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The Forces Between Water Molecules and the Second Virial Coefficient for Water

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In previous work on this subject, the second virial coefficient has been calculated with numerical success, but on the assumption of intermolecular forces which take inadequate cognizance of the known structure of the water molecule. In the present paper, all long range forces are computed in a semi-empirical way from dipole moment, quadrupole moment in accordance with the Bernal-Fowler analysis, and optical dispersion data. Interactions caused by quadrupole moments cannot be neglected. Short range repulsive forces are thus left undetermined. These are chosen in such a way that the second virial coefficient, in its dependence on temperature, approximates its measured values as closely as possible. It is found that a reasonable fit cannot be obtained with the use of the hard sphere model, nor with any model which permits the polar component of the force to be effective at arbitrarily small distances of separation. More satisfactory agreement results if the polar forces are eliminated at all distances smaller than the potential minimum. The best potential satisfying these various requirements is given at the end of the paper [formula (22)].

INTRODUCTION

THE present paper has as its principal purpose the determination of the forces acting between water molecules. To this end, we rely on the theory of van der Waals forces to provide an expression for the interaction at large distances of separation. The short range repulsive forces are at present beyond purely theoretical treatment. It might be expected, however, that when the attractive forces are known, available empirical data, such as the values of the second virial coefficient at different temperatures, would fix within reasonable limits the repulsive forces as well. This will prove to be the case.

To give a general survey, we list first the various types of forces which compose the total interaction and state their physical origins. Among the long range forces there are: (1) The attractions or repulsions between the permanent multipoles borne by a water molecule. These include not only the customary dipole forces to which the attention of most writers has been limited, but also quadrupole and higher types. For it will be seen that H_2O carries a sizable quadrupole moment whose presence may not be neglected. Since the Boltzmann factor makes alignment of the multipoles more probable than other orientations, the net effect, called alignment effect, is attractive. (2) Attractions caused by the induction of additional multipole moments by the fields of permanent moments—the so-called induction effect. (3) The forces arising from a mechanism similar to the preceding, but through fields caused by the rapidly rotating moments associated with electronic motions within a molecule instead of permanent moments. This is known as the dispersion effect. It is present regardless of whether the molecule has a multipole or not.

The short range forces are repulsive; their origin lies partly in the electrostatic repulsion between the molecular nuclei, partly in electron exchanges. They are not of spherical symmetry, but their angular dependence has not been described for the case of water molecules.

We now give a brief survey of the history of the present problem. The theory describing effect (1) of the preceding paragraph was developed by Keesom[1] at the time when all van der Waals forces were thought to originate in permanent multipoles. His treatment of dipole interactions is adequate for the problem at hand; his work on quadrupoles, which considers only *linear* structures, is in need of generalization before application to water molecules can be made. Furthermore, Keesom considers molecules having *only* a dipole, or *only* a quadrupole moment. The exact treatment for the combination of both is very unwieldy and will not be attempted here; an approximation will suffice for our purposes.

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[1] W. H. Keesom, Physik. Zeits. 22, 129 (1921).

The induction effect was considered by Debye[2] and Falkenhagen.[3] Formulas developed by them may be used in this work. For the theory of dispersion forces introduced by London, we refer the reader to a review article by one of the authors.[4]

An early analysis of the H_2O problem[5] which included consideration of all effects here mentioned resulted in the prediction that the molecule, in order to produce virial coefficients of the known magnitudes, possesses a quadrupole moment of about 5×10^{-26} e.s.u. In this work, the repulsive forces were treated somewhat inadequately, their effect being described by an infinite repulsion at a distance of separation equal to the kinetic theory diameter. (Hard sphere model.) This fiction, frequently employed in the past, makes the results extremely sensitive to the choice of that diameter, which is empirically ill defined and therefore sometimes leads to a specious semblance of success. Wohl[6] and Briegleb,[7] using similar methods and approximations, discussed the situation from a general chemical point of view.

More recently, the problem has been reconsidered by Stockmayer.[8] He shows that the temperature behavior of the second virial coefficients of water and ammonia is described with numerical correctness by assuming the molecules to be *point* dipoles. His calculation permits much latitude in the choice of other parameters of the interaction and shows, in fact, that the forces producing such agreement are far from unique. In a sense, this type of success is satisfying, but it teaches very little about the actual properties of the molecule and augments our knowledge in no fundamental way. Since our prime concern is with the actual forces, the assumption of point dipoles is inadequate.

The work of Goff, Anderson, and Gratch[9] contains the significant indication that the hard sphere model, when used in conjunction with a plausible set of force parameters, is not capable of yielding the correct temperature dependence of the second virial coefficient for water. This is true even when the essentially spherical force field, employed as an approximation by these authors, is replaced by a field of dipole symmetry as will later be shown in this paper.

We consider the various effects of interest in the order in which they were listed in the second paragraph of this introduction.

INTERACTION BETWEEN PERMANENT MULTIPOLES

For the sake of completeness and systematic development, we include in this section a few results that are known. The method is perhaps more direct than those found in the earlier literature.

