

## Aspects of the Statistical Thermodynamics of Real Fluids

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By extending the ideas previously applied to the statistical mechanical theory of hard sphere fluids of Reiss, Frisch, and Lebowitz, an approximate expression has been determined for the work of creating a spherical cavity in a real fluid. In turn the knowledge of this entity permits an evaluation of properties such as the surface tension and the normal heats of vaporization of fluids and the Henry's law constants of fluid mixtures. The agreement between the calculated and experimental properties is satisfactory.

## I. BASIC CONSIDERATIONS

IN a recent paper Reiss, Frisch, and Lebowitz<sup>1</sup> (henceforth referred to as I) obtained an approximate analytical expression for the equation of state of a hard sphere fluid which compared very favorably at all fluid densities with the results of previous machine computations<sup>2-4</sup> and which gave the first five virial coefficients quite accurately—the first three being in fact exact.

The techniques of this theory can be extended to the treatment of real fluids in a systematic manner, and at present this is being done. On the other hand the hard sphere results furnish a great deal of physical insight and suggest an approximate treatment of certain aspects of real fluids which can be carried out at once. The present paper will be devoted to this treatment.

The central idea of the development is that it is possible to write a very good estimate for the reversible work extended in the production of a spherical cavity of radius  $r$  in a fluid,  $W(r)$ . The work of expanding the spherical cavity's radius from  $r$  to  $r+dr$  can be written as a sum of a volume and surface contribution

$$dW(r) = p \cdot 4\pi r^2 dr + \sigma(r) \cdot 8\pi r dr,$$

with  $p$  the pressure of the fluid. For sufficiently large  $r$ ,  $\sigma(r) = \sigma_0$ , a surface tension, so that

$$W(r) \approx \frac{4}{3}\pi r^3 p + 4\pi r^2 \sigma_0. \quad (1.1)$$

The first term on the right-hand side of (1.1) is the volume work expended in creating the cavity of volume  $(4/3)\pi r^3$ . One may imagine this to be accomplished by the introduction of a hollow *rigid* sphere whose radius increases to the size  $r$ . During this expansion the total volume of the system remains con-

stant at  $V$  and the pressure also remains constant when  $V$  is chosen in such a way that

$$\lim_{N, V \rightarrow \infty} N/V = \rho, \quad (1.2)$$

where  $N$  is the number of molecules in the system and  $\rho$  is the number density.

The surface tension  $\sigma_0$  is then the interfacial tension between the fluid and a perfect rigid wall, and should not be confused with the surface tension at a liquid-vapor interface.

As  $r$  become somewhat smaller a term must be added which accounts for the curvature dependence of the surface work. We therefore write in place of (1.1) [cf. Eq. (6.2) of I],

$$W(r) = \left(\frac{4}{3}\pi r^3\right) p + 4\pi r^2 \sigma_0 [1 - (2\delta/r)], \quad (1.3)$$

where  $\delta$  is a distance of the order of the thickness of the inhomogeneous layer near the interface.

If the real molecules in the fluid are regarded as having rigid cores of diameter  $a$ , it is actually possible to compute  $W(r)$  exactly for  $r \leq a/2$ . This is so because a cavity of such small dimensions can contain at most the center of one molecule. For the details of the calculation the reader is referred to Eq. (3.1) through (3.3) of I. The work is given by

$$W(r) = -kT \ln(1 - \frac{4}{3}\pi r^3 \rho), \quad r \leq a/2, \quad (1.4)$$

where  $k$  is Boltzmann's constant and  $T$  is temperature. This is obviously different from Eq. (1.3), and the two must be matched at  $r = a/2$ .

Now the statistical considerations of reference I suggest that the density  $\rho G(r)$  just outside a cavity of radius  $r$  is specified very closely by

$$G(r) = A + (B/r) + (C/r^2) \quad (1.5)$$

for  $r > a/2$ , where  $A$ ,  $B$ , and  $C$  may depend upon density and temperature. This form should apply to both large and small cavities provided that  $r > a/2$ . Furthermore it is true [see Eq. (6.1) of I] that

$$G(r) = (4\pi r^2 k T \rho)^{-1} (\partial W / \partial r). \quad (1.6)$$

Insertion of (1.3) for  $W$  into (1.6) gives the form (1.5), and thus supports the conclusion that (1.3) which is

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<sup>1</sup> Reiss, Frisch, and Lebowitz, *J. Chem. Phys.* **31**, 369 (1959).

