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A small change in a at constant Q_f and V/RT affects these functions as follows:

$$\delta(F_H/T)/\delta a = H_H/aT$$

and

$$\delta(H_H/T)/\delta a = H_H/aT - C_H/a.$$

Since $S = (H - F)/T$, it follows that

$$\delta S_H/\delta a = -C_H/a$$

Thus the changes in the harmonic oscillator properties, and therefore also in the differences of Table I, are related in a simple way to the properties themselves. At $1/Q_f = 0$, a given small change in a will produce the same effect upon the entropy and free energy at all values of V/RT , while at the same time the heat content will remain unchanged at the classical value. When V/RT is low, the frequency remains low through the whole useful range of $1/Q_f$, and the effect of changing a will change only slightly as $1/Q_f$ increases. If V/RT is high, a change in a will

change the entropy and free energy by amounts varying from zero at high $1/Q_f$ to R times the percentage change in a at low $1/Q_f$.

This shows how the trend of 0.05 to 0.06 in the entropy and free energy differences found for the limiting harmonic oscillator at high V/RT can be effectively leveled out by the small change in a from $\pi^{1/2}$ to 1.74. The effect on the heat content and heat capacity is zero at both ends of the $1/Q_f$ scale and reaches a low maximum at some intermediate but fairly high $1/Q_f$. This maximum is less than one-half the maximum effect on the entropy and free energy.

It is reasonable that the most suitable harmonic oscillator for the comparison should have frequencies below the limiting ones, because in the useful range of the variables RT is always an appreciable fraction of V and, as a consequence, the average spacing of the more important energy levels will be less than that of the limiting oscillator.

Intermolecular Forces and Energies of Vaporization of Liquids

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By using a "smoothed potential" model for the liquid state and assuming isotropic, homogeneous expansion with temperature which involves no change in coordination, it is shown that it is possible to reduce the expression for the configurational energy of the liquid to a function of a single parameter, the density. If the intermolecular forces can be put into a polynomial form then the expression for the configurational energy can be factored, resulting in an algebraic equation of the form:

$$E_c = -B_1 D^2 - B_2 D^{3/2} - B_3 D^{-10/3} + B_4 D^4$$

INTRODUCTION

IN recent years, the problem of expressing analytically the thermodynamic properties of liquids has been shown capable of treatment using the methods of statistical mechanics. The most general and rigorous treatment made by Mayer and other workers,¹ has thrown consider-

able light on the phenomenon of condensation and raised fundamental questions concerning the region of the critical temperature. However, while fundamental in its approach, this method has not yielded functions susceptible to a simple, practical treatment.

Simpler models of the liquid state, based on

¹ Mayer and Mayer, *Statistical Mechanics*, Chaps. 13, 14 (John Wiley, 1940) (summarizes most of the recent work);

see also: Band *et al.*, *J. Chem. Phys.* 9, 123 (1941) and earlier papers.

somewhat crude formulations have yielded surprisingly good qualitative and even quantitative agreements with experimental data.²⁻⁵ These models may be termed "cage" models. They assume a quasi-crystalline structure for the liquid in which the molecules are restricted to motions in a cage of nearest neighbors. The main differences between such models and a true solid, lies in the ability of the liquid molecules to exchange cages, in the slightly weaker central forces acting on the molecule of the liquid as it moves from the center of its cage, and in the anisotropy of the solid.

The crudest of these models which has given significant results is the one proposed by Guggenheim,⁶ called the "smoothed potential" model. This model assumes that the liquid molecule, constrained to move within its cage, moves in a potential well with a flat floor and essentially infinite walls at the edges of the cage.

In this paper, it will be shown that the "smoothed potential" model for the liquid, when used in conjunction with intermolecular potentials of the London⁷ form will yield a simple relation connecting the energy of vaporization and the density of the liquid. This relation is in excellent agreement with the experimental values for these quantities over most of the liquid range.

