of activation relates to the probability of reaction. It includes contributions from requirements imposed by the orientation and steric bulk of the reactants and by their solvation. A unimolecular reaction may have $\Delta S^{\ddagger}$ near zero owing to the lack of orientational factors. If, however, the activation process involves dissociation, such as bond breaking within the single species, a large and positive value of $\Delta S^{\ddagger}$ is likely. As stated earlier, the numerical value of $\Delta S^{\ddagger}$ for a bimolecular reaction is dependent upon the choice of concentration scale. For rate constants in units dm^3 mol^{-1} s^{-1}, the value of $\Delta S^{\ddagger}$ is likely to be substantially negative, at least if the second-order kinetics is a manifestation of a bimolecular mechanism, not a more complicated scheme. The contributions of $\Delta S^{\ddagger}$ include the negative value resulting from bringing together two separate reactants each with 1 mol dm^{-3} concentration (roughly some -33 J mol^{-1} K^{-1}), as well as further contributions, negative as well, reflecting ionic charges (if any) and particular orientational factors, including loss of internal degrees of freedom in the transition state. The more negative the value of $\Delta S^{\ddagger}$, the lower

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†Although generally true, some caution is called for on two counts: (1) It may be possible to devise a mechanism in which a process having a negative enthalpy partly compensates. (2) For reasons considered in Chap. 7, certain chain reactions constitute exceptions.

the reaction rate, decreasing by a factor of 10 for a decrease of -19 J mol^{-1} K^{-1} in $\Delta S^{\ddagger}$.

6-4 RELATION OF FORWARD AND REVERSE REACTION RATES

The treatment of reversible reactions in Chap. 3 employed, for an elementary reaction, the following relation:

$$K = \frac{k_f}{k_r} \tag{6-23}$$

The validity of (6-23) is apparent, because at equilibrium the net rate of reaction becomes zero.

A slightly more complicated situation applies to the two-step process

$$\mathrm{A} \underset{-1}{\overset{1}{\rightleftarrows}} \mathrm{B} \tag{6-24}$$

$$\mathrm{B} \underset{-2}{\overset{2}{\rightleftarrows}} \mathrm{C} \tag{6-25}$$

$$\frac{-d[\mathrm{A}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] \tag{6-26}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] - k_2[\mathrm{B}] + k_{-2}[\mathrm{C}] \tag{6-27}$$

At equilibrium each of the rates is zero, and that gives the relation

$$K = \frac{[\mathrm{C}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_1 k_2}{k_{-1} k_{-2}} \tag{6-28}$$

Consider a reaction occurring by parallel pathways. The formation and dissociation of azidoiron(III) ion serves as an example[2] [Eq. (6-29)]. In terms of the

$$\mathrm{Fe^{3+} + HN_3 = FeN_3^{2+} + H^+} \tag{6-29}$$

predominant species in solution the net reaction rate is given by

$$\frac{d[\mathrm{FeN_3^{2+}}]}{dt} = \left(k_1 + \frac{k_2}{[\mathrm{H^+}]}\right)[\mathrm{Fe^{3+}}][\mathrm{HN_3}] - (k_{-1}[\mathrm{H^+}] + k_{-2})[\mathrm{FeN_3^{2+}}] \tag{6-30}$$

By equating forward and reverse rates at equilibrium and rearranging the resulting concentrations to correspond with the correct form of the equilibrium constant for Eq. (6-29), one obtains

$$K = \frac{[\mathrm{FeN_3^{2+}}]_{\mathrm{eq}}[\mathrm{H^+}]_{\mathrm{eq}}}{[\mathrm{Fe^{3+}}]_{\mathrm{eq}}[\mathrm{HN_3}]_{\mathrm{eq}}} = \frac{k_1 + k_2/[\mathrm{H^+}]}{k_{-1} + k_{-2}/[\mathrm{H^+}]} \tag{6-31}$$

This result poses a difficulty. The expression obtained suggests that K will depend upon $[H^+]$ as shown in Eq. (6-31), yet we know from thermodynamic considerations that K must be independent of $[H^+]$.

