Molecular Partition Functions in Terms of Local Properties

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The classical partition function for a polyatomic molecule is obtained in a form which has, for each atom, a factor that corresponds to free translational motion of the atom in an effective volume defined by the average vibrational amplitudes of the atom and the geometrical configuration of the neighboring atoms. A method is given for calculating the appropriate volume elements for any choice of internal coordinates. The treatment includes harmonic vibrations, internal rotations, and "reaction coordinates." Quantum mechanical corrections introduce additional factors which shrink the volume elements for high-frequency vibrations.

Since the principal factors in this form of the partition function are determined by local properties largely characteristic of the bonds in the vicinity of each atom, many of these factors remain practically constant and can be omitted in calculations which compare the reactants in a chemical reaction with the products or with the "activated complex."

IN applications of statistical thermodynamics and particularly in the transition state theory of chemical kinetics, the calculations often involve a ratio of the partition functions for two molecules having several atoms or groups in common, and to a practical approximation the contributions of many of the degrees of freedom associated with the common groups will cancel. However, this fact does not find natural expression in the usual formula for the partition function, as the moments of inertia for over-all and internal rotations and the vibrational frequencies (to a lesser extent) refer to the whole molecule.

In this paper a form of the classical partition function is obtained in which the principal factors are determined by local properties largely characteristic of the bonds in the vicinity of each atom. This formula, when augmented by quantum mechanical factors, is shown to involve no approximations beyond those required for the usual formula (neglect of vibration-rotation interactions and anharmonicity). The derivation extends to a general polyatomic molecule the serial method of integrating the classical partition function which Pitzer developed for chain hydrocarbons[1] and has recently applied to atom transfer reactions.[2]

The "classical" partition function or phase integral for a molecule of N atoms is

$$Q_{class} = h^{-3N} \int \cdots \int \exp(-H/kT) dp_{x_1} \cdots dp_{x_N} dx_1 \cdots dz_N.$$

$$(1)$$

It is related to the complete partition function by

$$Q = (Q_e/\sigma)(Q_q/Q_c)Q_{class},$$

$$(2)$$

where σ is the usual symmetry number required if some of the atoms are symmetrically equivalent; Q_e is the electronic partition function, in most cases given by the degeneracy of the electronic ground state; the ratio (Q_q/Q_c) contains the quantum correction factors which will be discussed later. Since the classical kinetic energy is $p_\alpha^2/2m$ for each atom α, the integrations over the momenta in Eq. (1) give

$$Q_{class} = Z \prod_{\alpha=1}^{N} \Lambda_\alpha^{-3},$$

$$(3)$$

where Λ_α is the de Broglie wavelength corresponding to the average momentum of atom α,

$$\Lambda_\alpha = h/(2\pi m_\alpha kT)^{\frac{1}{2}},$$

$$(4)$$

and Z is the "configurational integral" over the Boltzmann factor of the potential energy

$$Z = \int \cdots \int \exp(-U/kT) dx_1 \cdots dz_N.$$

$$(5)$$

Formally, at least, the configurational integral can always be regarded as a product of volume elements V_α available to the atoms of the molecule[3]

$$Z = \prod_{\alpha=1}^{N} V_\alpha.$$

$$(6)$$

If there were no forces between the atoms, each of them could move independently throughout V, the volume of the container, so that $V_\alpha = V$ for each atom and $Z = V^N$. When the N atoms belong to a molecule, one atom may still be regarded as "free to wander

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[1] (a) K. S. Pitzer, J. Chem. Phys. **8**, 711 (1940); **14**, 239 (1946). See also (b) W. B. Person and G. C. Pimentel, J. Am. Chem. Soc. **75**, 532 (1953); (c) G. J. Janz, *Estimation of Thermodynamic Properties* (Academic Press, New York, 1958).

[2] K. S. Pitzer, J. Am. Chem. Soc. **79**, 1804 (1957); O. Sinanoglu and K. S. Pitzer, J. Chem. Phys. **30**, 422 (1959).

[3] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), pp. 213–217, have described this viewpoint, for example; it is of course closely analogous to the cell theory of crystals and liquids.

about the whole system, dragging the molecule with it," while the other atoms of the molecule are constrained to lesser volumes in the vicinity of the first atom.[3] Thus $V_1 = V$, but the other effective volume elements V_α must be suitably defined averages. Our problem is to evaluate these in terms of the potential energy parameters and bond lengths and angles relating an atom to its neighbors in the molecule.

OVER-ALL TRANSLATION AND ROTATION

Since there is no potential energy associated with the over-all translations and rotations of the molecule (as long as gas imperfection is neglected), the integrations for these degrees of freedom are readily disposed of.[1,2] Any atom in the molecule may be arbitrarily chosen as atom 1, and the integration over $x_1 y_1 z_1$ yields just a factor V, as already mentioned. The cartesian coordinates of the second atom may be transformed to polar coordinates relative to the first atom, after which integration over the angles yields a factor of 4π. To integrate over the third rotational degree of freedom that exists if the molecule is nonlinear, we chose one of the coordinates of atom 3 to be its azimuthal angle about the direction of the 1–2 bond, and thus obtain another factor of 2π.

Thus Z is always proportional to $V8\pi^2$ for a nonlinear molecule or $V4\pi$ for a linear molecule.

HARMONIC VIBRATIONS

In carrying out the integrations over the vibrational degrees of freedom one can proceed atom by atom, referring the coordinates of the successive atoms to the positions of preceding atoms. Since the form of the potential energy will dictate the choice of coordinates to be used, it will be necessary to consider a rather general coordinate transformation. As a preliminary example which shows the principal features of the problem, we consider briefly the results for a nonlinear triatomic molecule with a valence force field.[4]

$$2U = F_r(\Delta r)^2 + F_{r'}(\Delta r')^2 + F_{\theta'}(\Delta\theta')^2, \quad (7)$$

where the Δ's denote displacements from the equilibrium values of the bond lengths r, r', and the interbond angle θ'. With this potential function, it is appropriate to use polar coordinates to locate both atoms 2 and 3. The coordinate transformation introduces a Jacobian factor of the form $r^2 \sin\theta$ for each atom. After the integrations over translation and rotation, we have

$$Z = V8\pi^2 \iiint \exp(-U/kT) r^2 r'^2 \sin\theta' dr dr' d\theta'.$$

If the remaining factors of the Jacobian are taken outside the integral and evaluated at the equilibrium configuration of the molecule (as shown below, this ap-

proximation amounts to neglecting the coupling between the vibrations and rotations), the integrations yield $Z = V_1 V_2 V_3$ where $V_1 = V$,

$$V_2 = 4\pi r^2 (2\pi kT/F_r)^{\frac{1}{2}}, \quad (8)$$

and

$$V_3 = 2\pi r' \sin\theta' (2\pi kT/F_{r'})^{\frac{1}{2}} r' (2\pi kT/F_{\theta'})^{\frac{1}{2}}. \quad (9)$$

