The Rotation and Vibration of Linear Triatomic Molecules

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(k, f, e); 874 (2) (k, e); 930 (4) (k, i, e); 998 (0) (k); 1059 $(\frac{1}{2})$ (k, e); 1245 (1vb) (k, e); 1420 (5b) (k, i, e); 1724 (6b) (e); 2938 (6b) (k, i, e).

21. *Trisodium tricarballylate*, $Na_3^{+++}[C_3H_5(COO)_3]^{---}$. Solution containing 45 percent Eastman tricarballylic acid and three equivalents NaOH. pH 7.6±0.2 to phenol red. $\Delta\nu$: 327 ($\frac{1}{2}$) (e); 428 (2b) (e); 802 (1b) (k, e); 883 (4) (k, e); 948 (5b) (k, e); 1009 (2) (k, e); 1050 (1) (k, e); 1105 (1) (k, e); 1164 (1) (k, e); 1207 (1) (k, e); 1333 (3b) (k, e); 1419 (8b) (k, i, e); 1571 (1b) (k, e); 2934 (9vb) (k, i, e).

22. *Citric acid*, $C_3H_4(OH)(COOH)_3$, (Merck). 50 percent solution in water, with 0.4 N HCl. $\Delta\nu$: 253 (1b) (e); 396 (3b) (e); 525 (1b) (e); 605 (1b) (e); 723 (1) (k, e); 800 (5) (k, i, f, e); 903 (1) (k, e); 939 (6) (k, e); 1056 (3) (k, e);

1130 (1b) (k, e); 1200 (1) (k, e); 1403 (3) (k, e); 1438 (2) (k, e); 1731 (6b) (e); 2948 (6) (k, i, e); 3001 (1) (k).

23. *Trisodium citrate*, $Na_3^{+++}[C_3H_4(OH)(COO)_3]^{---}$. Solution containing 30 percent Merck's citric acid in water, with 3 equivalents NaOH. pH 7.4−7.6 by phenol red. $\Delta\nu$: 233 ($\frac{1}{2}$) (e); 317 (0) (e); 409 (1b) (e); 583 ($\frac{1}{2}vb$) (e); 845 (4) (k, e); 956 (5) (k, i, f, e); 1045 (1b) (e); 1100 (1b) (k, e); 1210 ($\frac{1}{2}$) (e); 1302 (0) (e); 1415 (8b) (k, i, e); 1580 ($\frac{1}{2}b$) (e); 2929 (5) (k, e); 2982 (1) (k).

Polarization Studies: Examination by the technique previously described[3] showed the following lines to be strongly polarized ($\rho \ll 6/7$) malonic acid: 590, 773, 919, 1738. Disodium malonate: 590, 828, 935, 1361(?), 1439. Dipotassium oxalate: 902, 1457, 1489.

The Rotation and Vibration of Linear Triatomic Molecules

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The rotation and vibration of a linear molecule cannot be treated by the method of rotating axes if it contains more than three atoms. The definition of the axes for the triatomic case may be based on the fact that the three atoms always determine a plane. The relation of this definition to that for the nonlinear molecules is discussed, and the appropriate normal coordinates are introduced. The wave equation of the problem is derived and its approximate solution is discussed. The fact that the Eulerian angles do not enter into the zero- and first-order terms of the Hamiltonian makes it possible to calculate some of the second order terms of the expression for the energy values with complete generality. These are the terms that arise from the rotation and from the coupling between the rotation and vibration. They are found to be

$$\hbar^2[J(J+1)-l^2]/2A+C,$$

where A is the value of the moment of inertia at equilibrium, and

$$C = [\hbar^2(V_2+1)/2A]\{s^2(V_1+\tfrac{1}{2})[(\omega_1/\omega_2)+(\omega_2/\omega_1)] + c^2(V_3+\tfrac{1}{2})[(\omega_3/\omega_2)+(\omega_2/\omega_3)]\} - \hbar^2/2A.$$

In this expression, the V's are the vibrational quantum numbers and the ω's are the natural frequencies. The index 2 refers to the perpendicular vibration. The quantities c and s are determined by the potential energy function and are related by $c^2+s^2=1$. For symmetric molecules, $X-Y-X$, their values are $c=1$, $s=0$. If the natural frequencies are commensurable, the derivation ceases to be valid, but it appears likely that the result is essentially the same in this case.

