

## The Statistical Thermodynamics of Multicomponent Systems

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though not quantitative, change in the chromatographic behavior of the activity. In all probability it is a reducing agent for 43, as it is for rhenium and manganese.

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### CONCLUSIONS

From the foregoing experiments, the following conclusions regarding the electrochemistry of Element 43 may be drawn:

(1) The element may be obtained in an oxidized, anionic form by treatment with nitric and sulfuric acids.

(2) The element may be deposited electrolytically on a platinum cathode, with reduction to the metal very probably the principal process. No anodic deposition is observed.

(3) The deposition potential for the metal from its anionic form is  $-0.146$  volt *vs.* the normal hydrogen electrode in a solution of  $pH$  2.36. This corresponds to a standard electrode potential of  $-0.41$  volt for the process:



(4) The anionic form of the element is reduced and removed from solution by the metals: zinc, iron, nickel, tin, lead, copper, and mercury.

(5) Hydrochloric acid and stannous chloride reduce the anion to a cation.

## The Statistical Thermodynamics of Multicomponent Systems\*

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(Received September 4, 1944)

Distribution functions,  $F_n(\mathbf{z}, \{\mathbf{n}\})$ , for multicomponent systems are defined proportional to the probability density that  $\mathbf{n}$  molecules in an infinite isothermal system of fugacity set  $\mathbf{z}$  will occupy the configurational coordinates symbolized by  $\{\mathbf{n}\}$ . All thermodynamic functions may be obtained as certain sums of integrals of these distribution functions. These sums are always convergent, but impractically slow in convergence for numerical use without further transformation. In particular, the grand-partition function,  $\exp [VP(\mathbf{z})/kT]$ , may be expanded in a power series in the fugacities  $\mathbf{z}$  with coefficients given by integrals of the distribution functions  $F_n(0, \{\mathbf{n}\})$  at the fugacity set  $0$ . As has been previously demonstrated for one component systems, this is shown to be a special case of a more general relation permitting the calculation of the distribution functions (and therefore the thermodynamic functions) for one fugacity set from those at another set. The function  $-kT \ln F_n(\mathbf{z}, \{\mathbf{n}\})$  is the *potential of average force*,  $W_n(\mathbf{z}, \{\mathbf{n}\})$ , of  $\mathbf{n}$  molecules at the fugacity set  $\mathbf{z}$ ; at zero fugacities, the potential of average force is simply the potential energy. When only short range forces are present, by employing the procedure previously used for the im-

perfect gas, the integrals of the distribution functions may be simplified to integrals of lower order which become the coefficients in such expressions as the power-series expansion of the pressure increment in terms of the fugacity increments. These series have the advantage of a much higher rate of convergence than those involving integrals of the distribution functions, themselves; however, they do not converge when the initial and final fugacity sets bridge a phase transition. The general equations are applied to the imperfect multicomponent gas, to isotopic gas mixtures, and to condensed systems with the variables converted to the usual activities and activity coefficients. A change of independent variable with a corresponding change in coefficients then permits the evaluation of the pressure increment in terms of the solute concentrations. The equations for osmotic pressure are developed and found to be entirely analogous to those for the pressure of an imperfect gas. Finally, the osmotic pressure in a binary system and its behavior near phase transitions are discussed with emphasis on the critical mixing phenomenon, for which the existence of a region of anomalous first-order transition is shown to be probable.

### 1. INTRODUCTION

THE statistical derivation of the thermodynamic functions of a perfect gas\* from

a knowledge of the mechanical properties of the molecules has long been known. A simple state-

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\* Here by "perfect gas" we mean one which is non-degenerate as well as having negligible intermolecular forces.

ment of the solution is as follows: Consider a single molecule of species  $s$  in a volume  $V$  and let  $\epsilon_{ls}$  be its energy when in a particular quantum state  $ls$ . The partition function,  $Q_s$ , for such a system is a function of  $T$  and  $V$ , and is defined as

$$Q_s(V, T) = \sum_{ls} \exp(-\epsilon_{ls}/kT). \quad (1)$$

Since the Hamiltonian is separable in the coordinates and momenta of the center of mass, the partition function (1) becomes a product of two factors. One factor, due to the motion of the center of mass, is, for macroscopic volumes,  $(2\pi m_s kT/h^2)^{3/2} V$ ; the other,  $Q_{is}$ , is due only to the internal quantum states:

$$Q_s(V, T) = V(2\pi m_s kT/h^2)^{3/2} Q_{is}, \quad (1')$$

where  $m_s$  is the mass of the molecule of species  $s$ , and  $Q_{is}$  is the internal partition function,

$$Q_{is} = \sum_{js} \exp(-\epsilon_{js}/kT), \quad (1'')$$

in which the summation runs over all internal quantum states  $j_s$  of energy  $\epsilon_{js}$ .

The chemical potential per molecule,  $\mu_s$ , of a perfect gas composed of  $N_s$  molecules of species  $s$  in volume  $V$  at temperature  $T$  is given by

$$\mu_s = kT(\ln N_s - \ln Q_s). \quad (2)$$

If the particle density,  $\rho_s = N_s/V$ , is large, a system composed of real molecules is no longer a perfect gas, and (2) ceases to apply. Nevertheless, the formal method for obtaining the thermodynamic functions is still known: We now consider a system composed of the set  $\mathbf{N} = N_1, N_2, \dots, N_s, \dots, N_\sigma$  of molecules of species 1, 2,  $\dots$ ,  $s$ ,  $\dots$ ,  $\sigma$  in a volume  $V$ . Let  $l$  be a running index representing single quantum states of this system, and  $E_l$ , the energy of the  $l$ th state. The partition function  $\mathbf{Q}(\mathbf{N}, V, T)$  of such a system (which is calculated for the so-called *canonical* ensemble) is defined as<sup>1</sup>

$$\mathbf{Q}(\mathbf{N}, V, T) = \sum_l \exp(-E_l/kT). \quad (3)$$

The work function, or Helmholtz free energy  $A$ , of the system is then given by

$$A(\mathbf{N}, V, T) = -kT \ln \mathbf{Q}(\mathbf{N}, V, T). \quad (4)$$

<sup>1</sup> Cf. J. E. Mayer and M. Goeppert-Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940).

Two cases which have been successfully treated numerically by the use of this partition function (3) are those of a regular crystal (the Debye treatment which, however, is only approximate) and the perfect gas, which breaks down to Eqs. (1) and (2) since then,

$$\mathbf{Q}(\mathbf{N}, V, T) = \prod_s (Q_s^{N_s}/N_s!). \quad (5)$$

One may alternately employ the method of the *grand-canonical ensemble*, which will be elaborated upon in Section 4, since it forms the basis of the methods amplified here. This results in an expression for the pressure  $P$  in terms of the canonical partition function  $\mathbf{Q}$  as defined above and the chemical potentials  $\mu_s$  of the various molecular species  $s$ :

$$\exp(PV/kT) = \sum_{\mathbf{N}} [\exp(\sum_s N_s \mu_s/kT)] \mathbf{Q}(\mathbf{N}, V, T), \quad (6)$$

where the summation runs over all sets of numbers  $\mathbf{N} = N_1, N_2, \dots, N_s, \dots, N_\sigma$  of molecular species 1, 2,  $\dots$ ,  $s$ ,  $\dots$ ,  $\sigma$  ( $0 \leq N_s \leq \infty$ ), including  $\mathbf{N} = \mathbf{0}$ , for which we arbitrarily take

$$\mathbf{Q}(\mathbf{0}, V, T) = 1.$$

Although Eqs. (3) and (4) do not appear to be fundamentally more complicated than (1) and (2), there is a quantitative difference which is so great as to become qualitative in character. It is usually possible to determine the internal quantum states and the corresponding energies,  $\epsilon_{js}$ , of the *single*-molecule system by a combination of pure theory and spectrographic investigation, even for a relatively complicated molecule. The summation involved in (1'') may always be performed by a combination of analytical methods and straightforward, though frequently tedious, numerical evaluations. On the other hand, the quantum states and the corresponding energies,  $E_l$ , of a system composed of many *dependent* molecules can only be evaluated in a few extremely simple cases; for (3), involves summation over some  $\exp(10^{23})$  terms instead of the hundreds or possibly even only tens of terms entering in (1''). Unless analytical simplifications are available, Eq. (3) is therefore purely formal and of no use as far as numerical approximation is concerned.

Such analytical simplifications, based upon a

method first proposed by Ursell,<sup>2</sup> have been the subject of several recent papers.<sup>3-10</sup> The discussion of this article involves an attempt to present the mathematical procedures and arguments, particularly in connection with the method of the grand-partition function,<sup>10</sup> in detailed form, and to generalize this method for multicomponent systems. Although naturally it is not to be expected that rigorous equations will ever be obtained which lead to ready numerical evaluation for the more complicated systems, it appears that certain relationships can be derived which have the rigorous generality of the Gibbs statistics.

## 2a. SYMBOLISM

In treating a problem involving the coordinates of an extremely large number of molecules it will be necessary to adopt a system of symbols which are sufficiently complex in nature to make the resulting equations appear relatively simple. Thus, while the meaning of a symbol may be at first difficult to bear in mind, the compactness of the final expressions more than compensates for this initial inconvenience. Accordingly, we make the following definitions: The symbol

$$(i_s) = x_{is}, y_{is}, z_{is}, q_{1is}, q_{2is}, \dots \quad (7)$$

indicates the configurational coordinates of the  $i$ th molecule of species  $s$ , and in general will include internal coordinates,  $q_{1is}, q_{2is}, \dots$ , as well as the Cartesian coordinates,  $x_{is}, y_{is}, z_{is}$ , of the center of mass.

The coordinates of  $n_s$  molecules of a particular species  $s$  will be represented by

$$\{n_s\} = (1_s), (2_s), \dots, (i_s), \dots, (n_s). \quad (8)$$

In general, any **boldface** symbol will indicate a *set* of numbers or variables, *one for each species*.

<sup>2</sup> H. D. Ursell, Proc. Camb. Phil. Soc. **23**, 685 (1927).

<sup>3</sup> J. E. Mayer, J. Chem. Phys. **5**, 67 (1937).

<sup>4</sup> J. E. Mayer and P. G. Ackermann, J. Chem. Phys. **5**, 74 (1937).

<sup>5</sup> J. E. Mayer and S. F. Harrison, J. Chem. Phys. **6**, 87 (1938).

<sup>6</sup> M. Born and K. Fuchs, Proc. Roy. Soc. **A166**, 391 (1938).

<sup>7</sup> B. Kahn and G. E. Uhlenbeck, Physica **5**, 399 (1938).

<sup>8</sup> S. F. Streeter and J. E. Mayer, J. Chem. Phys. **7**, 1025 (1939).

<sup>9</sup> J. E. Mayer and Elliott Montroll, J. Chem. Phys. **9**, 2 (1941).

<sup>10</sup> J. E. Mayer, J. Chem. Phys. **10**, 629 (1942).

Thus, as in Section 1, the bold-face  $\mathbf{n}$  will be used to indicate a *set* of numbers of molecules of (a finite number,  $\sigma$ , of) different species,  $n_s$  of species  $s$ :

$$\mathbf{n} = n_1, n_2, n_3, \dots, n_s, \dots, n_\sigma, \quad (9)$$

the number of molecules under consideration being\*

$$n = \sum_{s=1}^{\sigma} n_s. \quad (9')$$

The coordinates of all the molecules of such a set  $\mathbf{n}$  will be represented by

$$\{\mathbf{n}\} = \{n_1\}, \{n_2\}, \dots, \{n_s\}, \dots, \{n_\sigma\}. \quad (10)$$

The differential volume elements are similarly defined by

$$d(i_s) = dx_{is} dy_{is} dz_{is} J[x/q] dq_{1is} dq_{2is} \dots, \quad (11)$$

$$d\{n_s\} = d(1_s) d(2_s) \dots d(i_s) \dots d(n_s), \quad (12)$$

and

$$d\{\mathbf{n}\} = d\{n_1\} d\{n_2\} \dots d\{n_s\} \dots d\{n_\sigma\}, \quad (13)$$

and are understood to be calculated in the Cartesian space of the atoms composing the molecules, i.e.,  $J[x/q]$  is the Jacobian of the transformation from the generalized internal coordinates,  $q_{1is}, q_{2is}, \dots$ .