Let a set of discrete point charges e_i be situated at vector distances $\mathbf{r}_i=(x_i, y_i, z_i)$ from an origin 0. Another set of charges ϵ_λ is placed at distances $\boldsymbol{\rho}_\lambda=(\xi_\lambda, \eta_\lambda, \rho_\lambda)$ from an origin Ω; the displacement of Ω relative to 0 is $\mathbf{R}$. The mutual static potential energy between these sets is then

$$V=\sum_{i\lambda}\frac{e_i\epsilon_\lambda}{|\mathbf{R}-\mathbf{r}_i+\boldsymbol{\rho}_\lambda|}.$$

If we introduce "relative displacement vectors" $\boldsymbol{\sigma}_{i\lambda}=\mathbf{r}_i-\boldsymbol{\rho}_\lambda$, V can be expressed in two equivalent simple forms, the operator form

$$V=\sum_{i\lambda} e_i\epsilon_\lambda \exp\left(-\boldsymbol{\sigma}_{i\lambda}\cdot\nabla\right)\left(\frac{1}{R}\right), \tag{1}$$

which results from a Taylor development, and the Legendre form

$$V=\sum_{i\lambda}\frac{e_i\epsilon_\lambda}{R}\sum_{l} P_l(\cos\alpha_{i\lambda})\left(\frac{\sigma_{i\lambda}}{R}\right)^l, \tag{2}$$

obtainable on application of a well-known expansion theorem in terms of Legendre polynomials. In the last expression, $\alpha_{i\lambda}$ is the angle between $\boldsymbol{\sigma}_{i\lambda}$ and $\mathbf{R}$: $\cos\alpha_{i\lambda}=(z_i-\zeta_\lambda/\sigma_{i\lambda})$ provided we take the Z axis along $\mathbf{R}$, as will henceforth be understood. Equation (2) is the more useful for our present purposes. If

$$\sum_i e_i=\sum_\lambda \epsilon_\lambda=0,$$

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[2] P. Debye, Physik. Zeits. **21**, 178 (1920).

[3] H. Falkenhagen, Physik. Zeits. Sowjetunion **23**, 87 (1922). For a correction to this paper, see reference 5.

[4] H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).

[5] H. Margenau, Phys. Rev. **36**, 1782 (1930).

[6] K. Wohl, Zeits. f. physik. Chemie **B23**, 105 (1933).

[7] G. Briegleb, Zeits. f. physik. Chemie **B14**, 36 (1931).

[8] W. H. Stockmayer, J. Chem. Phys. **9**, 398 (1941).

[9] J. A. Goff, J. R. Anderson, and S. Gratch, Heating, Piping and Air Conditioning **15**, 319 (1943).

as we are supposing, the terms for which $l=0$ and 1 make no contribution to (2). For sufficiently compact charge distributions and sufficiently large R, this series converges rapidly. In most molecular problems, terms beyond $l=4$ need not be considered. To this approximation, insertion of the Legendre polynomials gives

$$\begin{aligned} V= & -(1/R^3)\sum_{\substack{i\\ \lambda}} e_i\epsilon_\lambda(2z_i\zeta_\lambda-x_i\xi_\lambda-y_i\eta_\lambda) \\ & +(3/2R^4)\sum_{\substack{i\\ \lambda}} e_i\epsilon_\lambda[r_i^2\zeta_\lambda-z_i\rho_\lambda^2 \\ & +(2x_i\xi_\lambda+2y_i\eta_\lambda-3z_i\zeta_\lambda)(z_i-\zeta_\lambda)] \\ & +(3/4R^5)\sum_{\substack{i\\ \lambda}} e_i\epsilon_\lambda[r_i^2\rho_\lambda^2-5z_i^2\rho_\lambda^2-5r_i^2\zeta_\lambda^2 \\ & -15z_i^2\zeta_\lambda^2+2(4z_i\zeta_\lambda-x_i\xi_\lambda-y_i\eta_\lambda)^2] \\ & +(1/2R^5)\sum_{\substack{i\\ \lambda}} e_i\epsilon_\lambda[3(r_i^2+\rho_\lambda^2) \\ & \times(4z_i\zeta_\lambda-x_i\xi_\lambda-y_i\eta_\lambda) \\ & +5(z_i^2+\zeta_\lambda^2)(3x_i\xi_\lambda+3y_i\eta_\lambda-4z_i\zeta_\lambda)]. \end{aligned} \tag{3}$$

Summations 1 to 4 represent, respectively, dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, dipole-octupole interactions.

In physical problems, it is usually necessary to calculate

$$\int \exp(-V/kT)\sin\theta_1 d\theta_1 \sin\theta_2 d\theta_2 d\varphi \equiv \int \exp(-V/kT)d\Omega, \tag{4}$$

θ_1 and θ_2 being the polar angles between fixed lines in the molecules and Z, φ the relative azimuth. If only the first summation of V is retained, this integral can be evaluated exactly, for V then has the simple form

$$-(p_1p_2/R^3)(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\varphi), \tag{5}$$

where the p's are dipole moments. But in general, a series expansion of $\exp(-V/kT)$ must be performed before integration. The number of terms to be retained in this series depends on T. In the application to be made later, one should strictly use terms up to V^{10}, but the labor involved in such a computation appears prohibitive. We therefore adopt the following approximate procedure.

