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Statistical Mechanics of Fluid Mixtures*

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Expressions for the chemical potentials of the components of gas mixtures and liquid solutions are obtained in terms of relatively simple integrals in the configuration spaces of molecular pairs. The molecular pair distribution functions appearing in these integrals are investigated in some detail, in their dependence upon the composition and

density of the fluid. The equation of state of a real gas mixture is discussed, and an approximate molecular pair distribution function, typical of dense fluids, is calculated. Applications of the method to the theory of solutions will be the subject of a later article.

I.

ALTHOUGH statistical mechanics has met with considerable success in the interpretation of the properties of rarefied gases as well as those of crystalline solids, serious practical difficulties have retarded its application to dense gases and to liquids. In the present article, we shall describe a statistical treatment of fluid mixtures, which is formally applicable both to real gases and to liquids. It has the advantage of yielding expressions which lend themselves more readily than the usual statistical formulas, to approximations suitable for condensed systems. While we make no pretension to a resolution of the difficulties presented by the liquid state, the more serious of which resist more than a superficial treatment, we believe that the method to be described throws interesting light upon the problem, and that it may prove useful in opening up new lines of attack, particularly in the field of liquid solutions.

We must first ask whether classical statistical mechanics is competent to describe the dependence of the thermodynamic functions of fluids upon intermolecular forces. At ordinary temperatures, there is good reason to believe that the classical approximation is adequate for most gases and liquids consisting of chemically saturated molecules. When certain conditions involving the molecular masses, moments of inertia, and the intermolecular forces are satisfied, the partition function of a system of molecules is closely approximated by the product of a function of the temperature alone, and the Gibbs

phase integral in the phase space associated with the low frequency translational and rotational motion of the molecules.¹ The validity of the assumptions involved in this approximation is of course more questionable for liquids than for gases, particularly when there is strong coupling between the rotational motion of neighboring molecules as in polar liquids. We shall provisionally assume the adequacy of the classical approximation, remembering that our results are applicable only when this is true.

When the potential of the intermolecular force is of special form, for example a sum of terms depending upon the relative coordinates of molecular pairs, the explicit use of unwieldy integrals in a many dimensional phase space may be avoided. We shall show how the statistical formulas for certain important thermodynamic functions of a fluid mixture may be recast in terms of comparatively simple integrals in the configuration space associated with the relative motion of a molecular pair. The molecular pair distribution functions, which appear in these integrals are, to be sure, formally defined as ratios of many dimensional phase integrals. However, by certain transformations, they may be expressed in a form which leads to reasonable approximations both in condensed and rarefied systems. The approximation for rarefied systems leads to a novel approach to the problem of the equation of state of a real gas, while the approximation for condensed system promises to be of use in the theory of liquid solutions. On the other hand, the approximate distribution functions which have thus far been obtained do not

* The material of Section V of this article was presented at the eighty-ninth meeting of the American Chemical Society held in New York City during the week of April 22, 1935.

¹ E. Wigner, *Phys. Rev.* **40**, 749 (1932); Uhlenbeck and Gropper, *Phys. Rev.* **41**, 79 (1932); J. G. Kirkwood, *Phys. Rev.* **44**, 31 (1933); *J. Chem. Phys.* **1**, 597 (1933).

appear to be sufficiently exact for the calculation of the equations of state of liquids.

The method of the present treatment is based upon the same principle as the charging processes employed in the theory of electrolyte solutions. As Onsager has clearly pointed out, parameters which appear in the potential of the intermolecular forces have essentially the same status as the parameters of external force,² which determine the mechanical interaction between a thermodynamic system and its surroundings, and may be manipulated in the same manner. The application of this principle is by no means restricted to intermolecular forces of the Coulomb type, in the potential of which ionic charges enter as natural parameters. Arbitrary parameters may be introduced into the potential of intermolecular force in any system of molecules, by means of which the coupling between the molecules may be continuously varied in any convenient manner. This device allows one to express the chemical potential of any component of a fluid mixture in a particularly simple form. It also proves to be very useful in investigating the dependence of molecular pair distribution functions upon the composition and density of the fluid.

II.

The following analysis is formally applicable to all homogeneous fluids, whether real gas mixtures or liquid solutions. Differences arise only in the method of approximating distribution functions. We therefore consider a homogeneous fluid of ν substances, in thermodynamic equilibrium. By suitably restricting the ranges of composition and pressure so as to exclude coexistent phases containing any of its components, we may suppose that the fluid completely fills a vessel of volume v , which confines the motion of the system to a finite region of configuration space.³ We denote the absolute temperature by

² L. Onsager, Chem. Rev. **13**, 73 (1933); J. W. Gibbs, *Elementary Principles in Statistical Mechanics, Collected Works II*, Chap. VII (Longmans).

³ We postulate the absence of coexistent phases containing any of the components of the fluid, since we wish to represent the system by a petit ensemble, each example of which contains the same number of molecules. Actually this is a trivial restriction, for Gibbs has shown that although an open system is represented by a grand ensemble, its equilibrium properties do not differ sensibly from those of a closed system represented by a petit ensemble, each example of which is made up of the average

T , the numbers of molecules of the several components by N_1, \dots, N_ν , and the total number of molecules of all species, $\sum_{s=1}^{\nu} N_s$, by N . According to classical statistical mechanics, we represent the system by a canonically distributed petit ensemble, and obtain the usual expression for the Helmholtz free energy, F_N .

$$e^{-\beta F_N} = \left[\prod_{s=1}^{\nu} \frac{f_s(T)^{N_s}}{N_s!} \right] Z_N$$

$$Z_N = \int \dots \int e^{-\beta V_N} d\omega_1 \dots d\omega_N, \quad (1)$$

where β is equal to $1/kT$ and $d\omega_i$ is a differential element of the configuration space associated with the low frequency rotational and translational degrees of freedom of the molecule i . The integration in the sub-space of each molecule is extended over a region bounded by the volume of the vessel containing the fluid. In general

$$\int d\omega_i = \sigma_i v \quad (2)$$

where σ_i is equal to 4π for diatomic molecules which have only two low frequency rotational degrees of freedom and to $8\pi^2$ for polyatomic molecules which in general have three. The potential of the intermolecular forces, V_N , is a function of the configuration coordinates of all N molecules. The functions $f_s(T)$, depending upon the temperature alone, are products of certain momentum integrals associated with the low frequency degrees of freedom of a molecule of type s and the partition function associated with its high frequency vibrational degrees of freedom. For our present purposes we do not need to characterize these functions more closely.

The chemical potential per molecule of a component i of the fluid is thermodynamically defined by the relation

$$\mu_i = (\partial F / \partial N_i)_{T, v, N_1, \dots, N_{\nu-1}}. \quad (3)$$

It is statistically defined by Gibbs⁴ in terms of the grand ensemble. For our purposes, it is more convenient to define μ_i in terms of the petit ensemble upon which Eq. (1) is based. This may

number of molecules of a system of the grand ensemble. In case coexistent phases exist, we simply regard v as the volume of the homogeneous part in which we are interested.

⁴ J. W. Gibbs, *Elementary Principles in Statistical Mechanics, Collected Works II*, p. 187, Longmans.

be done in a very simple manner. We first observe that the treatment of N as a continuous variable in the thermodynamic definition (3) is simply a convenient mathematical device. A physical definition of chemical potential requires the use of finite differences, ΔF and ΔN_i , in the ratio $\Delta F/\Delta N_i$. For values of ΔN_i which do not sensibly affect the composition of the fluid, this ratio will not differ sensibly from the derivative on the right-hand side of Eq. (3). We are therefore justified in defining μ_i as the change in free energy produced by the subtraction or addition of a single molecule of type i from the macroscopic system, while maintaining the temperature, volume and the numbers of molecules of the other species constant.

$$\mu_i = F(N_1, \dots, N_i, \dots, N_r, T, v) - F(N_1, \dots, N_i - 1, \dots, N_r, T, v). \quad (4)$$

The fact that the removal of a single molecule is scarcely a physically realizable process does not alter the value of the definition (4) when used in conjunction with the petit ensemble, each system of which is supposed to comprise exactly the same number of molecules.