The ensemble or system treated will always be understood to have a fixed temperature  $T$ . Its thermodynamic state might be fully determined by giving  $T$  and the density set

$$\rho = \rho_1, \rho_2, \dots, \rho_s, \dots, \rho_\sigma, \quad (14)$$

where  $\rho_s$  is the number of molecules of species  $s$  per unit volume,

$$\rho_s = N_s/V, \quad (15)$$

or by specifying  $T$  and the chemical potential set

$$\mathbf{\mu} = \mu_1, \mu_2, \dots, \mu_s, \dots, \mu_\sigma, \quad (16)$$

with  $\mu_s$  the chemical potential of molecules of species  $s$ . Instead we shall find it more convenient to use  $T$  and the fugacity set

$$\mathbf{z} = z_1, z_2, \dots, z_s, \dots, z_\sigma, \quad (17)$$

in which  $z_s$ , the fugacity of molecules of type  $s$ ,

\* Unless otherwise stated, sums and products over the species  $s$  will be assumed to have the limits  $1 \leq s \leq \sigma$ .

is defined as proportional to  $\exp(\mu_s/kT)$  with the proportionality constant so chosen that at infinite dilution  $z_s = \rho_s$ . This definition may be written

$$z_s = [\exp(\mu_s/kT)] \lim_{\varrho_o \rightarrow 0} [\rho_{os} \exp(-\mu_{os}/kT)], \quad (18)^*$$

where  $\rho_{os}$  is the density in molecules of species  $s$  per unit volume at the chemical potential set  $\mu_o$ . The proportionality constant in (18) may be evaluated directly by considering a system of fixed volume  $V$  but containing a variable number,  $N_o$ , of molecules, i.e., having a variable density set  $\varrho_o$ . By Eq. (2) and (15), we have

$$\lim_{\varrho_o \rightarrow 0} [(N_{os}/Q_s) \exp(-\mu_{os}/kT)] = 1 \\ = (V/Q_s) \lim_{\varrho_o \rightarrow 0} [\rho_{os} \exp(-\mu_{os}/kT)],$$

since  $V$  and  $Q_s$  are independent of  $\varrho_o$ . (18) then becomes

$$z_s = (Q_s/V) \exp(\mu_s/kT). \quad (18')$$

The concentration activity coefficient  $\gamma_s(\mathbf{z})$  of species  $s$  may be defined by the equation

$$\gamma_s(\mathbf{z}) = z_s/\rho_s(\mathbf{z}). \quad (19)$$

The product of this dimensionless quantity with the concentration (density) of that species gives the concentration of an ideal substance having the same free energy.

Since the sum

$$\sum_s n_s \mu_s = n_1 \mu_1 + n_2 \mu_2 + \cdots + n_s \mu_s + \cdots + n_\sigma \mu_\sigma$$

occurs frequently it is convenient to introduce the notation

$$\mathbf{n} \cdot \boldsymbol{\mu} = n_1 \mu_1 + n_2 \mu_2 + \cdots + n_s \mu_s + \cdots + n_\sigma \mu_\sigma. \quad (20)$$

## 2b. THE DISTRIBUTION FUNCTIONS

The discussion of this article concerns itself primarily with certain distribution functions,  $F_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\})$ , of the coordinates of a set  $\mathbf{n}$  of molecules. These functions are defined by the statement that in an infinite system of fugacity set  $\mathbf{z}$ ,

$$[\prod_s \rho_s^{n_s}] F_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\}) d\{\mathbf{n}\}$$

is the probability that a set  $\mathbf{n}$  of molecules will be found at the coordinates  $\{\mathbf{n}\}$  in the con-

\* The fugacity  $z_s$  and its thermodynamic relationships are more fully discussed in Appendix A.

figuration element  $d\{\mathbf{n}\}$ . For such values of the coordinates  $\{\mathbf{n}\}$  that all intermolecular distances are large, this probability, integrated over the internal coordinates of each molecule, must have the average value  $\prod_s \rho_s^{n_s}$  per unit volume in the  $3n$ -dimensional Cartesian space of the centers of mass of the molecules. The definition of the functions  $F_{\mathbf{n}}$  is therefore such that their average value, under these conditions, is unity; i.e.,

$$\left. \begin{aligned} & \left\{ \prod_s [\rho_s(\mathbf{z})]^{n_s} F_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\}) \right\} \text{ is the probability} \\ & \text{density of the configuration } \{\mathbf{n}\} \text{ in an} \\ & \text{infinite system of fugacity set } \mathbf{z}, \end{aligned} \right\} \quad (21)$$

and

$$\lim_{V \rightarrow \infty} \left[ \frac{1}{V^n} \int \cdots \int_V F_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\}) d\{\mathbf{n}\} \right] = 1.$$

The definition includes the case  $\mathbf{z} = \mathbf{0}$  (that is  $z_s = 0$  for all  $s$ ) in which case, for a classical system,  $F_{\mathbf{n}}(\mathbf{0}, \{\mathbf{n}\})$  is proportional to  $\exp[-U_{\mathbf{n}}(\{\mathbf{n}\})/kT]$ , with  $U_{\mathbf{n}}(\{\mathbf{n}\})$  the potential energy of the molecules as a function of their coordinates  $\{\mathbf{n}\}$ . The general significance of  $-kT \ln F_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\})$  as a potential of average force is discussed in Section 6.

It will be shown that a detailed knowledge of these distribution functions would make possible the calculation of all the thermodynamic properties of the system.

As we proceed it will be evidently expedient to introduce new variables and functions, but to preserve the continuity of the development we postpone these definitions until they become necessary. For reference a summary of symbols is appended.

## 3. SUMMARY OF THE METHOD

Having defined the principal functions and quantities employed, the method and results can be summarized briefly before delving into the detailed derivations.

It is a simple consequence of the equations of the grand-partition function (Section 5) that  $\exp V P(\mathbf{z})/kT$  may be written as a sum over all sets  $\mathbf{n}$  of terms of the form

$$[\prod_s (z_s^{n_s}/n_s!)] \int \cdots \int_V F_{\mathbf{n}}(\mathbf{0}, \{\mathbf{n}\}) d\{\mathbf{n}\}.$$

Similarly it will be shown that one can write

$$(\prod_s [\rho_s(\mathbf{z})/z_s]^{N_s}) F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) \exp VP(\mathbf{z})/kT$$

as a sum of terms over all values of  $\mathbf{n}$ , the term for  $\mathbf{n}$  being

$$[\prod_s (z_s^{n_s}/n_s!)] \int \int \cdots \int_V F_{\mathbf{n}+\mathbf{N}}(\mathbf{0}, \{\mathbf{n}+\mathbf{N}\}) d\{\mathbf{n}\}$$

(Eq. (33)). We thus have an infinite set of equations, one for each  $\mathbf{N}$ , for the unknown functions  $F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})$ , each equation involving on the right-hand side an infinite series. There is no reason to expect that from such a set one can obtain explicit solutions for the *integrands* in these coefficients in terms of integrals of the functions  $F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})$ , but just that is the case! By an algebraic substitution, it is then possible to write for any fugacity set  $\mathbf{z}+\mathbf{y}$  a series for each function  $F_{\mathbf{N}}(\mathbf{z}+\mathbf{y}, \{\mathbf{N}\})$  permitting the calculation of these functions from the  $F_{\mathbf{N}+\mathbf{M}}(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\})$ ; i.e., one may calculate the distribution functions at  $\mathbf{z}+\mathbf{y}$  from a knowledge of those at any other fugacity set  $\mathbf{z}$ .

Now the particular feature of these equations which is of interest is the following: In going from any fugacity set  $\mathbf{z}$  to another,  $\mathbf{z}+\mathbf{y}$ , the series involve only the difference in fugacities,  $y_1, y_2, \dots, y_s, \dots, y_\sigma$ , raised to appropriate powers, the coefficients being functions of the original fugacities. The particular case for which  $z_1 = z_2 = \dots = z_s = \dots = z_\sigma = 0$  is not unique; in this case the difference-fugacity  $y_s$  is the complete fugacity.

Thus the whole method of the grand-partition function is generalized. The thermodynamic properties and the distribution functions at any fugacity are, in principle, calculable from those of any other fugacity, the case: density, pressure, and fugacity, equal zero being only one special case for which, incidentally, the logarithms of the distribution functions are (in a classical system) proportional to the true potential energies. The equations for calculating the properties from another set of fugacities are essentially the same as for the special case usually treated, the difference of the fugacities alone entering.

Although these series converge in the mathematical sense for all values of  $y_s$ , they are not suitable for numerical evaluations, for the convergence is far too slow. However, it is possible

to transform them into other series which, under certain conditions, lend themselves more readily to numerical approximation. One makes use of the fact that the functions  $F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})$ , according to (21), are unity (in the Cartesian space of the centers of mass after integration over the internal coordinates) for finite  $\mathbf{N}$  and large  $V$  over the considerable portion of space where all the molecules are distant from each other. We write the functions  $F_{\mathbf{N}}$  as unity plus a series of correction terms which differ from zero only where pairs, triples, or in general certain sets of molecules are close together. By appropriate definitions of the correction terms the equations still involve no approximations. By this means the integral over  $\{\mathbf{M}\}$  of each  $F_{\mathbf{N}+\mathbf{M}}$  may be written as a sum of products of integrals over these correction terms involving fewer molecules than  $\mathbf{M}$ . The coefficients occurring are such that the complete summation over  $\mathbf{M}$  may be written as an exponential of a power series in the fugacity differences  $\mathbf{y}$  and the activity coefficients  $\gamma(\mathbf{z})$ .

From the first equation so obtained,

$$[P(\mathbf{z}+\mathbf{y}) - P(\mathbf{z})]/kT$$

is expressed as a power series in  $y_s/\gamma_s(\mathbf{z})$  while the higher equations yield similar series (in the same variables) for the quantities

$$\ln F_{\mathbf{N}}(\mathbf{z}+\mathbf{y}, \{\mathbf{N}\}) - \ln F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}),$$

the coefficients in the latter case being, of course, functions of the coordinates  $\{\mathbf{N}\}$ . These power series have the property that for small values of the arguments they converge *numerically*, in the sense that the terms decrease rapidly in magnitude, and may therefore be used for numerical evaluation. They are not, however, convergent for all values of  $\mathbf{y}$ , and indeed diverge for such values of the temperature and fugacities that any phase transition occurs in the system between the fugacity  $\mathbf{z}$  and  $\mathbf{z}+\mathbf{y}$ . They thus lead to equations which are valid for the calculation of the properties at the fugacity set  $\mathbf{z}+\mathbf{y}$  from those at  $\mathbf{z}$  even if the phase present at  $\mathbf{z}$  is condensed, provided only that there is no phase change *between* the two fugacities  $\mathbf{z}$  and  $\mathbf{z}+\mathbf{y}$ .

The application of the general equations to binary liquid mixtures leads to the laws of ideal solutions and the specifications which must be met in order that the ideality be preserved throughout the whole concentration range.

## 4. THE GRAND-PARTITION FUNCTION FOR MULTICOMPONENT SYSTEMS

For the sake of completeness and consistency of notation we devote this section to a short derivation of the equations for the grand-partition function<sup>11, 12</sup> for an ensemble of constant energy having maximum entropy.

We consider a grand canonical ensemble consisting of a total volume  $MV$  divided into  $M$  similar regions each of volume  $V$ , the total energy and the total number of molecules of each species of the ensemble being fixed. The regions are separated, in thought, by semi-permeable membranes through which molecules and energy may flow, the separation being such that the total-phase space is the product of the independent phase spaces of the regions, i.e., the molecules in different regions interact with each other only negligibly.

Consider a number,  $\omega$ , of quantum states having energy between  $E$  and  $E+\Delta E$ , available to a system composed of the set  $\mathbf{N}$  of molecules in one such region.\* Further, let  $m$  be the number of such systems in these  $\omega$  states and let  $\Omega(m)$  be the total number of quantum states available to the ensemble of systems with the inhibition that exactly  $m$  are contained in the  $\omega$  states. Since the total number of particles in the ensemble is constant, as is the total energy, the criterion of equilibrium is that the entropy,  $S$ , of the ensemble be a maximum. Now the number of distinct ways in which we can select  $m$  systems is  $M!/m!(M-m)!$ , and one thus obtains for  $\Omega(m)$  the expression:

$$\Omega(m) = (M!/m!(M-m)!) \omega^m \Omega_r(M-m), \quad (22)$$

where  $\Omega_r(M-m)$  is the total number of quantum states available to the remaining  $M-m$  systems.

Employing a familiar definition of the entropy,

$$S(m) = k \ln \Omega(m) = k \ln M! - k \ln m! - k \ln (M-m)! + km \ln \omega + S_r(M-m)$$

and

$$S(m-1) = k \ln M! - k \ln (m-1)! - k \ln (M-m+1)! + k(m-1) \ln \omega + S_r(M-m+1).$$

At maximum,

$$\begin{aligned} \Delta S(m) &= S(m) - S(m-1) = 0 \\ &= k \ln \frac{(M-m+1)\omega}{m} + \Delta S_r(M-m) = 0, \end{aligned} \quad (23)$$

where  $\Delta S_r(M-m) = S_r(M-m) - S_r(M-m+1)$ .