Since $\int V^n d\Omega$ vanishes for odd n, the first term which occurs in the expansion is $\int V^2 d\Omega$. This will be computed exactly for the whole of expression (3). For sufficiently high temperatures this is the decisive contribution to (4), though that is not true in our application. We then evaluate (4) including the dipole term only, but augmenting the coefficient p_1p_2/R^3 in (5) in the proper way so that the mean square of the approximate V is nearly equal to $\int V^2 d\Omega$. This will require the addition of a term in R^{-5} to p_1p_2/R^3, a term characteristic of the quadrupole interaction. We proceed now to the calculation of $\int V^2 d\Omega \equiv 8\pi\langle V^2\rangle_{\text{Av}}$.

In squaring V, the cross terms between different summations of Eq. (3) may at once be omitted, for they will be seen to vanish when the integration over angles is performed. A great number of others may also be omitted; the justification for this curtailment will appear later on. The significant terms to be retained are given here in part:

$$\begin{aligned} V^2= & (1/R^6)\sum e_ie_j\epsilon_\lambda\epsilon_\mu(4z_iz_j\zeta_\lambda\zeta_\mu \\ & +x_ix_j\xi_\lambda\xi_\mu+y_iy_j\eta_\lambda\eta_\mu) \\ & +(9/4R^8)\sum e_ie_j\epsilon_\lambda\epsilon_\mu(r_i^2r_j^2\zeta_\lambda\zeta_\mu \\ & +z_iz_j\rho_\lambda^2\rho_\mu^2+4x_iz_ix_jz_j\xi_\lambda\xi_\mu+\cdots) \\ & +(9/16R^{10})\sum\cdots+(1/4R^{10})\sum\cdots. \end{aligned} \tag{6}$$

To obtain $\langle V^2\rangle_{\text{Av}}$ it is thus necessary to compute averages of the type $\langle x_i^n x_j^m\rangle_{\text{Av}}$, $\langle x_i^n y_j^m\rangle_{\text{Av}}$, etc. This procedure is somewhat complicated by the fact that the vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ are not independent—since the whole molecule is being oriented in the evaluation of the averages in question—but lie along rays always making a fixed angle θ_{ij} at 0. However, averages over Greek and Latin letters may be carried out independently because they refer to different molecules.

A convenient method for carrying out the averaging process with respect to connected coordinates appears to be this. We introduce Euler angles α, β, γ and let $\boldsymbol{R}(\alpha,\beta,\gamma)$ be the matrix which, when applied to the vector $\mathbf{r}$, produces rotation about the origin through α, β, γ. Starting with any special, permitted position of the vectors $\mathbf{r}_1$[10] and $\mathbf{r}_2$ such as

$$\mathbf{r}_1^0=r_1\mathbf{k},\quad \mathbf{r}_2^0=r_2(\sin\theta_{12}\mathbf{j}+\cos\theta_{12}\mathbf{k}),$$

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[10] We now write 1, 2 for the former indices i, j.

we obtain their most general position by applying to them the matrix $\boldsymbol{R}$:

$$\mathbf{r}_1=\boldsymbol{R}\mathbf{r}_1{}^0,\quad \mathbf{r}_2=\boldsymbol{R}\mathbf{r}_2{}^0.$$

These vectors have components

$$\begin{array}{l|l}
x_1=-r_1\sin\beta\cos\gamma & x_2=r_2\sin\theta_{12}(\sin\alpha\cos\beta\cos\gamma+\cos\alpha\sin\gamma)-r_2\cos\theta_{12}\sin\beta\cos\gamma \\
y_1=r_1\sin\beta\sin\gamma & y_2=r_2\sin\theta_{12}(-\sin\alpha\cos\beta\sin\gamma+\cos\alpha\cos\gamma)+r_2\cos\theta_{12}\sin\beta\sin\gamma \\
z_1=r_1\cos\beta & z_2=r_2\sin\theta_{12}\sin\alpha\sin\beta+r_2\cos\theta_{12}\cos\beta.
\end{array}$$

The desired average over any quantity Q is then simply

$$\langle Q\rangle_{\mathrm{Av}}=\frac{1}{8\pi^2}\int_0^{2\pi}d\alpha\int_0^{\pi}\sin\beta d\beta\int_0^{2\pi}d\gamma Q,$$

with θ_{12} held fixed and Q expressed through the preceding relations. The results needed here are:

$$\begin{aligned}
\langle x_ix_j\rangle_{\mathrm{Av}}&=(1/3)r_ir_j\cos\theta_{ij}\\
\langle x_iy_j\rangle_{\mathrm{Av}}&=0\\
\langle x_i{}^3x_j\rangle_{\mathrm{Av}}&=(1/5)r_i{}^3r_j\cos\theta_{ij}\\
\langle x_i{}^2x_j{}^2\rangle_{\mathrm{Av}}&=(1/15)r_i{}^2r_j{}^2(1+2\cos^2\theta_{ij})\\
\langle x_i{}^3y_j\rangle_{\mathrm{Av}}&=0\\
\langle x_iz_iz_j{}^2\rangle_{\mathrm{Av}}&=0\\
\langle x_i{}^2y_j{}^2\rangle_{\mathrm{Av}}&=(1/15)r_i{}^2r_j{}^2(1+\sin^2\theta_{ij})\\
\langle x_ix_jy_j{}^2\rangle_{\mathrm{Av}}&=(1/15)r_ir_j{}^3\cos\theta_{ij}
\end{aligned}$$