I. THE SMOOTHED POTENTIAL MODEL

If we assume a liquid composed of hard, spherical molecules of diameter d , moving in an average potential field $-U_c$, which is constant within the cage of a molecule, then we can write for the partition function of 1 mole:

$$Q_c = e^{Nv_f N e^{NU_c/kT}} = (ev_f e^{U_c/kT})^N. \quad (1)$$

N is Avogadro's number, v_f is the volume accessible to the center of the molecule (i.e., its free volume), and k is the Boltzmann constant.

For a rectangular potential well of the type which this model assumes, v_f may be represented by:

$$v_f = \frac{1}{8}\pi(a-d)^3 \quad (2)$$

² Fowler and Guggenheim, *Statistical Thermodynamics*, Chaps. 7, 8. (Presents a review of the work with simple liquid models, Cambridge University Press, London, 1939.)

³ Eyring and Hirschfelder, *J. Phys. Chem.* **41**, 250 (1937).

⁴ Newton and Eyring, *Trans. Faraday Soc.* **33**, 73 (1936).

⁵ H. S. Frank, *J. Chem. Phys.* **13**, 478-507 (1945).

⁶ Guggenheim, *Proc. Roy. Soc. A* **135**, 181 (1932).

⁷ London, *Zeits. f. physik. Chemie* **B11**, 222 (1930).

in which a is the average distance between the central molecule and its nearest neighbors. (The radius of the cage is equal to a .) We see then that " a " will be some function of the molar volume of the liquid, V . Thus, the free volume v_f becomes a function of V only.

The total partition function, Q , which will include the contributions of the external and internal degrees of freedom may be written as:

$$Q = Q_{\text{trans}} \cdot Q_{\text{rot}} \cdot Q_{\text{int}} \cdot Q_c. \quad (3)$$

This assumes that the various energies, internal and external, are all separable. From Q , the thermodynamic functions of the liquid may be obtained:

$$A = -kT \ln Q; \quad E = kT^2(d \ln Q/dT)_v; \quad \text{etc.} \quad (4)$$

II. THE CONFIGURATIONAL ENERGY

The expression for the partition function, Q_c , has been termed the configurational partition function⁸ since it represents that contribution to the total partition function which is caused by the intermolecular structure.

If we assume that the forces between molecules in a liquid are functions only of the distance of separation then it can be shown that U_c is a function only of the volume and Q_c will contribute exactly the quantity U_c to the total energy of the system. U_c is then the configurational energy of the system, and for molecules with no forces of interaction, U_c is equal to zero.

Let $E(r)$ represent the mutual potential energy averaged over-all configurations, of a pair of molecules, distant r from each other. Then the total potential energy of a molecule in the liquid, E_m will be the quantity $E(r)$ summed over all molecules in the liquid. This can be written as:

$$E_m = \sum_{i=1}^N n_i E(r_i). \quad (5)$$

In this equation n_i is the number of molecules at a distance r_i from the central molecule. Since n_i will increase roughly as r^2 , $E(r_i)$ must decrease faster than r_i^{-3} if E_m is to remain finite.

U_c represents the energy required to separate all the molecules in the liquid. If we think of the liquid as being composed of bonds between each pair of molecules, then U_c would be the energy required to break all of these bonds. We

then have the relation:

$$U_c = \frac{1}{2} N E_m = \frac{1}{2} N \sum_{i=1}^N n_i E(r_i). \quad (6)$$

The factor of $\frac{1}{2}$ is introduced to avoid counting all the bonds twice. Equation (6) assumes that E_m is the same for all the molecules in the liquid. This cannot be the case for the molecules in the surface, but for any large number of molecules in the aggregate the contribution of the surface molecules may be neglected.

If we now make the assumption that temperature expansion of the liquid is a regular, homogeneous, isotropic change in which the coordination of the molecules is unchanged (an assumption which is compatible with the type of potential well employed), then the quantities n_i become independent of temperature and the entire temperature dependence of U_c is to be found in $E(r_i)$.

This assumption of homogeneous temperature expansion means that all of the intermolecular distances may be related to any configuration of the liquid (chosen as a standard) by a single parameter. If r_1 is equal to the distance between the central molecule and its nearest neighbors ($r_1 = a$; see Eq. (2)) then it is possible to relate all the other distances in the liquid to r_1 by equations of the type:

$$r_i = c_i r_1. \quad (7)$$

The quantities c_i will be pure number ratios which will be independent of temperature and dependent only on the geometry or packing of the liquid.* If we choose a single temperature as a reference temperature, then for this standard state the ratios c_i are the ratios of the intermolecular distances to the distance r_1 .