INTRODUCTION

THE general theory of the interaction of the rotation and vibration of normal polyatomic molecules has been discussed by Eckart[1] and by Wilson and Howard.[2] They found it convenient to exclude linear molecules by their definition of normality. In an investigation preliminary to this one, it was found that the method developed by these authors cannot be extended, in general, to apply to linear molecules. More general schemes are needed, such as those

considered by Welker.[3] These methods are also applicable to other anomalous molecules, such as ethane.

However, the method of rotating axes can still be used for the particular case of a triatomic linear molecule. The definition of the axes is then essentially that used by Dennison.[4] In the first part of this paper, it will be shown how this definition is related to that given in references 1 and 2 for the nonlinear molecules. The Hamiltonian will be derived in the second part and in the third, the solution of the wave equation and calculation of the energy values will be discussed. In the concluding part, this calcu-

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* The first and second parts of this paper are based on a master's thesis entitled "The Quantum Mechanical Hamiltonian for Triatomic Linear Symmetric Molecules" submitted to the University of Chicago by A. W.

[1] C. Eckart, Phys. Rev. **47**, 552 (1935).

[2] E. B. Wilson, Jr., and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).

[3] H. Welker, Zeits. f. Physik **101**, 95 (1936).

[4] D. M. Dennison, Rev. Mod. Phys. **3**, 292 (1931).

lation will be compared with that made by Adel and Dennison[5] for the CO_2 molecule.

THE MOVING AXES

In order to define a set of rotating axes, the position of its origin and the directions of its axes must be specified; six independent equations are needed to accomplish this. In the general case of a nonlinear molecule, the requirement that the origin be at the centroid of the molecule furnishes three equations, and the remaining three are obtained from Casimir's condition.[6, 1, 2] This condition requires that the angular momentum of the molecule relative to the moving axes shall vanish as the equilibrium configuration is approached, regardless of the direction (in phase space) from which that approach is made. For a linear molecule, the three equations thus obtained are not independent. Additional independent and simple equations cannot be found in general, but for the triatomic molecule they are furnished by Dennison's requirement that the plane of the three atoms always coincide with one of the coordinate planes of the moving axes.

Using the notation of reference 1, let the rectangular coordinates of the ath atom relative to the moving system be y_{xa}, y_{ya}, y_{za}; in the present case, $a=1$, 2, 3. Let the equilibrium values of these coordinates be z_{ia}, and the normal coordinates be q_λ ($\lambda=1$, 2, 3). Then

$$y_{ia}=z_{ia}+\Sigma_\lambda q_\lambda z_{\lambda,ia} \qquad (1)$$

with $z_{\lambda,ia}$ independent of the q_λ. The equations defining the axes are to be expressed in terms of the y_{ia} and are not to involve the q_λ explicitly. However, they must be satisfied identically when the y_{ia} are eliminated by means of Eq. (1).

The requirement that the plane of the molecule is also the yz plane of the axes is

$$y_{xa}=0, \quad a=1, 2, 3. \qquad (2)$$

The equations fixing the origin at the centroid are (m_a mass of the ath atom)

$$\Sigma_a m_a y_{ia}=0, \qquad (3)$$

of which only two are independent of Eq. (2). The angular momentum relative to the moving axes will always be a vector parallel to the x axis (because of Eq. (2)) and hence Casimir's condition furnishes just one additional equation, bringing the total to six as required. This equation is

$$\lim_{y_{ia}\to z_{ia}} \{\Sigma_a m_a(y_{ya}\dot{y}_{za}-y_{za}\dot{y}_{ya})\}=0. \qquad (4)$$

The requirement that these equations be satisfied for all values of the q_λ and $\dot{q}_\lambda$ imposes certain restrictions on the constants z, but not enough to determine them uniquely. In other words, these equations define a class of moving coordinate systems, such that each is stationary relative to all others of the class. It is still possible to choose one member of the class at will. The requirement that the q_λ be normal coordinates also limits the values of the z's, but the choice may still be made so that at equilibrium, the z axis passes through each of the three atoms. It is usually supposed that the normal vibrations of a linear molecule are either of the ∥ or of the ⊥ type.[4] With this assumption, the selection just made reduces the Eq. (1) to the form

$$y_{ya}=Y_a q_2, \quad y_{za}=z_a+Z_a' q_1+Z_a'' q_2, \qquad (1.1)$$

where Y, Z', Z'' are constants replacing the $z_{\lambda,ia}$. The requirement that Eq. (3) be identically satisfied leads to