<sup>2</sup> M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem. Phys.* **22**, 881 (1954).

<sup>3</sup> W. W. Wood and J. D. Jacobsen, *J. Chem. Phys.* **27**, 1207 (1957).

<sup>4</sup> T. E. Wainwright and B. J. Alder, U. S. Atomic Energy Comm. Report, Contract No. W-7405-eng-48, Radiation Laboratory, Livermore, University of California.

asymptotically correct for large  $r$  is also valid for very small  $r$ . As a matter of fact (1.6) would still yield (1.5) if an arbitrary function of temperature and density were added to the right member of (1.3). The value of the function should be small enough so it can be ignored when  $r$  achieves macroscopic dimensions in which case the asymptotic equation (1.1) holds. Calling this arbitrary function  $K_0$ , we now have

$$W(r) = \left(\frac{4}{3}\pi r^3\right) p + 4\pi r^2 \sigma_0 [1 - (2\delta/r)] + K_0, \quad r > a/2. \quad (1.7)$$

Equation (1.7) can be written for  $r \geq a/2$  as

$$\begin{aligned} W(r) &= k_0 + k_1[r - (a/2)] + k_2[r - (a/2)]^2 \\ &\quad + k_3[r - (a/2)]^3 \\ &= K_0 + K_1 r + K_2 r^2 + K_3 r^3, \end{aligned} \quad (1.8)$$

where the  $K$ 's (and the  $k$ 's) may be functions of density and temperature. This is just an expansion of  $W(r)$  with terms up to cubic order retained. Actually we know<sup>1</sup> that  $W$  is nonanalytic at  $r = a/\sqrt{3}$  and other points beyond  $a/\sqrt{3}$  but there is strong evidence that the discontinuities occur in terms of higher order than those retained in (1.8) (see Sec. III of reference I).

In practice we will not need to know  $W$  for  $r$  very much greater than  $a/2$  (usually for  $r \leq a$ ) so that (1.8) may be regarded simply as an extrapolation formula. It should be emphasized that by (1.4) we know  $W$  exactly up to the point  $r = a/2$ , so we are already in possession of an appreciable part of  $W$  for larger values of  $r$ .

Comparison of Eq. (1.8) with Eq. (1.3) reveals that

$$K_3 = \frac{4}{3}\pi p. \quad (1.9)$$

The three remaining coefficients  $K_0$ ,  $K_1$ , and  $K_2$  can be determined by matching  $W$  and its first and second derivatives at  $r = a/2$  to the values obtained from Eq. (1.4). This is made possible by the fact that  $W$  and its first two derivatives are continuous. For the proof of this the reader is referred to Sec. III of reference I. There reference is made to hard spheres but it is easily seen that the same proof can be given for cavities in real fluids, although in Eq. (3.27) of reference I,  $G(a)$  must be replaced by  $g(a)$  (since  $G(a) \neq g(a)$  for real fluids).

When the coefficients are determined by this procedure, we obtain

$$\begin{aligned} K_0 &= kT \left\{ -\ln(1-y) + \frac{9}{2}[y/(1-y)]^2 \right\} - (\pi p a^3/6), \\ K_1 &= -(kT/a) \left\{ [6y/(1-y)] + 18[y/(1-y)]^2 \right\} + \pi p a^2, \\ K_2 &= (kT/a^2) \left\{ [12y/(1-y)] + 18[y/(1-y)]^2 \right\} - 2\pi p a, \\ K_3 &= \frac{4}{3}\pi p, \end{aligned} \quad (1.10)$$

where

$$y = \pi a^3 \rho / 6. \quad (1.11)$$

From the correspondence between the forms (1.7) and (1.8) for  $W$  we obtain, by using Eqs. (1.10),

$$\begin{aligned} \sigma_0 &= (kT/4\pi a^2) \left\{ [12y/(1-y)] + 18[y/(1-y)]^2 \right\} \\ &\quad - (pa/2), \\ \delta &= (a/4) \left\{ \frac{[6y/(1-y)] + 18[y/(1-y)]^2 - (\pi p a^3/kT)}{[6y/(1-y)] + 9[y/(1-y)]^2 - (\pi p a^3/kT)} \right\}. \end{aligned} \quad (1.12)$$