The solution to the dilemma lies in the principle of microscopic reversibility (considered more fully in Sec. 6-7), which states that at equilibrium the forward and reverse rates are the same *along each pathway*. Expressed algebraically, this statement is $k_1/k_{-1} = k_2/k_{-2}$, and substitution of that relation into Eq. (6-31) gives the result

$$K = \frac{k_1}{k_{-1}} = \frac{k_2}{k_{-2}} \tag{6-32}$$

The discussion in this section has shown that the forward and reverse rate expressions define the thermodynamics. The inverse is not exactly true. Given the forward rate law and the thermodynamic data, the reverse rate expression may be ambiguous,[3] because the coefficients in the thermodynamic equilibrium have relative significance only (in contrast to the reaction orders in the rate law). The hypothetical first-order conversion of A to B is consistent with a reverse rate of $k_{-1}[B]$ or with the expression $k'_{-1}[B]^2/[A]$ or with the general equation $k''_{-1}[B]^n/[A]^{n-1}$. This point tends to be of limited practical importance, since chemical reactions tend to occur by simple processes, and the family of possible expressions consists largely of highly unlikely forms.

Some caution[4] is called for if one seeks to compute an equilibrium constant by division of forward and reverse rate constants. Consider the two-step mechanism of Eqs. (6-24) and (6-25) under conditions in which B is *not* a steady-state intermediate. If the rate of disappearance of A were determined very early in an experiment, before appreciable B and C have accumulated, $-d[A]/dt \cong k_1[A]$. Similar measurements starting with product would afford $-d[C]/dt = k_{-2}[C]$. Clearly, the quotient k_1/k_{-2} is not the correct value of K. The point is that the apparent rate constants, k_1 and k_{-2}, are not the values that apply when the system is at equilibrium.

6-5 CONNECTIONS BETWEEN KINETICS AND THERMODYNAMICS

A useful family of relations can be derived by comparing the relations for the temperature dependence of a rate constant with the thermodynamic expression for the equilibrium constant.

Based on the Arrhenius equation, we have

$$\frac{k_f}{k_r} = \frac{A_f \exp(-E_f/RT)}{A_r \exp(-E_r/RT)} \tag{6-33}$$

Comparison with the thermodynamic relation

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(\frac{\Delta S^\circ}{R}\right)\exp\left(-\frac{\Delta H^\circ}{RT}\right) \tag{6-34}$$

leads to the equation[†]

$$E_f - E_r = \Delta H^\circ \tag{6-35}$$

Similar treatment starting the the equation of the activated complex theory gives the results

$$\Delta H_f^\ddagger - \Delta H_r^\ddagger = \Delta H^\circ \tag{6-36}$$

$$\Delta S_f^\ddagger - \Delta S_r^\ddagger = \Delta S^\circ \tag{6-37}$$

Those results, and a restatement of Eq. (6-23),

$$\frac{k_f}{k_r} = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$$

suggest that each rate constant is capable of expression in terms of a free energy of activation $\Delta G^\ddagger$:

$$\ln k_f = -\frac{\Delta G^\ddagger}{RT} + \text{constant} \tag{6-38a}$$

$$\ln k_r = -\frac{\Delta G^\ddagger}{RT} + \text{constant} \tag{6-38b}$$

Also, the expressions of (6-38) for the free energy of activation become

$$\ln k_f = -\Delta G_f^\ddagger + \ln \frac{RT}{Nh} \tag{6-39}$$

$$\Delta G_f^\ddagger = -RT \ln \frac{k_f Nh}{RT} \tag{6-40}$$

$$\Delta G_f^\ddagger = \Delta H_f^\ddagger - T\,\Delta S_f^\ddagger \tag{6-41}$$

6-6 THE HEAT CAPACITY OF ACTIVATION

It was pointed out earlier in this chapter that curvature in the plot of ln (k/T) versus T^{-1}, which might signal a complicated mechanism, may arise from a temperature-dependent enthalpy of activation. By analogy with the familiar thermodynamic equation, the heat capacity of activation, $\Delta C_p^\ddagger$, is defined by the equation

$$\Delta C_p^\ddagger = \frac{d\,\Delta H^\ddagger}{dT} \tag{6-42}$$

Highly precise kinetic data giving accurate values of rate constants and temperatures are needed to obtain values of $\Delta H^\ddagger$ which are sufficiently precise to warrant treatment by this method. Even for reactions in which the value of $\Delta C_p^\ddagger$ is appreciable, the values between ±100 and ±400 J mol^{-1} K^{-1}, the extent of curvature in a plot of

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[†] This equation is strictly applicable only in a condensed phase. In the gas phase, however, where the rate constants are defined in terms of concentration changes but the equilibrium constant in terms of partial pressures with $\Delta H^\circ = -Rd \ln K_p/d(1/T)$, then $E_f - E_r = \Delta E^\circ$.