$$\begin{aligned} \Sigma_a m_a z_a = \Sigma_a m_a Y_a = \\ \Sigma_a m_a Z_a' = \Sigma_a m_a Z_a'' = 0 \end{aligned} \qquad (3.1)$$

and Eq. (4) to

$$\Sigma_a m_a Y_a z_a=0. \qquad (4.1)$$

These equations determine Y_a as a function of z_a except for an arbitrary normalizing factor:

$$Y_1=(z_2-z_3)[m_2 m_3/m_1(m_1+m_2+m_3)]^{\frac{1}{2}}, \text{ etc. } (5.1)$$

The normalizing factor has been so chosen that

$$\Sigma_a m_a Y_a^2=\Sigma_a m_a z_a^2=A; \qquad (6)$$

A is thus the equilibrium value of the moment of inertia of the molecule. This choice makes the q_λ dimensionless; in quantum-mechanical prob-

[5] A. Adel and D. M. Dennison, Phys. Rev. 43, 716 (1933); 44, 99 (1933).
[6] H. B. G. Casimir, *The Rotation of a Rigid Body in Quantum Mechanics*, Chap. V. Dissertation, Leyden (1931).

lems they may be treated as small quantities of the order of magnitude $\epsilon = (\hbar/A\omega)^{\frac{1}{2}}$, ω being one of the natural frequencies. The constants Z_a' and Z_a'' are not completely determined, but the requirement that the q_λ be normal coordinates imposes the further conditions

$$\Sigma_a m_a Z_a'^2 = \Sigma_a m_a Z_a''^2 = A,$$
$$\Sigma_a m_a Z_a' Z_a'' = 0. \tag{7}$$

The Eqs. (3.1) and (7) are equivalent to

$$Z_a' = cz_a - s Y_a,$$
$$Z_a'' = sz_a + c Y_a, \tag{8}$$
$$c^2 + s^2 = 1,$$

so that only one constant is undetermined after the equilibrium configuration is given.

The Hamiltonian Operator

The determination of the classical Hamiltonian kinetic energy is now a straightforward algebraic calculation if the results of reference 1 are utilized. The first step is the calculation of the components of the moment of inertia tensor in the moving system. These are

$$A_{xx} = A_{yy} + A_{zz},$$
$$A_{yy} = A(f^2 + g^2),$$
$$A_{zz} = Aq_2^2, \tag{9}$$
$$A_{yz} = -Aq_2 f,$$
$$A_{xy} = A_{zz} = 0,$$

where $f = -sq_1 + cq_3$, $g = 1 + cq_1 + sq_3$.

The second step is the calculation of the angular momentum relative to the moving axes: the result is

$$\Lambda_x = \Sigma_a m_a (y_{ya} \dot{y}_{za} - y_{za} \dot{y}_{ya})$$
$$= A\{s(q_1 \dot{q}_2 - q_2 \dot{q}_1) + c(q_2 \dot{q}_3 - q_3 \dot{q}_2)\}, \tag{10}$$
$$\Lambda_y = \Lambda_z = 0.$$

The components of the total angular momentum of the molecule along the moving axes are (cf. Eq. (8), reference 1)

$$M_x = A_{xx}\Omega_x + \Lambda_x,$$
$$M_y = A_{yy}\Omega_y + A_{yz}\Omega_z, \tag{11}$$
$$M_z = A_{yz}\Omega_y + A_{zz}\Omega_z,$$

the Ω_i being the components of the angular velocity, again along the moving axes. The momenta conjugate to the q_λ are (cf. Eq. (11), reference 1)

$$p_\lambda = A\dot{q}_\lambda + \Omega_x(\partial \Lambda_x/\partial \dot{q}_\lambda). \tag{12}$$

The Eq. (11) and (12) are now to be solved for the Ω_i and $\dot{q}_\lambda$:

$$\Omega_x = [M_x - c\Lambda_1 - s\Lambda_3]/Ag^2,$$
$$\Omega_y = [M_y + fM_z q_2^{-1}]/Ag^2,$$
$$\Omega_z = M_z/Aq_2^2 + f\Omega_y/q_2;$$
$$\dot{q}_1 = p_1/A + sq_2\Omega_x, \tag{13}$$
$$\dot{q}_2 = p_2/A + f\Omega_x,$$
$$\dot{q}_3 = p_3/A - cq_2\Omega_x.$$

The following abbreviations have been used in Eq. (13):

$$\Lambda_1 = q_2 p_3 - p_2 q_3, \quad \Lambda_3 = q_1 p_2 - p_1 q_2. \tag{14}$$

The kinetic energy is then obtained by adding the products of the momenta with their corresponding velocities:

$$2AT = p_1^2 + p_2^2 + p_3^2 + M_z^2/q_2^2$$
$$+ [M_x - c\Lambda_1 - s\Lambda_3]^2/g^2 \tag{15}$$
$$+ [M_y + fM_z q_2^{-1}]^2/g^2.$$

It will be noted that the moments of inertia A_{xx} and A_{yy} do not appear in this equation.