Replacing the r_i in Eq. (6) by their values from Eq. (7), we have:

$$U_c = \frac{1}{2} N \sum_{i=1}^N n_i E(c_i r_1). \quad (8)$$

It is desirable to relate r_1 to some property of the liquid, and the most convenient property for this purpose is the molar density D . Generally the density will be inversely proportional to r_1^3

* If hexagonal packing is assumed, then $n_1 = 12$, $n_2 = 18$, $n_3 = 24$, etc., and $c_1 = 1$, $c_2 = (3/4)^{1/3}$, $c_3 = 2$, etc. For simple cubic packing, $n_1 = 6$, $n_2 = 12$, $n_3 = 8$, ... and $c_1 = 1$, $c_2 = 2^{1/3}$, $c_3 = 3^{1/3}$, etc.

and we can write,

$$r_1 = g D^{-1/3}, \quad (9)$$

in which g is again a geometrical constant independent of temperature.**

Substituting the value of r_1 from Eq. (9) into Eq. (8), we will have

$$U_c = \frac{1}{2} N \sum_{i=1}^N n_i E(c_i g D^{-1/3}). \quad (10)$$

In Eq. 10, U_c has been reduced to an expression which is a function of a single parameter, the molar density D , and it is now amenable to rather simple treatment.

III. ENERGY OF VAPORIZATION

The total energy E , of the liquid will be given by the expression (Eq. (4))

$$E = k T^2 (d \ln Q / d T)_V.$$

If we assume that the various degrees of freedom are separable then, from Eq. (3) we have,

$$E = k T^2 (d \ln Q_T \cdot Q_R \cdot Q_I) / d T)_V + U_c. \quad (11)$$

If we further assume that the rotation of the liquid is free or almost free (i.e., rotational barriers $< kT$) and that the internal modes of motion are the same in the liquid and vapor phases, then the partition functions Q_T , Q_R , and Q_I will be the same for both liquid and vapor.

To this degree of approximation then, we will have for the energy of vaporization,

$$E_{vap} = E(\text{gas}) - E(\text{liq}) = U_c(\text{gas}) - U_c(\text{liq}). \quad (12)$$

At temperatures at which the density of the gas is small, the energy of the gas may be neglected and we can write,

$$E_{vap} = U_c(\text{liq}). \quad (13)$$

As a next approximation of Eq. (13), we may assume the gas capable of the same treatment as the liquid, and in this case we can use the same function in Eq. (12) for the configurational energy of gas and liquid.

IV. INTERMOLECULAR POTENTIALS

London⁷ has shown that for non-polar molecules, the attractive forces are given by an

** For hexagonal packing: $g = 1.12 N^{-1/3}$. For simple cubic packing: $g = N^{-1/3}$.

expression,

$$E(r) = -\alpha/r^6 - \beta/r^8 - \gamma/r^{10} \quad (14)$$

in which the constants α , β , and γ are independent of temperature. Of these terms, the first (the "dipole-dipole" interaction) is dominant, although the other terms may become important at small distances. For molecules possessing dipole moments, the constant α is no longer temperature independent and has the form,

$$\alpha = \alpha_1 + \alpha_2/T. \quad (15)$$

The first term α_1 in Eq. (15) represents the sum of the London dispersion forces and the "induction" effect. For most substances, this latter is usually negligible. The term α_2/T in Eq. (15) arises from the orientation effect caused by the permanent dipoles. For most polar substances this term is usually small compared to the dispersion term. Only for substances such as NH_3 and H_2O , which are strongly hydrogen-bonded, does the orientation effect exceed the dispersion term. However, the orientation effect is not additive, whereas the dispersion and induction terms are. It is not therefore unreasonable to use Eq. (14) to represent the attractive forces without considering the temperature dependence of α in the case of very polar molecules.⁸