Table 6-1 Kinetic data[a] for the hydrolysis of methylchloroformate, Eq. (6-43)

Temp./°C	$10^4\ k/\mathrm{s}^{-1}$	$\overline{(\Delta H^{\ddagger})}/\mathrm{kJ\ mol}^{-1}$ [b]	$\frac{1}{2}(T'' - T')/°\mathrm{C}$
0.570	0.4209		
4.976	0.7016	73.50	2.77
10.031	1.229	72.60	7.50
14.987	2.087	72.53	12.51
19.569	3.323	71.09	17.28
25.025	5.642	70.42	22.30
29.832	8.812	69.68	27.43
35.012	14.05	69.51	32.44
40.133	21.72	68.72	37.59
45.135	32.65	67.51	42.63

[a] From Ref. 5; [b] Calculated from adjacent points according to Eq. (6-45).

ln (k/T) versus T^{-1} is slight. Consider the hydrolysis of methylchloroformate:

$$\mathrm{ClC(O)OCH_3 + H_2O = CO_2 + CH_3OH + H^+ + Cl^-} \tag{6-43}$$

Values of the first-order rate constant[5] are given in Table 6-1, and the plot of ln (k/T) versus T^{-1} in Fig. 6-2. The latter is barely curved on the scale of this graph. The graph

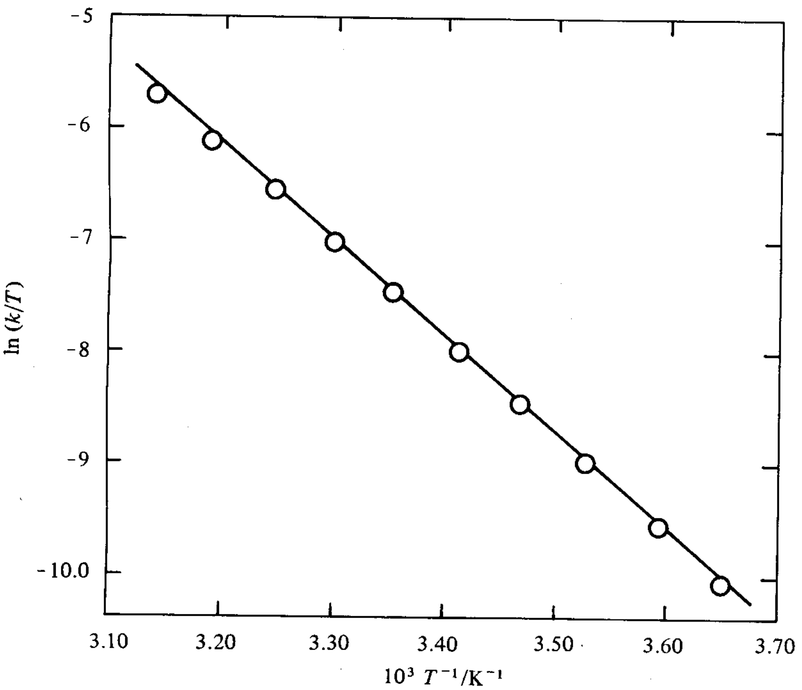


Figure 6-2 Plot of ln (k/T) versus $1/T$ for the hydrolysis of methylchloroformate (Ref. 5 and Table 6-1). The degree of curvature, although slight, is considered a real effect to which the scale of this graph cannot do justice.