Since the change from  $m-1$  to  $m$  of the number of regions in the  $\omega$  quantum states involves in the rest of the ensemble a decrease of  $V$  in the volume, a decrease of  $N_s$  in the number of molecules of type  $s$ , and a decrease of  $E$  in the energy,

$$\begin{aligned} \Delta S_r(M-m) &= -V \left( \frac{\partial S_r}{\partial V} \right)_{\mathbf{N}, E} - \sum_s N_s \left( \frac{\partial S_r}{\partial N_s} \right)_{N_t, V, E} - E \left( \frac{\partial S_r}{\partial E} \right)_{V, \mathbf{N}} \\ &= -\frac{PV}{T} + \frac{\mathbf{N} \cdot \mathbf{u}}{T} - \frac{E}{T}, \end{aligned} \quad (24)$$

<sup>11</sup> R. C. Tolman, Phys. Rev. **57**, 1160 (1940).

<sup>12</sup> E. A. Guggenheim, J. Chem. Phys. **7**, 103 (1939).

\* In the total-phase space the component parts belonging to the different regions are numbered due to the fact that these regions occupy different parts of the physical three-dimensional space, so that although for every quantum state of one region corresponding to a fixed number of molecules in that region in a definite state, there corresponds a similar quantum state of every other region differing only in a spatial translation, the corresponding quantum states of different regions are not identical.

in which it is understood that  $M$  approaches infinity. Thus, as  $M \gg m \gg 1$ , (23) and (24) give

$$\begin{aligned} \frac{m}{M\omega} &= \exp(-PV + \mathbf{N} \cdot \mathbf{u} - E_l)/kT \\ &= \phi_{l\mathbf{N}V}, \end{aligned} \quad (25)$$

the probability that a randomly selected region of volume  $V$  contain exactly the set  $\mathbf{N}$  of molecules and occupy a particular one of the  $\omega$  quantum states of energy  $E_l$ . The sum of  $\phi_{l\mathbf{N}V}$  over all possible quantum states  $l$  of each  $\mathbf{N}$ , and over all numbers of molecules  $\mathbf{N}$ , is unity:

$$\sum_{\mathbf{N}} \sum_l \phi_{l\mathbf{N}V} = 1 = \exp(-PV/kT) \sum_{\mathbf{N} \geq 0} \exp(\mathbf{N} \cdot \mathbf{u}/kT) \sum_l \exp(-E_l/kT), \quad (26)$$

where  $E_l$  is the energy of the  $l$ th quantum state. We thus obtain for the grand partition function of a multicomponent system:

$$\begin{aligned} \exp(PV/kT) &= \sum_{\mathbf{N} \geq 0} \exp(\mathbf{N} \cdot \mathbf{u}/kT) \sum \exp(-E_l/kT) \\ &= \sum_{\mathbf{N} \geq 0} [\exp(\mathbf{N} \cdot \mathbf{u}/kT)] Q(\mathbf{N}, V, T), \end{aligned} \quad (27)$$

in which  $Q(\mathbf{N}, V, T)$ , Eq. (3), is the partition function for the canonical ensemble containing the set  $\mathbf{N}$  of molecules in the volume  $V$  at temperature  $T$ , and has the value unity for  $\mathbf{N} = 0$ .

## 5. GENERALIZATION OF THE GRAND-PARTITION FUNCTION

In the last section it was shown that the probability that there be exactly the set  $\mathbf{N}$  of molecules in the volume  $V$  and that this system be in the quantum state  $l$  is:

$$\phi_{l\mathbf{N}V} = \exp(-PV + \mathbf{N} \cdot \mathbf{u} - E_l)/kT, \quad (25)$$

where  $E_l$  is the energy corresponding to the quantum state  $l$ . The probability that these molecules, being now for the moment numbered and collectively in the quantum state  $l$ , will occupy (respectively) the coordinates of configuration  $\{\mathbf{N}\}$  within the volume element  $d\{\mathbf{N}\}$  is  $|\psi_l\{\mathbf{N}\}|^2 d\{\mathbf{N}\}$ , where  $\psi_l$  is the normalized wave function of the system.

Let  $\phi_{\mathbf{N}V}\{\mathbf{N}\}$  be defined by the statement that  $\phi_{\mathbf{N}V}\{\mathbf{N}\} d\{\mathbf{N}\}$  is the probability that there is exactly the set  $\mathbf{N}$  of molecules in  $V$  and that these are located at the coordinates of configuration  $\{\mathbf{N}\}$  within  $d\{\mathbf{N}\}$  irrespective of the quantum state of the system. From (25) one sees that

$$\phi_{\mathbf{N}V}\{\mathbf{N}\} = \{\exp(1/kT)[-PV + \mathbf{N} \cdot \mathbf{u}]\} \sum_l \exp(-E_l/kT) |\psi_l\{\mathbf{N}\}|^2. \quad (28)^*$$

If the volume  $V$  is known to contain the set  $\mathbf{N} + \mathbf{n}$  of molecules then the probability density that there be  $\mathbf{N}$  molecules at the positions  $\{\mathbf{N}\}$  irrespective of the positions of the other  $\mathbf{n}$  molecules in the volume  $V$  is

$$\int \int \cdots \int_V \left[ \prod_s \frac{(N_s + n_s)!}{n_s!} \right] \phi_{\mathbf{N} + \mathbf{n}, V}\{\mathbf{N} + \mathbf{n}\} d\{\mathbf{n}\}, \quad (29)$$

since any  $N_s$  of the  $N_s + n_s$  molecules of species  $s$  may fill the  $\{N_s\}$  positions, and having chosen a particular set  $N_s$  of molecules of each type  $s$ , all permutations of the molecules among the positions

\* This is the probability that, having numbered the molecules, the  $i$ th molecule will be at the  $i$ th position, etc., and thus if integrated over all values of the coordinates within  $V$ , gives the probability that exactly this number of molecules are in  $V$  regardless of position. The probability that the positions  $\{\mathbf{N}\}$  be occupied by molecules of the appropriate species, irrespective of which molecule occupies which coordinate set, is  $(\prod_s N_s!)$  times (28); this latter quantity was used in reference 10.



are allowable. If we now sum (29) over all values of  $\mathbf{n}$ , we get the probability density that the configuration  $\{\mathbf{N}\}$  is occupied by the appropriate species of molecules at this temperature  $T$  and fugacity set  $\mathbf{z}$ , namely

$$\left( \prod_s [\rho_s(\mathbf{z})]^{N_s} \right) F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) = \exp(-PV/kT) \sum_{\mathbf{n} \geq 0} \exp((\mathbf{N} + \mathbf{n}) \cdot \mathbf{u}/kT) \prod_s \frac{(N_s + n_s)!}{n_s!} \\ \times \sum_l \exp(-E_l/kT) \int \int \cdots \int_V |\psi_l\{\mathbf{N} + \mathbf{n}\}|^2 d\{\mathbf{n}\}, \quad (30)^*$$

in which (28) has been substituted for  $\mathcal{P}_{\mathbf{N}+\mathbf{n},v}$ , and the expression defined in (21) has been used.

Employing our previous definition of the fugacity (18') in (30) we obtain

$$\left[ \prod_s \left( \frac{\rho_s(\mathbf{z})}{z_s} \right)^{N_s} \right] F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) = \exp(-PV/kT) \sum_{\mathbf{n} \geq 0} \left( \prod_s \frac{z_s^{n_s}}{n_s!} \right) \int \int \cdots \\ \cdots \int_V \left\{ \left[ \prod_s (N_s + n_s)! \left( \frac{V}{Q_s} \right)^{N_s + n_s} \right] \sum_l |\psi_l\{\mathbf{N} + \mathbf{n}\}|^2 \exp(-E_l/kT) \right\} d\{\mathbf{n}\}. \quad (31)$$

Taking the limit of this equation as all  $z_s$  approach zero, the only finite term remaining in the sum on the right is that for which  $\mathbf{n} = \mathbf{0}$ ; therefore,

$$F_{\mathbf{N}}(\mathbf{0}, \{\mathbf{N}\}) = \left[ \prod_s N_s! \left( \frac{V}{Q_s} \right)^{N_s} \right] \sum_l |\psi_l\{\mathbf{N}\}|^2 \exp(-E_l/kT), \quad (32)^{13}$$

and (31) may be written:

$$\left[ \prod_s \left( \frac{\rho_s(\mathbf{z})}{z_s} \right)^{N_s} \right] F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) = \exp(-PV/kT) \sum_{\mathbf{n}} \left( \prod_s \frac{z_s^{n_s}}{n_s!} \right) \int \int \cdots \int_V F_{\mathbf{N}+\mathbf{n}}(\mathbf{0}, \{\mathbf{N} + \mathbf{n}\}) d\{\mathbf{n}\}, \quad (33)$$

or, in more symmetrical form, introducing  $P(\mathbf{0}) = 0$ ,  $\gamma_s(\mathbf{0}) = 1$ ,

$$\exp(VP(\mathbf{z})/kT) \left\{ \prod_s [\gamma_s(\mathbf{z})]^{-N_s} \right\} F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) = \sum_{\mathbf{n} \geq 0} \left[ \prod_s \frac{z_s^{n_s}}{n_s!} \right] \int \int \cdots \int_V \exp(VP(\mathbf{0})/kT) \\ \times \left\{ \prod_s [\gamma_s(\mathbf{0})]^{-(N_s + n_s)} \right\} F_{\mathbf{N}+\mathbf{n}}(\mathbf{0}, \{\mathbf{n} + \mathbf{N}\}) d\{\mathbf{n}\}. \quad (34)^\dagger$$

Employing (21) for  $\mathbf{N} = \mathbf{0}$ ,  $F_{\mathbf{0}}(\mathbf{z}, \{\mathbf{0}\}) = 1$ , and we have, as a special case of (34),

$$\exp(VP(\mathbf{z})/kT) = \sum_{\mathbf{n} \geq 0} \left[ \prod_s \frac{z_s^{n_s}}{n_s!} \right] \int \int \cdots \int_V F_{\mathbf{n}}(\mathbf{0}, \{\mathbf{n}\}) d\{\mathbf{n}\}. \quad (35)$$

Now form the sum

$$I_{\mathbf{N}}\{\mathbf{N}\} = \sum_{\mathbf{m} \geq 0} \left( \prod_s \frac{(-z_s)^{m_s}}{m_s!} \right) \exp(VP(\mathbf{z})/kT) \int \int \cdots \int_V \left\{ \prod_s [\gamma_s(\mathbf{z})]^{-(N_s + m_s)} \right\} F_{\mathbf{N}+\mathbf{m}}(\mathbf{z}, \{\mathbf{N} + \mathbf{m}\}) d\{\mathbf{m}\}. \quad (36)$$

\* Actually, an equation of this type defines  $F_{\mathbf{N}}(\mathbf{0}, \{\mathbf{N}\})$  only for such values of the coordinates  $\{\mathbf{N}\}$  of the molecules as lie within the volume  $V$  for which the quantization of the right-hand side is performed. However, such a function defined within  $V$  is asymptotically equal, at all values of the coordinates  $\{\mathbf{N}\}$  for which it is defined, to the function defined by (30) for any volume greater than  $V$  which includes  $V$  provided only that  $V$  is large enough and of such a shape that surface effects may be neglected. We may consequently regard the distribution functions as defined over infinite space.

<sup>13</sup> J. C. Slater, Phys. Rev. **38**, 237 (1931).

† In reference 10 the quantities  $\{\gamma_s(\mathbf{z})\}^{-n} F_n(\mathbf{z}, \{\mathbf{n}\})$  were abbreviated as  $Q_n(\mathbf{z}, \{\mathbf{n}\})$ .