We now note that the introduction of a rigid sphere of diameter  $b$  into the fluid of real molecules is equivalent to the introduction of a cavity of radius

$$r = (a+b)/2, \quad (1.13)$$

since such a sphere excludes the centers of molecules (whose hard cores are of diameter  $a$ ) from a region of such radius. Thus (1.8) with  $r$  given by (1.13) is the reversible work expended in the introduction of a rigid sphere solute molecule of diameter  $b$ . To obtain the chemical potential  $\mu_h$  of such a solute we must add to the work  $W$  a term representing the free energy of mixing of the solute with solvent. This leads to the expression

$$\mu_h = kT \ln \rho_2 \Lambda_2^3 + W, \quad (1.14)$$

where  $\rho_2$  is the density of solute and  $\Lambda_2$  is

$$\Lambda_2 = h / (2\pi m_2 kT)^{1/2}, \quad (1.15)$$

$m_2$  being the mass of a solute molecule, and  $h$  Planck's constant. Of course, Eq. (1.14) only applies to dilute solutions in which the solute molecules remain independent of one another. By introducing Eq. (1.10) into Eq. (1.8) and the result into Eq. (1.14) we obtain,

$$\mu_h/kT = \ln \rho_2 \Lambda_2^3 + (W/kT),$$

$$\begin{aligned} W &= kT \left\{ [6y/(1-y)] [2(r/a)^2 - (r/a)] \right. \\ &\quad \left. + [18y^2/(1-y)^2] [(r/a)^2 - (r/a) + \frac{1}{4}] - \ln(1-y) \right\} \\ &\quad + \pi p a^3 \left[ \frac{4}{3}(r/a)^3 - 2(r/a)^2 + (r/a) - \frac{1}{6} \right], \end{aligned} \quad (1.16)$$

where  $r$  is given by Eq. (1.13) and  $y$  by Eq. (1.11).

For such a hard sphere solute, the partial pressure  $p_2$  can be computed, assuming the vapor phase to be ideal, for then the chemical potential  $\mu_2$  of the solute in the vapor must be given by

$$\mu_2/kT = \ln p_2 \Lambda_2^3 / kT. \quad (1.17)$$

Since in equilibrium  $\mu_2 = \mu_h$  we have by equating the right sides of (1.16) and (1.17)

$$\begin{aligned} p_2 &= [kT \rho_2 / (1-y)] \exp \left\{ (\pi p a^3 / kT) \right. \\ &\quad \cdot \left[ \frac{4}{3}(r/a)^3 - 2(r/a)^2 + (r/a) - \frac{1}{6} \right] \\ &\quad \left. + 6[y/(1-y)] [2(r/a)^2 - (r/a)] \right. \\ &\quad \left. + 18[y/(1-y)]^2 [(r/a)^2 - (r/a) + \frac{1}{4}] \right\}. \end{aligned} \quad (1.18)$$

From (1.18) the constant of Henry's law

$$k_H = p_2/\rho_2 \quad (1.19)$$

can easily be deduced.

## II. COMPARISON WITH EXPERIMENT

At this stage it is possible to test the validity of our expression for  $W(r)$ , the work required for the creation of a cavity of radius  $r$  by appeal to experiment. For example, by combining (1.14) with (1.17), using  $\mu_2 = \mu_h$ , and (1.19) we can derive

$$W(r) = kT \ln(k_H/kT), \quad (2.1)$$

which allows computation of  $W(r)$  from measured values of the constant of Henry's law. Comparison of the right sides of Eqs. (2.1) and (1.16) furnishes the necessary test.