In addition to the attractive forces, there exist repulsive forces at small distances which have been variously represented in the form δr^{-m} . With the aid of the quantum theory it has been shown⁹⁻¹¹ that the correct theoretical form for these repulsive forces is Ae^{-r/r_0} . Although A is a function of r , Slater⁹ has shown that no large error is involved in assuming A to be a constant for a given molecule. In any case, these forces of repulsion fall off very rapidly with the distance, and excellent agreement with experimental data has been obtained using either form.¹²⁻¹⁴

A general expression may then be written for

⁸ Margenau, Rev. Mod. Phys. **11**, 1 (1939), reviews the theories of intermolecular forces and discusses the importance of the various terms.

⁹ Slater, Phys. Rev. **32**, 349 (1928).

¹⁰ Buckingham, Proc. Roy. Soc. **A161**, 476 (1937).

¹¹ Huggins, J. Chem. Phys. **5**, 143 (1937).

¹² Hirschfelder and Roseveare, J. Phys. Chem. **43**, 15 (1939).

¹³ Buckingham, Proc. Roy. Soc. **A168**, 264 (1938).

¹⁴ Lennard-Jones, Proc. Phys. Soc. **43**, 461 (1931).

the total forces of interaction as follows:

$$E(r) = -\frac{\alpha}{r^6} - \frac{\beta}{r^8} - \frac{\gamma}{r^{10}} + \frac{\delta}{r^{12}}. \quad (16)$$

For the distances which occur in liquids this may be approximated by assuming hard molecules with attractive forces of the form,

$$E(r) = -\alpha_0/r^x. \quad (17)$$

This is justified to some extent by the fact that the higher dispersion terms in Eq. (16) are of about the order of magnitude and of opposite sign to the last repulsion term.⁸ If over the range of distances in the liquid at different temperatures the cancellation of these terms is very close, then x would have the value of 6. Estimating more closely, most of the intermolecular potential caused by these higher order terms will arise from the nearest neighbors and for these small distances the contribution of the repulsive forces is larger⁸ than the higher order dispersion terms, and we may expect to find values of x less than 6.

Substituting the value of $E(r)$ from Eq. (17) into Eq. (10), we find for the configurational energy,

$$U_c = -\frac{1}{2}N \sum_{i=1}^N n_i \alpha_0 c_i^{-x/3} g^{-x/3} D^{x/3} \quad (18)$$

$$= -(\frac{1}{2}N \alpha_0 g^{-x/3}) D^{x/3} \sum_{i=1}^N n_i c_i^{-x/3} \quad (19)$$

$$= -AD^{x/3}. \quad (20)$$

In Eq. (20), A is a constant containing only temperature independent quantities and so U_c is reduced to a simple function of the density. It can be seen from the form of U_c given in Eq. (10) that so long as we can express $E(r)$ as a polynomial in r , U_c can always be reduced to a simple polynomial expression in terms of D .

In the general case, using all the terms for the potential energy we would have:

$$U_c = -B_1 D^2 - B_2 D^{8/3} - B_3 D^{10/3} + B_4 D^4.$$

The term B_1 might be expected to show some temperature dependence for very polar or hydrogen-bonded molecules, and terms B_2 and B_3 would be of smaller magnitude with B_3 probably