The kinetic energy operator cannot be obtained from Eq. (15) by merely replacing the momenta by appropriate operators; if this were done, the result would not be a real operator. The appropriate additional factors are easily determined by the method of Wilson and Howard.[2] The resulting operator may be divided into two parts:

$$2AT_0 = g^{-2}p_1 g^2 p_1 + g^{-2}p_3 g^2 p_3$$
$$+ q_2^{-1}p_2 q_2 p_2 + M_z^2 q_2^{-2}, \tag{16}$$
and

$$2AT_2 = g^{-2}q_2^{-1}[M_x - c\Lambda_1 - s\Lambda_3]q_2[M_x - c\Lambda_1 - s\Lambda_3]$$
$$+ g^{-2}[M_y + fM_z q_2^{-1}]^2. \tag{17}$$

It is readily seen that the contribution of T_0 to the energy value is of the order of magnitude

$\hbar\omega$, while that of T_2 is of order $\epsilon^2\hbar\omega=\hbar^2/A$. There are no terms that make contributions of order $\epsilon\hbar\omega$, which is a direct consequence of Casimir's condition.

The potential energy, U, will depend only on the q_λ and will contain terms of every order of magnitude. The zero-order terms will be

$$U_0=(A/2)(\omega_1^2q_1^2+\omega_2^2q_2^2+\omega_3^2q_3^2)\,;\quad(18)$$

the appearance of the moment of inertia, A, in this expression is a purely formal consequence of the normalization of Eq. (6). The complete Hamiltonian operator is thus

$$H=(T_0+U_0)+U_1+(T_2+U_2)+\cdots,\quad(19)$$

the terms being bracketed according to order of magnitude.

In order to determine the characteristic values of this operator, it is necessary to consider the domain of the coordinates q_λ, and the conditions to be imposed on the wave function at the boundaries of that domain. Because of the small numerical value of ϵ in practical problems the wave function will have appreciable values only in a very small region in the interior of the domain, and it is easily seen that the characteristic values will not depend strongly on the boundary conditions. It is therefore desirable to transform the Hamiltonian in such a manner that the domain may be treated as infinite in all directions, and that the usual boundary conditions for such domains may be imposed. This end may be attained in three stages. The first is the contact transformation

$$H'=gHg^{-1}.\quad(20)$$

As is well known,[7] the characteristic values of H and H' are identical, provided that the boundary conditions for H' are suitably derived from those for H. This transformation eliminates g from T_0, but not from T_2. The second step is the replacement of g in T_2 by its Taylor expansion. The justification of this expansion is not obvious, but in view of the previous expansion of the potential energy, it is useless to consider its justification at this point. The final replacement of the correct domain and boundary

[7] Dirac, *Quantum Mechanics* (Oxford, 1935), p. 109; Condon and Morse, *Quantum Mechanics* (McGraw-Hill), pp. 59, 71.

conditions by the simpler ones will produce changes in the characteristic values, but these will presumably be negligible.

The kinetic energy operators as thus simplified are

$$2AT_0'=p_1^2+p_3^2+q_2^{-1}p_2q_2p_2+q_2^{-2}M_z^2,\quad(21)$$

$$2AT_2'$$
$$=g^{-1}q_2^{-1}[M_x-c\Lambda_1-s\Lambda_3]q_2[M_x-c\Lambda_1-s\Lambda_3]g^{-1}$$
$$+g^{-2}[M_y+fM_zq_2^{-1}]^2.\quad(22)$$

For many purposes, it is permissible to neglect terms of order $\epsilon^3\hbar\omega$ or smaller. Then g may be replaced by unity. This will be done for the remainder of this paper.