Of course it is necessary to have a solution containing a rigid sphere solute and approximately spherical solvent molecules, with effectively rigid cores. In any real solution the solute will have a partly attractive potential, which leads to a negative valued interaction free energy to be discussed more fully in Sec. III. Therefore, we expect our computed result to be higher than that found experimentally.

Two solutions for which data exist and which very nearly satisfy the requirements outlined above are helium in argon studied by Karasz and Halsey<sup>5</sup> and helium in benzene studied by Clever *et al.*<sup>6</sup> The benzene molecule is not truly spherical and we must rely upon angular averaging to provide such behavior. If it is assumed spherical and appeal is made to some independent phenomenon such as viscosity or second virial coefficient measurements, an internally consistent value of  $a$  should be derived.

If the solvent-solvent interaction is assumed to be described by a Lennard-Jones 6-12 potential, then a good choice for  $a$  is the point at which the rising potential, showing repulsion, is zero. The potential rises so steeply here that an increase of several  $kT$  in energy occurs with almost negligible decrease of distance between the two molecules. We have made this choice of  $a$ . The diameter  $b$  of the solute is chosen in the same manner.

The necessary data is available in Table 1-A of the Appendix of Hirschfelder, Curtiss, and Bird.<sup>7</sup> We find

$$\begin{aligned} \text{helium } b &= 2.56 \times 10^{-8} \text{ cm} \\ \text{argon } a &= 3.40 \times 10^{-8} \text{ cm} \\ \text{benzene } a &= 5.27 \times 10^{-8} \text{ cm.} \end{aligned} \quad (2.2)$$

The first two quantities are obtained from second virial coefficient measurements and the third from viscosity.

<sup>5</sup> F. E. Karasz and G. D. Halsey, *J. Chem. Phys.* **29**, 173 (1958).

<sup>6</sup> Clever, Battino, Saylor, and Gross, *J. Phys. Chem.* **61**, 1078 (1957).

<sup>7</sup> Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1110.

Densities were obtained from the critical tables.<sup>8</sup> Indicating  $W(r)$  obtained from Henry's law data by  $W(k_H)$ , and that obtained using (2.2), the proper values of density (concentration), and (1.16) by  $W$  we obtain the following:

Helium in argon ( $T=86.6^\circ\text{K}$ )

$$W(k_H) = 3.46 \times 10^{-14} \text{ erg}$$

$$W = 6.07 \times 10^{-14} \text{ erg}$$

Helium in Benzene ( $T=288^\circ\text{K}$ )

$$W(k_H) = 1.59 \times 10^{-13} \text{ erg}$$

$$W = 1.73 \times 10^{-13} \text{ erg.} \quad (2.3)$$

In the calculations leading to Eqs. (2.3) the term in Eq. (1.16) containing the pressure was neglected since at pressures of the order of an atmosphere it is entirely negligible. We see that  $W(k_H)$  is less than  $W$ , which is to be expected by the considerations of Sec. III.

The agreement between the calculated and experimental values of the constants of Henry's law may appear to be less satisfactory than that shown in (2.3). This arises from the logarithmic relation in Eq. (2.1). For example, if we denote  $k_H$  computed by combination of Eqs. (1.16) and (2.1) as  $k(W)$ , then we find for the cases exhibited by (2.3):

Helium in argon

$$k(W)/k_H = 8.8$$

Helium in benzene

$$k(W)/k_H = 1.42. \quad (2.4)$$

Nevertheless the real standard of agreement must be found in Eq. (2.3) since we are testing the validity of our expression for  $W(r)$ .

Another test of the validity of our relations is furnished by consideration of  $\sigma_0$  given in Eq. (1.12). It will be recalled that this represents the interfacial tension where the fluid contacts a perfectly rigid wall. This is not the same as  $\sigma$ , the interfacial tension between a liquid and its vapor, but ought to be of similar magnitude. This is especially true far below the critical temperature where the vapor is highly attenuated, for example at or below the normal boiling point. In Table I we compare  $\sigma_0$  and  $\sigma$  for a number of substances. The values of  $\sigma$  were taken from the handbook<sup>9</sup> and  $\sigma_0$  is calculated using (1.12) together with values of  $a$  from Table I-A in Hirschfelder, Curtiss, and Bird and values of density from the critical tables.<sup>8</sup> Once again, the term in  $p$  is negligible.