Substituting (34) for the integrand, (36) becomes

$$I_{\mathbf{N}}\{\mathbf{N}\} = \sum_{\mathbf{m} \geq 0} \sum_{\mathbf{n} \geq 0} \left( \prod_s \frac{(-)^{m_s} z_s^{m_s + n_s}}{m_s! n_s!} \right) \int \int \cdots \int_V F_{\mathbf{N}+\mathbf{m}+\mathbf{n}}(\mathbf{0}, \{\mathbf{N}+\mathbf{m}+\mathbf{n}\}) d\{\mathbf{m}+\mathbf{n}\}.$$

Regrouping the terms according to the value of  $\mathbf{m}+\mathbf{n}=\mathbf{j}$ , we have

$$\begin{aligned} I_{\mathbf{N}}\{\mathbf{N}\} &= \sum_{\mathbf{j} \geq 0} \left[ \sum_{\mathbf{i} \geq 0} \prod_s (-)^{i_s} j_s! / i_s! (j_s - i_s)! \right] \left( \prod_s \frac{z_s^{j_s}}{j_s!} \right) \int \int \cdots \int_V F_{\mathbf{N}+\mathbf{j}}(\mathbf{0}, \{\mathbf{N}+\mathbf{j}\}) d\{\mathbf{j}\} \\ &= \sum_{\mathbf{j} \geq 0} \left[ \prod_s (1-1)^{j_s} \right] \left( \prod_s \frac{z_s^{j_s}}{j_s!} \right) \int \int \cdots \int_V F_{\mathbf{N}+\mathbf{j}}(\mathbf{0}, \{\mathbf{N}+\mathbf{j}\}) d\{\mathbf{j}\} \\ &= F_{\mathbf{N}}(\mathbf{0}, \{\mathbf{N}\}). \end{aligned}$$

Therefore, (36) may be written

$$F_{\mathbf{N}}(\mathbf{0}, \{\mathbf{N}\}) = \sum_{\mathbf{m} \geq 0} \left( \prod_s \frac{(-z_s)^{m_s}}{m_s!} \right) \exp(VP(\mathbf{z})/kT) \int \int \cdots \int_V \left\{ \prod_s [\gamma_s(\mathbf{z})]^{-(N_s+m_s)} \right\} \times F_{\mathbf{N}+\mathbf{m}}(\mathbf{z}, \{\mathbf{N}+\mathbf{m}\}) d\{\mathbf{m}\}. \quad (37)$$

By rewriting (34) for the fugacity set  $\mathbf{z}+\mathbf{y}$ , and employing (37) in the integrand we obtain

$$\begin{aligned} \exp(VP(\mathbf{z}+\mathbf{y})/kT) \left\{ \prod_s [\gamma_s(\mathbf{z}+\mathbf{y})]^{-N_s} \right\} F_{\mathbf{N}}(\mathbf{z}+\mathbf{y}, \{\mathbf{N}\}) &= \sum_{\mathbf{n} \geq 0} \sum_{\mathbf{m} \geq 0} \left( \prod_s \frac{(-)^{m_s} (z_s + y_s)^{n_s} z_s^{m_s}}{m_s! n_s!} \right) \\ &\times \exp(VP(\mathbf{z})/kT) \int \int \cdots \int_V \left\{ \prod_s [\gamma_s(\mathbf{z})]^{-(N_s+m_s+n_s)} \right\} F_{\mathbf{N}+\mathbf{m}+\mathbf{n}}(\mathbf{z}, \{\mathbf{N}+\mathbf{m}+\mathbf{n}\}) d\{\mathbf{m}+\mathbf{n}\}. \end{aligned}$$

Regrouping terms according to the sum  $\mathbf{n}+\mathbf{m}=\mathbf{M}$ , and again using the multinomial expansion theorem, we find

$$\begin{aligned} \exp(VP(\mathbf{z}+\mathbf{y})/kT) \left\{ \prod_s [\gamma_s(\mathbf{z}+\mathbf{y})]^{-N_s} \right\} F_{\mathbf{N}}(\mathbf{z}+\mathbf{y}, \{\mathbf{N}\}) &= \sum_{\mathbf{M} \geq 0} \left( \prod_s \frac{y_s^{M_s}}{M_s!} \right) \\ &\times \exp(VP(\mathbf{z})/kT) \int \int \cdots \int_V \left\{ \prod_s [\gamma_s(\mathbf{z})]^{-(N_s+M_s)} \right\} F_{\mathbf{N}+\mathbf{M}}(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\}) d\{\mathbf{M}\}. \quad (38) \end{aligned}$$

This is a generalized form of the grand-partition function for a multicomponent system, enabling the calculation of the pressure,  $P(\mathbf{z}+\mathbf{y})$ , the activity coefficients  $\gamma_s(\mathbf{z}+\mathbf{y})$ , and the distribution functions,  $F_{\mathbf{N}}(\mathbf{z}+\mathbf{y}, \{\mathbf{N}\})$ , at any fugacity set  $\mathbf{z}+\mathbf{y}$ , in terms of the pressure,  $P(\mathbf{z})$ , the activity coefficients,  $\gamma_s(\mathbf{z})$ , and the distribution functions,  $F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})$ , at any other value  $\mathbf{z}$  of the fugacity set. Thus Eqs. (34) and (35) are special cases of (38) with  $\mathbf{z}=\mathbf{0}$ , while (37) is the special case  $y_s = -z_s$ ,  $\mathbf{y}+\mathbf{z}=\mathbf{0}$ .

So far the equations derived have not been restricted to any particular kind of system. As will be shown immediately, all of the series converge because of the finite size and low compressibility of real molecules, this being equally true even if, for instance, the fugacity sets  $\mathbf{z}$  and  $\mathbf{z}+\mathbf{y}$  in Eq. (38) correspond to two different phases.\* However, as has been previously pointed out (cf. Section 3), the convergence of these series is too slow to permit, even in principle, numerical evaluation. The demonstration that the series are absolutely convergent is simple: the functions  $F_{\mathbf{N}+\mathbf{M}}(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\})$

\* Note that, owing to the omission of gravitational forces, a condensed phase will not necessarily be found in any particular region of the containing vessel.

are all positive, and for exceedingly large values of  $\mathbf{M}$  approach zero in value for all values of the coordinates  $\{\mathbf{N}+\mathbf{M}\}$  within a finite volume  $V$ , for all real systems for which the molecules repel each other at small distances. Since, then, the integrals approach zero in value for infinite  $M$  values, the convergence is assured. However, the term which gives the largest contribution to the sum is that for which  $N+M$  represents the average molecular population of the volume  $V$ , and for ordinary macroscopic volumes is therefore of the order of magnitude of  $10^{20}$ .

An enormous improvement in the rate of convergence for systems satisfying certain requirements may be obtained by employing a method first suggested by Ursell,<sup>2</sup> and extended by Kahn and Uhlenbeck<sup>7</sup> to quantum mechanical systems. This procedure will be discussed in Section 7, but in order that the development there can proceed uninterruptedly, we pause to introduce the concept of the *potential of average force* which will be needed in simplifying later equations.

## 6. THE POTENTIALS OF AVERAGE FORCE

If we may treat the system consisting of  $\mathbf{N}$  molecules in volume  $V$  semi-classically, i.e., if the spacing of the quantum mechanical energy levels is small in comparison with  $kT$ , the probability density of finding the system in the configuration  $\{\mathbf{N}\}$  is given by the expression

$$\begin{aligned} \text{Semi classical} \\ \text{Limit} \quad & \left[ \frac{1}{Q} \sum_l |\psi_l\{\mathbf{N}\}|^2 \exp(-E_l/kT) \right] \\ &= \frac{1}{h^f Q \prod_s N_s!} \int \int \cdots \int \exp[-H(\{\mathbf{N}\}, \{\mathbf{P}_\mathbf{N}\})/kT] d\{\mathbf{P}_\mathbf{N}\} \quad (39)^* \end{aligned}$$

where  $f$  is the total number of degrees of freedom of the system, and the classical Hamiltonian,  $H(\{\mathbf{N}\}, \{\mathbf{P}_\mathbf{N}\})$ , is the sum of the kinetic and potential energies which in turn are functions of only the momenta and coordinates, respectively:

$$H(\{\mathbf{N}\}, \{\mathbf{P}_\mathbf{N}\}) = T\{\mathbf{P}_\mathbf{N}\} + U_\mathbf{N}\{\mathbf{N}\}. \quad (40)$$

By performing the integration indicated in (39) and recalling the equation obtained in the previous section for the distribution functions at zero fugacity,

$$F_\mathbf{N}(\mathbf{0}, \{\mathbf{N}\}) = \left[ \prod_s \left( \frac{V}{Q_s} \right)^{N_s} \frac{1}{N_s!} \right] \sum_l |\psi_l\{\mathbf{N}\}|^2 \exp(-E_l/kT), \quad (32)$$

it is evident that there is a direct proportionality between  $F_\mathbf{N}(\mathbf{0}, \{\mathbf{N}\})$  and  $\exp[-U_\mathbf{N}\{\mathbf{N}\}/kT]$  for any given  $\mathbf{N}$ . Indeed, by choosing the zero of potential energy correctly one may write:

$$F_\mathbf{N}(\mathbf{0}, \{\mathbf{N}\}) = \exp[-U_\mathbf{N}\{\mathbf{N}\}/kT]. \quad (41)$$

The correct zero of the potential energy may be easily obtained, but it is unessential in the argument which follows. (41) must, of course, satisfy the normalization condition (21).

If, for convenience of notation, we now consider a system of  $\mathbf{n}+\mathbf{N}$  molecules in volume  $V$ , the force acting along the coordinate  $q$  of the molecule  $i_s$  occupying one of the  $\{\mathbf{N}_s\}$  positions is given by

$$f_{qis}\{\mathbf{n}+\mathbf{N}\} = - \left( \frac{\partial U_{\mathbf{n}+\mathbf{N}}\{\mathbf{n}+\mathbf{N}\}}{\partial q_{is}} \right)_{q_{jt}}. \quad (42)$$

A comparison of Eqs. (28) and (32) shows that the probability density that there be exactly the set  $\mathbf{n}+\mathbf{N}$  of molecules in  $V$  and that of these,  $\mathbf{n}$  be located at the coordinates of configuration  $\{\mathbf{n}\}$ ,

\* See, for example, reference 1, p. 231.

and the other  $\mathbf{N}$  be distributed in any way among the  $\{\mathbf{N}\}$  remaining coordinates is (see Eq. (29))

$$\left[ \prod_s \frac{(n_s + N_s)!}{n_s!} \right] \phi_{\mathbf{n}+\mathbf{N}, v} \{\mathbf{n}+\mathbf{N}\} = \exp(-VP(\mathbf{z})/kT) \left[ \prod_s \frac{z_s^{n_s+N_s}}{n_s!} \right] F_{\mathbf{n}+\mathbf{N}}(0, \{\mathbf{n}+\mathbf{N}\}). \quad (43)$$

The *average force*,  $\langle f_{qis} \{\mathbf{N}\} \rangle$ , averaged over all positions of the coordinates  $\{\mathbf{n}\}$ , may now be found by multiplying (43) by (42), integrating over the coordinates  $\{\mathbf{n}\}$ , summing over all values of  $\mathbf{n}$ , and dividing this result by the sum and integrals of (43); that is

$$\langle f_{qis} \{\mathbf{N}\} \rangle = \frac{\exp(-VP(\mathbf{z})/kT) \sum \left( \prod_s \frac{z_s^{n_s}}{n_s!} \right) \int \int \cdots \int \left( -\frac{\partial U_{\mathbf{n}+\mathbf{N}}}{\partial q_{is}} \right) \exp(-U_{\mathbf{n}+\mathbf{N}} \{\mathbf{n}+\mathbf{N}\}/kT) d\{\mathbf{n}\}}{\exp(-VP(\mathbf{z})/kT) \sum \left( \prod_s \frac{z_s^{n_s}}{n_s!} \right) \int \int \cdots \int \exp(-U_{\mathbf{n}+\mathbf{N}} \{\mathbf{n}+\mathbf{N}\}/kT) d\{\mathbf{n}\}},$$

or,

$$\langle f_{qis} \{\mathbf{N}\} \rangle = \left( -\frac{\partial}{\partial q_{is}} [kT \ln F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})] \right)_{q_{jt}}, \quad (44)$$

in which (33) has been used. The quantity  $-kT \ln F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})$  is therefore such that its derivative with respect to one of the coordinates  $\{\mathbf{N}\}$  gives the statistical average force, as a function of  $\{\mathbf{N}\}$ , along that coordinate on the molecule occupying that position, the weighted average being taken over all positions  $\{\mathbf{n}\}$  of the other molecules in the system; or what is equivalent, the average is made over a long period of time during which the  $\{\mathbf{N}\}$ -coordinates are fixed and occupied by an appropriate set of molecules, and the remaining  $\mathbf{n}$ -molecules in the system are allowed to move freely. It thus is the *potential of average force*, denoted by  $W_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})$ , and we write

$$W_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) = -kT \ln F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}). \quad (45)$$

In the limit of zero fugacity, it is evident from Eq. (41) that

$$W_{\mathbf{N}}(0, \{\mathbf{N}\}) = U_{\mathbf{N}} \{\mathbf{N}\}. \quad (46)$$

In previous treatments it has been convenient to consider the potential energy  $U_{\mathbf{N}} \{\mathbf{N}\}$  as a sum of component potential energies,  $u_{ij}(r_{ij})$ , due to the interaction between pairs of molecules only. An extension of this method to the potentials of average force leads to some simplification of the equations of Section 7. If we denote a subset (consisting of the coordinates of  $\mathbf{n}$  molecules) of the set of coordinates  $\{\mathbf{N}\}$  of  $\mathbf{N}$ -molecules by the symbol  $\{\mathbf{n}\}_{\mathbf{N}}$ , we may express the function  $W_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\})$  in terms of the component potentials of average force by the equation

$$W_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) = \sum \{\mathbf{n}\}_{\mathbf{N}} w_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}}), \quad (47)$$

in which the sum is taken over all possible subsets, and the terms  $w_{\mathbf{n}}$  for  $n > 2$  may be thought of as corrections for the deviation of  $W_{\mathbf{N}}$  from a sum of pair terms only. The inverse of (47) is given by

$$w_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\}) = \sum \{\mathbf{N}\}_{\mathbf{n}} (-)^{n-N} W_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}_{\mathbf{n}}) \quad (48)$$

which is proved in the Appendix. It has been general practice to neglect terms  $w_{\mathbf{n}}$  for  $n > 2$ .