From Eqs. (1) and (4), we obtain the following expression for μ_i :

$$\mu_i = -kT \log \left[\frac{f_i(T)}{N_i} \frac{Z(N_1, \dots, N_i, \dots, N_r, T, v)}{Z(N_1, \dots, N_i - 1, \dots, N_r, T, v)} \right]. \quad (5)$$

Further simplification depends upon the form of the potential of the intermolecular forces, V_N . We shall treat here only systems, for which V_N may be expressed as a sum of terms V_{kl} , each depending only upon the relative coordinates of a molecular pair (kl).⁵

⁵ It is to be remarked that the potential of Eq. (6) in no way excludes the simultaneous interaction of groups of more than two molecules. It simply states that in such a group, the mutual potential energy of any pair is independent of the presence of the other molecules. For example the electrostatic energy of a system of point charges is of this type. London has shown that the potential of the attractive van der Waals forces between chemically saturated molecules satisfies the requirements of Eq. (6). [F. London, *Zeits. f. physik. Chemie* 11, 222 (1930).]

No such clear cut statement can be made regarding the repulsive forces, which operate at small distances, determining the effective collision diameters of molecules. However, it is plausible to assume that the potentials of these forces are approximately additive, and even if they are not exactly so, it is only necessary for our purposes that their narrow range of action is not sensibly displaced.

$$V_N = \sum_{k < l} V_{kl}. \quad (6)$$

We now define a fictitious potential of the following type

$$V_N(\lambda_1, \dots, \lambda_N) = \sum_{k < l} \lambda_k \lambda_l V_{kl}, \quad (7)$$

where $\lambda_1 \dots \lambda_N$ are arbitrary parameters. By varying these parameters between zero and unity, we can continuously vary the coupling between the N molecules from zero to its full value. In particular, we notice that when a value unity is assigned to each of the N parameters λ , we have

$$V_N(1, \dots, 1) = V_N, \quad (8)$$

where V_N is given by Eq. (6) and represents the actual coupling between the molecules. If, on the other hand, a value unity is assigned to $N-1$ of the parameters λ and a value zero to a single λ_i , we have

$$V_N(1, \dots, 0, \dots, 1) = V_{N-1}, \quad (9)$$

where V_{N-1} is the potential in a system of $N-1$ molecules formed by the removal of a single molecule i . Corresponding to $V_N(\lambda_1, \dots, \lambda_N)$, we define a phase integral,

$$Z_N(\lambda_1, \dots, \lambda_N) = \int \dots \int e^{-\beta V_N(\lambda_1, \dots, \lambda_N)} d\omega_1 \dots d\omega_N. \quad (10)$$

When each of the parameters, λ , is assigned the value unity, we have the following identity:

$$Z_N(1, \dots, 1) = Z(N_1, \dots, N_i, \dots, N_r). \quad (11)$$

When $N-1$ of the parameters λ are equal to unity, while a single λ_i corresponding, let us say,

In general, we should expect terms depending upon the relative coordinates of three or more molecules to be important only if the total intermolecular field is strong enough to produce a large perturbation in the electronic structure of a molecule in the fluid. Theoretical considerations suggest that not only in gases but also in liquids, this is not the case. Empirical arguments against any appreciable distortion of the electronic structure of molecules in most liquids are furnished by spectroscopic and optical evidence. For example, the molecular refractivity of most liquids is substantially the same as that of their vapor.

There are to be sure some types of intermolecular potential which do not satisfy Eq. (6), for example those of chemical forces of the homeopolar type. Another example is furnished by the energy of polarization of a molecule by a group of ions.

to a molecule of type i is equal to zero, we may write

$$Z_N(1, \dots, 0, \dots, 1) = \int \dots \int e^{-\beta V_{N-1}} d\omega_1 \dots d\omega_N. \quad (12)$$

Now since V_{N-1} contains no terms depending upon the coordinates of the molecule i , the integration over its configuration space in Eq. (12) may be carried out immediately. Performing this integration and making use of Eqs. (1) and (2), we obtain

$$Z_N(1, \dots, 0, \dots, 1) = \sigma_i v Z(N_1, \dots, N_i - 1, \dots, N_s). \quad (13)$$

From Eqs. (11) and (13) we may write

$$\frac{Z(N_1, \dots, N_i, \dots, N_s)}{Z(N_1, \dots, N_i - 1, \dots, N_s)} = \sigma_i v \frac{Z_N(1, \dots, 1, \dots, 1)}{Z_N(1, \dots, 0, \dots, 1)}. \quad (14)$$

Further we have the identity,

$$\log \frac{Z_N(1, \dots, 1, \dots, 1)}{Z_N(1, \dots, 0, \dots, 1)} = \int_0^1 \frac{\partial \log Z_N(\lambda_i)}{\partial \lambda_i} d\lambda_i. \quad (15)$$

To simplify notation, we write $Z_N(\lambda_i)$ for $Z_N(1, \dots, \lambda_i, \dots, 1)$. In the future this convention will be adopted for all functions of the parameters λ , only those differing from unity being explicitly indicated. Returning to Eq. (10), we observe that

$$Z_N(\lambda_i) = \int \dots \int e^{-\beta[V_{N-1} + \lambda_i V_i]} d\omega_1 \dots d\omega_N, \quad (16)$$

$$V_i = \sum_{k=1}^N V_{ik}.$$

Differentiation of (16) with respect to λ_i yields

$$\partial \log Z_N(\lambda_i) / \partial \lambda_i = -\beta \overline{V_i(\lambda_i)},$$

$$\overline{V_i(\lambda_i)} = \frac{\int \dots \int V_i e^{-\beta[V_{N-1} + \lambda_i V_i]} d\omega_1 \dots d\omega_N}{\int \dots \int e^{-\beta[V_{N-1} + \lambda_i V_i]} d\omega_1 \dots d\omega_N}. \quad (17)$$

Combining Eqs. (5), (14), (15) and (17), we obtain for the chemical potential:

$$\mu_i = kT \log N_i/v + \int_0^1 \overline{V_i(\lambda_i)} d\lambda_i + \varphi_i(T), \quad (18)$$

$$\varphi_i(T) = -kT \log \sigma_i f_i(T).$$

The mean potential energy $\overline{V_i(\lambda_i)}$ can be expressed as follows:

$$\overline{V_i(\lambda_i)} = \sum_{k=1}^N \overline{V_{ik}(\lambda_i)},$$

$$\overline{V_{ik}(\lambda_i)} = \frac{\int \dots \int V_{ik} e^{-\beta[V_{N-1} + \lambda_i V_i]} d\omega_1 \dots d\omega_N}{\int \dots \int e^{-\beta[V_{N-1} + \lambda_i V_i]} d\omega_1 \dots d\omega_N}. \quad (19)$$

Since V_{ik} depends only on the coordinates of the molecules i and k , we may write,

$$\overline{V_{ik}(\lambda_i)} = \frac{1}{\sigma_i \sigma_k v^2} \int \int V_{ik} e^{-\beta W_{ik}(\lambda_i)} d\omega_i d\omega_k, \quad (a)$$

$$e^{-\beta W_{ik}(\lambda_i)} = \frac{\sigma_i \sigma_k v^2 \int \dots \int e^{-\beta[V_{N-1} + \lambda_i V_i]} d\omega_1 \dots d\omega_{N-2}}{\int \dots \int e^{-\beta[V_{N-1} + \lambda_i V_i]} d\omega_1 \dots d\omega_N}. \quad (b)$$

The function $W_{ik}(\lambda_i)$, as we shall presently show, is the potential of the mean force acting between the molecules i and k . At present we merely observe that in the absence of external fields of force $W_{ik}(\lambda_i)$ can depend only upon the relative coordinate of the molecule pair i and k , except in a region of negligible volume near the surface of the fluid.