The temperatures have been chosen in Table I to correspond as closely as possible to measurements of

<sup>8</sup> *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1926).

<sup>9</sup> Lange, *Handbook of Chemistry* (Handbook Publishers, Sandusky, Ohio, 1941), fourth edition.

TABLE I. Comparison of  $\sigma$  and  $\sigma_0$  at or below the boiling points of various liquids.

Substance	Temp °K	$\sigma$ (dynes/cm)	$\sigma_0$ (dynes/cm)
Ne	27.2 °K	4.80	6.09
Ar	85.1 °K	13.2	16.4
He	4.2 °K	0.098	0.223
H <sub>2</sub>	20.4 °K	1.80	1.91
N <sub>2</sub>	70.1 °K	10.5	14.9
O <sub>2</sub>	70.1 °K	18.3	23.6
C <sub>6</sub> H <sub>6</sub>	273.1 °K	29.02	34.3

$\sigma$  under conditions of low vapor pressure. For very high vapor densities the agreement is less satisfactory.

### III. NONRIGID SPHERE SOLUTES

Until now we have been dealing with rigid sphere solutes whose potential energy of interaction with solvent molecules  $\phi_h$ , could be represented by

$$\begin{aligned} \phi_h &= \infty, & r \leq \frac{1}{2}(a+b); \\ \phi_h &= 0, & r > \frac{1}{2}(a+b), \end{aligned} \quad (3.1)$$

where  $r$  is the distance between the centers of the solute and solvent molecules. Real solute molecules have a nonrigid or soft potential in addition to  $\phi_h$ . If we call this part  $\phi_s$ , then the potential  $\phi$  is

$$\phi = \phi_h + \phi_s. \quad (3.2)$$

We will now compute the chemical potential of such an added solute molecule by using the coupling parameter method. We introduce coupling parameters<sup>10</sup>  $\xi_h$  and  $\xi_s$  as follows:

$$\phi(r, \xi_h, \xi_s) = \phi_h(r, \xi_h) + \xi_s \phi_s(r). \quad (3.3)$$

For  $\xi_h$  it is convenient to chose the radius of the hard core (as in reference I). Then the hard core is fully coupled to the rest of the system when  $\xi_h = \frac{1}{2}(a+b)$  so that (3.1) applies. The soft potential will be fully coupled when  $\xi_s = 1$ , i.e., when the second term on the right of (3.3) is just  $\phi_s$ .

We can now add the solute molecule to the solution in two stages. In the first  $\xi_h$  is charged from 0 to  $\frac{1}{2}(a+b)$ , while  $\xi_s = 0$ . The reversible work in this stage is simply  $\mu_h$ . Thus if the chemical potential of the added solute is represented as  $\mu(\xi_h, \xi_s)$

$$\mu_h = \mu\left[\frac{1}{2}(a+b), 0\right]. \quad (3.4)$$

In the next step the soft potential is brought into play by charging  $\xi_s$  from 0 to 1. Denoting the corresponding change in chemical potential by  $\mu_s$  we have

$$\mu_s = \mu\left[\frac{1}{2}(a+b), 1\right] - \mu\left[\frac{1}{2}(a+b), 0\right]. \quad (3.5)$$

Obviously the chemical potential of the added solute is

$$\mu = \mu_h + \mu_s. \quad (3.6)$$

<sup>10</sup> T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), p. 191.