An interesting and important observation regarding the general Eq. (33) for the distribution functions is that the integration over the internal coordinates of the  $N$  molecules may be performed *before* integration over the center of mass coordinates,  $\{\mathbf{N}_x\}$ , giving a distribution function dependent upon positions but independent of the internal coordinates of the molecules. This new distribution function, which will be referred to hereafter as the "spatial distribution function," may then be treated just as though it were for a system of monatomic molecules, except that the quantities corresponding to the potentials of average force are no longer even approximately equal to the sums of pair terms.

## 7. EXPANSION AND INTEGRATION OF THE DISTRIBUTION FUNCTIONS

According to (21), the spatial-distribution functions,  $F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}_x\})$ , are unity for finite  $\mathbf{M}$  and large  $V$  in the considerable portion of configuration space where *all* intermolecular distances between the  $\mathbf{M}$  molecules, are large. If it happens that the force between groups of molecules drops rapidly to zero at separation distances comparable to the molecular size, we may write a given spatial-distribution function as unity plus a series of correction terms which differ from zero only where pairs, triples, or in general certain sets of molecules are near each other. It will be shown convenient to choose the form of these correction terms so that  $F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}_x\})$  may be written as a sum of products of functions each of a smaller number of coordinates (Eq. (49)). The procedure is formal and generally rigorous, but to facilitate visualizing the method we apply it here to the spatial-distribution function only, and at such a fugacity set  $\mathbf{z}$  that the system is gaseous or liquid; actually we later deal (Eqs. (49) and (50)) with the complete distribution function (i.e., including internal coordinates) for whose expansion an analogous explanation may be given.

Before proceeding to an explicit definition of the correction terms it may be well to stress this feature of the distribution functions: When the center of mass coordinates,  $\{\mathbf{M}_x\}$  admit of a natural spatial separation into several mutually exclusive subsets of neighboring molecules—that is, when the  $\mathbf{M}$  molecules may be segregated according to position into several groups such that all the molecules of each group are at large distances (compared with the molecular diameter) from all the molecules of every other group, yet are “close” to each other—the spatial-distribution function  $F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}_x\})$ , being a probability, must be expressible as a product of probabilities, (i.e., distribution functions), one for each of the simultaneous independent events of having a particular subset of molecules close together. Thus, when one pair is in conjunction, with all other molecules mutually distant, we correct the value unity by adding a term for this pair. However, in order that the above requirement be fulfilled when a second pair of molecules are near each other we must add, in addition to the correction term for the second pair, another term which accounts for there being simultaneously two pairs present. This additional term is readily seen to be the product of the two different pair-correction terms.

If a triple were present we would have, in addition to the term corresponding to the triple, terms corresponding to all possible pairs which may be formed from the triple. In other words, if the coordinates  $\{\mathbf{M}_x\}$  are such that a particular aggregation exists, the expansion of the distribution function involves not only the term corresponding to this particular aggregation but in addition, correction terms for all *lower* aggregations which can be obtained from this aggregation by a process of dissociation. We begin with all molecules far apart, and correct first for pairs, then for triples, etc., until the desired state of aggregation is attained.

The correction term for having simultaneously pairs, triples, etc., must vanish if any one of the groups for which it corrects is dissociated. A simple form for the correction term, and one which satisfies the multiplicative property of the distribution functions discussed above, is thus a product of factors, each factor corresponding to a particular group and having the property of vanishing when that group dissociates in any way.

We denote as before (the coordinates of) a subset of  $\mathbf{m}$  particular molecules of the set  $\mathbf{M}$  by the symbol  $\{\mathbf{m}\}_{\mathbf{M}}$ , and a complete set of  $k$  unconnected (i.e., mutually exclusive) subsets  $\{\mathbf{m}_i\}_{\mathbf{M}} (1 \leq i \leq k)$  of the set  $\mathbf{M}$  by the symbol  $\{k\{\mathbf{m}_i\}_{\mathbf{M}}\}_u$ , with

$$\sum_{i=1}^k \mathbf{m}_i = \mathbf{M}.$$

We note that two subsets of identical size are different if they do not contain the same particular molecules. Let the correction term at fugacity  $\mathbf{z}$  for  $\{\mathbf{m}_i\}_{\mathbf{M}}$  proximate molecules be  $g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}_{\mathbf{M}})$ ; then the correction term for having the set of subsets  $\{k\{\mathbf{m}_i\}_{\mathbf{M}}\}_u$  will be

$$\prod_{i=1}^k g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}_{\mathbf{M}}),$$

and we may write the expansion of  $F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}\})$ , defining the  $g$ -functions implicitly, as

$$F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}\}) = \sum \{k \{\mathbf{m}_i\}_{\mathbf{M}}\}_u \prod_{i=1}^k g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}_{\mathbf{M}}), \quad (49)$$

where the sum is taken over all possible sets of unconnected subsets. An explicit definition of the  $g$ -functions is given by the inverse of (49):

$$g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}\}) = \sum \{l \{\mathbf{M}_j\}_{\mathbf{m}}\}_u (-1)^{l-1} (l-1)! \prod_{j=1}^l F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}_j\}_{\mathbf{m}}), \quad (50)$$

which is proved in the Appendix. Note that, according to (49), if all the positions  $\{\mathbf{M}\}$  are widely separated the integral of  $F_{\mathbf{M}}$  over the internal coordinates has the average value unity, so that the average value of  $g_1(\mathbf{z}, (i))$  is unity when integrated over the internal coordinates of the  $i$ th molecule. If the fugacity set  $\mathbf{z}$  has such a value that the system is liquid or gaseous then the integral of  $g_1(\mathbf{z}, (i))$  over the internal coordinates is unity. If the system is crystalline the integral over the internal coordinates may lead to a triply periodic function of the coordinates of the center of mass,<sup>10</sup> but the average value over an appreciable range of these coordinates is still unity.

The functions  $g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}\})$  are so defined that they approach zero if the values of the coordinates  $\{\mathbf{m}\}$  are such that there exist two subsets  $\{\mathbf{m}'\}_{\mathbf{m}}$  and  $\{\mathbf{m}\} - \{\mathbf{m}'\}_{\mathbf{m}}$  with all distances large between any molecule of  $\{\mathbf{m}'\}_{\mathbf{m}}$  and any molecule of  $\{\mathbf{m}\} - \{\mathbf{m}'\}_{\mathbf{m}}$ . The proof that this is the case is now given. By the multiplicative property of the distribution functions the following statement holds for  $F_{\mathbf{M}}$ : if the coordinates  $\{\mathbf{M}\}$  are such that there are two mutually exclusive subsets  $\{\mathbf{m}'\}_{\mathbf{M}}$  and  $\{\mathbf{M}\} - \{\mathbf{m}'\}_{\mathbf{M}}$  with all distances between the two subsets large, then

$$F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}\}) = F_{\mathbf{M}-\mathbf{m}'}(\mathbf{z}, \{\mathbf{M}-\mathbf{m}'\}_{\mathbf{M}}) F_{\mathbf{m}'}(\mathbf{z}, \{\mathbf{m}'\}_{\mathbf{M}}).$$

This relation is evidently consistent with (49) for  $F_{\mathbf{M}}$ ,  $F_{\mathbf{M}-\mathbf{m}'}$  and  $F_{\mathbf{m}'}$  only if all functions  $g_{\mathbf{m}}$  of the coordinates of sets  $\{\mathbf{m}\}_{\mathbf{M}}$  containing members from both  $\{\mathbf{m}'\}_{\mathbf{M}}$  and  $\{\mathbf{M}-\mathbf{m}'\}_{\mathbf{M}}$  are zero.

Since (38) necessitates the integration of the function  $F_{\mathbf{N}+\mathbf{M}}(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\})$  over the coordinates  $\{\mathbf{M}\}$  we require an expansion of this function similar to (49). If the coordinates  $\{\mathbf{N}+\mathbf{M}\}$  are such that they fall naturally into two isolated groups of  $\mathbf{N}$  and  $\mathbf{M}$  molecules respectively at the coordinate sets  $\{\mathbf{N}\}$  and  $\{\mathbf{M}\}$ , we may write

$$\begin{aligned} F_{\mathbf{N}+\mathbf{M}}(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\}) &= F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}\}) \\ &= F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) \sum \{k \{\mathbf{m}_i\}_{\mathbf{M}}\}_u \prod_{i=1}^k g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}_{\mathbf{M}}). \end{aligned}$$

However, if it happens that some of the  $\mathbf{N}$  molecules are close to some of the  $\mathbf{m}$  we need an additional correction. Denoting a subset of (the coordinates of)  $\mathbf{n}$  particular molecules of the set  $\mathbf{N}$  by the symbol  $\{\mathbf{n}\}_{\mathbf{N}}$ , the necessary corrections,  $g_{\mathbf{nm}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}}, \{\mathbf{m}\}_{\mathbf{M}})$ , may be applied to the functions  $g_{\mathbf{m}}$  in the form

$$g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}) + \sum \{\mathbf{n}\}_{\mathbf{N}} g_{\mathbf{nm}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}}, \{\mathbf{m}_i\}_{\mathbf{M}}),$$

and our complete expansion for  $F_{\mathbf{N}+\mathbf{M}}$  becomes\*

$$F_{\mathbf{N}+\mathbf{M}}(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\}) = F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) \sum \{k \{\mathbf{m}_i\}_{\mathbf{M}}\}_u \prod_{i=1}^k [g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}_{\mathbf{M}}) + \sum \{\mathbf{n}\}_{\mathbf{N}} g_{\mathbf{nm}}(\mathbf{z}, \{\mathbf{n}\}_{\mathbf{N}}, \{\mathbf{m}_i\}_{\mathbf{M}})]. \quad (51)$$

If we now integrate this expression over all values of the coordinates  $\{\mathbf{M}\}$ , the integrals

$$V(\prod_s m_s!) b_{\mathbf{m}}(\mathbf{z}) = \int \int \cdots \int_V g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}\}_{\mathbf{M}}) d\{\mathbf{m}\}_{\mathbf{M}}, \quad (52)$$

\* It should be noted that, though we wish to neglect higher terms in the numerical evaluation of some of our later expressions, these complete expansions involve no approximations whatever.

and

$$(\prod_s m_s!) b_{nm}(\mathbf{z}, \{\mathbf{n}\} \mathbf{N}) = \int \int \cdots \int_V g_{nm}(\mathbf{z}, \{\mathbf{n}\} \mathbf{N}, \{\mathbf{m}\} \mathbf{M}) d\{\mathbf{m}\} \mathbf{M} \quad (53)$$

depend only upon the numerical value of  $\mathbf{m} = m_1, m_2, \dots, m_s, \dots, m_\sigma$ , and not upon *which* of the  $M_s$  molecules constitute the  $m_s$ . (Note that if the interaction forces, i.e., the correction terms, drop sufficiently rapidly to zero with increasing separation distance of one molecule from all the other molecules of a group, the cluster integrals,  $b_{\mathbf{m}}(\mathbf{z})$  and  $b_{nm}(\mathbf{z})$ , of the first and second kinds defined by (52) and (53) are independent of the volume of the system.) A subdivision of the  $\{\mathbf{M}\}$  coordinates into  $\mu_{\mathbf{m}}$  subsets of size  $\mathbf{m}$  may be obtained in  $\prod_s M_s! / \prod_{\mathbf{m}} (\prod_s m_s!)^{\mu_{\mathbf{m}}} \mu_{\mathbf{m}}!$  different ways, all of which appear in the sum (41). Integration over  $\{\mathbf{M}\}$  thus leads to the equations

$$\begin{aligned} & \int \int \cdots \int_V F_{\mathbf{N}+\mathbf{M}}(\mathbf{z}, \{\mathbf{N}+\mathbf{M}\}) d\{\mathbf{M}\} \\ &= F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) \sum \{k\{\mathbf{m}_i\} \mathbf{M}\}_u \prod_{i=1}^k \int \int \cdots \int_V [g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\} \mathbf{M}) + \sum \{\mathbf{n}\} \mathbf{N} g_{nm}(\mathbf{z}, \{\mathbf{n}\} \mathbf{N}, \{\mathbf{m}_i\} \mathbf{M})] d\{\mathbf{m}_i\} \mathbf{M} \\ &= F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) (\prod_s M_s!) \sum_{\mu_{\mathbf{m}}} \prod_{\mathbf{m}} \frac{[V b_{\mathbf{m}}(\mathbf{z}) + \sum \{\mathbf{n}\} \mathbf{N} b_{nm}(\mathbf{z}, \{\mathbf{n}\} \mathbf{N})]^{\mu_{\mathbf{m}}}}{\mu_{\mathbf{m}}!} \end{aligned} \quad (54)$$

in which the sum over  $\mu_{\mathbf{m}}$  is subject to the restriction  $\sum_{\mathbf{m}} \mathbf{m} \mu_{\mathbf{m}} = \mathbf{M}$ , i.e.,  $\sum_{\mathbf{m}} m_s \mu_{\mathbf{m}} = M_s$  for all  $s$ .