$$\begin{aligned}
\langle x_iy_ix_jy_j\rangle_{\mathrm{Av}}&=(1/30)r_i{}^2r_j{}^2(3\cos^2\theta_{ij}-1)\\
\langle x_iy_iz_j{}^2\rangle_{\mathrm{Av}}&=0\\
\langle x_iy_iz_iz_j\rangle_{\mathrm{Av}}&=0\\
\langle x_iy_jz_j{}^2\rangle_{\mathrm{Av}}&=0\\
\langle x_iy_jx_jz_j\rangle_{\mathrm{Av}}&=0\\
\langle z_i{}^2z_j{}^2x_ix_j\rangle_{\mathrm{Av}}&=r_i{}^3r_j{}^3\frac{4\cos^3\theta_{ij}-\cos\theta_{ij}}{105}\\
\langle z_j{}^3z_j{}^3\rangle_{\mathrm{Av}}&=r_i{}^3r_j{}^3\frac{2\cos^3\theta_{ij}+3\cos\theta_{ij}}{35}\\
\langle z_i{}^2x_iz_j{}^2y_j\rangle_{\mathrm{Av}}&=0\\
\langle z_i{}^2x_iz_j{}^3\rangle_{\mathrm{Av}}&=0.
\end{aligned}\tag{7}$$

In addition to this list we note that averages over terms of odd power, such as x^2y, are always zero. Many other relations may be produced by noting two operations with respect to which the formulas above are invariant: (1) interchange of any two coordinates; (2) interchange of the indices i and j throughout. If averages over higher powers of V than the second were needed, similar integrations over a greater number of connected coordinates would have to be performed.

Combination of (6) and (7) yields finally a relatively simple result for $\langle V^2\rangle_{\mathrm{Av}}$:

$$\begin{aligned}
\langle V^2\rangle_{\mathrm{Av}}=\sum_{\substack{ij\\ \lambda\mu}}e_ie_j\epsilon_\lambda\epsilon_\mu\bigg\{&\frac{2}{3R^6}r_ir_jP_1(\cos\theta_{ij})\rho_\lambda\rho_\mu P_1(\cos\theta_{\lambda\mu})\\
&+\frac{1}{R^8}[r_i{}^2r_j{}^2P_2(\cos\theta_{ij})\rho_\lambda\rho_\mu P_1(\cos\theta_{\lambda\mu})\\
&+r_ir_jP_1(\cos\theta_{ij})\rho_\lambda{}^2\rho_\mu{}^2P_2(\cos\theta_{\lambda\mu})]\\
&+\frac{14}{5R^{10}}r_i{}^2r_j{}^2P_2(\cos\theta_{ij})\rho_\lambda{}^2\rho_\mu{}^2P_2(\cos\theta_{\lambda\mu})\\
&+\frac{4}{3R^{10}}[r_i{}^3r_j{}^3P_3(\cos\theta_{ij})\rho_\lambda\rho_\mu P_1(\cos\theta_{\lambda\mu})\\
&+r_ir_jP_1(\cos\theta_{ij})\rho_\lambda{}^3\rho_\mu{}^3P_3(\cos\theta_{\lambda\mu})]\bigg\}.
\end{aligned}\tag{8}$$

The P's are again Legendre polynomials. Here, obviously, the θ's with Latin indices refer to one, those with Greek indices to the other molecule. This answer, the general form of which (though hardly the numerical coefficients appearing in it) could have been predicted from symmetry considerations, immediately suggests the introduction of certain invariants:

Dipole-invariant: $L=\sum_{ij}e_ir_ie_jr_jP_1(\cos\theta_{ij})$,

Quadrupole-invariant: $M=\sum_{ij}e_ir_i{}^2e_jr_j{}^2P_2(\cos\theta_{ij})$,

Octupole-invariant: $M=\sum_{ij}e_ir_i{}^3e_jr_j{}^3P_3(\cos\theta_{ij})$.

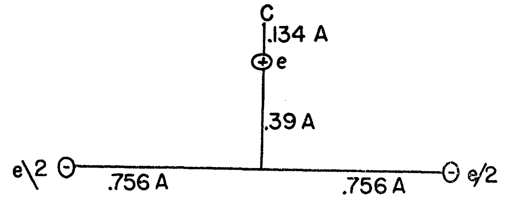

FIG. 1. Electrical structure of the water molecule assumed in calculation of moments. *Note:* In the figure the minus signs should be plus, and the plus sign should be minus.