TABLE I.*

Substance	M	T_c °C	D_c	A_{av}	A (x=6)		Range -°C	A_{av}	A (x=5)		Range -°C
					Av. dev. %	Max. dev. %			Av. dev. %	Max. dev. %	
Carbon dioxide	44	31.1	10.58	4.73	1.7	2.7	-60°/20°	13.6	2.4	4.1	-60°/20°
Sulfur dioxide	64	157.2	8.12	10.28	1.1	1.8	-40°/60°	28.9	2.5	5.9	-40°/60°
Ammonia	17	132.9	13.75	3.28	2.4	4.3	-50°/50°	10.97	0.6	1.3	-50°/50°
Water	18	374.4	17.72	3.29	2.3	4.5	0°/374.1°	11.68	1.3	3.6	0°/341°
Methyl alcohol	32	240.0	8.52	14.42	2.3	7.0	0°/238°	39.8	2.6	6.7	0°/210°
Ethyl alcohol	46	243.1	5.99	33.5	2.0	7.1	0°/230°	83.5	2.3	7.5	0°/200°
Propyl alcohol	60	263.7	4.55	59.0	3.1	9.5	0°/230°	135.5	4.4	11.2	0°/210°
Ethyl ether	74	193.8	3.55	65.1	1.9	4.0	0°/190°	134.8	0.5	3.1	0°/160°
Methyl formate	60	214.0	5.82	24.8	1.0	2.6	-20°/200°	68.2	1.5	4.0	-20°/170°
Ethyl formate	74	235.3	4.36	47.0	1.0	3.0	50°/220°	103.0	1.8	4.4	50°/200°
Propyl formate	88	264.9	3.52	79.3	1.1	3.5	70°/260°	160.5	1.7	4.0	70°/240°
Methyl acetate	74	233.7	4.40	48.2	1.5	2.8	50°/227°	105.5	1.8	6.0	50°/210°
Ethyl acetate	88	250.1	2.86	79.4	2.2	4.8	5°/245°	163.0	1.6	3.7	5°/210°
Propyl acetate	102	276.2	2.90	126.0	1.8	3.5	90°/266°	238	1.1	3.5	90°/250°
Methyl propionate	88	257.4	3.20	78.5	1.6	3.3	70°/250°	159.2	1.4	4.0	70°/230°
Ethyl propionate	102	272.9	2.91	121.8	1.7	3.5	0°/270°	238	2.0	4.7	0°/240°
Methyl butyrate	102	281.3	2.94	120.2	2.3	4.5	100°/278°	230	0.5	2.0	100°/250°
Methyl isobutyrate	102	267.6	2.95	116.3	1.0	3.8	90°/263°	223	1.3	3.2	90°/250°

* M = molecular weight, T_c = critical temperature in °C, D_c = critical density in moles/liter. $A_5 = E_{vap}/(D_{liq}^{5/3} - D_{gas}^{5/3})$ and $A_6 = E_{vap}/(D_{liq}^{6/3} - D_{gas}^{6/3})$ with E_{vap} in calories/mole and densities in moles/liter. Values for water from Keenan and Keyes, *Steam Tables*. Values for SO_2 and NH_3 from *International Critical Tables*. Values for CO_2 from *International Critical Tables*. The values at -60°C are for the super-cooled liquid. Values for the other substances are from Young, *Proc. Roy. Soc. Dublin* 12, 374 (1910).

TABLE II. Hydrocarbons*

Substance	M	T_c °C	D_c	A_{av}	A (x=6)		Range -°C	A_{av}	A (x=5)		Range -°C
					Av. dev. %	Max. dev. %			Av. dev. %	Max. dev. %	
Propane	44	96.85	5.10	24.0	3.0	6.7	-62°/93.3°	54.8	0.7	1.6	-62°/80°
n-pentane	72	197.2	3.23	79.2	1.6	3.3	30°/190°	154.3	1.6	4.2	30°/170°
iso-pentane	72	187.4	3.07	75.0	1.9	3.6	10°/183°	147.2	0.8	3.7	10°/160°
n-hexane	86	234.8	2.73	124.5	1.2	2.7	60°/226°	231.0	1.7	4.1	60°/200°
Cyclohexane	84	280	3.16	90.2	1.4	5.3	10°/277°	179.0	1.7	4.3	10°/250°
Benzene	78	288.5	3.91	63.1	2.5	4.5	0°/280°	134.1	0.8	3.0	0°/250°
n-heptane	100	266.9	2.34	187	2.1	3.8	70°/264°	330	1.7	3.8	70°/250°
n-octane	114	296.2	2.04	258	2.9	6.3	10°/280°	445	1.1	3.0	10°/270°
Di-isopropyl	86	227.4	2.80	113.7	0.7	3.4	50°/220°	212	2.2	4.7	50°/200°
Di-isobutyl	114	276.8	2.08	242	1.7	4.1	90°/274°	405	1.0	3.5	90°/250°

* See footnote, Table I for units. Values for propane, Stearns and George, *Ind. Eng. Chem.* 35, 602 (1943). All other hydrocarbons taken from Young (see reference to Table I).

negligible. Our assumption amounts to anticipating that the fourth term is of the same magnitude as the terms B_2 and B_3 or larger.

