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Free Volumes and Free Angle Ratios of Molecules in Liquids

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The free volume is defined as the total integral over that part of the potential energy of the molecule in the liquid which is due to thermal displacements of the center of gravity of the molecule from its equilibrium position. The free angle is the corresponding integral over angular displacements of the molecule. The free volume, V_f is related to the velocity of sound, u, in the liquid by

$$u \text{ (liquid)} = u \text{ (gas) } (V/V_f)^{\frac{1}{3}}.$$

This equation is used to derive a formula connecting the sound velocity in the liquid with its thermal conductivity. The quantity, $RT/p \exp (\Delta H/RT)$, gives the *product* of the free angle ratio and the free volume, rather than the free volume itself. Here p is the vapor pressure and ΔH is the heat of vaporization. The free volumes from sound velocities agree with those determined by independent methods. Specific heats, entropies of vaporization, the spectroscopic observations of Cartwright, and the differences between sound velocity, free volumes and the function RT/p $\times \exp (\Delta H/RT)$ are examined from the point of view of restricted rotation of the molecules in liquids. Lack of free rotation of molecules suffices to explain the abnormalities of the liquids examined. The dielectric constants of polar liquids are interpreted assuming restricted rotation and the following formula is derived:

$$\mu_l^2 \mu_g^{-2} = 1 - ((1 - \cos \theta_1)/2)^2,$$

where μ_l is the apparent dipole moment of the molecule in the liquid, μ_g is the dipole moment as determined from measurements in the gas phase, and θ_1, is the polar angle related to the free angle ratio, δ_2, by

$$\delta_2 = (1 - \cos \theta_1)/2.$$

The concept of restricted rotation of the molecules in the liquid accounts satisfactorily for the observed dielectric polarizations of water and methyl alcohol.

INTRODUCTION

IN the present paper certain kinetic theory formulae for gases are modified in such a way as to make them applicable to liquids. The point of view employed is to treat the molecule moving in its free volume in the liquid as equivalent to the molecule moving in the total volume in the gas phase. Using this notion it is possible to derive a new formula for the velocity of sound in liquids in terms of the velocity in the gas phase, the total volume and the free volume of the liquid. An equation very similar to that given by Bridgman[2] for the thermal conductivity of liquids also follows from such considerations.

The term, *free volume*, as employed here denotes the total integral over that part of the potential energy which is due to thermal displacements of the center of gravity of the molecule from its equilibrium position. The name, *free angle*, is introduced to refer to the corresponding integral over angular displacement of the molecule around its center of gravity. For linear molecules the *free angle ratio* is the free

angle divided by 4π, and for nonlinear ones an analogous definition holds. The free angle ratio is a convenient quantity to employ since it is given by the ratio of the partition functions for the restricted rotation of the molecule in the liquid, and its free rotation in the gas phase. The free angle ratio thus extends from a lower value (greater than zero) to unity depending on whether the molecule is held tightly in its position or is allowed to turn freely about its axes. For linear molecules the free angle ratio includes two degrees of rotational freedom, and is designated by the symbol, δ_2. For more complicated molecules, three degrees of rotational freedom must be taken into account and the corresponding symbol is δ_3.

To a first approximation both the free volume and the free angle ratio may be thought of as regions in which completely free displacement occurs, the regions being surrounded by infinite potential walls. This is the hard spheres approximation previously employed by Eyring, Hirschfelder and Stevenson[3, 4] to yield the ex-

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[1] Present address, University of Rochester, Rochester, New York.
[2] P. W. Bridgman, *The Physics of High Pressures* (Macmillan Co., 1931).

[3] H. Eyring and J. O. Hirschfelder, J. Phys. Chem. **41** 249 (1937).
[4] J. O. Hirschfelder, D. P. Stevenson and H. Eyring, J. Chem. Phys. **5**, 896 (1937).

pression for the free volume,

$$V_f = \frac{1}{V^2}\left[\frac{2RT}{P+(\partial E/\partial V)_T}\right]^3, \qquad (1)$$

where V is the molal volume of the liquid, R is the gas constant per mole, T is the absolute temperature, and E is the thermodynamic energy. It is, however, not necessary to consider the molecules as hard spheres, and Kincaid and Eyring[5] have given a treatment of liquid mercury in which the size of the molecules is presumed to vary both with temperature and volume. The dynamic potential curve[6] in this case is a parabola with a flat bottom.

For monatomic liquids, the free volume is defined by,

$$V_f = RT/p \exp(\Delta H/RT), \qquad (2)$$

where p is the vapor pressure of the liquid, and ΔH is the heat of vaporization. For liquids composed of polyatomic, nonspherical molecules, the expression on the right of Eq. (2) is equal to the product of the free volume, and the free angle ratio. When the molecules in the liquid do not rotate freely, this quantity will necessarily be smaller than the free volume.

THE USE OF KINETIC THEORY EQUATIONS FOR LIQUIDS

Velocity of sound in liquids

The velocity of sound, u, in any homogeneous medium is given by the general hydrodynamic formula:

$$u = (v/\beta_s)^{\frac{1}{2}}, \qquad (3)$$

where v is the specific volume and β_s is the adiabatic compressibility defined by $\beta_s \equiv -1/v \times (\partial v/\partial P)_s$. For the special case of an ideal gas, (3) becomes

$$u = (RT\gamma/M)^{\frac{1}{2}},$$

where γ is the ratio of the specific heat at constant pressure to that at constant volume, and M is the molecular weight of the gas.

[5] John F. Kincaid and H. Eyring, J. Chem. Phys. **5**, 587 (1937).