We may therefore refer the position of the center of gravity and the orientation of the molecule k to a coordinate system fixed in molecule i . Both V_{ik} and $W_{ik}(\lambda_i)$ will depend upon these relative coordinates alone. Moreover, the Jacobian of this transformation is unity. If we then integrate over the configuration space of molecule i , the expression for $\overline{V_{ik}(\lambda_i)}$, Eq. (20), becomes:

$$\overline{V_{ik}(\lambda_i)} = (1/\sigma_k v) \int V_{ik} e^{-\beta W_{ik}(\lambda_i)} d\omega_k, \quad (21)$$

where $d\omega_k$ is understood to refer to the coordinates of molecule k relative to a system of axes fixed in molecule i . Introducing Eq. (21) into Eq. (18), and remembering that $\overline{V_{ik}(\lambda_i)}$

is the same function for all molecules k of the same type, we may write:

$$\mu_i = kT \left\{ \log N_i/v + \sum_{k=1}^r \frac{N_k}{v} \int_0^1 B_{ik}(\lambda_i) d\lambda_i \right\} + \varphi_i(T), \quad (22)$$

$$B_{ik}(\lambda_i) = (1/\sigma_k kT) \int V_{ik} e^{-\beta W_i^k(\lambda_i)} d\omega_k,$$

where the summation extends over all molecular types k present in the fluid, and the function B_{ik} refers to a single pair of molecules of types i and k , respectively. Each B_{ik} is a function of temperature, volume and composition, since $W_i^k(\lambda_i)$ is a function of all of these variables. The notation $W_i^k(\lambda_i)$ means of course that all the parameters λ have the value unity except λ_i corresponding to a single molecule of type i .

The mean energy \bar{E} of the fluid may be expressed quite simply, if we assume classical equipartition with respect to the low frequency rotational and translational degrees of freedom

$$\bar{E} = E_0(T) + \bar{V}_N, \quad (23)$$

where \bar{V}_N is the mean potential energy associated with the intermolecular forces and $E_0(T)$, a function of the temperature alone, is sum of the internal energies of the molecules and their mean translational and rotational kinetic energies. Writing V_N in the form of Eq. (6), and remembering that V_{ik} depends only on the relative coordinates of molecules k and i , we may write*

$$\bar{V}_N = \sum_{i < k} \bar{V}_{ik} = \frac{1}{2} \sum_{i,k=1}^r (N_i N_k / v) \bar{V}_{ik},$$

$$\bar{V}_{ik} = (1/\sigma_k v) \int V_{ik} e^{-\beta W_i^k(1)} d\omega_k. \quad (24)$$

We note that W_i^k appearing in Eq. (24) is $W_i^k(1)$, the value of $W_i^k(\lambda_i)$ when molecule i has its full coupling with the other molecules of the system. Finally we may write,

$$\bar{E} = E_0(T) + \frac{1}{2} kT \sum_{i,k=1}^r (N_i N_k / v) B_{ik}. \quad (25)$$

The quantity B_{ik} in Eq. (25) is equal to $B_{ik}(1)$ of Eq. (22) when λ_i is unity. $E_0(T)$ may be

* Eq. (24) has been given by Hildebrand and Wood, J. Chem. Phys. 1, 817 (1933).

explicitly calculated if the internal partition functions of the molecules are known. We shall not be interested in this point here.

III.

The use of Eqs. (22) and (25) for purposes of calculation depends upon an investigation of the functions $W_i^k(\lambda_i)$ which determine the probability distribution of the pair of molecules i and k relative to each other. It may readily be shown that $W_i^k(\lambda_i)$ is the potential of the mean force acting between the molecules i and k , averaged over all configurations of the remaining $N-2$ molecules of the system. The force acting at the center of gravity of molecule i for a fixed configuration of the other molecules, is

$$F_i(\lambda_i) = -\nabla_i V_N(\lambda_i), \quad (26)$$

where ∇_i is the gradient operator associated with the coordinates of the center of gravity of molecule i . If we take a mean value with the pair of molecules i and k held fixed, we obtain

$$\overline{F_i(\lambda_i)}^{ik} = \frac{\int \cdots \int \nabla_i V_N(\lambda_i) e^{-\beta V_N(\lambda_i)} d\omega_1 \cdots d\omega_{N-2}}{\int \cdots \int e^{-\beta V_N(\lambda_i)} d\omega_1 \cdots d\omega_{N-2}}. \quad (27)$$

Differentiation of both sides of Eq. (20b), which defines $W_i^k(\lambda_i)$ and comparison with Eq. (27) yields

$$\overline{F_i(\lambda_i)}^{ik} = -\nabla_i W_i^k(\lambda_i). \quad (28)$$

The function $W_i^k(\lambda_i)$ is therefore the potential of the mean force acting at the center of gravity of molecule i when k is held fixed at some point in its vicinity. Similarly, it may be shown that $W_i^k(\lambda_i)$ is the potential of the mean generalized forces associated with the relative orientation of i and k . If the relative orientation is specified by the Eulerian angles ϑ , φ and ψ , the mean torque tending to produce rotation through the angle ϑ is $-\partial W_i^k(\lambda_i)/\partial \vartheta$. These relations have been used by Einstein, Schmoluchowski and others,⁶ who showed that the simple Boltzmann distribution is valid provided the potential of the mean force is employed in the exponential factor.

It is interesting to remark that the potential $W_i^k(1)$, corresponding to full coupling between molecule i and the other molecules, is susceptible

⁶ For a discussion of this point, see L. Onsager, Chem. Rev. 13, 73 (1933).

of experimental determination, at least in its dependence on the relative coordinates of the molecular centers of gravity. According to the theory of x-ray scattering by liquids, developed by Prins and Debye,⁷ the angular distribution of intensity of the scattered radiation is a sum of mean values of functions depending only upon the relative coordinates of pairs of molecules. Mean values of such functions are determined by the probability distribution function $e^{-\beta W_{ik}}$ in a system in thermodynamic equilibrium. By a Fourier integral inversion of the theoretical scattering formula, $(e^{-\beta W_{ik}} - 1)$ may be computed from the observed intensity measured as a function of the scattering angle. By Eq. (25), we see that a knowledge of $W_{ik}(1)$ suffices for the calculation of the mean energy of the fluid from the potentials V_{ik} . However, it does not suffice for the calculations of chemical potentials or the Gibbs free energy, ζ , which is equal to $\sum_{i=1}^p N_i \mu_i$. For the latter purpose we must know $W_{ik}(\lambda_i)$ for all values of λ_i between zero and unity. This information is not furnished by x-ray scattering experiments. Thus, while they yield valuable information concerning the statistical structure of liquids, they do not provide sufficient data for the calculation of entropy and free energy.