The quantity  $\mu_h$  has been discussed in the two previous sections and an approximation expression, Eq. (1.16), has been derived for it. Using a simple extension of the usual coupling parameter technique<sup>10</sup> it can be shown that

$$\mu_s = \rho \int_0^1 d\xi_s \int_0^\infty 4\pi r^2 \phi_s g[r, \xi_h = \frac{1}{2}(a+b), \xi_s] dr, \quad (3.7)$$

in which  $g[r, \xi_h = \frac{1}{2}(a+b), \xi_s]$  is the radial distribution function of solvent molecules about a solute whose rigid core is fully coupled and whose soft potential is coupled to the extent  $\xi_s$ . The evaluation of  $\mu_s$  therefore requires detailed knowledge of  $g(r, \xi_h, \xi_s)$ . Since  $g$  is positive and  $\phi_s$  is negative we can say that  $\mu_s$  is negative.

### IV. $\mu_h$ AND HEATS OF VAPORIZATION

In this section we apply what should be an even more severe criterion for testing the validity of  $\mu_h$  as given by (1.16). First (1.16) is specialized to the case in which  $r = a$  so that the solute now is a solvent molecule. Thus

$$\begin{aligned} \mu_h/kT &= \ln[\rho\Lambda^3/(1-y)] + 6[y/(1-y)] \\ &\quad + \frac{9}{2}[y/(1-y)]^2 + (\pi a^3 \rho / 6kT). \end{aligned} \quad (4.1)$$

If it is assumed that (4.1) applies to a liquid phase in equilibrium with an ideal vapor then [cf. Eq. (1.17)]

$$\mu = \mu_h + \mu_s = kT \ln(\rho\Lambda^3/kT). \quad (4.2)$$

If we use (4.1) in (4.2), we obtain

$$\begin{aligned} \mu/kT &= \ln(\rho\Lambda^3/kT) = \ln\{(6\Lambda^3/\pi a^3)[y/(1-y)] \\ &\quad + 6[y/(1-y)] + \frac{9}{2}[y/(1-y)]^2 \\ &\quad + (\pi a^3 \rho / 6kT) + (\mu_s/kT)\}. \end{aligned} \quad (4.3)$$

The process in Eq. (3.7) in which  $\xi_s$  is charged from 0 to 1 may be approximated by setting  $\xi_s = 1$  in  $g$  from the beginning. It is asymptotically correct for that part of the integral in which  $\xi_s$  is approaching 1 and should not introduce a large error. In general  $\mu_s$  can be decomposed as follows:

$$\mu_s = e_s + p v_s - T s_s, \quad (4.4)$$

where  $e_s$  is the internal energy change during charging of the soft potential,  $v_s$  is a volume associated with the process and  $s_s$  an entropy. The term in  $p v_s$  may be shown to be small for a condensed system and will be neglected.

Now the change in internal energy during charging is obviously

$$e_s = \rho \int_a^\infty 4\pi r^2 \phi_s g(r, \xi_h = \frac{1}{2}(a+b), \xi_s = 1) dr, \quad (4.5)$$

so that  $e_s$  is just what is obtained by setting  $\xi_s$  equal to unity in  $g$  in Eq. (3.7). Thus the error in doing this involves neglect of the entropy of charging. The

system becomes more organized upon charging since the attractive forces lead to greater correlation between molecules. As a result

$$s_s < 0 \quad (4.6)$$

and

$$\mu_s > e_s. \quad (4.7)$$

Further, if the vapor is ideal it can be shown<sup>11</sup> that

$$e_s = 2kT - 2\lambda_v, \quad (4.8)$$

where  $\lambda_v$  is the heat of vaporization per molecule. Thus

$$\mu_s = 2kT - 2\lambda_v - Ts_s \approx 2kT - 2\lambda_v. \quad (4.9)$$

Substituting (4.9) into (4.3) we obtain, with neglect of terms of the order  $pv$ ,

$$\lambda_v/kT = 1 - \frac{1}{2} \{ \ln(\pi a^3 p / 6kT) [(1-y)/y] - 6[y/(1-y)] - \frac{9}{2}[y/(1-y)]^2 \} - (s_s/2k). \quad (4.10)$$

In view of (4.6) the last term on the right is positive. If we then approximate  $\lambda_v$  by  $\lambda_v'$  which we define to be equal to the first two terms on the right (i.e., we ignore the entropy contribution) then

$$\lambda_v' < \lambda_v. \quad (4.11)$$

If the measured vapor pressure and the measured density are used (in Eq. 4.10) together with values of  $a$  obtained by the procedure used previously, then  $\lambda_v'$  can be computed. This can be compared with the measured  $\lambda_v$  which it should approximate on the low side. In Table II we list values of  $\lambda_v'$  computed in this manner together with measured values of  $\lambda_v$  for various substances. The data all refer to the boiling points of the various substances.