[6] The *dynamic potential curve* is defined as the curve for which the corresponding partition function, when raised to the $3N$th power, is the translational partition function for the liquid as a whole aside from an exponential potential energy factor.

Equation (4) may be compared to that for $\bar{c}$, the average kinetic theory velocity of the molecules.

$$\bar{c} = (8RT/\pi M)^{\frac{1}{2}}. \qquad (5)$$

It is seen that u is proportional to $\bar{c}$ but is slightly smaller since the factor $(8/\pi)^{\frac{1}{2}}$ is always greater than $\gamma^{\frac{1}{2}}$. This is what one might suppose since a wave propagated by matter would hardly be expected to travel faster than the molecules which carry it. However, when the velocity of sound in liquids is compared to the kinetic theory velocity of the molecules it is found that u for most liquids is greater than $\bar{c}$ by factors ranging from five to ten. For example for benzene at 25°C, $\bar{c}$ is 2.83×10^4, u(gas) is 1.88×10^4, while u(liquid) is 13.0×10^4 cm/sec. Fig. I illustrates the mechanism responsible for the fact that the velocity of sound in liquids can be so much greater than the kinetic theory velocity of the molecules. The wave front is assumed to travel from the edge of molecule A to the adjacent edge of molecule B with the velocity given by Eq. (4). As A collides with B, however, the signal is transmitted almost instantaneously to the opposite edge of molecule B. Since the ratio of the total distance to the free space between two points in a liquid is given by
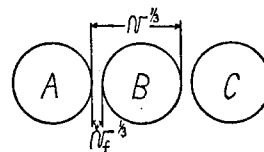

FIG. 1. Illustration of the mechanism which explains the observation that the velocity of sound in liquids is greater than the kinetic theory velocity of the molecules.

the ratio $(V/V_f)^{\frac{1}{3}}$, this leads at once to the equation,[7]

[7] Equation (1) of this paper is Eq. (13) of the paper by Eyring and Hirschfelder and was there derived from the expression $V_f^{\frac{1}{3}} = 2(V^{\frac{1}{3}} - d)$ assuming $(\partial d/\partial V)_T$ equals zero, i.e., the hard sphere model. Eq. (1) is obtained by the same procedure from the expression $V_f = (V^{\frac{1}{3}} - d)$ provided $(\partial d/\partial V)_T$ has the appropriate negative value. This corresponds to getting more free volume from increasing $(V^{\frac{1}{3}} - d)$ than one would get if the sides of the free volume were flat faces. Since the sides of the free volume are spheres this sign of $(\partial d/\partial V)_T$ is obvious *a priori*. The necessity of going beyond the simplest hard sphere model has been encountered in two previous papers. See Eq. (22) of Kincaid and Eyring[4] and Eq. (21) of Hirschfelder, Stevenson and Eyring.[3] However, it is possible that Eq. (6) should be employed in the more general form, u(liquid) $= cu$(gas) $(V/V_f)^{\frac{1}{3}}$ when c is a proportionality constant not necessarily equal to unity.

$$u(\text{liquid}) = u(\text{gas})(V/V_f)^{\frac{1}{3}}$$
$$= (RT\gamma/M)^{\frac{1}{2}}(V/V_f)^{\frac{1}{3}}. \quad (6)$$

Equation (6) may be employed either to find the velocity of sound in liquids if V_f is known from some other source, or to determine free volumes if sound velocity measurements have been made. A detailed comparison of free volumes computed by this and various other methods will be made in a later section.

Thermal conductivity of liquids

A straightforward application of the kinetic theory of gases gives the relation for the thermal conductivity K,

$$K(\text{gas}) = \frac{1}{3}(V/V_f)^{\frac{1}{3}}\bar{c}Lc_v, \quad (7)$$

where $(V/V_f)^{\frac{1}{3}}$ is the number of molecules per cc, L is the mean free path, and c_v is the specific heat per molecule. It is found, however, that Eq. (7) gives values which are too low for the thermal conductivity of gases, and Loeb[8] gives the correction factor $\frac{1}{4}(9\gamma' - 5)$, where γ' is the ratio of c_p to c_v. Eq. (7) may now be rewritten,

$$K(\text{gas}) = \frac{1}{3}[\frac{1}{4}(9\gamma' - 5)](V/V_f)^{\frac{1}{3}}\bar{c}Lc_v, \quad (8)$$

a relation which may be tested in the form,

$$K(\text{gas}) = \eta(c_v/m)\frac{1}{4}(9\gamma' - 5), \quad (9)$$

since the viscosity, η, is given by $\frac{1}{3}(N/V)m\bar{c}L$. Eq. (9) has been observed to give excellent agreement with experiment.[8]

In order to convert Eq. (8) into a form applicable to liquids the following identifications may be made. (N/V) becomes the number of molecules per cc of liquid rather than per cc of gas. The average velocity $\bar{c}$ must be multiplied by the ratio, $(V/V_f)^{\frac{1}{3}}$, for the same reasons as are given above for justifying Eq. (6). The distance that the energy is carried is now $(V/N)^{\frac{1}{3}}$ rather than L, the mean free path for the gas. c_v for the gas is replaced by αc_v, where α is the accommodation coefficient which takes account of the number of degrees of freedom which come into equilibrium in the thermal conduction process. Making all these substitutions we have:

$$K(\text{liquid}) = 1/12(9\gamma' - 5)(N/V)(8RT/\pi M)^{\frac{1}{2}}$$
$$\times (V/V_f)^{\frac{1}{3}}(V/N)^{\frac{1}{3}}(\alpha c_v), \quad (10)$$

[8] Leonard B. Loeb, *Kinetic Theory of Gases* (McGraw-Hill Book Co., 1927).