THE PERTURBATION CALCULATION

This Hamiltonian has certain characteristics that simplify some parts of the second order perturbation calculation. For convenience, let u always denote a function independent of the Eulerian angles α, β, γ, and v always denote a function of α, β only, independent of the other variables. Then, since the zero-order Hamiltonian depends only on M_z^2, on the q_λ, and on their momenta, the zero-order wave function will have the form

$$\psi_0=vu(N,l)\exp(\pm il\gamma),\quad(23)$$

where v and the sign of the exponent are undetermined. The determination of $u(N,l)$ and of the zero-order energy, W_0, has been discussed in detail by Dennison;[4] they are

$$W_0(N)=(V_1+\tfrac{1}{2})\hbar\omega_1+(V_2+1)\hbar\omega_2+(V_3+\tfrac{1}{2})\hbar\omega_3,$$
$$u(N,l)=\psi^{V_1}(q_1)\psi^{V_3}(q_3)R^{V_2,\ l}(q_2),\quad(24)$$

where ψ^V and $R^{V,\ l}$ are one- and two-dimensional Hermite functions, respectively. The three quantum numbers V_λ have been abbreviated as N; all the quantum numbers have integral values, and

$$l=V_2,\ V_2-2,\ V_2-4,\cdots\ 1\ \text{or}\ 0.\quad(25)$$

For the present, it will be supposed that ω_1, ω_2 and ω_3 are incommensurable numbers, so that accidental degeneracy may be avoided. Since the first-order terms of the Hamiltonian depend only on the q_λ, the function v will re-

main undetermined by the first-order calculation. The first-order wave function will be

$$\psi = [v_+ \exp (il\gamma) + v_- \exp (-il\gamma)]$$
$$\times [u(N, l) + \sum_{n \neq N} u(n, l)a(n)], \quad (26)$$

the constants $a(n)$ being given by the usual formula.

The second-order terms of the Hamiltonian involve all coordinates or their momenta; since some of these have not appeared in earlier terms, the usual linear secular equations will be replaced by differential equations determining the functions v_+ and v_-. These equations can be written most conveniently by first defining the four linear operators T_{++}, T_{+-}, etc.:

$$T_{\pm\pm}v = \int\int \{u(N, l)^* \exp (\mp il\gamma)$$

$$\times [T_2'u(N, l)v \exp (\pm il\gamma)]\} q_2 dq d\alpha. \quad (27)$$

The secular differential equations are then

$$T_{++}v_+ + T_{+-}v_- = W''v_+,$$
$$T_{-+}v_+ + T_{--}v_- = W''v_-, \quad (28)$$

and the second-order energy correction is

$$W_2 = W'' + \text{terms arising from } U_1 \text{ and } U_2.$$

On substituting the expression for T_2' from Eq. (22) into Eq. (27), it is found that many terms vanish because of the properties of the M operators, and without reference to the special form of $u(N, l)$. The result of the calculation is that

$$T_{+-} = T_{-+} = 0,$$
$$T_{++} = T_{--} = [(M_x^2 + M_y^2)/2A] + C, \quad (29)$$

where

$$C = \frac{\hbar^2 l^2}{2A} \int q_2^{-1} |(-sq_1 + cq_3)u(N, l)|^2 dq$$

$$+ (1/2A) \int q_2 |(c\Lambda_1 + s\Lambda_3)u(N, l)|^2 dq. \quad (30)$$

From Eq. (29) it follows that the $\pm$ degeneracy is not removed by the second-order perturbation. Since the characteristic values of $M_x^2 + M_y^2$ are

$\hbar^2[J(J+1) - l^2]$ with $J = l, l+1, \cdots$, the values of W'' can be written down at once. The functions $v_\pm$ are also immediately available: they are essentially the wave functions of the symmetric rotator.[4]

Using the explicit form of $u(N, l)$ (Eq. (24)) the quantity C can be evaluated. For this calculation it is convenient to use the relation

$$\int q_2\{(\partial R/\partial q_2)^2 + R^2 l^2/q_2^2\} dq_2 = A\omega_2(V_2 + 1)/\hbar,$$

which follows at once from the differential equation for R. The result is that

$$C = [\hbar^2(V_2 + 1)/2A]\{s^2(V_1 + \tfrac{1}{2})[(\omega_1/\omega_2) + (\omega_2/\omega_1)]$$
$$+ c^2(V_3 + \tfrac{1}{2})[(\omega_3/\omega_2) + (\omega_2/\omega_3)]\} - \hbar^2/2A. \quad (31)$$

The appearance of the ratios of the natural frequencies in this expression is in accord with expectation.[1] This part of the energy expression is determined by the lack of rigidity of the molecule, and in quantum theory, a small natural frequency implies a large amplitude of oscillation. This part of the energy expression should therefore become large when any one of the natural frequencies becomes small. Thus each frequency should appear as a denominator. Since dimensional arguments show that the frequencies can enter into the second-order energy only as ratios, the general form of Eq. (31) may be expected to be valid in more general cases than the one here treated.