V. TEST OF EQ. (20) USING ENERGIES OF VAPORIZATION

We showed in Section III, Eq. (12) that the energy of vaporization of a liquid should be equal to the difference in configurational energies of the liquid and gas. Substituting the values of the configurational energies from Eq. (20) into Eq. (12), we have

$$E_{vap} = A(D_{liq}^{x/3} - D_{gas}^{x/3}). \quad (21)$$

For most of the liquid range, the density of the saturated vapor is small compared to the density of the liquid and Eq. (21) may be reduced to

$$E_{vap} = A D_{liq}^{x/3}. \quad (22)$$

To test Eq. (21), it is solved for the constant A and the ratio of E_{vap} to the difference in the $x/3$ power of the densities of liquid and vapor is computed from their experimental values. Values of x equal to 3, 4, 5, 6, 7 were tried for a number of different substances and the values for x of 3, 5, and 6 for all of the substances listed in Tables I, II, and III.

TABLE III. Halogen compounds.

Substance	<i>M</i>	<i>T_c</i> °C	<i>D_c</i>	<i>A_{av}</i>	<i>A</i> (<i>x</i> =6)		Range —°C	<i>A_{av}</i>	<i>A</i> (<i>x</i> =5)		Range —°C
					Av. dev. %	Max. dev. %			Av. dev. %	Max. dev. %	
Stannic chloride	260.5	318.7	2.85	131.0	1.2	2.8	100°/280°	242.0	1.5	4.3	100°/280°
Carbon tetrachloride	154	283.2	3.62	70.5	2.0	3.9	70°/280°	145.8	1.0	3.0	0°/260°
Methyl chloride	50.5	143.1	7.3	12.3	2.8	5.9	−62°/77°	32.4	0.3	2.0	−62°/77°
Dichloro-difluoro-methane	121	111.7		29.6	2.3	4.0	−40°/49°	67.0	0.4	1.3	−40°/49°
Trichloro-mono-fluoromethane	137.4	198.0		46.2	2.4	4.2	−40°/71°	103.0	0.7	1.5	−40°/71°
Dichloro-mono-fluoromethane	102.9	178.5		28.9	1.7	2.8	−40°/71°	68.8	0.2	1.0	−40°/71°
Difluoro-mono-chloro-methane	86.5	96.0		16.6	3.0	4.8	−104°/49°	41.6	0.6	2.6	−104°/49°
Unsymmetrical tri-chloro-trifluoro-ethane	187.4	214.1		90.5	2.3	3.9	−30°/105°	182.6	0.5	0.9	−30°/105°
Fluorobenzene	96	286.6	3.69	72.8	0.9	2.3	80°/280°	148.4	2.0	3.8	80°/260°
Chlorobenzene	112.5	359.2	3.08	104.0	2.1	4.3	130°/270°	207.5	0.4	1.1	130°/270°
Bromobenzene	157	397*	3.09*	118.5	2.0	3.6	150°/270°	235.0	0.5	1.2	150°/270°
Iodobenzene	204	448*	3.50*	149	1.4	2.8	180°/280°	290.5	0.6	1.3	180°/280°

* Values estimated by Young. See footnote, Table I for units. Values for methyl chloride and the chlorine-fluorine substituted compounds from the latest thermodynamic tables issued by the DuPont Company, Wilmington, Delaware. All other compounds taken from Young (see reference to Table I).

When the values 3, 4, or 7 are used for *x*, the values of *A* so obtained for a single liquid over a temperature range show considerable variation. Only the values for *x* of 5 and 6 will fit the data and give reasonably constant values for *A*.

In Table I are presented the data for CO₂, SO₂, and substances which are expected to show hydrogen bonding. Table II presents the data for hydrocarbons and Table III the data for halogenated compounds.