Equation (8) then takes the form

$$\langle V^2\rangle_{\text{Av}}=\frac{2}{3R^6}L^{(1)}L^{(2)}+\frac{1}{R^8}(M^{(1)}L^{(2)}+L^{(1)}M^{(2)})+\frac{1}{R^{10}}\left[\frac{14}{5}M^{(1)}M^{(2)}+\frac{4}{3}(L^{(1)}N^{(2)}+N^{(1)}L^{(2)})\right]. \tag{9}$$

The invariants may also be expressed as functions of multipole moments. On defining, as usual,

$$\text{dipole moment}=\mathbf{p}=\textstyle\sum_i e_i\mathbf{r}_i,$$

components of quadrupole moment

$$=Q_{xx}=\textstyle\sum_i e_ix_i^2,\quad Q_{xy}=\sum_i e_ix_iy_i,\ \text{etc.},$$

components of octupole moments

$$=O_{xxx}=\textstyle\sum_i e_ix_i^3,\quad O_{xxy}=\sum_i e_ix_i^2y_i,\ \text{etc.},$$

they read:

$$\begin{aligned}L&=p^2,\\ M&=Q_{xx}^2+Q_{yy}^2+Q_{zz}^2+(3Q_{xy}^2-Q_{xx}Q_{yy})\\&\quad+(3Q_{xz}^2-Q_{xx}Q_{zz})+(3Q_{yz}^2-Q_{yy}Q_{zz}),\\ N&=O_{xxx}^2+O_{yyy}^2+O_{zzz}^2+6O_{xxy}^2+6O_{xxz}^2+6O_{xyy}^2\\&\quad+6O_{yyz}^2+6O_{xzz}^2+6O_{yzz}^2+15O_{xyz}^2\\&\quad-3O_{xxx}(O_{xyy}+O_{xzz})-3O_{yyy}(O_{xxy}+O_{yzz})\\&\quad-3O_{zzz}(O_{xxz}-O_{yyz})-3O_{xxz}O_{yyz}\\&\quad-3O_{xxy}O_{zzy}-3O_{xyy}O_{xzz}.\end{aligned} \tag{10}$$

We now return to our original plan for the calculation of $\int \exp(-V/kT)d\Omega$. This involved the replacement of the correct V of Eq. (3) by an approximate V' of the form

$$V'=-\left[\frac{L}{R^3}+u(R)\right]f$$

where

$$f=2\cos\theta_1\cos\theta_2-\sin\theta_1\sin\theta_2\cos\varphi$$

in such a way that $\langle V^2\rangle_{\text{Av}}=\langle V'^2\rangle_{\text{Av}}$ as nearly as possible. Since $\langle f^2\rangle_{\text{Av}}=\frac{2}{3}$ we have

$$\langle V'^2\rangle_{\text{Av}}=\frac{2}{3}\left[\frac{L^2}{R^6}+\frac{2Lu}{R^3}+u^2\right].$$

On comparing this with (9), in which all superscripts may now be omitted because we are dealing with two similar molecules, we find $u=(3M/2R^5)$ so far as the first two terms on the right of (9) are concerned. This choice makes the contribution of the $1/R^{10}$ term somewhat too small for the case of H_2O, but this is not a serious matter since that contribution turns out to be small anyway. Henceforth, then, we use

$$V=-\left(\frac{L}{R^3}+\frac{3}{2}\frac{M}{R^5}\right)f(\theta_1\theta_2\varphi). \tag{11}$$

In calculating the constants of Eq. (10) for the water molecule we have assumed the electrical structure proposed by Bernal and Fowler,[11] who place a charge $+\frac{1}{2}e$ at each of the H nuclei, and a charge $-e$ on the bisector of the H–H distance, 0.20A away from the 0 nucleus. The mass structure, needed to locate the center of mass about which quadrupole and octupole moments must be computed, is that determined by Mecke and Baumann.[12] Details are depicted in Fig. 1, where C represents the center of mass. They give the known value $p=1.87\times10^{-18}$ e.s.u. for the dipole moment. Furthermore, we find

$$L=35.2\times10^{-37}\ \text{e.s.u.},\quad M=56.6\times10^{-53}\ \text{e.s.u.},\quad N=99.6\times10^{-69}\ \text{e.s.u.}$$

With these values, Eq. (9) becomes

$$\langle V^2\rangle_{\text{Av}}=\left(\frac{8.27\times10^{-72}}{R^6}+\frac{39.9\times10^{-88}}{R^8}+\frac{183\times10^{-104}}{R^{10}}\right)\text{ergs}^2. \tag{12}$$

At $R=3\text{A}$, which is near the distance of closest approach of two molecules, the three terms here retained are, respectively, 11.3, 6.1, and 3.1

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[11] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).

[12] R. Mecke and W. Baumann, Physik. Zeits. Sowjetunion **33**, 833 (1932). K. Freudenberg and R. Mecke, Zeits. f. Physik **81**, 465 (1933).

$\times 10^{-27}$ erg^2 which shows that omission of the quadrupole moment entails a very serious error. On the other hand, the approximate V of Eq. (11) becomes

$$V=-\left(\frac{3.52\times 10^{-36}}{R^3}+\frac{8.50\times 10^{-52}}{R^5}\right)f(\theta_1\theta_2\varphi). \quad (13)$$

It gives a $\langle V^2\rangle_{\mathrm{Av}}$ which agrees with (12) in the first two terms, of course, but makes the coefficient of the last term much too small (48.2 instead of 183). This, however, will be regarded as acceptable in view of the inaccuracies of the model.