The volume factor for atom 2 is thus a spherical shell centered on atom 1; the thickness of the shell $(2\pi kT/F_r)^{\frac{1}{2}}$ is a measure of the average vibrational amplitude of the 1–2 bond stretch. V_3 is a doughnut shaped volume with radius $2\pi r' \sin\theta'$ about its axis along the extension of the 1–2 bond, and with a cross section given by the product of the vibrational amplitudes of the 2–3 bond stretch and the 1–2–3 bond bend. (The factor of r' is included in the bending amplitude because $F_{\theta'}$ refers to angle rather than distance.) In Pitzer's treatment of n-paraffin hydrocarbons,[1] each new link in the chain introduces a factor having the same form as Eq. (9), except that $2\pi r' \sin\theta'$ is replaced by a suitable average which takes account of the steric effects associated with internal rotation.

In extending this approach to molecules having a more complicated geometry and potential energy function, the main problem is to obtain a convenient general method for evaluation of the Jacobian factors.

It will prove convenient first to make a comparison with the usual formula for the partition functions.[3,5] Instead of cartesian coordinates for the individual atoms, as used in Eq. (3), the usual derivation employs coordinates defined with respect to the whole molecule: the center of mass coordinates, the Eulerian angles specifying the orientation of the principal axes of inertia, and the normal coordinates for vibrations. In these coordinates the molecular energy is separable, provided the coupling between rotation and vibration and the anharmonicity of the vibrations are neglected. The resulting formula for the classical partition function is

$$Q_{\text{class}} = V8\pi^2 (2\pi kT/h^2)^3 M^{\frac{3}{2}} |I|^{\frac{1}{2}} \prod_{i=1}^{3N-6} u_i^{-1}, \quad (10)$$

where M is the molecular mass, $|I|$ the determinant of the moment of inertia tensor, and $u_i = h\nu_i/kT$, where ν_i is the fundamental frequency of the ith normal mode of vibration. A comparison of Eq. (3) and (10) shows that, under the approximations made in deriving (10), the configurational integral satisfies the relation
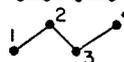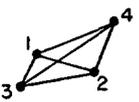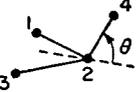
$$Z = V8\pi^2 (2\pi kT/h^2)^{-\frac{1}{2}(3N-6)} M^{\frac{3}{2}} |I|^{\frac{1}{2}} \prod_{\alpha=1}^{N} m_\alpha^{-\frac{3}{2}} \prod_{i=1}^{3N-6} u_i^{-1}. \quad (11)$$

We may separate out the dependence on the vibrational

[4] Sinanoglu and Pitzer[2] have given a detailed treatment of the triatomic molecule from a somewhat different point of view.

[5] G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), pp. 501–530.

TABLE I. Jacobian factors.

Atom	Configuration	Coordinates	J_α
$\alpha=1$		x, y, z	V
$\alpha=2^a$		$r_{12}, \theta_{ex}, \phi_{ex}$	$4\pi r_{12}{}^2$
$\alpha=3^a$		$r_{23}, \phi_{123}, \phi_{123}{}'$	$r_{23}{}^2$
		$r_{23}, \phi_{123}, \phi_{ex}$	$2\pi r_{23}{}^2 \sin\phi_{123}$
		$r_{23}, r_{13}, \phi_{ex}$	$2\pi (r_{23}r_{13}/r_{12})$
$\alpha=4$		$r_{34}, \phi_{234}, \phi_{234}{}'$	$r_{34}{}^2$
		r_{34}, ϕ_{234}, τ	$r_{34}{}^2 \sin\phi_{234}$
		$r_{24}, \phi_{124}, \phi_{324}$	$r_{24}{}^2/\sin\psi_{341}$
		r_{24}, r_{14}, r_{34}	$(r_{14}r_{34}/r_{12}r_{32}) (e_{21}xe_{23}\cdot e_{24})^{-1}$
		$r_{24}, \phi_{124}, \theta$	$r_{24}{}^2 \cos\theta/\cos\psi_{413}$
		r_{14}, r_{34}, θ	$r_{24}/[\sin\phi_{143} - (e_{14}x\ e_{24}\cdot e_{34}) \tan\theta]$
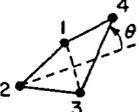
^a For $\alpha=2$ and $\alpha=3$ the angles θ_{ex} and ϕ_{ex} are the external rotation angles; upon integration these give rise to the factors 4π and 2π in J_α.

force constants by making use of the identity

$$| F_S || G_S | = \prod_{i=1}^{3N-6} \lambda_i, \qquad (12)$$

where $\lambda_i = (2\pi\nu_i)^2$ and $| F_S |$ and $| G_S |$ are the determinants of the $3N-6\times3N-6$ matrices of the coefficients which appear in the vibrational energy

$$\tfrac{1}{2}\sum G_{tt'} P_t P_{t'} + \tfrac{1}{2}\sum F_{tt'} \Delta S_t \Delta S_{t'},$$

in Wilson's treatment of molecular vibrations.[6,7] $S_1, \cdots, S_{3N-6}$ are internal coordinates (bond lengths and angles) and the P_t's are the vibrational momenta conjugate to the S_t's. The result of combining Eqs.

[6] Wilson, Decius, and Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955). We shall follow the notation in this book as closely as is practicable.

[7] In Eq. (12) and (13) the subscript S is used to emphasize that the form taken by the elements of the F_s and G_s matrices and the Jacobian J_s depends on the choice of internal coordinates. For our purposes it is important to note that as long as the coordinates used are geometrical ones (in contrast to dynamical coordinates such as normal modes), the F matrix will not involve the masses and the G matrix will not involve the force constants.

(11) and (12) may be rearranged as follows:

$$J_S = \frac{| F_S |^{\frac{1}{2}}}{(2\pi kT)^{\frac{1}{2}(3N-6)}} \int \cdots \int \exp(-U/kT) dx_1 \cdots dz_N \qquad (13a)$$

$$= V 8\pi^2 M^{\frac{3}{2}} | I |^{\frac{1}{2}} \prod m_\alpha^{-\frac{3}{2}} | G_S |^{-\frac{1}{2}}. \qquad (13b)$$

Now one side of the Eq. (13a) does not involve masses, the other (13b) does not involve the force constants. Hence the quantity denoted by J_S is independent of both the force constants and masses, and consequently depends only on the geometrical parameters.