We must consequently depend upon theoretical information about the potentials of mean force $W_{ik}(\lambda_i)$. Since the many dimensional phase integrals of Eq. (20b), which defines $W_{ik}(\lambda_i)$, are inconvenient to handle, we follow an indirect method of attack, leading to reasonable approximations both for condensed and rarefied systems. Logarithmic differentiation of both sides of Eq. (20b) yields

$$\partial W_{ik}(\lambda_i) / \partial \lambda_i = \overline{V_{is}(\lambda_i)} - \overline{V_i(\lambda_i)}, \quad (29)$$

where

$$\overline{V_{is}(\lambda_i)} = \frac{\int \dots \int V_{is} e^{-\beta [V_{N-1} + \lambda_i V_i]} d\omega_1 \dots d\omega_{N-2}}{\int \dots \int e^{-\beta [V_{N-1} + \lambda_i V_i]} d\omega_1 \dots d\omega_{N-2}}, \quad (30)$$

$\overline{V_{is}(\lambda_i)}$ is the mean value of V_{is} for a fixed configuration of the molecular pair i and k , while $\overline{V_i(\lambda_i)}$ is the mean value of the same function taken over all configurations of all molecules of

⁷ Zernicke and Prins, *Zeits. f. Physik* **41**, 184 (1927); Debye and Mencke, *Physik. Zeits.* **31**, 797 (1930).

the system. By Eq. (10), we may write

$$\overline{V_{is}(\lambda_i)} = V_{ik} + \sum_{\substack{s=1 \\ s \neq k}}^N \overline{V_{is}(\lambda_i)}, \quad (31)$$

since the term V_{ik} is constant for fixed configurations of molecules i and k and is unaffected by a mean value operation in which these are held fixed. Because V_{is} depends only on the relative coordinates of i and s , we have

$$\overline{V_{is}(\lambda_i)} = (1/\sigma_s v) \int V_{is} e^{-\beta W_{ik}(\lambda_i)} d\omega_s, \quad (a)$$

$$(32)$$

$$e^{-\beta W_{ik}(\lambda_i)} = \frac{\sigma_s v \int \dots \int e^{-\beta [V_{N-1} + \lambda_i V_i]} d\omega_1 \dots d\omega_{N-3}}{\int \dots \int e^{-\beta [V_{N-1} + \lambda_i V_i]} d\omega_1 \dots d\omega_{N-2}}, \quad (b)$$

where the integration in the numerator of (32b) is to extend over the coordinates of all molecules except i , k and s and in the denominator over all but those of i and k . It will be seen at once that $W_{ik}(\lambda_i)$ is the potential of the mean force acting upon molecule s , averaged over the configurations of all molecules except i , k and s . We note that $W_{ik}(\lambda_i)$ is not invariant under a permutation of upper and lower indices, although $W_{ik}(\lambda_i)$ is. It is possible to define a potential of mean force which is symmetric in the coordinates of i , k and s , differing from $W_{ik}(\lambda_i)$ by a term independent of the coordinates of s , but the latter form is not the most convenient for the present purposes. The second term of Eq.

(29) is the sum $\sum_{s=1}^N \overline{V_{is}(\lambda_i)}$, each member of which is given by an expression of the form (21). Moreover, each of the mean values $\overline{V_{is}}$ and $\overline{V_{is}}$ are identical molecules of the same type s , so that we may write,

$$\partial W_{ik}(\lambda_i) / \partial \lambda_i = V_{ik} + \sum_{s=1}^v \frac{N_s}{v} \frac{1}{\sigma_s} \int V_{is} [e^{-\beta W_{ik}(\lambda_i)} - e^{-\beta W_{ik'}(\lambda_i)}] d\omega_s, \quad (33)$$

where the sum is extended over all types s . Each of the integrals refers to a single group of three molecules, i , k , and a single molecule of type s . Properly a term, $(v\sigma_k)^{-1} \int V_{ik'} e^{-\beta W_{ik'}(\lambda_i)} d\omega_{k'}$, where k' is a single molecule of the same type as k , should be omitted from the sum in Eq. (33). Since, however, this term bears a ratio of the

order of $1/N_k$ to terms retained, it can be ignored altogether. This is not true of V_{ik} , which is of dominant importance when k is situated in the immediate neighborhood of i .

Before integrating Eq. (33) we shall find it convenient to investigate the behavior of $W_i^k(\lambda_i)$ in the neighborhood of $\lambda_i=0$. First we note that $W_i^k(0)$ must be independent of the coordinates of i , since the mean force on i vanishes when λ_i is equal to zero. Moreover, it must also be independent of the coordinates of k except in the surface region, since the mean force on k must also vanish when λ_i is equal to zero. From these facts we conclude that $W_i^k(0)$

must be a constant. Making use of Eq. (20b), we write

$$e^{-\beta W_i^k(0)} = \frac{\sigma_i \sigma_k v^2 \int \cdots \int e^{-\beta V_{N-1}} d\omega_1 \cdots d\omega_{N-2}}{\int \cdots \int e^{-\beta V_{N-1}} d\omega_1 \cdots d\omega_N}. \quad (34)$$

Now the integral in the denominator of (34) is obviously independent of the coordinate of i and k , since it includes integrations over these coordinates. Since $W_i^k(0)$ is independent of the coordinates of i and k , we must conclude that the integral in the numerator is also independent of them. The factor $\sigma_i \sigma_k v^2$ may therefore be written as an integration over the configuration spaces of molecules i and k ,

$$\sigma_i \sigma_k v^2 \int \cdots \int e^{-\beta V_{N-1}} d\omega_1 \cdots d\omega_{N-2} = \int \cdots \int e^{-\beta V_{N-1}} d\omega_1 \cdots d\omega_N. \quad (35)$$

From Eqs. (34) and (35) we conclude that $e^{-\beta W_i^k(0)}$ has the value unity and that $W_i^k(0)$ vanishes. Bearing this fact in mind, we integrate Eq. (33) between zero and λ_i with the result:

$$W_i^k(\lambda_i) = \lambda_i V_{ik} + \sum_{s=1}^r (N_s/v) (1/\sigma_s) \int_0^{\lambda_i} \int V_{is} [e^{-\beta W_{ik}^s(\lambda_i)} - e^{-\beta W_i^s(\lambda_i)}] d\omega_s d\lambda_i. \quad (36)$$

From Eq. (36), we observe that $W_i^k(\lambda_i)$ approaches $\lambda_i V_{ik}$ as the densities of the several components of the fluid approach zero. This approximation is also obtained by neglecting the influence of the fixed molecule k on the distribution of a third molecule s in the vicinity of molecule i , that is by ignoring the difference between $W_{ik}^s(\lambda_i)$ and $W_i^s(\lambda_i)$. In the theory of the equation of state of a rarefied gas, this is essentially the approximation which is made. To obtain a more accurate expression for $W_i^k(\lambda_i)$ we must know something about the potential $W_{ik}^s(\lambda_i)$ involving the group of three molecules i , k and s . Proceeding from Eq. (32b), which defines $W_{ik}^s(\lambda_i)$, we obtain by differentiation with respect to λ_i

$$\begin{aligned} \partial W_{ik}^s(\lambda_i) / \partial \lambda_i &= \lambda_i V_{is} + \sum_{l=1}^r (N_l/v\sigma_l) \int V_{il} [e^{-\beta W_{ik}^l(\lambda_i)} - e^{-\beta W_{ik}^l(\lambda_i)}] d\omega_l, \\ e^{-\beta W_{ik}^s(\lambda_i)} &= \frac{\sigma_l \int \cdots \int e^{-\beta [V_{N-1} + \lambda_i V_{il}]} d\omega_1 \cdots d\omega_{N-4}}{\int \cdots \int e^{-\beta (V_{N-1} + \lambda_i V_{il})} d\omega_1 \cdots d\omega_{N-3}}. \end{aligned} \quad (37)$$

Examination of (32b) shows at once that $W_{ik}^s(0)$ is merely W_k^s in a system containing N_i-1 molecules of type i . It is apparent that this function can differ from W_k^s in the original system only by a quantity of completely negligible order, $O(1/N_i)$. Thus when Eq. (37) is integrated with respect to λ_i , there is obtained

$$W_{ik}^s(\lambda_i) = W_k^s + \lambda_i V_{is} + \sum_{l=1}^r (N_l/v\sigma_l) \int_0^{\lambda_i} \int V_{il} [e^{-\beta W_{ik}^l(\lambda_i)} - e^{-\beta W_{ik}^l(\lambda_i)}] d\omega_l d\lambda_i. \quad (38)$$