INDUCTION EFFECT

In describing the induction effect, the analysis of reference 4 will be followed. If the potential energy produced by one molecule at the position of the other is φ, the energy induced in the latter is $-\frac{1}{2}\alpha(\nabla\varphi)^2$, where α is the molecular polarizability. To be sure, this energy depends on the orientation of the inducing molecule (and to the extent to which α is a tensor upon the orientation of the other as well), but this dependence is much less pronounced than in the preceding effect. In particular, the energy cannot change sign. Instead of introducing an angular function in the integral $\int \exp(-V/kT)d\Omega$, we shall therefore average over directions at once. This leads to the induction energy

$$-\tfrac{1}{2}\alpha\langle(\nabla\varphi)^2\rangle_{\mathrm{Av}}=-\alpha\left(\frac{L}{R^6}+\frac{3}{2}\frac{M}{R^8}+\cdots\right), \quad (14)$$

wherein L and M are the former invariants. For the two interacting molecules, this expression has to be multiplied by 2. In the next section, reasons will be given for choosing the value of α to be 1.44×10^{-24} cm^3. We thus obtain as the contribution of the induction effect to the intermolecular energy in water

$$V=-\left(\frac{10^{-59}}{R^6}+\frac{24\times 10^{-76}}{R^8}+\cdots\right)\text{ ergs.} \quad (15)$$

The leading term of this expression is only about 10 percent of the first part of (13) at $R=3$A, which indicates the relative importance of the two effects.

DISPERSION EFFECT

The dispersion effect produces an interaction energy also of the form $-(C/R^6)-(D/R^8)$. The value of C calculated in reference 4 and used in previous work on the second virial coefficient[8, 9] was obtained with the use of London's[13] formula in which the "resonance" energy was set equal to the ionization energy of the molecule, and α was taken to be 1.5×10^{-24} cm^3. This procedure can be improved by employing optical dispersion formulas, two of which are available.[14]

Dorsey,[15] in his valuable compendium on water, assumes as the best value of the polarizability $\alpha=1.59\times 10^{-24}$ cm^3. This is derived from Stranathan's[16] and other measurements of the dielectric constants. As might be expected in that type of work, the measurements are somewhat discordant, and Stranathan admits a possible error of 10 percent in α.

On the other hand, Dorsey lists, without comment on the implied discrepancy, two one-term dispersion formulas, one due to Cuthbertson,

$$n-1=\frac{2.63\times 10^{27}}{10700\times 10^{27}-\nu^2}, \quad (16)$$

and one proposed by Hölemann and Goldschmidt,

$$n-1=\frac{3.07\times 10^{27}}{12500\times 10^{27}-\nu^2}. \quad (17)$$

They permit computation of α by extrapolation to $\nu=0$. Both yield $\alpha=1.44\times 10^{-24}$ cm^3. We believe this extrapolation to be more accurate than the former value and shall, therefore, use it in the present work.

In a similar way, the force parameters C and D will be computed from (16) and (17). Equation (16) involves a resonance energy of 13.55 ev and an oscillator strength of 2.41; the respective quantities in (17) being 14.7 and 2.81 ev. Both resonance energies are smaller than the ionization energy (18 ev). The constant D may be computed from a formula previously published.[17]

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[13] F. London, Zeits. f. physik. Chemie **B11**, 222 (1930).

[14] C. and M. Cuthbertson, Phil. Trans. **A213**, 1 (1913). P. Hölemann and H. Goldschmidt, Zeits. f. physik. Chemie **B24**, 199 (1934).

[15] N. E. Dorsey, *Properties of Ordinary Water-Substance* (Reinhold Publishing Corporation, New York, 1940).

[16] J. D. Stranathan, Phys. Rev. **48**, 538 (1935).

[17] H. Margenau, J. Chem. Phys. **6**, 896 (1938).

This procedure leads to $C=33.7\times 10^{-60}$ erg cm^6, $D=95\times 10^{-76}$ erg cm^8 on the basis of (16); $C=36.4\times 10^{-60}$ erg cm^6, $D=95\times 10^{-76}$ erg cm^8 from (17). The value of D is to be regarded as quite uncertain. We take as the contribution of the dispersion effect to the intermolecular potential

$$V=-\left(\frac{35\times 10^{-60}}{R^6}+\frac{95\times 10^{-76}}{R^8}\right)\text{ ergs.} \quad (18)$$

SECOND VIRIAL COEFFICIENT

After determination of all constituents of the long range van der Waals energy, attention will now be directed to the short range repulsive forces. Concerning them there is but meager information. Attempts to derive specific details from a large variety of empirical data led us to abandon the search for a potential the uniqueness of which could plausibly be accepted before calculating the equation of state:

$$\frac{pv}{RT}=1+\frac{B}{v}+\cdots,$$

in particular the second virial coefficient B. The procedure has therefore been inverted: The repulsive potential is to be determined by seeking agreement with known values of B at different temperatures.