In calculating J_S we are free to use any convenient values for the force constants and masses. Although Eq. (13b) can be considerably simplified by setting the atomic masses equal to unity, it is still feasible to use only for simple molecules. Therefore Eq. (13a) will be used for the general treatment. The integrations over the vibrational motions of the atoms are effected merely by taking the limit in which the diagonal force constants become very large and the nondiagonal force constants vanish. Before taking this limit, we must

replace the cartesian volume element in Eq. (13a) by $dS_1 \cdots dS_{3N-6}$ times the Jacobian associated with the transformation to internal coordinates and integrate over translation and rotation: thus the result is that Eq. (13a) reduces to $V8\pi^2$ times the value of the Jacobian at the equilibrium configuration of the molecule. Since this result has been obtained from Eq. (10) without further approximations, the evaluation of the Jacobian at the equilibrium position is equivalent to the neglect of vibration-rotation interactions in the usual treatment.

In the next section it will be found that J_S may be written as a product of factors, one for each atom,

$$J_S = \prod_{\alpha=1}^{N} J_\alpha. \qquad (14)$$

(See Table I.) The final formula for the configurational integral will then take the form:

$$Z = \frac{(2\pi kT)^{\frac{1}{2}(3N-6)}}{|F_S|^{\frac{1}{2}}} \prod_{\alpha=1}^{N} J_\alpha. \qquad (15a)$$

Thus in the classical partition function of Eq. (3), the dependence on the atomic masses, the vibrational force constants, and the molecular geometry appears in separate factors. An effective volume V_α may be assigned to each atom, as in Eq. (6), by assuming that the force constant matrix is diagonal in the internal coordinates chosen so that the determinant in Eq. (15) becomes the product of the diagonal force constants, as in Eq. (8) and (9); however, this may also be done without neglecting the nondiagonal force constants, since the force constant matrix can always be diagonalized without changing the value of its determinant.[8] In computations it is convenient to associate a vibrational amplitude

$$\ell_i = (2\pi kT/F_{ii})^{\frac{1}{2}}$$

with each of the diagonal force constants, so that Eq. (15a) can be written as

$$Z = w^{-1} \prod_{i=1}^{3N-6} \ell_i \prod_{\alpha=1}^{N} J_\alpha, \qquad (15b)$$

where the factor

$$w = \left[|F_S| / \prod_{i=1}^{3N-6} F_{ii} \right]^{\frac{1}{2}} \qquad (16)$$

corrects for the correlations which are introduced by the presence of the off-diagonal force constants.

CALCULATION OF THE JACOBIAN FACTORS

If the transformation to internal coordinates is carried out in the serial fashion illustrated above for the triatomic example, it is readily shown that the Jacobian

can be factored as indicated in Eq. (14). After the initial steps involving the translational and rotational degrees of freedom associated with the first three atoms, we replace x_α, y_α, z_α for each of the succeeding atoms by internal coordinates $S_{i\alpha}$, $S_{j\alpha}$, $S_{k\alpha}$ which locate the atom relative to the preceding atoms. The transformation equations thus take the form

$x_\alpha = f(S_{i\alpha}, S_{j\alpha}, S_{k\alpha})$ +functions of the new coordinates
of the preceding atoms (17)

and, similarly, for y_α and z_α.

The required Jacobian is the absolute value of the determinant whose elements are the derivatives of the original cartesian coordinates with respect to the new coordinates. In calculating a derivative such as $(\partial x_\alpha / \partial S_{i\beta})$, all the internal coordinates except $S_{i\beta}$ are held at fixed values; this means that all the atoms preceding atom β are fixed while those following atom β are displaced as a rigid body when $S_{i\beta}$ is varied. It follows from Eq. (17) that the derivatives of x_α, y_α, z_α with respect to the new coordinates of any later atom β all vanish: if $\beta > \alpha$,

$$(\partial x_\alpha / \partial S_{i\beta}) = 0,$$

etc. Accordingly the $3N \times 3N$ Jacobian determinant assumes a triangular form and factors into the product of its diagonal blocks which are 3×3 determinants, one for each atom. We need, therefore, to calculate only derivatives such as $(\partial x_\alpha / \partial S_{i\alpha})$, in which the new and old coordinates of a single atom are involved. Also, as shown under Eq. (13), we need only the equilibrium value of the Jacobian factors.

Actually, in order to be able to make direct use of Wilson's convenient vector methods, we shall calculate instead the determinant whose elements are $(\partial S_{i\alpha} / \partial x_\alpha)_0$, etc., which is the reciprocal of the desired Jacobian.[9] From Taylor's theorem we have

$$\Delta S_{i\alpha} = (\partial S_{i\alpha} / \partial x_\alpha)_0 \Delta x_\alpha + (\partial S_{i\alpha} / \partial y_\alpha)_0 \Delta y_\alpha$$

$$+ (\partial S_{i\alpha} / \partial z_\alpha)_0 \Delta z_\alpha + \text{terms involving other atoms} (18)$$

and analogous equations for $\Delta S_{j\alpha}$ and $\Delta S_{k\alpha}$; the Δ's again denote displacements from equilibrium values. In Wilson's treatment,[6] a displacement vector ϱ_α is introduced whose components are Δx_α, Δy_α, Δz_α; the three differential coefficients are likewise considered as the components of a vector $s_{i\alpha}$ associated with the coordinate $S_{i\alpha}$ of atom α. Equation (18) may then be written as the scalar product of these vectors,

$$\Delta S_{i\alpha} = s_{i\alpha} \cdot \varrho_\alpha + \cdots. \qquad (19)$$

This form has the advantage that it is unnecessary to

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[8] See, for example, H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1943), p. 308.

[9] In calculating a derivative of the type $(\partial S_{i\alpha} / \partial x_\beta)$ the cartesian coordinates of all atoms except atom β remain fixed. This condition differs from that implied in calculating $(\partial x_\alpha / \partial S_{i\beta})$, where all atoms following β were shifted. However, since by inverting Eq. (17) we may define $S_{i\alpha}$ in terms of the cartesian coordinates of the preceding atoms, we have $(\partial S_{i\alpha} / \partial x_\beta) = 0$ if $\beta > \alpha$, so that again a triangular determinant is obtained.
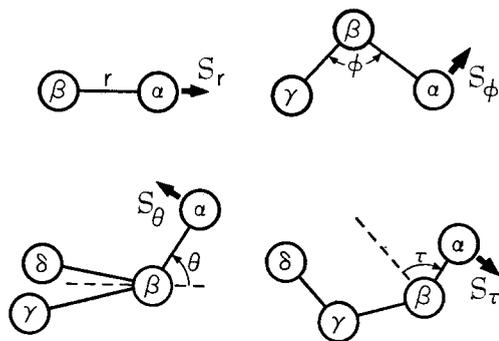
FIG. 1. Internal coordinates and **s** vectors.

specify any axes for the displacement coordinates; for example, the $\mathbf{s}_{i\alpha}$ vector can be expressed in terms of unit vectors along the various chemical bonds in the vicinity of atom α.