This equation is entirely analogous to Eq. (36). Since W_k^s is given by an equation of the form of (36), a first approximation to $W_{ik}^s(\lambda_i)$ is evidently $V_{is} + \lambda_i V_{il}$. Similarly a first approximation to $W_i^s(\lambda_i)$ is $\lambda_i V_{is}$. If these approximations are employed in the integrals of Eq. (36), we obtain a second approximation to $W_i^k(\lambda_i)$, namely

$$W_i^k(\lambda_i) = \lambda_i V_{ik} - kT \sum_{s=1}^r (N_s/v) (1/\sigma_s) \int (e^{-\beta \lambda_i V_{is}} - 1) (e^{-\beta V_{ks}} - 1) d\omega_s. \quad (39)$$

We should expect this approximation to be adequate in gases of moderate density. The method of successive approximation employed to obtain Eq. (39), can of course be extended without great difficulty, by transforming the potentials $W_{ik,l}(\lambda_i)$, involving groups of four molecules; in exactly the same manner as $W_i^k(\lambda_i)$ and $W_{ik}^s(\lambda_i)$. Presumably any desired degree of approximation could be attained in this fashion, but the expressions become very cumbersome. It should also be remarked that the method of approximation just outlined can only be employed when no long range forces, such as the Coulomb forces, act between the molecules, for in such cases the integral of Eq. (39) diverges. It converges whenever the individual potentials decrease asymptotically at least as rapidly as r_{ik}^{-4} .

For an exact calculation of $W_i^k(\lambda_i)$, it would be necessary to solve a set of $N-1$ simultaneous integral equations of the type of Eqs. (36) and (38), involving potentials $W_{ik,\dots,l}^s$ in which the number of fixed molecules i, k, \dots, l , ranges from one to $N-1$. Moreover, when the number of fixed molecules becomes comparable with the total number of molecules, N , the equations become more complicated than (36) and (38), due to growth of terms, which are of zero order in the latter equations. Since this is not a practicable procedure, we must resort to some means of approximation. Eq. (39) represents a possible method of approximation in which $W_i^k(\lambda_i)$ is developed in powers of the densities of the components of the fluid. However, we should like to find an approximation more suitable in condensed systems than Eq. (39) is likely to be. An obvious and simple approximation may be obtained by assuming superposition in the potentials of mean force,

$$W_{ik}^s(\lambda_i) = W_k^s + W_i^s(\lambda_i). \quad (40)$$

Although the additivity expressed in Eq. (40) holds for the direct action of i and k on s through the terms $V_{ks} + \lambda_i V_{is}$, it cannot hold exactly for their indirect action upon s through their effect on the distribution of the remaining $N-3$ molecules. The magnitude of this discrepancy will be discussed later. If we introduce the approximation (40) into Eq. (36), we obtain the following integral equation:

$$W_i^k(\lambda_i) = \lambda_i V_{ik} + \sum_{s=1}^{\nu} (N_s/v)(1/\sigma_s) \int_0^{\lambda_i} \int V_{is} e^{-\beta W_i^s(\lambda_i)} [e^{-\beta W_k^s(1)} - 1] d\omega_s d\lambda_i. \quad (41)$$

The potentials $W_i^k(\lambda_i)$ will have the same form for any pair of molecules of the same type. From the ν types of molecules present in the fluid, $\nu(\nu+1)/2$ types of molecular pairs can be formed. There will, therefore, be $\nu(\nu+1)/2$ types of functions $W_i^k(\lambda_i)$, each satisfying an equation like (41). Simultaneous solution of these integral equations will yield values of the functions $W_i^k(\lambda_i)$ consistent with the approximation expressed in Eq. (40). Of course for a pure fluid, having only one component, only one integral equation has to be solved.

$$W(q_{12}, \lambda) = \lambda V(q_{12}) + (N\rho/M\sigma) \int_0^{\lambda} \int V(q_{13}) e^{-\beta W(q_{13}, \lambda)} [e^{-\beta W(q_{23}, 1)} - 1] d\omega_3 d\lambda, \quad (42)$$

where q_{12} , q_{13} and q_{23} are the relative coordinates of a set of three molecules, N is Avogadro's number, M the molecular weight of the substance, and ρ its density. We note that the approximation (39) is obtainable from Eq. (41) as the first step in its solution by successive substitution. In general, it will not be feasible to seek analytic solutions of Eqs. (41) or (42). However, by graphical or mechanical quadrature, it should be possible to determine self-consistent functions satisfying these equations. We remark that this process provides a theoretical means of calculating the x-ray scattering curves of liquids, since they are determined by $W_i^k(1)$. In some cases the potentials of intermolecular force can be calculated from atomic structure. Although this can be done in relatively few cases, quantum mechanics prescribes an approximate functional form for the V_{ik} . With this functional form, the numerical values of V_{ik} may be deduced from the temperature dependence of the second virial coefficient of the substance in the gaseous state.

While Eq. (40) represents an approximation which is intuitively attractive, it is of course not exact. Although a numerical estimate of the error involved is difficult, we can say something quite

definite about the nature of the approximation. To facilitate discussion, we shall introduce the symbol ϵ_{ik}^s to denote the deviation from additivity

$$\epsilon_{ik}^s = W_{ik}^s(\lambda_i) - [W_k^s + W_i^s(\lambda_i)]. \quad (43)$$

It is possible to express ϵ_{ik}^s in terms of a third order fluctuation in the potential energy of molecule i . Without entering into the details of the calculation, we state the following result.

$$\epsilon_{ik}^s = \beta^2 \int_0^{\lambda_i} \int_0^1 \int_0^1 \overline{(V_i - \overline{V_i})(V_k - \overline{V_k})(V_s - \overline{V_s})} d\lambda_k d\lambda_s d\lambda_i, \quad (44)$$

where the fluctuation is understood to be a function of the variables $\lambda_i, \lambda_k, \lambda_s$, mean values being taken with the distribution function $e^{-\beta V_N(\lambda_i, \lambda_k, \lambda_s)}$. A more useful expression for ϵ_{ik}^s is obtained simply by subtracting the equation for $W_i^s(\lambda_i)$ corresponding to (36) from Eq. (38). The result is,

$$\epsilon_{ik}^s = \sum_{l=1}^r (N_l/v\sigma_l) \int_0^{\lambda_i} \int_0^1 V_{il} \{e^{-\beta W_{ik}^l(\lambda_i)} + e^{-\beta W_i^l(\lambda_i)} - e^{-\beta W_{ik}^l(\lambda_i)} - e^{-\beta W_i^l(\lambda_i)}\} d\omega_l d\lambda_i. \quad (45)$$

An exact calculation of ϵ_{ik}^s from Eq. (45) is of course impossible without a knowledge of the potential $W_{ik}^l(\lambda_i)$. However, we should expect to obtain at least a rough estimate of ϵ_{ik}^s by using the additivity approximation for the potentials $W_{ik}^l(\lambda_i)$, $W_{ik}^l(\lambda_i)$, and $W_i^l(\lambda_i)$. Introduction of this approximation yields

$$\epsilon_{ik}^s = \sum_{l=1}^r (N_l/v\sigma_l) \int_0^{\lambda_i} \int_0^1 V_{il} e^{-\beta W_i^l(\lambda_i)} (e^{-\beta W_k^l} - 1)(e^{-\beta W_s^l} - 1) d\omega_l d\lambda_i. \quad (46)$$