Now employing (54) in (38) we obtain

$$\begin{aligned} \exp (VP(\mathbf{z}+\mathbf{y})/kT) F_{\mathbf{N}}(\mathbf{z}+\mathbf{y}, \{\mathbf{N}\}) / \prod_s [\gamma_s(\mathbf{z}+\mathbf{y})]^{N_s} &= \exp (VP(\mathbf{z})/kT) F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) / \prod_s [\gamma_s(\mathbf{z})]^{N_s} \\ &\times \sum_{\mathbf{M} \geq 0} \sum_{\mu_{\mathbf{m}}} \prod_{\mathbf{m}} \frac{1}{\mu_{\mathbf{m}}!} \left\{ V b_{\mathbf{m}}(\mathbf{z}) \prod_s \left[ \frac{y_s}{\gamma_s(\mathbf{z})} \right]^{m_s} + \sum \{\mathbf{n}\} \mathbf{N} b_{nm}(\mathbf{z}, \{\mathbf{n}\} \mathbf{N}) \prod_s \left[ \frac{y_s}{\gamma_s(\mathbf{z})} \right]^{m_s} \right\}^{\mu_{\mathbf{m}}}. \end{aligned} \quad (55)$$

The summation over  $\mathbf{M}$  removes the restriction on the  $\mu_{\mathbf{m}}$ , and it is seen that the sum in the right of (55) is the expansion of an exponential, so that

$$\begin{aligned} \exp (VP(\mathbf{z}+\mathbf{y})/kT) F_{\mathbf{N}}(\mathbf{z}+\mathbf{y}, \{\mathbf{N}\}) / \prod_s [\gamma_s(\mathbf{z}+\mathbf{y})]^{N_s} &= \exp (VP(\mathbf{z})/kT) F_{\mathbf{N}}(\mathbf{z}, \{\mathbf{N}\}) / \prod_s [\gamma_s(\mathbf{z})]^{N_s} \\ &\times \exp \sum_{\mathbf{m} \geq 0} \left\{ V b_{\mathbf{m}}(\mathbf{z}) \prod_s \left[ \frac{y_s}{\gamma_s(\mathbf{z})} \right]^{m_s} + \sum \{\mathbf{n}\} \mathbf{N} b_{nm}(\mathbf{z}, \{\mathbf{n}\} \mathbf{N}) \prod_s \left[ \frac{y_s}{\gamma_s(\mathbf{z})} \right]^{m_s} \right\}, \end{aligned} \quad (56)$$

for all values of the fugacity set  $\mathbf{y}$  which are smaller than the corresponding set of associated convergence radii of the series in the last expression. If we now employ (45) with the expansion (47) for the potentials of average force, and collect terms in (56) according to their dependence on  $V$  and the coordinate sets  $\{\mathbf{n}\} \mathbf{N}$ , we find\*

$$P(\mathbf{z}+\mathbf{y}) - P(\mathbf{z}) = kT \sum_{\mathbf{m} \geq 0} b_{\mathbf{m}}(\mathbf{z}) \prod_s [y_s/\gamma_s(\mathbf{z})]^{m_s} \quad (57)$$

$$w_{1s}(\mathbf{z}+\mathbf{y}, (i_s)) + kT \ln \gamma_s(\mathbf{z}+\mathbf{y}) = w_{1s}(\mathbf{z}, (i_s)) + kT \ln \gamma_s(\mathbf{z}) - kT \sum_{\mathbf{m} \geq 0} b_{1s, \mathbf{m}}(\mathbf{z}, (i_s)) \prod_s [y_s/\gamma_s(\mathbf{z})]^{m_s} \quad (58)$$

and

$$w_{\mathbf{n}}(\mathbf{z}+\mathbf{y}, \{\mathbf{n}\} \mathbf{N}) = w_{\mathbf{n}}(\mathbf{z}, \{\mathbf{n}\} \mathbf{N}) - kT \sum_{\mathbf{m} \geq 0} b_{nm}(\mathbf{z}, \{\mathbf{n}\} \mathbf{N}) \prod_s [y_s/\gamma_s(\mathbf{z})]^{m_s}, \quad (59)$$

where the subscript  $1_{s, \mathbf{m}}$  of  $b$  in the sum of (58) means that all  $n_r$  are zero except  $n_s = 1$ .

These equations are analogous to those obtained by Mayer,<sup>10,†</sup> and reduce to those for a one component system. Particularly, equation (57) permits the calculation of the pressure at the fugacity

\* For convenience in writing summation limits,  $b_0$  is taken equal to zero.

† Incidentally, Eqs. (43) and (44) of this reference contain several incorrect signs.

set  $\mathbf{z}+\mathbf{y}$  from the cluster integrals and the activity coefficients evaluated at the fugacity set  $\mathbf{z}$ , whenever the sum converges. This remark will be elaborated upon in Sections 8 and 9.

### 8. THE CHANGE OF INDEPENDENT VARIABLE

In the integration of the  $g$ -functions (Eq. (52)) for simplified systems in which  $w_n=0$  for  $n>2$ , it has been found convenient to use *irreducible integrals*,  $B_n$ , which may be physically defined for such systems as the integral of a certain function of the potential energies between pairs of molecules in a group which is more than singly connected, i.e., one in which it is possible to pass from any molecule to any other molecule of the group by at least two alternate paths having only the initial and final molecules in common. The cluster integrals,  $b_m(\mathbf{z})$ , have been found to be sums of products of these irreducible integrals.<sup>1</sup>

The physical meaning of the irreducible integrals is somewhat obscured if the molecules are not perfectly symmetrical or if, in general, there are internal coordinates. However, as was previously pointed out in Section 6, an examination of Eq. (33) shows that we might have integrated  $F_N(\mathbf{z}, \{\mathbf{N}\})$  immediately over the internal coordinates and applied the discussion of Section 7 entirely to the spatial distribution functions so obtained. Under these conditions the irreducible integrals have a perfectly definite physical meaning as solutions, in terms of the  $b_m(\mathbf{z})$ , of the implicit equation which defines them (see Eq. (60) below). In the actual calculation of the cluster integrals one would normally perform the integrations leading to the irreducible integrals first; add to this the simplification of having the readily measurable density rather than the fugacity as independent variable in our equations when the irreducible integrals are employed and there results sufficient reason for their use.

The expression of the cluster integrals in terms of the irreducible integrals has been solved for one and two component systems by Mayer,<sup>5,14</sup> and for any number of components by Fuchs.<sup>15</sup> A brief outline of the general mathematical theorems proved by Fuchs will be given, and these will then be used to convert our series for the pressure (57) into one having irreducible integrals as coefficients.

The solution to the combinatorial problem of expressing the cluster integrals,  $b_m$ , in terms of the irreducible integrals,  $B_n$ , for a system of  $\sigma$  components may be written

$$m_r b_m = \sum \mathbf{v}_n \left| \delta_{st} - \frac{1}{n_t} \sum_n (n_s - \delta_{st}) \nu_{tn} \right| \prod_{s=1}^{\sigma} \prod_n \frac{\{m_s n_s B_n\}^{\nu_{sn}}}{\nu_{sn}!}, \quad (60)$$

in which the summation extends over all integers  $\mathbf{v}_n \geq 0$  subject to the condition that

$$\sum_{t=1}^{\sigma} \sum_n (n_s - \delta_{st}) \nu_{tn} = m_s - \delta_{sr},$$

and  $|\cdot|_{\sigma}$  symbolizes a determinant of  $\sigma$ th order. Fuchs further shows that (60) may be written as a Cauchy integral:

$$m_r b_m = \left( \frac{1}{2\pi i} \right)^{\sigma} \oint \oint \cdots \oint \xi_r | \delta_{st} - \xi_s G_{st} |_{\sigma} \prod_{s=1}^{\sigma} \frac{\exp(m_s G_s(\xi, B_n))}{\xi_s^{\mu_s+1}} d\xi_s, \quad (61)$$

where  $G(\xi, B_n)$  and its derivatives are defined by the equations

$$G(\xi, B_n) = \sum_{n \geq 0} B_n \prod_s \xi_s^{n_s}, \quad (62)^*$$

and

$$G_s(\xi, B_n) = \left( \frac{\partial G}{\partial \xi_s} \right)_{\xi_t}$$

<sup>14</sup> J. E. Mayer, J. Phys. Chem. **43**, 71 (1939).

<sup>15</sup> K. Fuchs, Proc. Roy. Soc. **A179**, 408 (1942).

\* For convenience  $B_0$  is taken equal to zero.



Multiplying (61) by  $\prod_s Z_s^{m_s}$  and summing over  $\mathbf{m} \geq 0$ , one obtains, on integration, the equations

$$Z_r G_r(\mathbf{Z}, b_{\mathbf{m}}) = Y_r, \quad r = 1, 2, \dots, \sigma, \quad (63)$$

where the  $Y_r$  are solutions of the equations

$$Z_r = Y_r \exp [-G_r(\mathbf{Y}, B_{\mathbf{n}})], \quad r = 1, 2, \dots, \sigma. \quad (64)$$

Employing (63) and (64) it is then easy to show that

$$G(\mathbf{Z}, b_{\mathbf{m}}) = G(\mathbf{Y}, B_{\mathbf{n}}) + \sum_{s=1}^{\sigma} Y_s [1 - G_s(\mathbf{Y}, B_{\mathbf{n}})]. \quad (65)$$

This last result (65) is precisely what is needed to enable us to express the pressure difference between the fugacities  $\mathbf{z} + \mathbf{y}$  and  $\mathbf{z}$  in terms of the irreducible integrals, for (57) may be written in the form

$$P(\mathbf{z} + \mathbf{y}) - P(\mathbf{z}) = kT \sum_{\mathbf{m} \geq 0} b_{\mathbf{m}}(\mathbf{z}) \prod_s \left[ \frac{\rho_s(\mathbf{z})}{z_s} \right]^{m_s} = kT G(\mathbf{Z}, b_{\mathbf{m}}) \quad (66)$$

with  $Z_s = y_s \rho_s(\mathbf{z}) / z_s$ . It is evident that when  $z_r$  is held fixed,

$$Y_r = \frac{Z_r}{kT} \left( \frac{\partial [P(\mathbf{z} + \mathbf{y}) - P(\mathbf{z})]}{\partial Z_r} \right)_{T, z_s} = \frac{y_r}{kT} \left( \frac{\partial P(\mathbf{z} + \mathbf{y})}{\partial (z_r + y_r)} \right)_{T, z, y_s}$$

or

$$Y_r = y_r \frac{\rho_r(\mathbf{z} + \mathbf{y})}{(z_r + y_r)}; \quad (67)$$

(66) with (67) in (65) then gives

$$P(\mathbf{z} + \mathbf{y}) - P(\mathbf{z}) = kT \left\{ \sum_{s=1}^{\sigma} y_s \frac{\rho_s(\mathbf{z} + \mathbf{y})}{z_r + y_r} - \sum_{\mathbf{n} \geq 0} \left( \sum_{s=1}^{\sigma} n_s - 1 \right) B_{\mathbf{n}}(\mathbf{z}) \prod_{s=1}^{\sigma} \left[ \frac{\rho_s(\mathbf{z} + \mathbf{y})}{z_s + y_s} \right]^{n_s} \right\}. \quad (68)$$

Since the appearance of a new phase in general causes singularities in the thermodynamic functions such as that given by (66), we conversely associate singularities in the fugacity function,  $G(\mathbf{Z}, b_{\mathbf{m}})$ , with phase transitions. By the general theorem for implicit functions,<sup>16</sup> the  $\sigma$ -Eqs. (64) inversely define the variables  $\mathbf{Y}$  in terms of the variables  $\mathbf{Z}$  whenever the Jacobian of the transformation,  $J[\mathbf{Z}/\mathbf{Y}]$ , does not vanish or become singular anywhere in the accessible domains of the variables. This Jacobian, by (64) has the value

$$J \left[ \frac{\mathbf{Z}}{\mathbf{Y}} \right] = |\delta_{sr} - Y_s G_{sr}(\mathbf{Y}, B_{\mathbf{n}})|_{\sigma} \exp \left[ \sum_{s=1}^{\sigma} G_s(\mathbf{Y}, B_{\mathbf{n}}) \right], \quad (69)$$

from which it is evident that a singularity in the function  $G(\mathbf{Z}, b_{\mathbf{m}})$  may arise either from singularities in the functions  $G(\mathbf{Y}, B_{\mathbf{n}})$  or from the vanishing of the determinant in (69). This remark will be employed in some of the arguments of Section 10 in applying (68) to solutions.