THE CARBON DIOXIDE MOLECULE

The most interesting linear triatomic molecule is that of carbon dioxide. It has two special characteristics: it is symmetric, the structure being $O-C-O$, and the frequency ω_1 is very nearly equal to $2\omega_2$. The first results in fixing the values of c and s at 1 and 0, respectively. The second results in accidental degeneracy, which was excluded in the previous section. However all conclusions there derived, except Eq. (31), remain valid if the functions $u(N, l)$ are replaced by the appropriate linear combinations obtained from the solution of the first-order secular equations. These combinations have been calculated by Adel and Dennison.[5]

A comparison of their Hamiltonian with the

present one reveals only one important differ-ence, though there are numerous minor ones. Using $c=1$, $s=0$, it is seen that Λ_3 will disappear from the Hamiltonian, but $\Lambda_1 = q_2 p_3 - p_2 q_3$ will remain. In the Hamiltonian of Dennison and Adel, only the term $q_2 p_3$ appears.[8] Had there been no accidental degeneracy, this would have resulted in the omission of the term ω_2/ω_3 in Eq. (31), and the retention of the term ω_3/ω_2.

[8] In their notation, $q_2{}^2 p_3{}^2 = (\omega_2/2\omega_3 I)\rho^2 p_\xi{}^2$.

Apparently, it will have a similar effect when there is accidental degeneracy. Fortunately, $\omega_3/\omega_2 = 3.55$, so that the relative numerical error is small. From an examination of the published calculations, it is not possible to con-clude with certainty that this is the only effect of the omission. If there are no others, one may also conclude that Eq. (31) remains valid even when the accidental degeneracy is taken into account.

The Diffusion Constant of an Electrolyte, and Its Relation to Concentration

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A semi-empirical equation is proposed which predicts for potassium chloride, sodium chloride and potassium nitrate in aqueous solution, differential diffusion constants which agree with the experimentally determined values for the three salts within the limits of error of the experiments. The relation of the effective diffusion constant determined in the Northrop-McBain diaphragm cell to the differential diffusion constant is discussed; it is shown that Cole and Gordon's rule that the effective diffusion constant meas-ured in such a cell is equal to the differential diffusion con-stant for the mean concentration, is still a valid approxima-tion even when there is a nonlinear dependence of diffusion constant on cencentration, provided the total concentra-tion range involved is less than 0.1 N.

IT has long been recognized that there is a rela-tion between the thermodynamic properties of solutions of a given solute and the diffusion constant k of that solute; the Nernst equation connecting the osmotic pressures and mobilities of the ions of an electrolyte with diffusion con-stant at infinite dilution is a familiar example. It has also been recognized that the diffusion constant k, defined by the Fick equation (for uni-directional diffusion in the x direction)

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(k\frac{\partial c}{\partial x}\right), \qquad (1)$$

where c is the concentration and t the time, is in general itself a function of concentration. As a result, it is necessary to distinguish between the true "differential" diffusion constant at a given concentration, and "integral" diffusion constants which represent some sort of average depending on the kind of apparatus used. Since in most cases it is the integral diffusion constant that is measured, and since it is necessary to know the

relation between the differential diffusion con-stant and concentration to interpret the integral values, it is evident that this relation is a matter of some importance.

Onsager and Fuoss[1] in an important paper seem to have made the first attempt to compute the dependence of k on c. Their method con-sisted essentially in equating the diffusion con-stant to the product of two terms; the first of these involved the change in thermodynamic potential of the solute with concentration, and the second was a "mobility" term which for infinite dilution reduced to the familiar Nernst expression. The thermodynamic term was evalu-ated from the empirically determined activity coefficients of the electrolyte, and the mobility term was calculated by means of the Debye-Onsager theory of conductivity. Their evalua-tion of this latter item was admittedly unsatis-factory, and the agreement with experiment in the two cases they studied (sodium and potassium

[1] Onsager and Fuoss, J. Phys. Chem. 36, 2689 (1932).