TABLE I. *Comparison of the observed thermal conductivities of liquids at 30°C with those computed from Eq. (12).*

SUBSTANCE	K(OBS.)[9]	K(CALC.)[10]	$\frac{K(\text{OBS.})}{K(\text{CALC.})}$
Methyl Alcohol	21.1×10^3 c.g.s. Units	22.3	0.95
Ethyl Alcohol	18.0	19.2	.94
Propyl Alcohol	15.4	17.3	.89
Butyl Alcohol	16.7	13.3	1.26
Iso-Amyl Alcohol	14.8	14.1	1.05
Ether	13.7	10.9	1.26
Acetone	17.9	16.3	1.10
Carbon Bisulfide	15.9	16.1	0.99
Ethyl Bromide	12.0	12.8	.94
Ethyl Iodide	11.1	10.6	1.05
Water	60.1	51.7	1.16

a formula which reduces to

$$K(\text{liquid}) = 1/12(9\gamma' - 5)(8/\pi\gamma)^{\frac{1}{2}}$$
$$\times (NV)^{\frac{1}{3}}u(\alpha c_v). \quad (11)$$

Here u is the velocity of sound in the liquid, γ' is the effective value of the ratio of c_p to c_v for thermal conduction in the gas, and γ is the same quantity for the transmission of sound.

In order to have formula (11) reduce to the one successfully employed by Brdigman,[2] αc_v must be assigned the value $3k$ per molecule. For the polyatomic liquids which Bridgman studied, this is understandable if only the kinetic energy of translation and rotation transfer appreciable energy in the process of thermal conduction. Using a value of c_v equal to $3k$, γ' becomes $4/3$ and (11) reduces to,

$$K(\text{liquid}) = 0.931(1/\gamma)^{\frac{1}{2}}3k(N/V)^{\frac{2}{3}}u. \quad (12)$$

This formula has the same form as that employed by Bridgman,[2] but the numerical coefficient is about 12 percent smaller, as a result of the factor $0.931/\gamma^{\frac{1}{2}}$ replacing unity in his expression.

Table I shows values for K at 30° for a number of liquids computed by (12) for comparison with Bridgman's experimental values. The agreement is somewhat better than Bridgman's earlier computations. Since carbon bisulfide is a linear molecule, the computation for this substance was made with a value of αc_v equal to $2.5k$, and a corresponding value of γ' of 1.40. The excellent agreement of the observed value with the one calculated in this way suggests that the liquid rare gases would be interesting substances with which to check the theory. A value for αc_v of

[9] P. W. Bridgman, Proc. Am. Acad. **59**, 109 (1923).
[10] γ values secured from K. Bennewitz, and W. Rossner, Zeits. f. physik. Chemie **B39**, 126 (1938). Sound velocity measurements from Bridgman[9] or Freyer, Hubbard and Andrews.[12]

about $3k$ would also be obtained from the translational contribution alone, if potential energy were included. Thus from data for the condensed rare gases, one will be able to determine whether or not potential as well as kinetic energy comes into equilibrium in the thermal conduction process in liquids.

Equation (12) not only works remarkably well for the variation of K from liquid to liquid at atmospheric pressure, but, as Bridgman has pointed out, it also gives approximately the temperature variation of K. It is therefore quite surprising that it does not predict the pressure effect correctly. Whereas most liquids increase their thermal conductivity by approximately a factor of 2 on going from atmospheric pressure to 12,000 atmospheres,[2] the formula predicts an increase by about a factor of 4. This is plausibly explained by a decrease in the value of α due to quantization of the mass motions of the molecules at high pressures. The effective heat capacity, αc_v, would have to become $1.5k$ in order to explain the observations at the highest pressures to which the experiments extend.

Debye[11] has treated the problem of the thermal conductivity of solids, with special reference to effects at low temperatures. The essential difference between his treatment and the one given above is that the identification of L with $(V/N)^{\frac{1}{3}}$ in the derivation of Eq. (12) is equivalent to assuming that each molecule acts independently while the essence of Debye's treatment lies in his assumption that the molecules are strongly coupled in such a way as to produce elastic waves of long wave-length. The effect of coupling, enabling the heat impulses to be transmitted by distances greater than the intermolecular distances without scattering is, however, important only at low temperatures. For most liquids it appears to be more satisfactory to treat the problem in essentially the manner indicated.

A comparison of values for free volumes of liquids computed by various methods

Since more complete data exist for benzene than for any other nonmetallic and nonpolar liquid, its free volume was computed by all avail-

TABLE II. *The free volume of benzene as a function of temperature at atmospheric pressure.*

$\tau °C$	V_f FROM[12, 13] EQ. (6) (SOUND VELOCITY)	$\delta_3 V_f$ FROM[14] EQ. (2) (VAPOR PRESSURE)	V_f FROM[15] EQ. (1) (ENERGY VOLUME COEFFICIENT)
5°	0.193 cc		0.214 cc
25°	.272	0.238 cc	.288
50°	.411	.419	.423
75°		.727	.633
100°		1.24	.99

able methods. The agreement between the various methods is seen by inspection of Table II to be very satisfactory. C_v for liquid benzene exceeds the gaseous value by 5 calories per mole per degree. This suggests lack of free rotation about two axes for the molecules in the liquid. On the other hand the sound velocity method gives a free volume only slightly greater than the product of free volume with free angle ratio as determined from vapor pressures, indicating a free angle ratio not greatly less than unity.