hardly does justice to the accuracy of the data, however, and the extent of the curvature must be determined by other means.[5,6] The most reliable method is a numerical least-squares fit of the data to the relation

$$\ln k = A + BT^{-1} + C \ln T \tag{6-44}$$

This fit gives parameters A, B, and C from which $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta C_p^{\ddagger}$ are then calculated.[6] Unfortunately, however, the method is not very instructive of the magnitude of the effect or the physical situation. For that reason a cruder but more intuitive method has been developed for the data at hand, a method less correct but considerably easier to appreciate. Approximately, it is this: Over a sufficiently narrow range of temperature, $\Delta H^{\ddagger}$ is constant. One can approximate a series of such values by calculating a mean value of the activation enthalpy $\overline{\Delta H^{\ddagger}}$ from successive pairs of values of (k', T'), (k'', T''):

$$\overline{(\Delta H^{\ddagger})} = \frac{R \ln (k''/k')}{1/T' - 1/T''} \tag{6-45}$$

The third column of Table 6-1 presents such values, which are seen to decrease smoothly from 73.50 to 67.51 kJ mol^{-1} with increasing temperature. According to Eq. (6-42), the average values are then plotted as $\overline{(\Delta H^{\ddagger})}$ versus T_{avg}, giving a straight line of slope $\Delta C_p^{\ddagger}$. The graph is shown in Fig. 6-3, and it is seen to define a reasonably straight line having a slope $\Delta C_p^{\ddagger} = -150$ J mol^{-1} K^{-1}, which agrees with the accepted value.

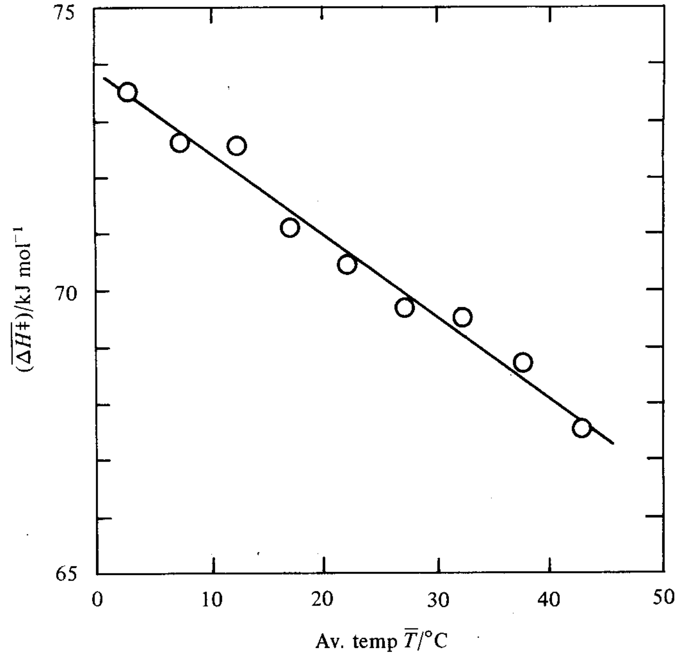


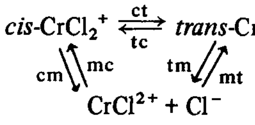
Figure 6-3 Evaluation of $\Delta C_p^{\ddagger}$ for the hydrolysis of methylchloroformate (Table 6-1 and Ref. 5). This plot shows the incremental, average enthalpy of activation from Eq. (6-45) versus the average temperature in the interval.

The value of $\Delta C_p^\ddagger$ may provide insight into the nature of the transition state, especially with respect to solvation and charge separation. Large values are often found for reactions leading to the formation of ions from neutral molecules. To evaluate $\Delta C_p^\ddagger$ requires kinetic data of unusually high accuracy. The differential temperature method of Albery and Robinson[7] can be used to provide activation parameters of high accuracy. The authors point out that if concentrations are measured to an accuracy of 1 percent at two temperatures at which the ratio of rate constants is 1.1, the uncertainty in $\Delta H^\ddagger$ is of the order of 20 percent. On the other hand, it is possible to obtain highly precise values of $\Delta H^\ddagger$ by measuring the *difference* in concentration between two reactions held at different known temperatures. For example, one might use a double-beam spectrophotometer with reactions in progress in both sample and reference compartments. The two reactions would be made up identically but thermostatted at different temperatures. The instrument recording presents, as a function of time, the concentration difference between the two, measured far more accurately than if each run were conducted independently. Results from such an experiment are considered in Prob. 6-4.