Two facts, however, may be assumed. A survey of the material on the crystal structure of ice,[18] considerations by Bernal and Fowler, the density of water, etc., indicate that the minimum of the total potential must lie somewhere between 2.7 and 2.9A. While the concept of a minimum has no precise meaning for forces which depend on angles, this realization nevertheless proves to be a guide. It is possible, for example, to calculate the average orientation of adjacent water molecules in ice and fix the minimum with some precision. The value of R chosen for this was about 2.80A. Such deliberations, however, serve only for preliminary orientation; it develops that choices widely different from this do not yield proper values of B.

The second fact concerns the form of the repulsive force law. Calculations on simpler molecules and atoms of spherical symmetry show that the exchange energy, in a sufficiently large range of distances, may be represented in the form $A\exp(-R/\rho)$, which will here be chosen.

At first thought, then, one would try a total potential pieced together from (13), (15), (18) and the latter expression, i.e.,

$$V=a(R)+b(R)f(\theta_1,\theta_2,\varphi) \quad (19)$$

in which[19]

$$a(R)=A\exp(-R/\rho)-\left(\frac{45\times 10^{-60}}{R^6}+\frac{119\times 10^{-76}}{R^8}\right),$$

$$b(R)=\frac{3.52\times 10^{-36}}{R^3}+\frac{8.5\times 10^{-52}}{R^5}.$$

The parameters A and ρ are not quite as disposable as they might seem, even if no condition is imposed on the position of the minimum. The condition that there be a minimum at all drastically limits the choice. Result (19) is to be inserted into the well-known formula

$$B=2\pi N^2\int^{\infty}R^2dR\int_{\Omega}(1-\exp(-V/kT))\frac{d\Omega}{8\pi}. \quad (20)$$

The second integration yields

$$1-\exp[-a(R)/kT]\int\exp(-bf/kT)\frac{d\Omega}{2\pi}$$
$$=1-\exp(-a/kT)F(b/kT).$$

Let $b/kT\equiv x$. Then

$$F(x)=\sum_{\lambda}\int\frac{(-xf)^{\lambda}}{\lambda!}\frac{d\Omega}{8\pi}=\sum_{n=0}^{\infty}\int\frac{(xf)^{2n}}{(2n)!}\frac{d\Omega}{8\pi},$$

the last because $\int f^{\lambda}d\Omega=0$ for odd λ. Now

$$\int f^{2n}\frac{d\Omega}{8\pi}=\frac{1}{2n+1}\cdot\frac{2.4\cdots 2n}{1\cdot 3\cdots(2n+1)}\sum_{l=0}^{n}\left(\frac{2l}{l}\right)\equiv G_{2n},$$

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[18] W. H. Bragg, Proc. Phys. Soc. London **34**, 98 (1922). B. E. Warren, J. Chem. Phys. **6**, 666 (1938).

[19] Because of an oversight, a different value of the coefficient in the last term of $a(R)$ has been used in the subsequent numerical calculations. We have, unfortunately, neglected the quadrupole moment in computing the induction effect, so that the coefficient in question was 95 instead of 119. Revision was not made because this term makes only a minor contribution to B and is not known with sufficient accuracy.

TABLE I. Comparison of experimental and calculated values of B in cm³/mole on the basis of the hard sphere model.

T	B_{calc}	B_{exp}	Rel. error
700°K	−65.9	−65.4	−0.8 percent
600°K	−112.4	−99.0	−13.5 percent
500°K	−215.2	−166.4	−29.3 percent
400°K	−542	−346.9	−56.2 percent

TABLE II. Comparison of experimental and values of B in cm³/mole calculated on the assumption of a potential minimum.

T	B_{calc}	B_{exp}	Rel. error
700°K	−65.9	−65.4	−0.8 percent
600°K	−109.9	−99.0	−11 percent
500°K	−200.2	−166.4	−20 percent

so that

$$F(x)=\sum_{n=0}^{\infty}\frac{G_{2n}}{(2n)!}x^{2n}. \tag{21}$$

While it is quite possible to integrate e^{-xf} without expansion—the result being either a series in Bessel functions or a definite integral over Bessel functions—the present form of $F(x)$ has been found most convenient for problems of this type. We have prepared a numerical table of $F(x)$ with x ranging from 0 to 10. The remaining integration,

$$B=2\pi N\int R_2\left\{1-\exp\left[-a(R)/kT\right]F\left[\frac{b(R)}{kT}\right]\right\}dR$$

was carried out graphically. This is much less tedious than expansion of the integrand and subsequent term-by-term integration.

If $A\rightarrow\infty$ while $\rho\rightarrow 0$, V reduces to the potential characteristic of hard spheres. This was one of the first models tried. It involves only one disposable parameter, and this is adjusted by making B come out correctly at one temperature. Measurements with which comparison is here made are those of Keyes, Smith, and Gerry.[20]

In the calculation with the hard sphere model, only the attractive terms of the potential are used. If the infinite barrier is placed at $R=2.87$A, sufficient agreement results for $T=700$°K. Table I shows what happens at lower temperatures.

This outcome, while at first unpleasant, is particularly interesting in view of the fact that Stockmayer[8] was able to obtain good agreement at all temperatures with the use of the hard sphere model, when he neglected the quadrupole moment. The discrepancies incurred can, however, be made to tell us more about the repulsive interaction. They are due, it seems, to the large coefficient of the angular part of the potential, which makes a proportionately larger contribution to B at lower temperatures. We therefore attempt to neutralize this effect by using finite values for A and ρ.