In general reliable values for heats of vaporization are not available over a sufficiently large temperature range to make possible a significant comparison of the absolute magnitude and temperature coefficients of the free volumes from vapor pressure with free volumes from sound velocity. However, although Eq. (1) is an approximate relation based on a very simple model, inspection of Table II reveals good agreement between values based on this relation and those calculated from vapor pressures. On the strength of this agreement, free volumes were computed by Eqs. (1) and (6) for a number of liquids for which the necessary data are given by Freyer, Hubbard and Andrews.[12] The results are shown in Table III. Although the computation of free volumes from vapor pressures and heats of vaporization is not a practical procedure for many liquids because of uncertainties in experimental heats of vaporization, the converse calcu-

[11] P. Debye, *Wolfskehl-Vorträge zu Göttingen* (Leipzig, 1914), Anhang p. 46. See also, Max Born, *Atomtheorie des Festen Zustandes* (B. G. Teubner, Leipzig, 1923), p. 707.

[12] Sound velocity data from E. B. Freyer, J. C. Hubbard and D. H. Andrews, J. Am. Chem. Soc. 51, 759 (1929).

[13] Values of γ for computing μ for the gas were secured from the frequencies given by R. C. Lord and D. H. Andrews, J. Phys. Chem. 41, 141 (1937).

[14] E. F. Frock, D. C. Ginnings and W. B. Holton, Nat. Bur. Stand. J. Research 6, 881 (1931). δ_3 is the free angle ratio.

[15] Data from 25° to 65°C from R. E. Gibson and John F. Kincaid, J. Am. Chem. Soc. 60, 511 (1938). Data at other temperatures extrapolated by a method to be published later.

TABLE III. *Values of the free volume for various liquids.*

SUB-STANCE	ACETONE		ETHER		CHLOROFORM		TOLUENE		CARBON TETRACHLORIDE		CARBON DISULFIDE	
$t°C$	V_f FROM EQ. (6)	V_f FROM EQ. (1)	V_f FROM EQ. (6)	V_f FROM EQ. (1)	V_f FROM EQ. (6)	V_f FROM EQ. (1)	V_f FROM EQ. (6)	V_f FROM EQ. (1)	V_f FROM EQ. (6)	V_f FROM EQ. (1)	V_f FROM EQ. (6)	V_f FROM EQ. (1)
0			0.48	0.47	0.21	0.25	0.16	0.16	0.16	0.21	0.23	0.45
10			.57	.55	.24	.29	.19	.19	.24	.26	.26	.52
20	0.45	0.54	.70	.65	.29	.34	.22	.22	.28	.31	.30	.58
30			.90	.79	.34	.40	.26	.26	.33	.37	.36	.66
40	.64	.63			.40	.47	.31	.31	.38	.43	.39	.75
50					.48		.36	.36	.45	.50	.47	.84

lation of heats of vaporization from vapor pressures and "sound velocity" free volumes appears to be a useful method.

In order to test the applicability of the sound velocity method of computing free volumes for a metallic liquid, free volumes of mercury as computed from Eq. (6) were compared with those given by the partition function previously published.[5] The expression for V_f is,

$$V_f = N \left[\frac{T/\Theta}{(2\pi mkT)^{\frac{1}{2}}/h} + 2\left(\frac{V}{N}\right)^{\frac{1}{3}} - 2\left(\frac{V_0}{N}\right)^{\frac{1}{3}} \right]^3. \quad (13)$$

Here Θ is the characteristic temperature of the liquid and V_0 is identified as the volume of the liquid at the melting point. Taking Θ equal to 79°, a value consistent with the experimental entropy of fusion, the free volumes shown in Table IV are obtained. It may be noted that the agreement between the values at both low and high pressures is quite satisfactory. This is of particular interest since the free volumes for mercury are of a different order of magnitude than those of the nonmetallic liquids discussed above. However, only a more exact investigation of mercury can establish how satisfactory these values really are.

In order to test the theory for another monatomic liquid, an attempt was made to utilize the somewhat inadequate data for liquid argon. The entropy of liquid argon at its melting point at atmospheric pressure, as computed from the data of Euken[16] is 12.5 E.U. The general formula for the entropy of a liquid is,[17]

$$S = 4R + R \ln (2\pi mkT)^{\frac{3}{2}} V_f / h^3 N \quad (14)$$

and this leads to a value of 0.15 cc for the free volume of liquid argon at its melting point. Taking the specific heats at constant volume and constant pressure given by Euken and Hauck,[18] and the volumes determined by Baly and Donnan,[19] we estimate β_s at the melting point to be 1.29×10^{-10} c.g.s. unit. This corresponds to a value of u equal to 0.74×10^5 cm/sec. and a free volume of 0.35 cc. The agreement to within a factor of two is considered satisfactory in view of the uncertainties in the data. The free volume for argon at its boiling point was determined from its heat of vaporization to be 1.25 cc. Since other methods yield much smaller values, it appears to us that the accepted figure for the heat of vaporization must be too low. A value of 1.65

TABLE IV. *Free volumes for liquid mercury at different temperatures and pressures.*

$t°C$	P(ATM.)	V_f FROM EQ. (6)	V_f FROM EQ. (13)
−39°	1		0.0081 cc
0	1	0.0120 cc	.0120
100°	1	.0220	.0256
200°	1		.0434
300°	1		.0718
357°	1		.0904
0°	1	.0120	.0120
0°	1000	.0117	.0116
0°	2000	.0114	.0114
0°	3000	.0111	.0111
0°	4000	.0107	.0109
0°	5000	.0104	.0107
0°	6000	.0101	.0105
0°	7000	.0098	.0103

the communal sharing of the free volume. It also is dependent on the assumption that each molecule moves on a parabolic dynamic energy curve, and on the vanishing of the derivative $(\partial E_s / \partial T)_T$, where E_s is the static energy previously defined (Ref. 5). It is believed that these simplifications do not lead to serious error in this case.