6-7 THE PRINCIPLE OF MICROSCOPIC REVERSIBILITY

The basic statement is that the forward and reverse of a particular pathway are related as mirror images. In mechanistic terms this requires that the mechanism of the reverse reaction is the same as that of the forward one (determined under comparable conditions). The positions of the atoms as the reactions move along the reaction coordinate to form and later destroy the activated complex are identical in both directions, save that the signs of the momentum vectors are reversed. Consequently, a condition of equilibrium is not just that gross forward and reverse rates are identical but that the opposing rates along each pathway are equal.

We shall consider two examples, the first being Cl^- loss from the geometrical isomers of the dichlorochromium(III) ion.[8,9] The reaction scheme is that shown in Eq. (6-46). The reaction has been studied by two methods. In the first instance,[8] samples were removed from the mixture, quenched, and the components separated chromatographically. Later, a method was developed to disentangle the rate constants from simultaneous multiwavelength spectrophotometric determinations on the unseparated mixture.[9] The latter constitutes an example of the techniques of numerical integration applied to a complex kinetic pattern.



(6-46)

The rate constants applicable to the reaction are given in Table 6-2. The principle of microscopic reversibility provides this relation:

$$K_{ct} = \frac{k_{ct}}{k_{tc}} = \frac{k_{mt}}{k_{tm}} \times \frac{k_{cm}}{k_{mc}} \tag{6-47}$$

Since cis-trans isomerization proceeds directly, as well as by reaction of $CrCl^{2+}$ and Cl^-, experiments starting with, say, initially pure *trans*-$CrCl_2^+$ must properly take

Table 6-2 Kinetic and thermodynamic parameters[a] for reactions of *cis*-$CrCl_2^+$, *trans*-$CrCl_2^+$, and $CrCl^{2+}$

Reaction	k_f	k_r/s^{-1}	K
$CrCl^{2+} + Cl^- \rightleftharpoons$ *cis*-$CrCl_2^+$	$k_{mc} = 3.6 \times 10^{-7}\ M^{-1}\ s^{-1}$	$k_{cm} = 1.8 \times 10^{-6}$	$2.0 \times 10^{-3}\ M^{-1}$
$CrCl^{2+} + Cl^- \rightleftharpoons$ *trans*-$CrCl_2^+$	$k_{mt} = 1.3 \times 10^{-7}\ M^{-1}\ s^{-1}$	$k_{tm} = 8.3 \times 10^{-5}$	$1.6 \times 10^{-3}\ M^{-1}$
cis-$CrCl_2^+ \rightleftharpoons$ *trans*-$CrCl_2^+$	$k_{ct} = 6.2 \times 10^{-5}\ s^{-1}$	$k_{tc} = 7.8 \times 10^{-5}$	0.78

[a] Refer to Eq. (6-47). Values, taken from Ref. 8, are at 34.8°C.

into account the parallel reactions of isomerization and aquation. (Particularly so, since in the absence of added Cl^- the reactions of $CrCl^{2+}$ and Cl^- are of negligible importance.) The kinetic expressions, with such terms neglected, are

$$\frac{d[CrCl^{2+}]}{dt} = k_{tm}[\text{trans}] + k_{cm}[\text{cis}] \tag{6-48}$$

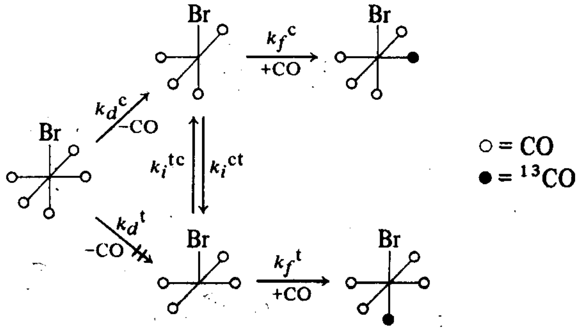
$$\frac{-d[\text{cis}]}{dt} = k_{tc}[\text{trans}] - (k_{ct} + k_{cm})[\text{cis}] \tag{6-49}$$

$$\frac{-d[\text{trans}]}{dt} = -(k_{tc} + k_{tm})[\text{trans}] + k_{ct}[\text{cis}] \tag{6-50}$$

The numerical values are such that the steady-state approximation is not valid. The experimental data are depicted in Fig. 6-4, and in the same figure are shown solid lines calculated from a numerical integration of these equations.