## 9. RESULTS

The net results of importance for the evaluation of the pressure and, therefore, through the use of the equations of appendix A of all of the more usual thermodynamics functions, may now be summarized.

<sup>16</sup> See, for example, Goursat-Hedrick, *Mathematical Analysis*, first edition (Ginn and Company, New York, 1904), Vol. I, pp. 45, 50.

Equation (57) expresses the pressure change in the system as a power series in the fugacity change:

$$P(\mathbf{z}+\mathbf{y})-P(\mathbf{z})=kT \sum_{\mathbf{m} \geq 0} b_{\mathbf{m}}(\mathbf{z}) \prod_s [y_s/\gamma_s(\mathbf{z})]^{m_s} \quad (70)$$

in which it is important to note that the coefficients of all the linear terms in the sum are unity, that is,  $b_{\mathbf{m}}(\mathbf{z})=1$  for the subscript set  $m_s=\delta_{rs}$ .

Using the thermodynamic relation (A13) of the appendix,

$$[\partial P(\mathbf{z}+\mathbf{y})/\partial y_s]_{T, \mathbf{z}, y_r} = kT \rho_s(\mathbf{z}+\mathbf{y})/(z_s+y_s);$$

applying this to (70) one obtains

$$\rho_s(\mathbf{z}+\mathbf{y}) = \frac{z_s+y_s}{y_s} \sum_{\mathbf{m} \geq 0} m_s b_{\mathbf{m}}(\mathbf{z}) \prod_r [y_r/\gamma_r(\mathbf{z})]^{m_r}, \quad (71)$$

as an expression for the density in molecules per unit volume of species  $s$ .

Equation (64) with  $Z_r=[y_r/\gamma_r(\mathbf{z})]$  and  $Y_r=[y_r/\gamma_r(\mathbf{z}+\mathbf{y})]$ , Eq. (67), leads to the relationship:

$$\ln \gamma_s(\mathbf{z}) - \ln \gamma_s(\mathbf{z}+\mathbf{y}) = \frac{\gamma_s(\mathbf{z}+\mathbf{y})}{y_s} \sum_{\mathbf{n} \geq 0} n_s B_{\mathbf{n}}(\mathbf{z}) \prod_r [y_r/\gamma_r(\mathbf{z}+\mathbf{y})]^{n_r}, \quad (72)$$

while (68) is

$$P(\mathbf{z}+\mathbf{y})-P(\mathbf{z})=kT \left\{ \sum_s \frac{y_s}{\gamma_s(\mathbf{z}+\mathbf{y})} - \sum_{\mathbf{n} \geq 0} \left( \sum_s n_s - 1 \right) B_{\mathbf{n}}(\mathbf{z}) \prod_s \left[ \frac{y_s}{\gamma_s(\mathbf{z}+\mathbf{y})} \right]^{n_s} \right\}. \quad (73)$$

If the species of molecules were such that all the mutual potential energies were independent of the species (e.g., for isotopes which are distinguishable in principle but negligibly different in mechanical properties) then

$$b_{\mathbf{m}} = (m!/\prod_s m_s!) b_m,$$

where, as usual  $m = \sum_s m_s$ , and

$$B_{\mathbf{n}} = (n!/\prod_s n_s!) B_n$$

so that the integrals depend only upon the number of particles and not on their kind. If, in addition  $\mathbf{z} = \sum_s \mathbf{z}_s$  and  $\rho = \sum_s \rho_s$ , the activity coefficients for all species are identical and the foregoing equations become

$$\begin{aligned} P(\mathbf{z}+\mathbf{y})-P(\mathbf{z}) &= kT \sum_{m \geq 0} b_m(\mathbf{z}) \sum_{\mathbf{m} \geq 0} \frac{m!}{\prod_s m_s!} \prod_s \left[ \frac{y_s}{\gamma_s(\mathbf{z})} \right]^{m_s} \\ &= kT \sum_{m \geq 0} b_m(\mathbf{z}) \left[ \sum_s \frac{y_s}{\gamma_s(\mathbf{z})} \right]^m = kT \sum_{m \geq 0} b_m(\mathbf{z}) \left[ \frac{y}{\gamma(\mathbf{z})} \right]^m, \end{aligned} \quad (70')$$

$$\rho(\mathbf{z}+\mathbf{y}) = \frac{z+y}{y} \sum_{m \geq 0} m b_m(\mathbf{z}) [y/\gamma(\mathbf{z})]^m, \quad (71')$$

and

$$\ln \gamma(\mathbf{z}) - \ln \gamma(\mathbf{z}+\mathbf{y}) = \frac{\gamma(\mathbf{z}+\mathbf{y})}{y} \sum_{n \geq 0} n B_n(\mathbf{z}) [y/\gamma(\mathbf{z}+\mathbf{y})]^n, \quad (72')$$

$$P(\mathbf{z}+\mathbf{y})-P(\mathbf{z}) = kT \left\{ \frac{y}{\gamma(\mathbf{z}+\mathbf{y})} - \sum_{n \geq 0} (n-1) B_n(\mathbf{z}) \left[ \frac{y}{\gamma(\mathbf{z}+\mathbf{y})} \right]^n \right\}, \quad (73')$$

where (71') and (72') are obtained from (71) and (72) by a summation over  $s$ . These equations are seen to be just those for the one component case.<sup>10</sup>

The application to a gas may be made most conveniently by setting  $\mathbf{z} \equiv \mathbf{0}$ , in which case  $\gamma_s(\mathbf{z}) = 1$  for all components, and  $y_s/\gamma_s(\mathbf{z} + \mathbf{y}) = y_s/\gamma_s(\mathbf{y}) = y_s \rho_s(\mathbf{y})/y_s = \rho_s(\mathbf{y})$ , while  $P(\mathbf{z}) = 0$ , so that Eqs. (70) to (73) become

$$\begin{aligned} P(\mathbf{y}) &= kT \sum_{\mathbf{m} \geq 0} b_{\mathbf{m}}^0 \prod_s y_s^{m_s}, \\ &= kT \left\{ \sum_s y_s + \sum_{\mathbf{m} \geq 1} b_{\mathbf{m}}^0 \prod_s y_s^{m_s} \right\}, \end{aligned} \quad (74)$$

$$= kT \left\{ \sum_s \rho_s(\mathbf{y}) - \sum_{\mathbf{n} \geq 0} (\sum_s n_s - 1) B_{\mathbf{n}}^0 \prod_r \rho_r^{n_r} \right\},$$

$$\rho_s(\mathbf{y}) = \sum_{\mathbf{m} \geq 0} m_s b_{\mathbf{m}}^0 \prod_r y_r^{m_r} \quad (75)$$

and

$$\ln Y_s = \ln \rho_s(\mathbf{y}) - \frac{1}{\rho_s} \sum_{\mathbf{n} \geq 0} n_s B_{\mathbf{n}}^0 \prod_r \rho_r^{n_r}, \quad (76)$$

where the superscript zeros are used on the integrals to indicate that they are evaluated at zero fugacity of all components. The second line of Eq. (74) is written in this form to emphasize the fact that the coefficients of all the linear terms are unity.

Essentially these equations for gaseous mixtures have been given before by Fuchs<sup>15</sup> and their equivalents for two components were derived by Mayer.<sup>14</sup> They deserve no further discussion here but are listed for comparison.

The more novel application of Eqs. (70) to (73) is given if we consider the case of one or more solutes in a solvent.\* For this case we shall find it convenient to use as the reference fugacity set  $\mathbf{z}$ , at which the integrals are calculated, that at which the fugacities of the solutes are zero and the fugacity of the solvent is such that the pure liquid has some convenient pressure  $P^*$ , say one atmosphere, or possibly its orthobaric vapor pressure. These conditions will be referred to hereafter as the standard state,  $\mathbf{z}^*$ . The activity of each component will be chosen with such a proportionality factor that it becomes equal to the density or, in more usual chemical terminology, the concentration, of that species in molecules per unit volume as the composition approaches that of the standard state.

The notation will be altered to emphasize the unique position of the solvent, for which Greek symbols will be employed, while Latin letters will be adopted for the solutes. The solute quantities which appear turn out to be their concentrations in molecules per unit volume (which we shall now write  $c_s$  instead of  $\rho_s$ ) and their activities  $a_s$  in the same concentration units. The solvent quantities that enter are its concentration  $\rho$  in molecules per unit volume, its activity  $\alpha$  (equal to the concentration in the limiting case of the pure solvent), and the activity coefficient  $\gamma = \alpha/\rho$ . For the standard state these quantities will be marked with an asterisk.

If in our previous notation we choose the subscript zero to indicate the solvent† the standard state  $\mathbf{z}^*$  is given by  $z_s = z_0 \delta_{0s}$ , and the new symbols are related to the old through the equations:

$$\begin{aligned} \text{Solvent quantities} \quad & \left\{ \begin{aligned} \rho &= \rho_0(\mathbf{z}^* + \mathbf{y}) & (77a) \\ \rho^* &= \rho_0(\mathbf{z}^*) = \alpha^* & (b) \\ \alpha &= (z_0^* + y_0)/\gamma_0(\mathbf{z}^*) & (c) \\ \gamma &= \gamma_0(\mathbf{z}^* + \mathbf{y})/\gamma_0(\mathbf{z}^*). & (d) \end{aligned} \right. \end{aligned}$$

\* J. G. Kirkwood has treated similar problems by a different method. See J. Chem. Phys. **3**, 300 (1935) and Chem. Rev. **19**, 275 (1936).

† So that the *solutes* are numbered from 1 to  $\sigma$ .

$$\text{Solute quantities} \begin{cases} c_s = \rho_s(\mathbf{z}^* + \mathbf{y}) = (z_s^* + y_s)/\gamma_s(\mathbf{z}^* + \mathbf{y}) & (78a) \\ 0 = \rho_s(\mathbf{z}^*) & (b) \\ a_s = y_s/\gamma_s(\mathbf{z}^*). & (c) \end{cases}$$

Since only the quantity  $y_o/\gamma_o(\mathbf{z}^*)$  and not  $\alpha$  itself appears in the equations we assign it the symbol  $\Delta\alpha$ ,

$$\Delta\alpha = y_o/\gamma_o(\mathbf{z}^*) = \alpha - \alpha^*, \quad (79)$$

it being the change in the solvent activity in going from the standard state  $\mathbf{z}^*$  to the state  $\mathbf{z}^* + \mathbf{y}$ . For a solute, the change in activity between these two states is the total activity, the activity in the standard state being zero. The dissymmetry of the equations results entirely from the choice of the standard state.

Employing the new symbols, Eqs. (70) to (73) become<sup>†</sup>

$$P(\alpha, \mathbf{a}) = P^* + kT \sum_{\mu, \mathbf{m}} b^*_{\mu\mathbf{m}} (\Delta\alpha)^\mu \prod_r a_r^{m_r}; \quad (80)$$

$$\rho(\alpha, \mathbf{a}) = \frac{\alpha}{\Delta\alpha} \sum_{\mu, \mathbf{m}} \mu b^*_{\mu\mathbf{m}} (\Delta\alpha)^\mu \prod_r a_r^{m_r}; \quad (81a)$$

$$\ln \alpha = \ln \rho - \frac{\gamma}{\Delta\alpha} \sum_{\nu, \mathbf{n}} \nu B^*_{\nu\mathbf{n}} \left( \frac{\Delta\alpha}{\gamma} \right)^\nu \prod_r c_r^{n_r}; \quad (b)$$

$$c_s(\alpha, \mathbf{a}) = \sum_{\mu, \mathbf{m}} m_s b^*_{\mu\mathbf{m}} (\Delta\alpha)^\mu \prod_r a_r^{m_r}, \quad (82a)$$

$$\ln a_s = \ln c_s - \frac{1}{c_s} \sum_{\nu, \mathbf{n}} n_s B^*_{\nu\mathbf{n}} \left( \frac{\Delta\alpha}{\gamma} \right)^\nu \prod_r c_r^{n_r}; \quad (b)$$

$$P(\alpha, \mathbf{a}) = P^* + kT \left[ \sum_s c_s + \frac{\Delta\alpha}{\gamma} - \sum_{\nu, \mathbf{n}} (\sum_s n_s - 1 + \nu) B^*_{\nu\mathbf{n}} \left( \frac{\Delta\alpha}{\gamma} \right)^\nu \prod_r c_r^{n_r} \right], \quad (83)$$

where the asterisk on the integrals  $b$  and  $B$  indicates that the integration is carried out with the potentials of average force occurring in the pure solvent, that is at infinite dilution of all solute species.