If we rely on Eq. (46) for the order of magnitude of ϵ_{ik}^s , we see that the integrand will be very small except for configurations of molecule such that W_k^l and W_s^l are simultaneously large. If s and k are situated at some distance from each other so that their spheres of influence on the distribution of a third molecule l , do not overlap appreciably, ϵ_{ik}^s will be small. Returning to Eq. (36) we remark that for the calculation of $W_i^k(\lambda_i)$, it is only necessary to know $W_{ik}^s(\lambda_i)$ accurately in a region in the vicinity of molecule i , where V_{is} is sensibly different from zero. If the molecules i and k are separated by an appreciable distance, s will be distant from k in the greater part of this region, and we may conclude that ϵ_{ik}^s is small. Thus we may expect Eq. (41) to provide a good approximation to $W_i^k(\lambda_i)$ at least when the molecules i and k are separated by an appreciable distance, and that $W_i^k(\lambda_i)$ will approach the solution of Eq. (41) asymptotically as the distance between i and k is increased. This point is of some importance in the case of long range intermolecular forces, such as those between electrolyte ions. At small distances between i and k the dominant term in $W_i^k(\lambda_i)$ becomes V_{ik} , and although the terms depending on the density may still be large, it is not necessary to know them with such great accuracy. Once solutions of Eq. (41) have been obtained, they may be used in Eq. (46) to obtain a rough estimate of ϵ_{ik}^s . If this turns out to be small, the solutions of Eq. (41) can be accepted with some degree of assurance as reasonable approximations to the potentials $W_i^k(\lambda_i)$. It would be desirable to have a more rigid criterion for judging the adequacy of these approximations, but unfortunately this cannot be obtained without introducing distribution functions involving larger and larger groups of fixed molecules. Unless some approximation such as superposition is introduced at some early stage in this sequence of distribution functions, we are driven back to the many dimensional phase integrals with which we started.

Having obtained approximate expressions for $W_i^k(\lambda_i)$ by solution of Eqs. (41), we can calculate the chemical potential of any component of the fluid by means of Eq. (22), as well as the total energy of the fluid by Eq. (25). From the chemical potentials, we may obtain the Gibbs free energy, ζ , of the system.

$$\zeta = E + pv - TS = \sum_{i=1}^r N_i \mu_i = kT \left\{ \sum_{i=1}^r N_i \log N_i/v + \sum_{i,k=1}^r \frac{N_i N_k}{v} \int_0^1 B_{ik}(\lambda_i) d\lambda_i \right\} + \sum_{i=1}^r N_i \varphi_i(T). \quad (47)$$

In principle one can obtain the compressibility, κ , of the fluid by means of the thermodynamic formula,

$$1/\kappa = -v(\partial p/\partial v)_T = -(\partial \zeta/\partial v)_{T, N_1, \dots, N_r} \quad (48)$$

However the $B_{ik}(\lambda_i)$ depend upon v through the $W_i^k(\lambda_i)$. Even though Eq. (41) may provide good approximations to the $W_i^k(\lambda_i)$, it is by no means certain that the derivatives of these solutions with respect to v will be good approximations to $\partial W_i^k(\lambda_i)/\partial v$. Thus while Eqs. (22), (35) and (47) may express the dependence of the μ_i , \bar{E} and ζ upon the composition of the fluid with some accuracy, the compressibility calculated from Eqs. (47) and (48) may be a much poorer approximation. Quite formally, we may write

$$\left(\frac{\partial p}{\partial v}\right)_T = -kT \left\{ \sum_{i=1}^r \frac{N_i}{v^2} + \sum_{i,k=1}^r \frac{N_i N_k}{v^3} \int_0^1 \left[B_{ik}(\lambda_i) - v \frac{\partial B_{ik}(\lambda_i)}{\partial v} \right] d\lambda_i \right\}. \quad (49)$$

In case the fluid under consideration is a gas, we know that as the volume is increased to infinity, the pressure decreases continuously to zero. In this case we may integrate Eq. (49) between the limits v and infinity. After a simple partial integration, the following equation of state is obtained.

$$\frac{p\bar{v}}{RT} = 1 + \sum_{i,k=1}^r \frac{x_i x_k}{\bar{v}} \left\{ \int_0^1 N \left[B_{ik}(\lambda_i) + \bar{v}^2 \int_{\infty}^{\bar{v}} \frac{B_{ik}(\lambda_i)}{\bar{v}^3} d\bar{v} \right] d\lambda_i \right\} \quad (50)$$

$$n_i = N_i/N; \quad x_i = n_i/\sum n_k; \quad \bar{v} = v/\sum n_k,$$

where N is Avogadro's number, n_i the number of moles of component i present in the gas and x_i the mole fraction of that component. Eq. (50) may be made the basis for a statistical calculation of the equation of state of a real gas mixture. When the potentials $W_i^k(\lambda_i)$ in the $B_{ik}(\lambda_i)$ are approximated simply by $\lambda_i V_{ik}$ the usual expressions for the second virial coefficients are obtained.

IV.

The present method provides a particularly simple means of determining the equation of state of a real gas mixture. We shall derive expressions for the second and third coefficients in the virial expansion of the equation of state, indicating how the method may be extended to higher coefficients. Results are obtained which are in agreement with those of Ursell, who has treated the same problem from a somewhat different point of view.⁸

If the function $W_i^k(\lambda_i)$ is approximated by Eq. (39), we obtain the following expression for $B_{ik}(\lambda_i)$.

$$B_{ik}(\lambda_i) = \frac{1}{\sigma_k kT} \int V_{ik} \exp \left\{ -\beta \lambda_i V_{ik} + \sum_{s=1}^r \frac{N_s}{v \sigma_s} \int (1 - e^{-\beta \lambda_i V_{is}})(1 - e^{-\beta V_{ks}}) d\omega_s \right\} d\omega_k. \quad (51)$$

Substitution of this expression in Eqs. (22) and (50) would yield the chemical potentials of the several components and the equation of state of the gas mixture. We should expect the equation of state, although approximate, to be much more satisfactory than a virial expansion. However, the integrals involved cannot be expressed in terms of elementary functions, and we shall not concern ourselves with their simplification here. We note that Eq. (39) is exact to terms in $1/v^2$, so that the first two terms of an expansion of the right-hand side of Eq. (51) are exact. The expansion is

$$B_{ik}(\lambda_i) = \frac{1}{kT} \left\{ \frac{1}{\sigma_k} \int V_{ik} e^{-\beta \lambda_i V_{ik}} d\omega_k + \sum_{s=1}^r \frac{N_s}{v} \frac{1}{\sigma_s \sigma_k} \int \int V_{ik} e^{-\beta \lambda_i V_{ik}} (1 - e^{-\beta \lambda_i V_{is}})(1 - e^{-\beta V_{ks}}) d\omega_k d\omega_s + O(1/v^3) \right\}. \quad (52)$$

⁸ Ursell, Proc. Camb. Phil. Soc. **23**, 685 (1927); R. H. Fowler, *Statistical Mechanics*, Cambridge University Press (1929), p. 173.

Substitution of this expansion in Eq. (22), integration with respect to λ_i and a rearrangement of terms yields⁹

$$\mu_i = kT \left\{ \log N_i/v + \sum_{k=1}^v \frac{N_k}{v\sigma_k} \int (1 - e^{-\beta V_{ik}}) d\omega_k \right. \\ \left. + \frac{1}{2} \sum_{k,s=1}^v \frac{N_k N_s}{v^2} \frac{1}{\sigma_k \sigma_s} \int \int (1 - e^{-\beta V_{ik}})(1 - e^{-\beta V_{is}})(1 - e^{-\beta V_{ks}}) d\omega_k d\omega_s + O(1/v^3) \right\}. \quad (53)$$

When the approximate expressions for the μ_i given by Eq. (53) are introduced into Eqs. (47) and (48), we obtain

$$\left(\frac{\partial p}{\partial v} \right)_T = -kT \left\{ \sum_{i=1}^v \frac{N_i}{v^2} + \sum_{i,k=1}^v \frac{N_i N_k}{v^3} \frac{1}{\sigma_k} \int (1 - e^{-\beta V_{ik}}) d\omega_k \right. \\ \left. + \sum_{i,k,s=1}^v \frac{N_i N_k N_s}{v^4} \frac{1}{\sigma_k \sigma_s} \int \int (1 - e^{-\beta V_{ik}})(1 - e^{-\beta V_{is}})(1 - e^{-\beta V_{ks}}) d\omega_k d\omega_s + O(1/v^5) \right\}. \quad (54)$$