Now the Jacobian we require is the reciprocal of the determinant formed from the components of the three vectors $\mathbf{s}_{i\alpha}$, $\mathbf{s}_{j\alpha}$, $\mathbf{s}_{k\alpha}$. This determinant represents the "volume" of the parallelepiped whose sides are formed by the three **s** vectors and is equal to their scalar triple product (or "box" product).[10] Thus we have the general formula

$$J_\alpha = (\mathbf{s}_{i\alpha} \times \mathbf{s}_{j\alpha} \cdot \mathbf{s}_{k\alpha})^{-1}. \qquad (20)$$

Rules for evaluating the **s** vectors for various kinds of internal coordinates are given in reference 6. The direction of $\mathbf{s}_{i\alpha}$ is that in which a given displacement of atom α will produce the greatest increase of $\Delta S_{i\alpha}$, and the magnitude of $\mathbf{s}_{i\alpha}$ is equal to the increase in $\Delta S_{i\alpha}$ produced by unit displacement in this most effective direction. These properties follow from the fact that $\mathbf{s}_{i\alpha}$ is the gradient of $S_{i\alpha}$; they may also be inferred from Eq. (19), since the scalar product of two vectors is the product of their magnitudes and the cosine of the angle between them.

For reference, we list here the appropriate **s** vectors, expressed in terms of unit vectors between the atoms, for the four most common types of internal coordinates (see Fig. 1).[11] The unit vector directed from atom β toward atom α is written $\mathbf{e}_{\beta\alpha}$.

Bond stretching. $\Delta S_{i\alpha} = \Delta r_{\beta\alpha}$, the extension of the distance between atoms β and α,

$$\mathbf{s}_r = \mathbf{e}_{\beta\alpha}. \qquad (21)$$

Valence angle bending. $\Delta S_{i\alpha} = \Delta\phi_{\alpha\beta\gamma}$, the displace-

ment of the angle between the $\alpha-\beta$ and $\beta-\gamma$ bonds,

$$\mathbf{s}_\phi = (\cos\phi_{\alpha\beta\gamma}\mathbf{e}_{\beta\alpha} - \mathbf{e}_{\beta\gamma})(r_{\beta\alpha}\sin\phi_{\alpha\beta\gamma})^{-1}. \qquad (22)$$

Angle between a bond and a plane defined by two bonds. $\Delta S_{i\alpha} = \Delta\theta$, where θ is the angle formed by the bond $\beta\alpha$ and the plane of the three atoms $\beta\gamma\delta$ (If the four atoms are coplanar, $\theta = 0$),

$$\mathbf{s}_\theta = [(\mathbf{e}_{\beta\gamma} \times \mathbf{e}_{\beta\delta})(\sin\phi_{\gamma\delta\beta})^{-1} - (\sin\theta\mathbf{e}_{\beta\alpha})](r_{\beta\alpha}\cos\theta)^{-1}. \qquad (23)$$

Torsion. $\Delta S_{i\alpha} = \Delta\tau$, where $-\pi < \tau < \pi$ is the angle between the two dihedral planes formed by the atoms $\alpha\beta\gamma$ and $\beta\gamma\delta$, respectively, when atoms α to δ are bonded in sequence,

$$\mathbf{s}_\tau = (\mathbf{e}_{\beta\alpha} \times \mathbf{e}_{\beta\gamma})(r_{\beta\alpha}\sin^2\phi_{\gamma\beta\alpha})^{-1}. \qquad (24)$$

Table I gives formulas for the types of Jacobian factors which occur most often in practice. These and others may be readily derived from Eqs. (20)–(24) by straightforward vector algebra. The results for the simpler cases are easily visualized and can also be obtained by more elementary methods. For example, J_s for a linear molecule is made up of the factors for a diatomic molecule, $J_1 J_2 = V4\pi r^2$, times a factor of $(\mathbf{s}_r \times \mathbf{s}_\phi \cdot \mathbf{s}_{\phi'})^{-1} = r^2$ for each successive link. Similarly, for a zigzag chain one has the factors for a triatomic molecule times a factor of $(\mathbf{s}_r \times \mathbf{s}_\phi \cdot \mathbf{s}_r)^{-1} = r^2 \sin\phi$ for each new link. When branched configurations and rings are considered, several possibilities arise. If a "branching atom" is added to form a pyramidal configuration, one would usually choose the bond stretch r and two interbond bends ϕ, ϕ' to locate the branching atom (denoted by $\alpha = 4$ in Table I) relative to its three neighbors ($\beta = 2$, $\gamma = 3$, $\delta = 1$); then

$$J_\alpha = (\mathbf{s}_r \times \mathbf{s}_\phi \cdot \mathbf{s}_{\phi'})^{-1}$$

$$= (r_{\beta\alpha}^2 \sin\phi_{\alpha\beta\gamma} \sin\phi_{\alpha\beta\delta})/(\mathbf{e}_{\beta\alpha} \times \mathbf{e}_{\beta\gamma} \cdot \mathbf{e}_{\beta\delta}), \qquad (25)$$

where $(\mathbf{e}_{\beta\alpha} \times \mathbf{e}_{\beta\gamma} \cdot \mathbf{e}_{\beta\delta})$ is the volume of the parallelepiped formed by the three unit vectors along the bonds. This quantity, which appears in the J_α factors for several types of coordinates and configurations, can be expressed in terms of angles (see Fig. 1),

$$(\mathbf{e}_{\beta\alpha} \times \mathbf{e}_{\beta\gamma} \cdot \mathbf{e}_{\beta\delta}) = S\psi_{\gamma\alpha\delta}S\phi_{\alpha\beta\gamma}S\phi_{\alpha\beta\gamma} \qquad (26a)$$

$$= [1 - (C^2\phi_{\alpha\beta\gamma} + C^2\phi_{\alpha\beta\delta} + C^2\phi_{\gamma\beta\delta}) + 2C\phi_{\alpha\beta\gamma}C\phi_{\alpha\beta\delta}C\phi_{\gamma\beta\delta}]^{\frac{1}{2}} \qquad (26b)$$

where $\psi_{\gamma\alpha\delta}$ is the dihedral angle between the $\alpha\beta\gamma$ and $\alpha\beta\delta$ planes, and here S and C denote sine and cosine, respectively. If one wished to employ a central force field rather than a valence force field, one would use instead the distances $r_{\beta\alpha}$, $r_{\gamma\alpha}$, $r_{\delta\alpha}$ and the corresponding formula for $J_\alpha = (\mathbf{s}_r \times \mathbf{s}_{r'} \cdot \mathbf{s}_{r''})^{-1}$ as given in Table I. For an atom belonging to a branched group of four coplanar atoms, the usual choice of coordinates would be the bond stretch r, the out-of-plane bend θ, and one of the interbond bends, ϕ (both cannot be used in the

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[10] For vector and matrix algebra, see reference 8, pp. 132–146; 287–316.