The agreement between  $\lambda_v'$  and  $\lambda_v$  is really quite good. In all cases  $\lambda_v'$  is lower than  $\lambda_v$  by about 15%. This agrees with Eq. (4.11) and furthermore shows that the entropy contribution is small. The successful approximate computation of  $\lambda_v(\lambda_v')$  by this technique strengthens the validity of Eq. (1.16) since the method is based on this expression for  $\mu_h$ .

What is perhaps an even more stringent test of Eq. (1.16) is possible. This depends on the fact that if  $\mu_s$  is known over a range of values of the state variables

TABLE II. Comparison of  $\lambda_v'$  and  $\lambda_v$ , the heat of vaporization.

Substance	$\lambda_v'$ (cal)	$\lambda_v$ (cal)
Ar	1 360	1 558
Ne	361	416
Xe	2 830	3 200
He	23.2	24
CH <sub>4</sub>	1 850	2 218
N <sub>2</sub>	1 260	1 340
H <sub>2</sub>	188	218
C <sub>6</sub> H <sub>6</sub>	6 300	7 360

<sup>11</sup> Reference 10, p. 189.

TABLE III. Comparison of  $\lambda_v$  calculated by (4.18) with experimental values at the boiling point.

Substance	$\lambda_v$ (cal.) calc.	$\lambda_v$ (cal.) exp.
Ar	1510	1558
CH <sub>4</sub>	2280	2218

then  $s_s$  and  $v_s$  can be computed from the thermodynamic formulas

$$s_s = -(\partial\mu_s/\partial T)_p, \quad (4.12)$$

$$v_s = (\partial\mu_s/\partial p)_T. \quad (4.13)$$

For reasons connected with the Clapeyron-Clausius relation it will be useful to examine the temperature derivative of  $\mu_s$  along the line of coexistence between liquid and vapor phases. Using subscript  $c$  for such derivatives we have

$$(d\mu_s/dT)_c = -s_s + v_s(dp/dT)_c. \quad (4.14)$$

Another expression for this quantity, obtained by solving (4.3) for  $\mu_s$  and differentiating, is

$$(d\mu_s/dT)_c = -s_s + (e_s/T) + (pv_s/T) + (\pi a^3 p / 6T) - k + [(kT/p) - (\pi a^3 / 6)](dp/dT)_c - kT \frac{(1+2y)^2}{y(1-y)^3} (dy/dT)_c. \quad (4.15)$$

All coexistence derivatives can be written in terms of  $(dp/dT)_c$  if  $T$  and  $p$  are regarded as the independent variables. The value of this arises from the fact that the Clapeyron-Clausius relation says

$$(d \ln p / dT)_c = \lambda_v / kT^2. \quad (4.16)$$

Recall that  $e_s$  is also given in terms of  $\lambda_v$  by (4.8).

The quantity  $v_s$  can be written as

$$v_s = v - v_h, \quad (4.17)$$

where  $v_h = (\partial\mu_h/\partial p)_T$  by Eq. (4.1) is

$$v_h = kT[(1+2y)^2/y(1-y)^3](\partial y/\partial p)_T + (\pi a^3/6). \quad (4.18)$$

If we use the facts that  $pa^3/kT \ll 1$ ,  $v=0(a^3)$ , and  $(\partial \ln y/\partial \ln p)_T \ll 1$  then combination of (4.8) and (4.14-18) yields

$$\lambda_v = kT + kT^2\alpha[(1+2y)^2/(1-y)^3], \quad (4.19)$$

where  $\alpha$  is the coefficient of thermal expansion,

$$(1/v)(\partial v/\partial T)_p = -(1/y)(\partial y/\partial T)_p.$$

This expression for the heat of vaporization is essentially an exact consequence of the assumed form of  $\mu_h$  and thus serves as an important criterion for the validity of the latter. To apply it, however, requires reliable data for  $\alpha$  and the molecular core diameter of simple liquids. For argon and methane the coefficients

of thermal expansion at the boiling point are available from the critical tables,<sup>8</sup> while  $a$  may be taken from Hirschfelder, Curtiss, and Bird.<sup>7</sup> Comparison of the calculated and experimental heats of vaporization are made in Table III. The agreement seems to be very good.