Integration between the volume limits ∞ and v leads to the following equation of state

$$\frac{p\bar{v}}{RT} = 1 + \sum_{i,k=1}^v \frac{x_i x_k}{\bar{v}} B_{ik}^0 + \sum_{i,k,s=1}^v \frac{x_i x_k x_s}{\bar{v}^2} C_{iks}^0 + O(1/\bar{v}^3) \\ B_{ik}^0 = \frac{N}{2\sigma_k} \int (1 - e^{-\beta V_{ik}}) d\omega_k \\ C_{iks}^0 = \frac{N^2}{3\sigma_k \sigma_s} \int \int (1 - e^{-\beta V_{ik}})(1 - e^{-\beta V_{is}})(1 - e^{-\beta V_{ks}}) d\omega_k d\omega_s. \quad (55)$$

If the method of approximating $W_i^k(\lambda_i)$ embodied in Eq. (39) is carried one stage farther, one more term may be retained in the expansion of $B_{ik}(\lambda_i)$ and the fourth virial coefficient may be calculated. The process can be continued indefinitely, but of course the algebraic operations become tedious, and the final expressions unwieldy. The method consists simply of continued substitution and

⁹ After integration with respect to λ_i , the terms in μ_i involving $1/v^2$ have the form

$$\sum_{\substack{k,s=1 \\ k \neq s \neq i}}^N \frac{1}{v^2 \sigma_k \sigma_s} \int \int (1 - e^{-\beta V_{ks}}) \left\{ \frac{V_{ik}}{V_{ik} + V_{is}} (e^{-\beta(V_{ik} + V_{is})} - 1) - (e^{-\beta V_{ik}} - 1) \right\} d\omega_k d\omega_s,$$

where the original summation indices, referring to the individual molecules, have been restored for clearness. For every term in the sum with the integrand

$$\left\{ \frac{V_{ik}}{V_{ik} + V_{is}} (e^{-\beta(V_{ik} + V_{is})} - 1) - (e^{-\beta V_{ik}} - 1) \right\} (1 - e^{-\beta V_{ks}}),$$

corresponding to any specified pair of molecules k and s , there is also a term involving the same pair, having the form

$$\left\{ \frac{V_{is}}{V_{is} + V_{ik}} (e^{-\beta(V_{ik} + V_{is})} - 1) - (e^{-\beta V_{is}} - 1) \right\} (1 - e^{-\beta V_{ks}}).$$

The sum of this pair of terms is readily seen to be

$$(1 - e^{-\beta V_{ik}})(1 - e^{-\beta V_{is}})(1 - e^{-\beta V_{ks}})$$

so that the double sum may be rearranged as follows:

$$\frac{1}{2} \sum_{\substack{k,s=1 \\ k \neq s \neq i}}^N \frac{1}{v^2 \sigma_k \sigma_s} \int \int (1 - e^{-\beta V_{ks}})(1 - e^{-\beta V_{is}})(1 - e^{-\beta V_{ik}}) d\omega_k d\omega_s.$$

This sum contains $(N-1)(N-2)$ terms of similar magnitude. It differs from the sum over molecular types appearing in Eq. (55) by $(3N-2)$ terms of the same magnitude. The aggregate of these terms bears a ratio of the order of $1/N$ to either sum and is consequently entirely negligible.

expansion. If one wishes a virial expansion including terms of the order of $1/v^n$, one begins by approximating the $W_{ik\dots l}^s$, involving n fixed molecules, by sums of the form $\lambda_i V_{is} + \sum_{l=1}^{n-1} V_{ls}$. These expressions, substituted in an equation similar to (38), yield an approximate $W_{ik\dots l}^s$ involving $(n-1)$ fixed molecules. Continued substitution finally leads to an expression for $W_i^k(\lambda_i)$, which when expanded in powers of $1/v$, is exact to terms involving $1/v^n$. It is only necessary to have the expression for $W_{ik\dots l}^s$ involving $(n-1)$ molecules, exact to terms in $1/v$, since in the final expansion, it is multiplied by a factor $1/v^{n-1}$.

V.

It is interesting to investigate the form of the molecular pair distribution function, $e^{-\beta W_i^k}$ by means of the approximation, Eq. (39). Although Eq. (39) can scarcely be accurate at liquid densities, we might expect it to be adequate up to moderately high densities. Moreover, even where inexact, it should serve to illustrate the form of the distribution function.

We shall restrict our attention to a pure fluid, consisting of spherically symmetrical molecules. For such a fluid, Eq. (39) reduces to the following expression when λ_i is equal to unity

$$W(r) = V(r) - (NkT/v)$$

$$\times \int (1 - e^{-\beta V(r_{13})})(1 - e^{-\beta V(r_{23})}) dv_3,$$

$$r = |\mathbf{r}_1 - \mathbf{r}_2|; \quad r_{13} = |\mathbf{r}_1 - \mathbf{r}_3|; \quad r_{23} = |\mathbf{r}_2 - \mathbf{r}_3|. \quad (56)$$

Since all molecules are of the same type, W_i^k and V_{ik} have the same functional form for every molecular pair, and we may omit the indices i and k . We shall suppose the molecules to be rigid spheres of diameter b , so that when r is less than b , $V(r)$ becomes positively infinite. Attractive forces outside of the sphere a should properly be represented by a potential of the form, $-\gamma/r^6$. However to simplify calculations, we shall represent this potential by a trough of depth u_0 and width, $a-b$. Between the concentric spheres of radii b and a , $V(r)$ is thus equal to $-u_0$. The potential $V(r)$, upon which the following calculations are based is represented by the following step function.

$$\begin{aligned} V(r) &= \infty, & 0 \leq r \leq b \\ &= -u_0, & b \leq r \leq a \\ &= 0, & a < r. \end{aligned} \quad (57)$$

With this potential, the integral on the left-hand side of Eq. (56) may be expressed in terms of the

volumes of intersection of spheres of radii a and b .

$$W(r)/kT = V(r)/kT - (N\omega_0/v)J(r),$$

$$\omega_0 = 4\pi b^3/3, \quad (58)$$

$$J(r) = \frac{1}{\omega_0} \{ \omega_{bb} + 2(\omega_{ab} - \omega_{bb})(1 - e^{\beta u_0}) + (\omega_{aa} - 2\omega_{ab} + \omega_{bb})(1 - e^{\beta u_0})^2 \},$$

where ω_{bb} is volume of intersection of two spheres of equal radii b , ω_{aa} that of two spheres of equal radii a , and ω_{ab} that of two spheres of unequal radii a and b , the distance between the centers of each pair of spheres being r . A simple calculation yields

$$\begin{aligned} \frac{\omega_{bb}}{\omega_0} &= 1 - 3r/4b + \frac{1}{16}(r/b)^3; & 0 < r \leq 2b \\ &= 0, & r > 2b \\ \frac{\omega_{aa}}{\omega_0} &= (a/b)^3 [1 - 3r/4a + \frac{1}{16}(r/a)^3]; & 0 < r \leq 2a \\ &= 0, & r > 2a \\ \frac{\omega_{ab}}{\omega_0} &= \frac{1}{2} \{ [1 - \frac{3}{4}(1 - (\alpha/r^2))(r/b) + \frac{1}{16}(1 - (\alpha/r^2)^3)(r/b)^3] + (a/b)^3 \\ &\quad \times [1 - \frac{3}{4}(1 + (\alpha/r^2))(r/a) + \frac{1}{16}(1 + (\alpha/r^2)^3)(r/a)^3] \}; \\ &\quad (a^2 - b^2)^{\frac{1}{2}} < r \leq a + b \\ &= 0, & r > a + b; \quad \alpha = a^2 - b^2. \end{aligned} \quad (59)$$