[11] These formulas are derived in reference 6, pp. 54–61. The other **s** vectors given in reference 6 for these coordinates are not needed in the present application, as they would appear in the nondiagonal blocks of the original $3N \times 3N$ Jacobian. Also we may ignore the signs of the **s** vectors, and take them in any order in Eq. (20), as always $J_\alpha > 0$.

planar case since they are redundant). One then has $J_\alpha = (\mathbf{s}_r \times \mathbf{s}_\phi \cdot \mathbf{s}_\theta)^{-1} = r_{\beta\alpha}{}^2$. If the coplanar atoms formed a ring, however, one might use two stretches and the out-of-plane bend, for which $J_\alpha = (\mathbf{s}_r \times \mathbf{s}_{r'} \cdot \mathbf{s}_\theta)^{-1} = r_{\beta\alpha}/\sin\phi_{\gamma\alpha\delta}$. (The more general formulas given in Table I for these two examples also hold for nonplanar configurations.)

The configurations considered in Table I for the fourth atom ($\alpha = 4$) include all the common ones encountered with five or more atoms.[12] The table is therefore sufficient to treat a large class of molecules; one only needs to form the appropriate product of the J_α factors.

Redundancies will frequently occur for branched or ring configurations. This causes no difficulty in evaluating the J_α factors: if one tried to use redundant coordinates, the triple scalar product of the $\mathbf{s}$ vectors would vanish. However, a particular choice among the alternative sets of nonredundant coordinates must be made, and one must be careful to express the potential energy in these same coordinates when evaluating the $|F_S|$ determinant.[13] A typical example arises when a second branching atom (atom 5) is added to the pyramidal configuration discussed above. This gives a configuration in which four bonds stem from a common atom, as in methane derivatives. The portion of J_S involving these five atoms would comprise three factors, $J_1 J_2 J_3$, for the atoms bonded in sequence and two factors, $J_4 J_5$, for the branching atoms. J_4 and J_5 each have the form of Eq. (25). However, there are three interbond angles relating atom 5 to the preceding atoms, and the dihedral angle which enters J_5 via Eq. (26b) will differ according to which two interbond angles are used: $\psi_{153} \leftrightarrow \phi_{125}$, ϕ_{325}; $\psi_{354} \leftrightarrow \phi_{325}$, ϕ_{425}; and $\psi_{451} \leftrightarrow \phi_{425}$, ϕ_{125}. The usual practice in defining the force constants is to include all the redundant coordinates in the potential energy, as it is convenient to treat similar coordinates on the same basis. Proper allowance must be made for this if we wish to use such force constants. For example, Herzberg's valence force field for methane involves four C—H stretches and all six of the H—C—H bends, which appear with the force constants k_r and k_ϕ, respectively.[14] On eliminating one of the angles by use of the redundancy relation, we find the angular part of the potential energy has five diagonal terms, each with force constant $2k_\phi$, and ten pairs of nondiagonal terms, each member of a pair with force constant k_ϕ. The value of the $|F_S|$ determinant is then found to be $6k_r{}^4k_\phi{}^5$. The factor corresponding to 6 here is $b(b-1)/2$, in the more general case of the redundancy among the angles between b bonds which radiate from a common atom.

In deriving Eq. (14) and in writing down the factors

J_S we have found it most convenient to proceed atom by atom, referring the positions of the successive atoms to those of previous atoms, as in the examples above, but it should be emphasized that the results are not restricted to coordinates defined in this serial fashion. Let us represent this set of internal coordinates by a column matrix $\mathbf{S}$, and introduce after Eq. (18) a linear transformation to some new set of coordinates, $\mathbf{S}' = \mathbf{A}^{-1}\mathbf{S}$, where $\mathbf{A}$ is the matrix of the transformation. Then the corresponding Jacobian is given by $J_{S'} = |A| J_S$ and the force constant determinant by $|F_{S'}| = |A|^2 |F_S|$. Since the determinant of the new transformation cancels out of the configurational integral of Eq. (15a), either set of coordinates gives the same result; we need only maintain consistency between our calculations of the Jacobian and the force constant determinant. In some problems it will be convenient to rewrite Eq. (15a) as

$$Z = \frac{(2\pi kT)^{\frac{1}{2}(3N-6)}}{|F_{S'}|^{\frac{1}{2}}} |A| \prod_{\alpha=1}^{N} J_\alpha, \qquad (15c)$$

that is, to retain the serial coordinates $\mathbf{S}$ in calculating J_S and use more general coordinates $\mathbf{S}'$ in calculating the vibrational amplitudes, which may now refer to various linear combinations of geometrical coordinates rather than to individual atoms. For example, it is often convenient to express the potential energy in terms of symmetry coordinates,[15] which give the maximum possible factorization of the force constant matrix and are particularly useful when redundancies are to be eliminated. For symmetry coordinates, $|A| = 1$, as they are defined by a unitary transformation.

INTERNAL ROTATIONS

For a molecule having r internal rotational or torsional degrees of freedom, the usual treatment[16] replaces r of the u_i^{-1} factors in Eq. (10) and (11) by

$$(2\pi kT/h^2)^{r/2} |I_r|^{\frac{1}{2}} \int_0^{2\pi/n_1} \cdots \int_0^{2\pi/n_1}$$
$$\cdot \exp(-U_{ir}/kT) d\tau_1 \cdots d\tau_r. \quad (27)$$

Here the coupling of internal rotation with the vibrations and with over-all rotations is neglected; $|I_r|$ is an $r \times r$ determinant containing the reduced moments of inertia for internal rotations; and the torsional potential energy is usually approximated by a sum of terms of the form $\frac{1}{2}V_i(1-\cos n_i\tau_i)$. Since in Eq. (27) the mass dependent quantities are separate from those involving the potential energy, just as in Eq. (12), the contribution of internal rotations in our treatment is readily derived by the same method followed for ordinary vibrations.

[12] J. C. Decius, J. Chem. Phys. **17**, 1315 (1949).