A second example is that given by T. L. Brown[10] for the mechanism of exchange of carbon monoxide between free CO and the metal carbonyl complex $Mn(CO)_5Br$. The experimental finding is that (1) reaction of ^{13}CO with $Mn(CO)_5Br$ forms $Mn(CO)_4(^{13}CO)Br$ in which (*a*) it can be unambiguously shown by infrared spectroscopy that both cis and trans positions have incorporated the ^{13}C label and (*b*) the rate of exchange consists of a single term, $k_{ex}[Mn(CO)_5Br]$, independent of [CO] and (2) the ^{13}CO stretching frequencies in cis and trans products grow in at the same rate.

Those observations originally suggested a mechanism rejected by Brown because it violates the principle of microscopic reversibility. The original proposal invoked these steps: rate-limiting dissociation of a *cis*-CO (the *trans*-CO was presumed to be inert), with capture of a ^{13}CO by either isomer of the stereochemically labile five-coordinate intermediate. The sequence is depicted in Eq. (6-51).



(6-51)

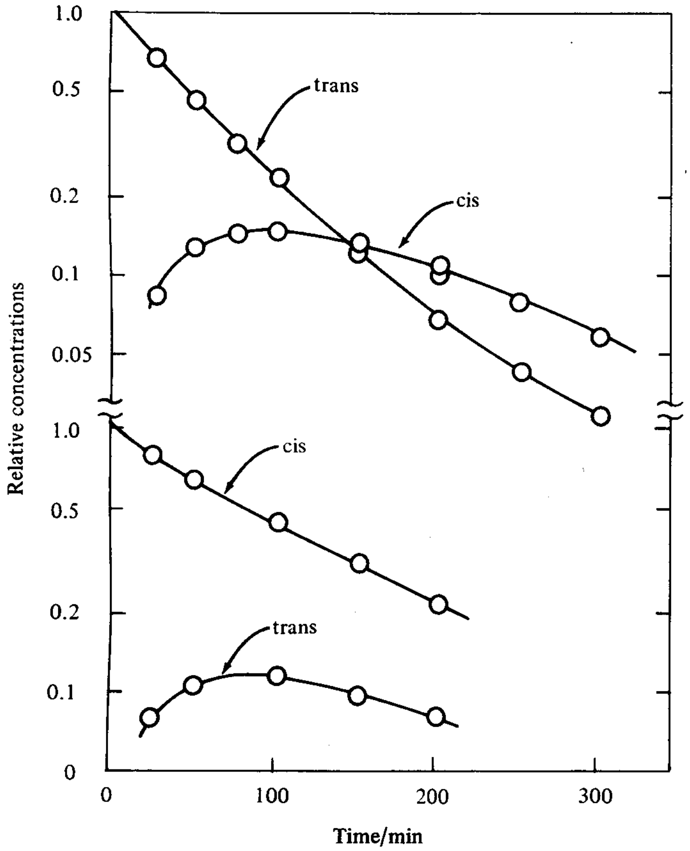


Figure 6-4 Relative concentrations (log scale) versus time, depicting [*trans*-CrCl$_2^+$] (○) and [*cis*-CrCl$_2^+$] (○–). The upper part refers to a run starting with pure trans isomer, the lower to a run starting with pure cis. The points are experimental data,[6] and lines are those calculated from the rate constants in Table 6-1.

Brown points out that such a mechanism violates the principle of microscopic reversibility in that the relative rates of capture of CO must be in proportion to their dissociation, $k_f^c/k_f^t = k_d^c/k_d^t$. The resolution in this case originates because the exchange reaction necessarily has a perfectly symmetrical reaction coordinate, which the proposal in (6-52) disregards. Brown states:

> If there is preferential loss of CO from the equatorial position, then, no matter what modes of equilibration may prevail in the five-coordinate intermediate, addition of CO must occur at the equatorial position, with the same degree of preference which characterizes loss of CO. This conclusion follows directly from the principle of microscopic reversibility. If the transition state for loss of axial CO possesses a higher free energy than that for loss of radial CO, the transition state for addition of CO to the intermediate along the axis must be correspondingly higher. The key to the application of this concept in the present context is that the labeling which is observed resides in the group being added to the intermediate and not in the parent molecule.