### V. SUMMARY

It appears that it is possible to give an excellent approximation for the chemical potential of (or the work of adding) a hard sphere in a real fluid. Systems exist, such as helium in benzene, which are close to

this model so that an experimental test of the theoretical expression may be obtained directly from Henry's law constants. In addition, for very large hard spheres the work of expanding the sphere can be related to the surface tension. Thus this rigid wall-liquid surface tension can be calculated. Lastly, the heat of vaporization can be related to the difference between the work of adding a real molecule and the work of adding a hard sphere to a fluid, and in this way determined. The agreement between these calculations and experimental data lends support to the basic concept involved in the estimation of  $\mu_h$ .

## Evaluation of One-Center Electron Repulsion Integrals between Certain $s$ -Type Atomic Orbitals\*

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A general formula is derived for one center  $s$ -type electron repulsion integrals for the set of basic atomic orbitals which involve the complete set of associated Laguerre functions of order  $(2l+1)$  and degree  $(n+l+1)$  with a single orbital exponent.

SEVERAL investigators have suggested the orthonormal set of functions

$$\psi_{nlm} = R_{nl}(r) Y_l^m(\theta, \varphi),$$

where, in atomic units,

$$R_{nl}(r) = \frac{(2Z)^{\frac{1}{2}}}{(n+l+1)} \left[ \frac{(n-l-1)!}{(n+l+1)!} \right]^{\frac{1}{2}} \cdot (2Zr)^l L_{n+l+1}^{2l+2}(2Zr) \exp(-Zr),$$

and

$$Y_l^m(\theta, \varphi) = \left[ \frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right]^{\frac{1}{2}} P_l^m(\cos\theta) \exp(im\varphi),$$

as a useful set of basic atomic orbitals.

In the early days of quantum mechanics it was pointed out by E. Schrödinger that this set might have advantages for variational treatments in as much as it is a discrete and complete set, in contrast to the set of hydrogenic orbitals. Recently, Löwdin and Shull have successfully used this basis for certain problems.

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<sup>1</sup> The associated Laguerre polynomials  $L_{n+l+1}^{2l+2}$  and associated Legendre polynomials  $P_l^m$  are defined as in L. C. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935).

In order to use these functions in a variation or second-order perturbation theory treatment one must evaluate kinetic energy, potential energy, and electron repulsion integrals. Kinetic and potential energy integrals may be evaluated by using formulas which may be trivially obtained from the formulas derived for a hydrogen atom by Hirschfelder and Löwdin.<sup>2</sup> However, general formulas for the electron repulsion integrals do not seem to be available.

Although a single general formula for all electron repulsion integrals is not readily obtainable, a formula may be derived for each set of angular types not zero by symmetry. We have derived a formula for electron repulsion integrals of the  $s$  type ( $l=m=0$  for all four functions) and other derivations may be patterned accordingly.

First we abbreviate as follows:

$$\langle ac | 1/r_{12} | bd \rangle \equiv \iint a^*(1) c^*(2) (1/r_{12}) b(1) d(2) d\tau_1 d\tau_2,$$

where

$$x(\mu) = \psi_{x00}(\mu), \quad x = a, b, c, d.$$

Next we introduce the customary expansion for  $1/r_{12}$

<sup>2</sup> J. O. Hirschfelder and P.-O. Löwdin, *Long Range Interaction of Two 1s Hydrogen Atoms Expressed in Terms of Natural Spin Orbitals*, Technical Report of the Quantum Chemistry Group, Uppsala University (1957).