[13] Methods for the elimination of redundant coordinates are discussed in reference 6, pp. 140–145. The coordinates used must also be kinematically complete (see reference 12).

[14] Reference 5, pp. 181–182.

[15] Reference 6, pp. 113–140.

[16] (a) K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. **10**, 428 (1942); (b) K. S. Pitzer, *Quantum Chemistry* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1953), pp. 239–243; 482–487; 492–500; (c) J. C. M. Li and K. S. Pitzer, J. Phys. Chem. **60**, 466 (1956).

TABLE II. Quantum corrections.[a]

u	Q_q/Q_c	$(S_q-S_c)/R$	$(F_q-F_c)/RT$	$(H_q-H_c)/RT$
0.00	1.0000	0.0000	0.0000	0.0000
0.50	0.9897	0.0105	0.0103	0.0208
1.00	0.9595	0.0407	0.0413	0.0820
1.50	0.9120	0.0888	0.0920	0.1808
2.00	0.8508	0.1515	0.1615	0.3130
2.50	0.7804	0.2255	0.2481	0.4736
3.00	0.7045	0.3069	0.3503	0.6572
3.50	0.6273	0.3925	0.4665	0.8590
4.00	0.5512	0.4794	0.5952	1.0746
4.50	0.4801	0.5659	0.7347	1.3006
5.00	0.4030	0.6501	0.8838	1.5339
5.50	0.3535	0.7314	1.0412	1.7726
6.00	0.2895	0.8092	1.2057	2.0149
6.50	0.2525	0.8831	1.3767	2.2598
7.00	0.1996	0.9532	1.5532	2.5064
7.50	0.1765	1.0196	1.7346	2.7542
8.00	0.1466	1.0825	1.9202	3.0027
8.50	0.1213	1.1420	2.1097	3.2517
9.00	0.1000	1.1985	2.3026	3.5011
9.50	0.0822	1.2521	2.4986	3.7507
10.00	0.0674	1.3031	2.6974	4.0005
10.50	0.0551	1.3517	2.8986	4.2503
11.00	0.0450	1.3981	3.1021	4.5002
11.50	0.0366	1.4425	3.3076	4.7501
12.00	0.0297	1.4849	3.5152	5.0001
12.50	0.0241	1.5258	3.7242	5.2500
13.00	0.0195	1.5649	3.9351	5.5000
13.50	0.0158	1.6027	4.1473	5.7500
14.00	0.0128	1.6391	4.3609	6.0000
14.50	0.0103	1.6742	4.5758	6.2500
15.00	0.0083	1.7080	4.7920	6.5000

[a] Definitions:

$Q_q/Q_c = \Gamma(u) = (u/2)/\sinh(u/2) = (C_p/R)_{ho}^{\frac{1}{2}}$

$(S_q-S_c)/R = ue^{-u}(1-e^{-u})^{-1} - \ln(1-e^{-u}) - \ln(e/u)$

$(F_q-F_c)/RT = -\ln(Q_q/Q_c) = \ln(1-e^{-u}) + (u/2) - \ln u$

$(H_q-H_c)/RT = ue^{-u}(1-e^{-u})^{-1} + (u/2) - 1$.

The result is to modify the vibrational amplitude factor in Eq. (15) as follows: r rows and columns are omitted in the $|F_s|$ determinant, and r factors of $(2\pi kT)^{\frac{1}{2}}$ are likewise omitted; these are replaced by the integral in Eq. (27). The factors before the integral do not appear in this treatment, as they have been absorbed into the de Broglie wavelengths of Eq. (3) and the Jacobian factors. The Jacobian factor remains the same as for ordinary vibrations. One introduces a torsional angle to locate the first atom of each internal rotor group, and makes use of the s_r vector of Eq. (24).

If the interactions between the internal rotor groups can be neglected, the integral in Eq. (27) breaks up into factors each of the form

$$\ell_r = \int_0^{2\pi/n} \exp[-\tfrac{1}{2}V(1-\cos n\tau)/kT]d\tau$$

$$= (2\pi/n)\exp[-(F-F_f)/RT], \quad (28)$$

where the quantity $(F-F_f)/T$ refers to the increase in free energy from the free rotor case and has been tabulated as a function of V/RT by Pitzer and Gwinn.[16] The value appropriate to Eq. (28) is found in the column labeled $1/Q_f=0$, which represents the classical limit. If the potential barrier is very large, the harmonic

oscillator approximation obtains, with

$$\tfrac{1}{2}F_\tau\tau^2 = \tfrac{1}{4}n^2V\tau^2,$$

and the right hand side of Eq. (28) becomes

$$(2\pi kT/F_\tau)^{\frac{1}{2}} = (2\pi/n)(RT/V\pi)^{\frac{1}{2}}. \quad (29)$$

This approximation holds to 2% or better when $V/RT>16$, and to 10% when $V/RT>4$.

Equation (28) will usually not be sufficient for molecules with compound rotations involving rotating groups attached to rotating groups. For some groups the effective potential barrier may change significantly for different conformations of the molecule, as the amount of steric interference between groups will vary. A correction for these effects may be made[1] by inserting a steric factor, $\sum_c \exp(-E_c/RT)$, where the sum is over all the molecular conformations, each of which is assigned an extra interaction energy E_c.

QUANTUM CORRECTIONS

The classical expression for a volume element V_α is not valid whenever any of its dimensions become comparable to or less than Λ_α, the de Broglie wavelength of the atom. At ordinary temperatures, the volumes associated with over-all transitions and rotations are sufficiently large to make these degrees of freedom effectively classical, but in most molecules the vibrational amplitudes of some atoms will be considerably less than their de Broglie wavelength. To correct the classical partition function, as indicated in Eq. (2), one has only to multiply by the ratio of the quantum to the classical harmonic oscillator partition functions,

$$Q_q/Q_c = \prod_{i=1}^{3N-6} \Gamma(u_i),$$

where

$$\Gamma(u) = u\exp(-u/2)(1-e^{-u})^{-1}. \quad (30)$$

This ratio and the corresponding corrections to the thermodynamic properties may be readily evaluated from extensive tabulations of the harmonic oscillator functions.[1c, 16b] A small table adequate for most applications is given as Table II. The factor Γ_i to be supplied for each vibrational frequency is less than unity.[17] To a first approximation, $\Gamma_i = 1-(u_i^2/24)$; thus for $u_i < 1.5$ ($\nu_i < 330$ cm^{-1} at room temperature or in general $\nu_i < 1.1T$), the error in the classical partition function is not more than 10%, which corresponds to an error in the entropy of only 0.2 cal deg^{-1} mole^{-1} or less.