[18] A. Euken, and F. Hauck, Zeits. f. physik. Chemie **134**, 161 (1928).
[19] E. C. C. Baly, and F. G. Donnan, J. Chem. Soc. **81**, 907 (1902).

[16] A. Euken, Verh. D. phys. Ges. **18**, 4 (1916).
[17] This formula in the exact form given depends on a contribution of R to the entropy of fusion resulting from

kcal./mole, 10 percent greater than that given in the *International Critical Tables*, is indicated by the theory.

Determination of free volumes from spectroscopy

The frequency of vibration of molecules in liquids is related to the free volume by the approximate relationship,

$$\frac{(2\pi mkT)^{\frac{1}{2}}}{h}\frac{V^{\frac{1}{3}}}{u}\left(\frac{RT\gamma}{M}\right)^{\frac{1}{2}}=N^{\frac{1}{3}}\frac{kT}{h\nu}$$

$$=\frac{(2\pi mkT)^{\frac{1}{2}}}{h}V_f^{\frac{1}{3}}, \quad (15)$$

which connects the velocity of sound in the liquid with the energy $h\nu$ for a translational degree of freedom. Thus one would expect the light scattered from liquids to show the familiar Stokes and anti-Stokes lines of the Raman spectrum corresponding to energies from 10 to 100 cm^{-1}. Such lines have been observed[20] and as Debye[21] has remarked they show the same correlation between frequency and sound velocity to be expected from Eq. (15). This method of arriving at free volumes will no doubt become of increasing importance.

RESTRICTED ROTATION OF MOLECULES IN LIQUIDS

Heat capacity as a criterion of restricted rotation

Most of the available data for the quantity C_v(liquid) minus C_v(ideal gas) has been summarized in Table V. It is seen that in all cases the heat capacity at constant volume for the liquid is greater than the ideal gas value and that this inequality persists up to the critical point. Considering first the two examples of monatomic liquids which are given in the table, we note differences of 2.6 and 3.1 calories per mole per degree for argon and mercury respectively at their melting points. These are just the differences to be expected if three degrees of translational freedom for the molecule in the vapor have become vibrations in the liquid.

The data for liquids composed of more complex molecules can be interpreted in terms of hindered rotation of the molecules. If rotational degrees of freedom of the molecules in the vapor become librations[22] in the liquid we would expect a specific heat difference between liquid and ideal gas of about one calorie per mole per degree for each degree of freedom so affected. This may, of course, be modified by anharmonic terms in the

TABLE V. *Difference between the specific heats at constant volume for the ideal gas and the liquid for various substances at different temperatures.*[29]

ARGON[23] $T°$K	C_v(LIQ) $-C_v$(IDEAL GAS)	MERCURY[b] $T°$K	C_v(LIQ) $-C_v$(IDEAL GAS)	CARBON DISFULIDE[12, 24] $T°$K	C_v(LIQ) $-C_v$(IDEAL GAS)	CARBON TETRACHLORIDE[12, 26] $T°$K	C_v(LIQ) $-C_v$(IDEAL GAS)	
84°	(2.6)	234°	3.1	160°	(4.7)	250°	(4.0)	Melting Point
		370°	2.6	210°	(3.9)	280°	3.8	
		500°	2.4	265°	3.1	310°	3.4	
87°	2.5	630°	2.3	319°	2.3	349°	(3.0)	Boiling Point
156°	1.1							Critical Point

T CHLOROFORM[12, 26] $T°$K	C_v(LIQ) $-C_v$(IDEAL GAS)	BENZENE[12, 27] $T°$K	C_v(LIQ) $-C_v$(IDEAL GAS)	ETHYLENE[23, 25, 28] $T°$K	C_v(LIQ) $-C_v$(IDEAL GAS)	
203°	(6.7)	278°	5.3	104°	5.3	Melting Point
250°	(6.3)	300°	5.0	125°	5.3	
290°	5.3	325°	4.9	150°	5.3	
334°	4.7	353°	4.9	170°	5.3	Boiling Point
				283°	(4.2)	Critical Point

[20] E. Gross, and M. Vuks, Nature **135**, 998 (1935).
[21] P. Debye, Chem. Rev. **19**, 171 (1936).
[22] Libration is used here to mean restricted rotation.
[23] A. Euken and Hauck, Zeits. f. physik. Chemie **134**, 161 (1938).
[24] Paul C. Cross, J. Chem. Phys. **3**, 825 (1935).
[25] G. B. Kistiakowsky and Falih Nazmi, J. Chem. Phys. **6**, 18 (1938).
[26] Robert D. Vold, J. Am. Chem. Soc. **59**, 1192 (1935).
[27] R. C. Lord and D. H. Andrews, J. Phys. Chem. **41**, 149 (1937).
[28] Mathies E. Haas and Gebhart Stegeman, J. Phys. Chem. **36**, 2125 (1932).
[29] The data for specific heats at constant volume for the vapors are, in most cases, calculations from spectroscopic data. The references give either the computations or the necessary data for making them. Extrapolated values are given in parentheses.