The correct application of this principle has proved of occasional difficulty; particular aspects are discussed more fully in the literature.[11,12]

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PROBLEMS

6-1 *Temperature dependence.* The reaction in Prob. 3-1 was also studied under the same conditions at 35.0°C. Use the data below to evaluate (*a*) K at 35.0°C, (*b*) k_f and k_r at 35.0°C, (*c*) $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for forward and reverse rate constants, (*d*) ΔH° and ΔS°.

Time/s	0.0	600	1200	1800	3600	18,000
Absorbance 285 nm, 35.0°C	0.450	0.573	0.655	0.708	0.783	0.814

6-2 *Forward and reverse reaction rates.* The rate of isotopic exchange between $U^{4+}(aq)$ and UO_2^{2+} in dilute perchloric acid is given by (see Prob. 5-14):

$$R_{ex} = k_{ex} \frac{[U^{4+}][UO_2^{2+}]}{[H^+]^3}$$

with $k = 2.1 \times 10^{-7}$ M^2 s^{-1} at 25°C. The equilibrium constant is 2×10^{-10} M^4 (25°C) for the reaction

$$U^{4+} + UO_2^{2+} + 2H_2O = 2UO_2^{+} + 4H^+$$

Assuming that the latter reaction constitutes the major pathway for U(IV)-U(VI) exchange, determine the form of the rate law for U(V) disproportionation and its rate constant.

6-3 *Kinetics and thermodynamics; microscopic reversibility.* The elementary gas-phase reaction

$$NO + ClNO_2 = NO_2 + ClNO$$

is characterized by these thermodynamic parameters at 298 K: $\Delta H^\circ = -16.5$ kJ mol^{-1} and $\Delta G^\circ = -22.9$ kJ mol^{-1}. The forward rate constant can be expressed in Arrhenius form [Eq. (6-9)] and by an activated complex theory expression [Eq. (6-13)]. (In both cases use 1 mol/dm^3 standard state.)

(*a*) Express k_r in the same two forms. Compute k_r at 298 K.

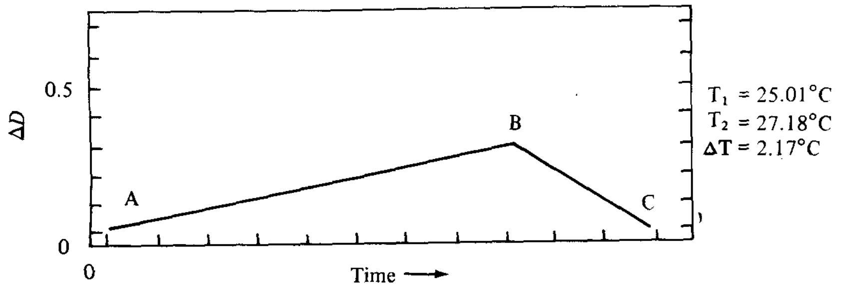
(*b*) What experiments using nitrogen-15-labeled compounds might distinguish the molecular mechanisms of chlorine atom and oxygen atom transfer?

6-4 *Differential temperature method.* The method described in the text has been applied[7] to a study of the iodination of acetone, a pseudo-zero-order reaction under the conditions employed ($[(CH_3)_2CO] \gg [I_2]$)

$$\frac{-d[I_2]}{dt} = k[(CH_3)_2CO] = k'$$

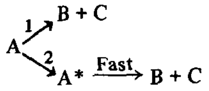
Two identical reaction solutions were prepared, one at the lower temperature T_1 in the sample compartment of a double-beam spectrophotometer, the other at T_2 in the reference beam. A direct recording of $\Delta D = D_1 - D_2$ was made as a function of time while the difference in reaction temperature was maintained to ±0.001°C.