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[17] Since the factors $\exp(-u_i/2)$ have been included in Eq. (29), the energy zero for the partition function is the minimum of the potential energy surface for the molecule. These factors would be omitted under the alternative convention in which the lowest real quantum state is taken as the energy zero; the corresponding quantum correction factors, $u_i/[1-\exp(-u_i)]$, would then be greater than unity. Cf. reference 3, page 217. It may be noted that the $G(u)$ function tabulated by J. Bigeleisen and M. G. Mayer, J. Chem. Phys. **15**, 261 (1947) and J. Bigeleisen, ibid. **21**, 1333 (1953) is the derivative with respect to u of $(F_q-F_c)/RT$.

Pitzer and Gwinn have shown that the harmonic oscillator function, Eq. (30), provides a good approximation to the correction factor for internal rotations.[18] In many cases the torsional frequencies, even for methyl groups, are low enough to be effective classical.

EQUILIBRIUM CONSTANT AND THERMODYNAMIC PROPERTIES

Our results may now be summarized in terms of the thermodynamic functions. The usual statistical thermodynamic formulas[5] and Eq. (2) and (3) give the equilibrium constant as

$$\ln K_p = -\Delta F/RT$$

$$= -\Delta E_0/RT + \Delta \ln[(Q_e/\sigma)(Q_q/Q_c)(Z/N_0)], \quad (31)$$

where Δ denotes the sum over the product molecules minus that over the reactants; the de Broglie wavelengths Λ_α of Eq. (4) cancel in taking this difference. Since the configurational integral Z for each molecule, as evaluated in Eqs. (15) and (28), can be broken up into a product of volume elements (expressed in terms of vibrational amplitudes, Jacobian factors, and the quantum corrections), the equilibrium constant is proportional to

$$\Pi \frac{V_\alpha(\text{products})}{V_\alpha(\text{reactants})},$$

the ratio of the product over all the atoms of the effective volumes available to them in the product and reactant molecules. In most cases the only volume elements that do not cancel to a practical approximation are those for the atoms in the vicinity of the reaction site. Thus the important factors, in particular the large volume changes associated with transforming vibrational degrees of freedom into rotational and translational ones, are readily visualized and written down with the aid of Tables I–III.

The Gibbs free energy, for one mole of ideal gas, is given by

$$F = E_0 - RT \ln(Q/N_0)$$

$$= E_0 + F_e + F_\sigma + F_K + F_U + \sum_{i=1}^{3N-6}(F_q - F_c)_i, \quad (32)$$

where $F_e = -RT \ln Q_e$ and $F_\sigma = RT \ln \sigma$ are the usual terms arising from electronic multiplicity and from molecular symmetry, and

$$F_K = 3RT \sum_{\alpha=1}^{N} \ln \Lambda_\alpha$$

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[18] This could also be obtained by using in Eq. (28) the tabulated value[16] of $(F-F_f)/T$ at the proper value of $1/Q_f$, and multiplying by $\exp(-u/2)$ to conform with our convention.[17] This method would usually be less convenient than Eq. (30), since it requires one to calculate Q_f, which involves a reduced moment of inertia.

TABLE III. Numerical formulas.[a]

$\Lambda = (h^2/2\pi mkT)^{\frac{1}{2}} = 17.457\,(mT)^{-\frac{1}{2}}$	A
$\ell = (2\pi kT/F)^{\frac{1}{2}} = 0.009\,312\,6\,(T/F)^{\frac{1}{2}}$	A
$u = h\nu/kT = 1.4387\,(\nu/T)$	
$V/N_0 = RT/N_0P = 136.22\,(T/P)$	A³
$kT/h = (2.0828 \times 10^{10})\,T$	sec⁻¹

[a] The physical constants quoted in reference 16b, page 521, were used. The units are: T, °K; P, atmos.; m, g mole⁻¹; ν, cm⁻¹; stretching force constant, 10⁵ dynes/cm; bending force constant, 10⁻¹¹ erg/radian². To be consistent with these formulas, the lengths which enter the J_α factors of Table I and Eq. (15) are to be expressed in angstrom units.

and

$$F_U = -RT \ln(Z/N_0)$$

$$= -RT\left[\sum_{i=1}^{3N-6} \ln \ell_i - \ln w + \ln(V/N_0) + \sum_{\alpha=2}^{N} \ln J_\alpha\right]$$

are the contributions from the classical kinetic and potential energy phase integrals of Eq. (3). Alternative ways of expressing the vibrational amplitudes ℓ_i in terms of the force constants are given in Eq. (15a-c); for internal rotations, ℓ_r is given by Eq. (28). The $J_1 = V$ factor has been combined with the division by Avogadro's number: $V/N_0 = RT/N_0P$ is the volume per molecule at pressure P. In the units of Table III,

$$-(F_K + F_U)/RT = (3N-2)\ln T + \frac{3}{2}\sum_{\alpha=1}^{N} \ln m_\alpha$$

$$-\frac{1}{2}\ln|F_S| - \ln P + \sum_{\alpha=2}^{N} \ln J_\alpha - 22.6084N + 32.9726. \quad (33)$$

The entropy is given by

$$S = R + R \ln(Q/N_0) + RT(\partial \ln Q/\partial T)$$

$$= R + S_e + S_\sigma + S_K + S_U + \sum_{i=1}^{3N-6}(S_q - S_c)_i, \quad (34)$$

where

$$S_K = -3R \sum_{\alpha=1}^{N} \ln \Lambda_\alpha + \frac{3}{2}(NR)$$

and

$$S_U = R \ln(Z/N_0) + \frac{1}{2}(3N-6)R$$

so that $(S_K + S_U)/R$ is given by the right hand side of Eq. (33) plus $\frac{1}{2}(6N-6)$.

To treat internal rotations, the tables prepared by Pitzer and Gwinn[16] may be used if Eq. (33) is modified as follows: For each internal rotational degree of freedom, one omits a row and column in $|F_S|$ and a $\frac{1}{2}\ln T$ term and replaces them by

$$-\ln n - (F-F_f)/RT + 6.5143$$

when calculating the free energy, or by

$$-\ln n - (S-S_f)/R + 6.0143$$

when calculating the entropy.

As written, Eq. (33) applies to a nonlinear molecule of N atoms. For a linear molecule, the presence of $(3N-5)$ vibrations requires that the coefficient of $\ln T$ be changed to $3N-\frac{3}{2}$ and the constant term replaced by 28.2962; to obtain $(S_K+S_U)/R$ one adds $\frac{1}{2}(6N-5)$.