potential functions. On this basis the difference of 5.3 calories per mole per degree shown by benzene and ethylene near their melting points is interpreted as being due to vibrations for five of the degrees of freedom and free rotation about the axis perpendicular to the plane of the molecule for the other. It is significant that carbon tetrachloride, a symmetrical molecule, has a smaller difference between the specific heats of liquid and vapor than chloroform, a relatively unsymmetrical one. The data indicate that even carbon disulfide does not rotate freely in the liquid, but the figures at the two lowest temperatures recorded must be interpreted with some caution since they represent long extrapolations. The same is true of the chloroform data. The high value of 4.2 calories per mole per degree for the difference between the observed and the ideal gas value for ethylene at the critical point may be due to a change with temperature of association into double and triple molecules, assuming, of course, that the data are correct. Any hypothesis of hindered rotation at such large volumes appears unlikely.

Since the data indicate that the effect of rising temperature, and thus of increasing volume, is to reduce the potential restricting rotation, it is of interest to examine the effect of volume changes alone on this potential. This can be done by examining the effect of pressure on the specific heat at constant volume of those liquids for which adequate data are available. Table VI shows values of C_v for liquid benzene at various pressures and temperatures. The contribution of the internal vibrations to the specific heat have been subtracted from the thermodynamic C_v. It is necessary to assume that this contribution is independent of pressure since no data are available on the effect of high pressures on the frequencies corresponding to the normal modes of vibration of molecules. Assuming that this effect will not change the qualitative aspects of the data we have the result that the heat capacity at constant volume is considerably greater at 1000 bars[31] than at low pressures. The fact that C_v rises to as high a value as 12.1 calories per mole per degree appears to indicate that at high pressures there is restricted rotation even about the axis perpendicular to the plane of the ring.

The free angle ratio from spectroscopy

When the velocity of sound in liquid water is used to compute V_f at room temperature a value of about 0.4 cc is secured. On the other hand, the product $\delta_3 V_f$ as determined from heats of vaporization and vapor pressures at the same temperature is about 0.02 cc. A reasonable interpretation is to assign the discrepancy of a factor of about 20 to a small free angle ratio. A

TABLE VI. *The heat capacity at constant volume of liquid benzene under pressure.*[30]

$t°K$	1 BAR	250 BARS	500 BARS	750 BARS	1000 BARS
298.1°	11.0	11.1	11.3	11.5	11.7
308.1°	10.9	11.0	11.2	11.5	11.7
318.1°	10.8	11.1	11.3	11.6	11.8
328.1°	10.8	11.2	11.4	11.7	11.9
338.1°	10.7	11.2	11.4	11.8	12.1

[30] The units are calories per mole per degree. The changes of specific heat with pressure were computed from the data of Gibson and Kincaid[15] using the thermodynamic equations,

$$dC_p/dP = -Td^2V/dT^2 \quad \text{and} \quad C_p - C_v = T\alpha^2 V/\beta,$$

where C_p is the specific heat at constant pressure, and α and β are defined as,

$$\alpha = 1/V(\partial V/\partial T)_p, \quad \beta = -1/V(\partial V/\partial P)_T.$$

The values for C_p at one bar are the weighted mean of the data given in Landolt-Börnstein, *Tabellen*. The contributions to the specific heat made by the internal vibrations were computed from the frequencies given by Lord and Andrews.[27]

TABLE VII. *Free volumes for liquid water.*

$t°C$	V_f FROM[32] EQ. (6) (SOUND VELOCITY)	$\delta_3 V_f$ FROM EQ. (2) (VAPOR PRESSURE)	$1/\delta_3$[33] (FROM SPECTROSCOPY)	$(\delta_3 V_f)1/\delta_3$
0	0.44 cc	0.0095 cc	26	0.25 cc
10	.43	.012	25	.36
20	.42	.014	25	.35
30	.42	.017	24	.41
40	.43	.021	24	.50
50		.025	24	.60
75		.040	24	.96
100		.062	24	1.5

[31] The bar, or metric atmosphere, is equal to 10^6 dynes per square centimeter. This is approximately one normal atmosphere.

[32] Sound velocity data from J. C. Hubbard and A. L. Loomis, Phil. Mag. 5, 1177 (1928).

[33] $1/\delta_3$ computed from the relation

$$1/\delta_3 = \left[\frac{8\pi^2(8\pi^3(kT)^3ABC)^{\frac{1}{2}}}{h^3}\right]\left[\left(\frac{1}{1-\exp(-hc167/kT)}\right)^2 \right.$$
$$\left. \times \left(\frac{1}{1-\exp(-hc500/kT)}\right)\right]^{-1}$$

with a value of ABC, the products of the principal moments of inertia, equal to 6.1×10^{-120}.

check of this hypothesis is possible. Cartwright[34] has observed frequencies of 167 and 500 cm^{-1} in liquid water at room temperature. These frequencies were interpreted by him as arising from restricted rotation of the molecules. Since three degrees of rotational freedom must be accounted for, at least one of the rather broad absorption regions probably arises from two frequencies, and Stearn and Eyring[35] have employed a doubly degenerate frequency at 167 cm^{-1} to represent approximately this absorption band. Using this approximation we have the values for the free angle ratio shown in Table VII. These were secured by taking the ratio of the partition function for free rotation of the water molecule and the product of the Einstein function corresponding to frequencies of (2) 167 cm^{-1} and 500 cm^{-1}.