The energies of vaporization were usually not given directly in the literature cited in the footnotes to the tables, but were calculated by subtracting $P(V_g - V_l)$ from the heats of vaporization. The heats of vaporization given in the literature are not calorimetric heats but calculated values obtained from precise vapor pressure data and data on the molar volumes of liquid and vapor. The Clausius-Clapeyron relation— $H_v = T(V_g - V_l)dP/dT$ —was used to obtain H_{vap} from this data. In almost every case where direct calorimetric data was available, the calculated values agree to within 1–2 percent. The values of the energy of vaporization calculated in this manner are probably good to about 1–2 percent over most of the temperature range and probably good to only about 5 percent in the neighborhood of the critical temperature.

For most of the substances over the temperature range for which data were available, the energies of vaporization changed by a factor of from 50 percent to 300 percent. In a few cases like that of water, the range is represented by a factor of 20.

In each case, values for *A₅* and *A₆* were calculated at 10°C intervals over the temperature range indicated in the tables. In a few cases where good data was available up to the critical, calculations were made at smaller intervals in this region. Because of the large number of individual calculations, only the average results presented in Tables I, II, and III are given.

From the tables it can be seen that both *A₅* and *A₆* represent the data to within a few percent. The detailed calculations show that *A₅* gives a better fit for the data over a temperature range which extends from low temperatures (below the boiling point) up to temperatures not too close to the critical. For a temperature range which does not go beyond a reduced temperature of 0.9 the constancy of *A₅* is within the limits of experimental error of the data. This is most evident for the halogenated compounds in Table III. For some of these compounds (e.g., the freons) the data does fall below $T_r < 0.9$ and for these *A₅* is well within the limits of experimental error.

A_6 shows its largest deviations at temperatures below the boiling point. For temperatures near the boiling point and extending up to the critical temperature, A_6 is a better constant than A_5 and fits within the limits of experimental error. This was rather surprising, since the use of the same function to represent both the configurational energies of liquid and vapor (see Eq. (21)) was originally considered a dubious approximation.

However, a reconsideration of Eq. (16) indicates a possible explanation for the behavior of the quantities A_5 and A_6 . A large part of the total expansion of the liquid takes place in a short temperature interval in the neighborhood of the critical point. In the temperature range from the melting point extending up to $T_r=0.9$ the total variation in the intermolecular liquid distances has been about 20 percent. In this small range of distances, the repulsive energies are probably large enough to overbalance the higher order dispersion terms, and $E(r)$ will probably not fall off as rapidly as r^{-6} . It should not be unexpected then to find that for this range r^{-5} provides a good representation of the intermolecular potentials.

Above a reduced temperature of 0.9 the liquid is expanded and intermolecular distances are changing rather rapidly. The repulsive forces fall off most rapidly and in this region they are probably equal to or smaller than the higher order dispersion terms. All of these terms have become proportionately smaller than the r^{-6} term and so it seems reasonable that this term should provide a good fit for both the liquid and the gas which is even more expanded. The Beattie-Bridgman equation of state gives,

$$E_c = C_1 D^2 - C_2 D. \quad (23)$$

At large densities the first term in Eq. (23) is dominant, and the energy reduces to the form used in this paper. These large densities are certainly the case in the critical region.

Also rather surprising at first was the fact that such strongly hydrogen-bonded liquids as water, ammonia, and the alcohols (Table I) show such excellent agreement with the simple liquid model used. Of the substances reported in Table I, propyl alcohol shows the poorest agreement. Calculations not reported were made for acetic acid from Young's data (see reference to Table I) and the calculated values of E_{vap} could not be fit by any simple function of the densities. This is to be expected since it is well known that acetic acid is largely dimeric in the vapor phase, and we are dealing in this case with a rather complex system of largely associated molecules. Acetic acid is also rather anomalous in that its heat of vaporization increases with increasing temperature up to approximately the boiling point. In the case of propyl alcohol it would be of some interest to check the experimental data to see if the large deviations are real.

The good agreement for hydrogen-bonded liquids suggests that the bonding energies must vary with the intermolecular distances in the same fashion as the London forces, namely, r^{-6} . The agreement which is obtained for liquids at temperatures where it seems likely that there is restricted rotation suggests that the potential energy of the restricting barriers must show the same dependence on temperatures also.

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