By means of Eqs. (58) and (59), $W(r)/kT$ may be computed as a function of the ratios, r/b , a/b , $N\omega_0/v$ and u_0/kT . The probability distribution function, which we shall designate by $G(r)$ may then be calculated from the relation $G(r) = e^{-W(r)/kT}$. We note that $N\omega_0$ is equal to eight times the total volume of the molecules,

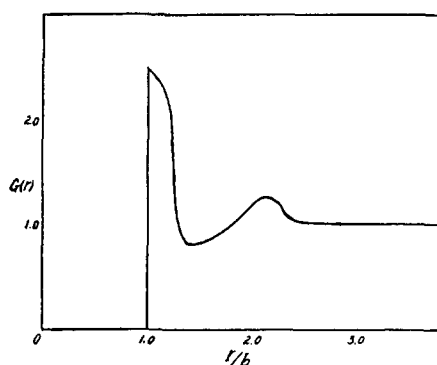


FIG. 1. Molecular pair distribution function based upon Eq. (58).

their radii being $b/2$. For most liquids the ratio $N\omega_0/v$ would have a value between 4 and 6. Moreover, we should expect u_0/kT to be at least unity in liquids. The ratio a/b is somewhat arbitrary. However, in order to make the rectangular trough approximate the actual potential of the attractive forces, which diminishes rapidly with increasing distance, a/b cannot differ much from unity. In order to approach conditions in the liquid state, we assign the following values to the constants in question: $N\omega_0/v = 2$; $u_0/kT = 1$; $a/b = 1.25$. The above value of $N\omega_0/v$ corresponds to a density about a third of ordinary liquid densities. With the above values of the constants, $G(r)$ has been calculated with the aid of Eqs. (58) and (59). It is plotted as a function of r/b in Fig. 1, and tabulated in Table I. Actually there is a discon-

TABLE I.

r/b	$G(r)$	r/b	$G(r)$
0.0	0.00	1.6	0.86
0.8	0.00	1.8	0.98
1.0	2.48	2.0	1.20
1.2	2.23	2.2	1.25
1.4	0.81	2.4	1.03
		2.5	1.00

tinuity in the curve at $r/b = 1.25$, arising from the artificial nature of the step function potential. In the figure, this discontinuity has been eliminated by drawing a smooth curve through points calculated at r/b intervals of 0.2. It will be observed that the calculated $G(r)$ bears a close resemblance to the molecular distribution

functions in liquids derived from measurements of x-ray scattering, exhibiting the characteristic maxima and minima of the empirically determined functions. While we realize that at the temperature and density of the above calculation, the approximation (39) is being pushed to the limit of its applicability, we believe that it adequately illustrates the mechanism by which the intermolecular forces operate to establish molecular pair distribution functions in dense fluids.

It is interesting to observe that the attractive van der Waals forces play a dominant role in the production of the secondary maximum and minimum in the $G(r)$ of Fig. 1. On the basis of Eq. (39), the distribution function in a fluid of rigid spheres with no attractive forces would exhibit a single maximum at $r=b$. The absence of secondary maxima and minima for rigid spheres is of course the fault of Eq. (39). If the approximation were carried one stage farther, they would begin to appear. However, the point to be emphasized is that probability distribution functions derived from the packing of rigid spheres can scarcely be applied to actual fluids, where the attractive forces play a dominant role in determining the form of the distribution function.

A further limitation of the approximation (39) is that it fails to produce more than a single pair of secondary maxima and minima. For a more exact calculation, it is suggested that the distribution function derived from Eq. (39) be used as a starting point for the self-consistent solution of the more exact integral Eqs. (41) and (42). Thus, it will be observed that tertiary maxima and minima would doubtless arise from the secondary maximum and minimum of the approximate $W(r, \lambda)$ based on Eq. (39), if the latter function were substituted in the integral of Eq. (42). The computational difficulties involved in the self-consistent solution of Eq. (42) are unfortunately rather serious, since even for spherically symmetrical molecules, a triple numerical or mechanical integration is required at each stage of the process. However, these difficulties are not insurmountable.

The formulation of a theory of solutions on the basis of the present ideas offers intriguing possibilities. Several methods of approach are open,

the direct use of our expressions for the chemical potentials being the most obvious. An alternative and more phenomenological treatment applicable to dilute solutions has also been undertaken. These investigations will be described in a future article.

Note added in proof:

(a) A remark about the normalization of the molecular pair distribution functions is perhaps worth while. In defining the potential of mean force, $W_i^k(\lambda_i)$, an arbitrary constant is at our disposal. This constant has been so chosen that

$$(1/v\sigma_k) \int e^{-\beta W_i^k(\lambda_i)} d\omega_k = 1$$

a relation which may be verified by reference to Eq. (20b). The approximate forms for $W_i^k(\lambda_i)$ of course do not exactly satisfy this condition.

(b) At sufficiently high temperatures, the exponentials

of Eq. (41) may be expanded and the following approximate linear integral equation is obtained

$$W_i^k(\lambda_i) = \lambda_i V_{ik} - \frac{\lambda_i}{kT} \sum_s \frac{N_s}{v} \frac{1}{\sigma_s} \int V_{is} W_k^s(1) d\omega_s$$

where regions in which W_i^s and W_k^s become infinite due to repulsive forces, are excluded from the integration. If we apply the equation to the ions of an electrolyte solution, the solvent being treated as a continuous medium of dielectric constant D , we know that V_{ik} is equal $e_i e_k / Dr_{ik}$ where e_i and e_k are the ionic charges. For this potential, it may be verified without difficulty that the above set of linear integral equations has the following solutions

$$W_i^k(\lambda_i) = \lambda_i \frac{e_i e_k}{Dr_{ik}} e^{-\kappa r_{ik}}; \quad \kappa^2 = \frac{4\pi}{DkT} \sum_s \frac{N_s}{v} e_s^2$$

if molecular size is neglected. These solutions, together with Eq. (22) lead to the Debye-Hückel limiting law for the chemical potentials of the ions.

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Some Critical Remarks Concerning Bailli Nilsen's Paper: "On the Theory of Free Radicals and Organo-Alkali Compounds"¹ *

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LATELY, a paper by Bailli Nilsen on the above title appeared in this journal, the main subject of the article being a computation of the electron affinities of free aromatic radicals.

The author first mentions two possible ways of a quantum-mechanical calculation of the electron affinities of such free radicals,—the "first method" certainly alluding to some ordinary first order perturbation method for an atom, or, a molecule when adding an extra electron on an unoccupied orbit—whereas the "second method," as he says, is closely connected with Pauling and Wheland's theory for free radicals.

If now, for instance, we apply such an ordinary perturbation method to the simplest of all atoms, the hydrogen atom, we will find a very poor approximate value of the electron affinity—even the sign being wrong—viz., the negative value -0.25 Rh or -3.385 electron volts—whereas an exact calculation provides a positive value 0.0506 Rh or 0.685 electron volt.

It is true, therefore, that there are many difficulties in determining the energy difference caused by putting an extra electron into an atom or a molecule. We also know that these difficulties are closely connected with considerable changes of the electronic configuration of the atom, because the electron orbits are deformed by the mutual interaction of the electrons. These changes can only be accounted for by the aid of complicated variational methods.

The author of the above paper now seems to be of the opinion that such difficulties may be conquered simply by dropping them out of sight and by making use of the essentially different "second method" of Pauling and Wheland, which is especially suited for quite other purposes, viz., the computation of binding forces between atoms of **given electronic configurations**.

We will, however, quite overlook the considerable errors introduced in this way by neglecting energy changes in the individual atoms themselves, and only analyze the author's application of the "second method."

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