It may be seen that the free volume from the vapor pressure, the heat of vaporization, and the observed frequencies is almost exactly equal to the free volume from sound velocity at room temperature, the point at which the spectroscopic observations were made. The discrepancies at other temperatures indicate that the frequencies corresponding to restricted rotation should be greater than those observed at lower temperatures, and smaller at higher temperatures. Such a temperature drift will probably be difficult to observe spectroscopically because rising temperature simply makes the absorption bands broader and more diffuse, as has been observed.[36]

The dielectric constant as a criterion for restricted rotation

In order to have available a new tool for the determination and interpretation of restricted rotation of molecules in liquids, formulas connecting the free angle ratio with the dielectric
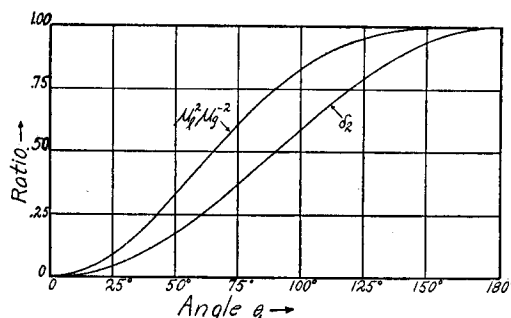

FIG. 2. $\mu_l{}^2\mu_v{}^{-2}$ plotted against the polar angle θ_1. This ratio is determined from equation (17) and the relation, $\bar{m} = \mu^2 F/3kT$ which holds for the gas.

constant are given. The importance of the free angle ratio in determining vapor pressures and boiling points of liquids may be seen by inspection of Fig. 2 where δ_2 is plotted as a function of the polar angle, θ_1, through which the molecule is free to turn. Here θ_1 is analogous to the angle of colatitude as measured on a globe from the north pole down to a given "parallel," and δ_2 is the corresponding solid angle divided by 4π. The two are connected by the equation,

$$\delta_2 = 1 - \cos\theta_1/2. \tag{15}$$

Here δ_2 is analogous to δ_2 previously defined for linear molecules, but differs from δ_3 for nonlinear ones since it does not take account of the restricted rotation of the molecule about the axis in which the dipole lies. If the potential curves for the rotation of the molecule about the three axes are symmetrical, then δ_2 is equal to the two-thirds power of δ_3. In some actual cases this relation is approximately correct as we shall see later.

We next consider dipoles free to orient under the influence of the field in the region between the pole and colatitude θ_1, assuming the poles are distributed at random with respect to the field direction. The expression for the average moment $\bar{m}$, using classical statistics is then:

$$\bar{m} = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi}\left[\frac{\int_0^{2\pi}\int_0^{\theta_1}\exp\left(\frac{\mu F}{kT}\cos\theta_{12}\right)\mu\cos\theta_{12}\sin\theta_1 d\theta_1 d\varphi_1}{\int_0^{2\pi}\int_0^{\theta_1}\exp\left(\frac{\mu F}{kT}\cos\theta_{12}\right)\sin\theta_1 d\theta_1 d\varphi_1}\right]\sin\theta_2 d\theta_2 d\varphi_2. \tag{16}$$

[34] C. H. Cartwright, Phys. Rev. 49, 470 (1936).
[35] A. E. Stearn and Henry Eyring, J. Chem. Phys. 5, 113 (1937).
[36] Paul C. Cross, John Burnham, and Philip A. Leighton, J. Am. Chem. Soc. 59, 1134 (1937).

Here θ_{12} is the angle between the dipole and the applied field, F, and μ is the dipole moment. θ_1 and φ_1 are the polar coordinates of the dipole

with respect to an axis chosen in such a way that the dipole can move with a potential energy which depends only on θ. This potential energy arises from interaction with neighbors. θ_2 and φ_2 give the direction of the applied electric field with respect to the same axis. The evaluation of $\bar{m}$ follows without difficulty using the expansion $\exp(x) = 1 + x + x^2/2 + \cdots$ and the identity $\cos\theta_{12} \equiv \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2(\sin\varphi_1 \sin\varphi_2 + \cos\varphi_1 \cos\varphi_2)$. The result is

$$\bar{m} = \frac{\mu^2 F}{3kT}\left[1 - \left(\frac{1 + \cos\theta_1}{2}\right)^2\right]. \qquad (17)$$

Higher powers of $\mu F/kT$ are readily calculable, but are in general negligible.

The values for δ_2 and $\mu_l^2\mu_g^{-2}$ as a function of θ_1 are tabulated in Table VIII and shown in Fig. 2. Here μ_g is the dipole moment which is calculated from measurements on the gas, while μ_l is the value calculated in the same way if the rotation is restricted to lie between the polar angles 0 to θ_1.

If in addition to moving freely between 0 and θ_1 an extra potential energy E permits the dipole to move between θ_1 and 180°, the equation corresponding to (16) gives,

$$\bar{m} = \frac{\mu^2 F}{3kT}\left[1 - \left(\frac{\sin^2\theta_1(1 - \exp(-E/RT))}{2(1 - \cos\theta_1 + (1 + \cos\theta_1)\exp(-E/RT))}\right)^2\right]. \qquad (18)$$

Finally if the potential energy for rotation between 0° and θ_1° is zero, between θ_1 and θ_2 is E, and between θ_2 and 180° is again zero, then the analog to (16) gives

$$\bar{m} = \frac{\mu^2 F}{3kT}\left[1 - \frac{1}{4}\left(\frac{(\sin^2\theta_1 - \sin^2\theta_2)(1 - \exp(-E/RT))}{2 + (\cos\theta_2 - \cos\theta_1)(1 - \exp(-E/RT))}\right)^2\right]. \qquad (19)$$

Other cases can be obtained in a similar way but these will suffice for our purpose.