Evaluate k'_2/k'_1 and $\Delta H^\ddagger$ for the run shown.



6-5 *Composite temperature dependence.* Consider the two mechanisms shown, each of which leads to an expression $-d[A]/dt = k_{app}[A]$. In each case show the shape of a plot of $\ln k_{app}$ versus $1/T$.

Mechanism 1:



Mechanism 2:

$$A \underset{-3}{\overset{3}{\rightleftharpoons}} A^*$$

$$^*A \xrightarrow{4} B + C$$

6-6 *Kinetics and equilibrium.* Rabinovitch and Michel [*J. Am. Chem. Soc.*, 81:5065 (1959)] report that the cis-trans isomerization of 2-butene follows first-order kinetics at high pressures. The value of k_f is $1.9 \times 10^{-5}\ s^{-1}$ at 742°K and has $E_a = 2.67 \times 10^4\ J\ mol^{-1}$. The equilibrium constant is 1.53 and has $\Delta H^\circ = 0$. Consider an experiment with $[cis]_0 = 7.16 \times 10^{-4}\ mol\ dm^{-3}$ and $[trans]_0$. Compute (*a*) the apparent rate constant for approach to equilibrium at 742 K, (*b*) [cis] at time 6×10^4 s, and (*c*) the apparent rate constant at 686 K.

6-7 *Composite temperature dependence.* A. Burg [*J. Am. Chem. Soc.*, 74:3482 (1955)] and M. E. Garabadian and S. W. Benson [*J. Am. Chem. Soc.*, 86:186 (1964)] have found that the rate of the gas-phase reaction $2BH_3CO = B_2H_6 + 2CO$ is

$$\frac{-d[BH_3CO]}{dt} = k_{exp}\frac{[BH_3CO]^2}{[CO]}$$

with k_{exp}, in Arrhenius form, given by

$$k_{\mathrm{exp}}/\mathrm{s}^{-1} = 7.6 \times 10^{13} \exp\left(-\frac{111{,}900\ \mathrm{J\ mol^{-1}}}{RT}\right)$$

Chien and Bauer [*Inorg. Chem.*, 16:867 (1977)] give thermodynamic data at 298 K (converted to a standard state of 1 mol/cm^3):

	BH_3CO	BH_3	CO
ΔH_f°/kJ mol^{-1}	-111.0	+99.9	-111.5
S°/J mol^{-1} K^{-1}	+165.7	+103.8	+113.5

This reaction involves BH_3 as a steady-state intermediate reacting in this rate-limiting step:

$$BH_3CO + BH_3 \xrightarrow{2} B_2H_6 + CO$$

Evaluate k_2 in an Arrhenius form.

6-8 *Temperature dependence.* Derive a general relation between $\Delta S^\ddagger$ of activated complex theory and A of the Arrhenius equation. Compute A for a first-order reaction with $\Delta S^\ddagger = -20$ J mol^{-1} K^{-1} at 298 K.

6-9 *Elementary reactions.* Castellano and Schumacher [*Z. Phys. Chem.*, 24:198 (1962)] considered the photochemical decomposition of ozone:

$$O_3 + h\nu \longrightarrow O_2 + O$$

The O atoms so produced either reacted to form O_2 or returned to ozone in the presence of a third body M:

$$O + O_3 \xrightarrow{1} 2O_2$$

$$O + O_2 + M \xrightarrow{2} O_3 + M$$

The ratios of rate constants are as follows for different M's.

M	Ar	He	N_2	O_2	CO_2	O_3
$k_1k_2^{-1}$/mol dm^{-3}	550	420	370	310	150	140

Consider now the thermal dissociation of O_3:

$$O_3 + M \xrightarrow{3} O + O_2 + M$$

Compute the relative values of k_3 for different M's.

6-10 *Composite temperature dependence.* Show that a plot of the apparent first-order rate constant of Eq. (6-22) as $\ln(k_{\mathrm{app}}/T)$ versus $1/T$ will always be curved downward, corresponding to an apparent $\Delta H^\ddagger$ which decreases with increasing temperature. What will the shape of the plot be if, by chance, $\Delta H_6^\ddagger = \Delta H_{-5}^\ddagger$?