The expressions for the enthalpy and the heat capacity functions are the same in the present treatment and in the usual one, since $\partial \ln Q/\partial T$ is the same. Because of our choice of the energy zero,[17] it is necessary to add $\frac{1}{2}RT\sum u_i$ to the enthalpy formula given in reference 5, which then may be written as

$$H = E_0 + RT + RT^2(\partial \ln Q/\partial T)$$
$$= E_0 + 4RT + (3N-6)RT + \sum_{i=1}^{3N-6}(H_q-H_c)_i. \quad (35)$$

The classical configurational integral for an ideal gas molecule is unchanged by isotopic substitution, to a very good approximation. Therefore when Eq. (31–35) are applied to equilibrium isotope effects, all terms cancel except the quantum corrections and the symmetry numbers. When Eq. (38–40) are applied to kinetic isotope effects, the only additional quantities which contribute are the transmission coefficient κ and the "effective mass" m^* associated with the reaction coordinate. The resulting formulas for isotope effects thus reduce immediately to those obtained by Bigeleisen.[19,20]

REACTION COORDINATES AND RATE CONSTANTS

For the "activated complex" of transition state theory,[21] one of the vibrational factors u_i^{-1} in Eq. (10) and (11) is replaced by the factor

$$(2\pi m^*kT/h^2)^{\frac{1}{2}}\delta = \delta/\Lambda^* \quad (36)$$

which arises from the assumptions that, in a region of length δ at the top of the energy barrier, the motion in the reaction coordinate is separable from the other internal degrees of freedom, and corresponds to a free translation of the reduced mass, m^*. After multiplying by the average rate of crossing the barrier,

$$\kappa(kT/2\pi m^*)^{\frac{1}{2}}/\delta = \kappa(kT/h)(\Lambda^*/\delta), \quad (37)$$

one obtains the familiar formula for the rate constant,

$$k = \kappa(kT/h)K^{\ddagger}, \quad (38)$$

where κ is the transmission coefficient and $K^{\ddagger}$ is the quasi-equilibrium constant for formation of the activated complex. The cancellation of (δ/Λ^*) which occurs between Eq. (36) and (37) leads to Eyring's prescription: the partition function for the activated complex that enters $K^{\ddagger}$ is to be calculated with the omission of any reference to the reaction coordinate.

These steps have been reviewed in order to contrast them with the present treatment, in which the result is formally somewhat different. As a consequence of Eq. (36), we find that one of the vibrational amplitudes in Eq. (15) is replaced by δ; the mass dependent quantity $1/\Lambda^*$ does not appear here since it has been absorbed into the de Broglie wavelengths of Eq. (3) and the Jacobian factors. [Compare the discussion under Eq. (27).] Therefore when we multiply by the factor, Eq. (37), the length δ cancels but Λ^* does not. The final result is that we may again write the rate constant in the form of Eq. (38), where $K^{\ddagger}$ is given by Eq. (31). Now, however, in Eq. (31–34) the configurational integral for the activated complex, $Z^{\ddagger}$, has the wavelength Λ^* in place of the vibrational amplitude which would have appeared if the reaction coordinate were an ordinary vibration. To obtain $S^{\ddagger}$ and $H^{\ddagger}$ one has also to subtract R and RT, respectively, from Eq. (34) and (35), since this Λ^* factor contributes to

$$(T\partial \ln Q^{\ddagger}/\partial T),$$

$a-\frac{1}{2}$ rather than the $+\frac{1}{2}$ given by a vibrational amplitude. Thus, if $Z^{\ddagger}$ is written as $\Lambda^* Z_{\ddagger}$, then $S^{\ddagger}$ maybe obtained from Eq. (34) with

$$S_U^{\ddagger} = R \ln\Lambda^* - \frac{1}{2}R + R \ln(Z_{\ddagger}/N_0) + \frac{1}{2}(3N-7)R. \quad (39)$$

The effective mass m^* that enters Λ^* may be calculated in terms of the F and G matrix elements of the activated complex by the general method described by Johnston, Bonner, and Wilson.[22] The quantum correction which is required if there is substantial negative curvature along the reaction coordinate has recently been reexamined by Bell.[23] For a parabolic barrier with

$u^* < 2\pi$, he obtains

$$(Q_q/Q_c)^* = (u^*/2)/\sin(u^*/2),$$

where $u^* = h\nu^*/kT = \Lambda^*/(2\pi kT/F^*)^{\frac{1}{2}}$; ν^* is the absolute value of the imaginary frequency associated with the reaction coordinate and $-F^*$ is the negative curvature.

The parameters in the Arrhenius equation, $k=$

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[19] See J. Bigeleisen and M. Wolfsberg in *Advances in Chemical Physics*, I. Prigogine, editor (Interscience Publishers, Inc., New York, 1958), Vol. I, pp. 15–76, and references cited therein.

[20] As pointed out by Bigeleisen [*Proceedings of the Amsterdam Symposium on Isotope Separation* (North-Holland Publishing Company, 1958), pp. 122–23], if the comparison indicated in Eq. (11) is made for two isotopic molecules, one obtains a proof of the Teller–Redlich product rule (see reference 6, pp. 182–186) relating the vibrational frequencies of isotopic molecules.

[21] Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

[22] Johnston, Bonner, and Wilson, J. Chem. Phys. **26**, 1002 (1957). The parameter λ in this paper equals $(2\pi\nu^*)^2 = F^*/m^*$. See also refernces 2 and 19.

[23] R. P. Bell, Trans. Faraday Soc. **55**, 1 (1959). For small u^*, Bell's formula reduces to the $1+(u^{*2}/24)$ correction obtained by Wigner.[21]

$A \exp(-E_{act}/RT)$, are given by

$$E_{act} = \Delta H^{\ddagger} + (1+x) RT$$

$$\log A = \log \kappa + 10.7524 + 2.3484x + (1+x) \log T$$

$$+ 0.4343(\Delta S^{\ddagger}/R), \quad (40)$$

where k and A are in the customary units of $\sec^{-1}$ cc^x $mole^{-x}$, $(1+x)$ is the molecularity of the reaction, and the entropy of activation $\Delta S^{\ddagger}$ refers to a standard state of 1 atm. A number of terms cancel exactly from $\Delta S^{\ddagger}$, including all terms in m_α and N, and in particular $\Delta S_K^{\ddagger} = 0$. Furthermore, it is usually a satisfactory approximation to cancel all vibrational amplitudes and Jacobian factors [and to neglect the contributions from the off-diagonal force constants of Eq. (16)], except for the atoms and bonds directly involved in the reaction coordinate. Many of the quantum corrections likewise cancel. In any case they are significant only for high-frequency vibrations, whereas, in typical examples, most of the new vibrations which appear as the activated complex is formed are low-frequency modes arising from rotations and translations of the reactants. These cancellations reduce to a minimum the number of force constants and structural parameters that need to be estimated for the activated complex.