Consider first the application of the theory to a solution of a polar substance in a nonpolar solvent. If the solution is sufficiently dilute for interactions between the dipoles to be negligible, any restriction on the free rotation of the polar molecule is imposed by the nonpolar molecules around it. Under these conditions, the polar molecules can orient in the solution with almost exactly the same ease that they can do so in the gas phase, *provided the frequency of the applied field is well below the natural frequency of rotation of the solute molecules in the solution.* For small solute molecules in relatively nonviscous solvents, the frequencies at which derivations due to dispersion can be expected are well above the present experimental range.

In pure polar liquids, however, an entirely different situation exists. Under these conditions all the molecules are not free to orient in the field both because of dipole coupling and because of the size and shape of the molecules. As we have already seen for the case of water, spectroscopic considerations and the velocity of sound, in conjunction with the vapor pressures, agree in giving a value for δ_3 of about 0.04, corresponding to a δ_2 of 0.12($=0.04^{\frac{2}{3}}$). We use the familiar equations,

$$\frac{\epsilon - 1}{\epsilon + 2}V = \frac{4\pi}{3}N\left(\alpha + \frac{\mu^2}{3kT}\right) \qquad (20)$$

TABLE VIII

θ_1	0°	10°	20°	30°	40°	50°	60°
$\mu_l^2\mu_g^{-2}$	0	.0153	.0594	.1296	.2202	.3252	.4374
δ_2	0	.0076	.0301	.0665	.1170	.1786	.2500

θ_1	70°	80°	90°	100°	110°	120°
$\mu_l^2\mu_g^{-2}$	.5508	.6555	.7500	.8292	.8919	.9375
δ_2	.3290	.4131	.5000	.5869	.6710	.7500

θ_1	130°	140°	150°	160°	170°	180°
$\mu_l^2\mu_g^{-2}$	.9681	.9864	.9954	.9990	1.0000	1.0000
δ_2	.8214	.8830	.9335	.9699	.9924	1.0000

and
$$\frac{n^2-1}{n^2+2}V = \frac{4\pi}{3}N\alpha. \quad (21)$$

At 20° and one atmosphere water has an index of refraction for sodium light of n equal to 1.3330, a molal volume, V, of 18.05 cc and a dielectric constant, ϵ, of 80. This leads to a value for $(4\pi/3)N\alpha$ of 3.7 cc and $(4\pi N/3)\mu^2/3kT = 13.7$ cc for the liquid. For the gas $(4\pi N/3)\mu^2/3kT = 71$ cc.[37] From Fig. 2 we see that this value of $\mu_l^2\mu_g^{-2}$ of 0.194 leads to a value of δ_2 of 0.10 to be compared to 0.12 found above.

The same calculations for methyl alcohol at 0°C yield the following results. $V_f\delta_3$ from vapor pressures and heats of vaporization is 0.026 cc, and V_f from sound velocity is 0.54 cc. The value of δ_3 from these results is 0.048, corresponding to δ_2 equal to 0.13. Utilizing the data of Åkerlöf[38] we obtain the value of 0.25 for δ_2 at the same temperature from the dielectric constant and dipole moment of the molecule.[39] It is of interest to observe that δ_2, as determined from dielectric constant, increases with the temperature being 0.34 to 60°C. Such a result is, of course, to be expected.

There is a tendency for δ_2 from the dielectric constant to be greater than $(\delta_3)^{\frac{2}{3}}$ determined from other sources. This might be interpreted as due to a restriction on rotation about the axis in which the electric moment of the molecule lies which is greater than that about the other two axes. This is probably a valid argument in the case of water since the higher of the two frequencies which were employed to account for restricted rotation undoubtedly corresponds to a mode of motion involving only the hydrogens, and thus is a libration about the axis in which the dipole lies. Computing this correction from the Einstein functions corresponding to these frequencies gives a value of δ_2 of 0.09 to be compared to 0.10 from the dielectric constant.

It is not unreasonable that the discrepancy in the case of methyl alcohol might be accounted for on a similar basis, but the data for making such a computation are not at present available.

However, various factors which might cause deviations from the theory have been neglected. Thus, the coupling of dipoles in the liquid may operate in such a way as to either increase or reduce the apparent moment of the molecule in the liquid. Also the adequacy of equation (20) for pure polar liquids is by no means always conceded, even after account is taken of the restricted rotation of the molecules.[40]

However, it appears that any explanation of the deviations from (20) which is not compatible with restricted rotation of the molecules in many liquids is not in agreement with other lines of evidence. Fowler,[41] and Debye and Ramm[42] have also interpreted the dielectric properties of condensed phases from the point of view of restricted rotation.

CONCLUSION

The results of this work lead us to suggest that the abnormalities of the so-called associated liquids can be explained entirely from the standpoint of restricted rotation of the molecules. Thus although water and methyl alcohol are ordinarily classed as highly abnormal, their free volumes from sound velocity are not markedly different from those of other liquids. It is only the product, $V_f\delta_3$, rather than V_f itself, which is a different order of magnitude for "hydrogen bonded" as compared to normal liquids. The values recorded here for δ_3 for water and methyl alcohol thus account for their abnormally high entropies of vaporization.

[37] P. Debye, Chem. Rev. **19**, 171 (1936).
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[41] R. H. Fowler, Proc. Roy. Soc. **149A**, 1 (1935).
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