A typical calculation involved the use of $\rho=0.28$A (a value in this neighborhood seems to be required in order to produce a minimum at all; cf. also the findings of R. Heller[21]) and $A=3.155\times 10^{-9}$ erg. These correspond to a potential minimum, computed with the proper value of $\bar{f}$ as explained, at 2.80A. The results are given in Table II. While the correct B is obtained at 700°K, the same sort of discrepancy appears at lower temperatures, though it has diminished somewhat in magnitude. Numerous trials were made with other sets of parameters, notably those corresponding to a minimum at 2.76A ($0-0$ distance in ice), at 2.90A (intermolecular distance in liquid water), and at 3.10A. These yielded no better success.

The conclusion is therefore inescapable that a potential of the form (19) cannot be used for the purpose at hand. This might indeed have been expected, for it implies that the function f, which is characteristic of polar behavior, is effective all the way into the origin $R=0$. On the other hand, the repulsive potential which is taken to be independent of angles provides no mechanism for counteracting this fictitious polarity at close distances of separation. A more reasonable representation of the potential appears to be this. Assume the polar forces to be active for $R>R_{\text{min}}$, the range in which the molecules may indeed be regarded as permanent multipoles. But for $R<R_{\text{min}}$, let all interactions be of spherical symmetry. Though the latter hypothesis is but an approximation to the truth, it is a better approximation than the very extreme and specific one of dipolar symmetry.

Such a representation does not yield a con-

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[20] F. G. Keyes, L. B. Smith, and H. T. Gerry, Proc. Am. Acad. Arts Sci. 70, 319 (1936).

[21] R. Heller, J. Chem. Phys. 9, 154 (1941).

tinuous curve for all orientations of the molecules. This analytic fault will have to be accepted in order to avoid the artificial difficulties which the construction of a continuous function would entail. Thus we take

$$V=\begin{cases} V_1=a'(R), \quad R<R_{\min} \\ V_2=a(R)+b(R)f(\theta_1\theta_2\varphi)R>R_{\min}, \end{cases}$$

where a' differs from a in having a different set of constants A', ρ'. For A and ρ, the preceding calculations strongly suggest 3.25×10^{-9} erg, $\rho=0.28\text{A}$ as most likely values. This leaves A' and ρ' to be determined. There appears to be some latitude in their choice, and we cannot be sure that the adjustment here proposed is unique. But the effect of reasonable alterations on B is not large.

One relation between them will be obtained by requiring continuity between V_1 and V_2 at $R_{\min}$, that is, at 2.80A for some definite temperature, say 700°K. Thus

$$\exp(-V_1/kT)=\int\exp(-V_2/kT)\frac{d\Omega}{8\pi}$$
$$=\exp[-a(R)/kT]\cdot F[b(R)/kT]$$

at $T=700°\text{K}$ and $R=2.80\text{A}$. (If this fit were tried at $R=2.90\text{A}$, it would require the use of a negative A'. This again shows one of the self-stabilizing aspects of the procedure.) The second relation is provided by the requirement that B shall have its experimental value at some temperature at the middle of the range. The work involved here is obviously tedious, and no claim will be made that the present investigation is exhaustive; slightly different values of the constant may produce an even better fit. On taking $A'=2.4\times10^{-6}$ erg, $\rho'=0.15\text{A}$—a model which approaches the hard sphere case—the temperature dependence of B (see Table III) is obtained. While the agreement is not perfect, the improvement is very considerable and indicates that the repulsive potential adopted is not far from correct.

TABLE III. Experimental and calculated values of B in cm^3/mole by use of adjusted constants.

T	B_{calc}	B_{exp}	Rel. error
700°K	−68.9	−65.4	−5.4 percent
600°K	−101.1	−99.0	−2.1 percent
500°K	−164.4	−166.4	+1.2 percent
400°K	−329.8	−346.9	+4.9 percent

The small quantum correction, computed by Stockmayer[8] for dipoles, does not improve the calculated values materially. An estimate for the present case shows that it reduces the error at 700°K to about −5 percent while increasing that at 400°K to about 5.5 percent.

Summarizing the work, we find that

$$V=\begin{cases} 2.4\times10^{-6}\exp(-R/0.15\text{A}-c(R) \\ \qquad\qquad\qquad\qquad \text{if } R<2.80\text{A} \\ 3.25\times10^{-9}\exp(-R/0.28\text{A}) \\ \quad -c(R)-b(R)(2\cos\theta_1\cos\theta_2 \\ \quad -\sin\theta_1\sin\theta_2\cos\varphi) \quad \text{if } R>2.80\text{A} \end{cases} \tag{22}$$

with

$$c(R)=\left(\frac{45\times10^{-60}}{R^6}+\frac{95\times10^{-76}}{R^8}\right)\text{ ergs,}$$

$$b(R)=\left(\frac{3.52\times10^{-36}}{R^3}+\frac{8.50\times10^{-52}}{R^5}\right)\text{ ergs}$$

represents the best intermolecular potential for water molecules in view of available facts.