Of particular interest is the case for which  $\Delta\alpha = 0$ , i.e., the activity of the solvent is held constant. The pressure difference

$$P(\alpha, \mathbf{a}) - P(\rho^*, 0) = \pi(\rho^*, \mathbf{a}), \quad (84)$$

is the osmotic pressure. We find

$$\pi(\rho^*, \mathbf{a}) = kT \sum_{\mathbf{m}} b^*_{0\mathbf{m}} \prod_s a_s^{m_s}, \quad (85a)$$

$$= kT \left[ \sum_s a_s + \sum_{m>1} b^*_{0\mathbf{m}} \prod_s a_s^{m_s} \right]; \quad (b)$$

or,

$$\pi(\rho^*, \mathbf{c}) = kT \left[ \sum_s c_s - \sum_{\mathbf{n}} (\sum_s n_s - 1) B^*_{0\mathbf{n}} \prod_s c_s^{n_s} \right] \quad (c)$$

where the second line is so written to draw attention to the fact that the integrals  $b^*_{0\mathbf{m}}$  are unity for such  $\mathbf{m}$  values that  $m_s = \delta_{rs}$ .

By comparison with Eq. (74) for the imperfect gas it is seen that the osmotic-pressure equation corresponds exactly to that for the pressure of a gaseous solute, except that the activity  $a_s$  replaces

<sup>†</sup> The cluster integrals  $b^*_{\mu\mathbf{m}}$ , in which the solvent subscript is written explicitly, should not be confused with the cluster integrals  $b_{\mathbf{m}\mathbf{m}}$  of the second kind (Eq. (53)) which appear only in Section 7. Also the solvent subscript  $\mu$  should not be confused with the chemical potential,  $\mu_s$ .

the fugacity  $y_s$ , and the integrals occurring as coefficients are calculated by the use of the potentials of average force in the infinitely dilute solution, involving only the mutual potentials of solute molecules and never explicitly the potentials of solvent with solute or solvent with solvent molecules.

The other equations are:

$$c_s(\rho^*, \mathbf{a}) = \sum_{\mathbf{m}} m_s b_{0\mathbf{m}}^* \prod_r a_r^{m_r}, \quad (86a)$$

$$\begin{aligned} \rho(\rho^*, \mathbf{a}) &= \rho^* \sum_{\mathbf{m}} b_{1,\mathbf{m}}^* \prod_r a_r^{m_r} \\ &= \rho^* \exp \sum_{\mathbf{n}} B_{1,\mathbf{n}}^* \prod_r c_r^{n_r}; \end{aligned} \quad (b)$$

and

$$\ln a_s = \ln c_s - \frac{1}{c_s} \sum_{\mathbf{n}} n_s B_{0\mathbf{n}}^* \prod_r c_r^{n_r}, \quad (87)$$

where the second form of (86b) comes from (81b).

It is thus to be noted that, for a world at constant temperature at least, the presence of intangible molecules which act with forces on the ordinary molecules but which could pass through them, would not alter the applicability of the Gibbs statistics to equilibrium systems. Since the intangible molecules pass through all barriers their fugacity would everywhere be constant, though not their concentration, and all measured pressures would be osmotic pressures. The measured forces between ordinary molecules would all be average forces, influenced by the all-pervading fluid molecules, but the potentials calculated from them, the potentials of average force, would be strictly applicable to the calculation of all observed thermodynamic properties.

Rather than measuring osmotic pressures, a more usual laboratory practice is to vary the concentrations of solutions under constant (atmospheric) pressure, a process corresponding to the equation:

$$\sum_{\mu, \mathbf{m}} b_{\mu, \mathbf{m}}^* (\Delta\alpha)^\mu \prod_s a_s^{m_s} = 0. \quad (88)$$

The question now arises as to the dependence of one of the variables of Eq. (88) (for example the solvent activity increment,  $\Delta\alpha$ ) on the other variables (the solute activities), i.e., the determination of the coefficients  $\lambda_i$  in the equation

$$\Delta\alpha = \sum_i \lambda_i \prod_s a_s^{i_s}. \quad (89)$$

We note that

$$(\Delta\alpha)^\mu = \sum_{\mu_i} (\sum_i \mu_i = \mu) \mu! \prod_i \frac{(\lambda_i \prod_s a_s^{m_s})^{\mu_i}}{\mu_i!}$$

which, when employed in (88) gives

$$\begin{aligned} &\sum_{\mu, \mathbf{m}} b_{\mu, \mathbf{m}}^* \sum_{\mu_i} (\sum_i \mu_i = \mu) \mu! \left( \prod_i \frac{\lambda_i^{\mu_i}}{\mu_i!} \right) \prod_s a_s^{\sum_i i_s \mu_i + m_s} = 0, \\ &= \sum_{\mathbf{k}} \left[ \sum_{\mathbf{m} > 0} \sum_{\mu_i} (\sum_i i \mu_i = \mathbf{k} - \mathbf{m}) b_{\sum \mu_i, \mathbf{m}}^* (\sum \mu_i)! \prod_i \frac{\lambda_i^{\mu_i}}{\mu_i!} \right] \prod_s a_s^{k_s} \\ &= \sum_{\mathbf{k}} \left[ \sum_{\mu=0}^k \sum_{\mu_i} b_{\mu, \mathbf{k} - \sum i \mu_i}^* \binom{\mu}{\mu_i} \prod_i \lambda_i^{\mu_i} \right] \prod_s a_s^{k_s} = 0 \end{aligned} \quad (90)$$

where the last two lines are obtained through the substitution  $\mathbf{k} = \sum_i i \mu_i + \mathbf{m}$ .

Since (90) must hold for all values of the variable  $\mathbf{a}$ , the coefficient in brackets must be identically zero for each  $\mathbf{k}$ :

$$\sum_{\mu=0}^k \sum_{\mu_i} b_{\mu, \mathbf{k} - \sum i \mu_i}^* \binom{\mu}{\mu_i} \prod_i \lambda_i^{\mu_i} = 0 \quad (\text{all } \mathbf{k}). \quad (91)$$

While for many-component systems this gives fairly complicated relations between the  $\lambda$ 's and  $b$ 's for which no general analytic solution has yet been found, the first several  $\lambda$ 's are easily obtainable for two components. (91) becomes

$$\sum_{\mu=0}^k \sum_{\mu_i} b_{\mu, k-\Sigma \mu_i}^* \binom{\mu}{\mu_i} \prod_i \lambda_i^{\mu_i} = 0 \quad (91')$$

which for various values of  $k$  yields the relations:

$$\begin{aligned} k=1 \quad & b_{01}^* + b_{10}^* \lambda_1 = 0, \quad \therefore \lambda_1 = -1; \\ k=2 \quad & b_{02}^* + b_{11}^* \lambda_1 + b_{20}^* \lambda_1^2 + b_{10}^* \lambda_2 = 0, \quad \therefore \lambda_2 = b_{11}^* - b_{02}^* - b_{20}^*; \\ k=3 \quad & b_{03}^* + b_{12}^* \lambda_1 + b_{21}^* \lambda_1^2 + b_{30}^* \lambda_1^3 + (b_{11}^* + 2b_{20}^* \lambda_1) \lambda_2 + b_{10}^* \lambda_3 = 0, \\ \text{or,} \quad & \lambda_3 = (b_{30}^* - b_{21}^* + b_{12}^* - b_{03}^*) + (2b_{20}^* - b_{11}^*)(b_{11}^* - b_{02}^* - b_{20}^*); \text{ etc.} \end{aligned}$$

Thus, for a binary system, the solvent activity as a function of the solute activity at constant pressure is given by the expression

$$\alpha = \rho^* - a + (b_{11}^* - b_{02}^* - b_{20}^*) a^2 + [(b_{30}^* - b_{21}^* + b_{12}^* - b_{03}^*) + (2b_{20}^* - b_{11}^*)(b_{11}^* - b_{02}^* - b_{20}^*)] a^3 + \dots \quad (92)$$

The discussion of the application of the general equations to binary systems will be continued in the following section.

## 10. TWO-COMPONENT SYSTEMS

Because systems of three or more components have not been so exhaustively studied and are less familiar to most than are those of two components, we propose to devote this section to an application of the general equations to binary systems.

In the series notation of Section 8, Eq. (85c), expressing the osmotic pressure in a solution containing a single solute, assumes the form:

$$\begin{aligned} \pi(\rho^*, c) &= kT [c - \sum_n (n-1) B_{on}^* c^n] \\ &= kT [c + G(c, B_{on}^*) - cG'(c, B_{on}^*)] \end{aligned} \quad (93)$$

where the prime indicates differentiation with respect to  $c$ . It is seen that for the special case in which the solute concentration,  $c$ , becomes so small that powers higher than first be neglected, this equation reduces to the familiar law of van't Hoff. Equation (93) is identical with that obtained previously, for example by Mayer and Harrison,<sup>5</sup> † for the pressure of an imperfect gas, except that here the irreducible integrals are evaluated under the conditions which exist in the infinitely dilute solution rather than in the infinitely rarefied gas.

The coefficients,  $B_{on}^*$ , involve integrals over the coordinate space of the *solute* molecules only, and the integrands are functionals of the potentials of average force between *solute* molecules only. The functional dependence of the integrands on the potentials of average force of the solute molecules in the infinitely dilute solution is exactly the same as the functional dependence of the integrands of the virial coefficients of the gas on the potentials between isolated molecules. The presence of the solvent does not appear explicitly at all in Eq. (93), and appears only implicitly as the potentials of average force of the solute molecules are influenced by the presence of the solvent.

The equations are derived under the assumption that the integration over the internal coordinates of one molecule of the solute converges to a value independent of the volume. This means that the assumption is made that dissociation of the solute is negligible. If it were not, an appropriate transformation of coordinates, changing the description of numbers of molecules, and of "internal coor-

† Note that here  $B_{on} = \beta_{n-1}/n$  used in this reference.

ordinates" *versus* coordinates of center of mass, must be made. In any case, the van't Hoff law holds for the molecular weight appropriate to the solute in the solvent, and holds at low densities as long as the potentials of average force between the molecular entities chosen are sufficiently weak to lead to small values of the product of "virial coefficients"  $B_{on}^*$  times the solute density (concentration)  $c$ , measured in molecules per unit volume. Evidently, then, the osmotic pressure for solutions plays the role analogous to the total pressure of a gaseous mixture.

We now examine the conditions under which phase transitions may occur. For our two-component system, Eq. (85a) has the form

$$\pi(\rho^*, a) = kT G(a, b_{on}^*) = kT \sum_{m \geq 1} b_{on}^* a^m, \quad (94)$$

where  $a$  is the conventional *liquid phase activity* measured in molecules per unit volume (cf. Section 9).

The slope of the curve obtained by plotting the osmotic pressure against the density of the solute\* is given by the expression

$$\left( \frac{\partial \pi}{\partial c} \right)_{z, T} = \frac{kT}{c} \sum_{m \geq 1} m b_{on}^* a^m \cdot \left( \frac{\partial \ln y}{\partial \ln c} \right)_{z, T}, \quad (95)$$

since  $a$  is proportional to  $y$  by Eq. (78c). From (86a),

$$c = \sum_{m \geq 1} m b_{on}^* a^m, \quad (96)^\dagger$$

and (95) becomes

$$\left( \frac{\partial \pi}{\partial c} \right)_{z, T} = kT \left( \frac{\partial \ln y}{\partial \ln c} \right)_{z, T}. \quad (97)$$

To evaluate the derivative in the right of (97), we note from (96) that

$$\left( \frac{\partial}{\partial \ln c} \right)_{z, T} \left[ \frac{1}{c} \sum_{m \geq 1} m b_{on}^* a^m \right] = 0 = \sum_{m \geq 1} m^2 b_{on}^* a^m \left( \frac{\partial \ln y}{\partial \ln c} \right)_{z, T} - 1, \quad (98)$$

whence,

$$\left( \frac{\partial \pi}{\partial c} \right)_{z, T} = kT c / \sum_{m \geq 1} m^2 b_{on}^* a^m. \quad (99)$$

It is now apparent that if the sum in the denominator of (99) has an infinite discontinuity for some value  $\bar{y}$  of the fugacity of the solute (corresponding to the concentration  $\bar{c}$ ), the slope of the osmotic pressure *vs.* density curve is zero for all densities above  $\bar{c}$  which satisfy (96). (The divergence of the sum  $\sum_{m \geq 1} m^2 b_{on}^* a^m$  does not necessarily require an infinite discontinuity in the density function (96).) If we wish to investigate the slope for fugacities greater than  $\bar{y}$ , we must use the analytical continuation of the divergent sum.

Returning now to the discussion at the end of Section 8, the singularity,  $\bar{y}$ , of  $G(a, b_{on}^*)$  may correspond either to the vanishing of the determinant in (69), which now becomes

$$1 - cG''(c, B_{on}^*) = 0, \quad (100)$$

or a singularity at  $\bar{c}$  in the function  $G(c, B_{on})$ . By (93) we write

$$\left( \frac{\partial \pi}{\partial c} \right)_{z, T} = kT [1 - cG''(c, B_{on})] \quad (101)$$

\* This corresponds to the physical process of adding solute to a given quantity of pure solvent and always readjusting the pressure on the solution so as to maintain osmotic equilibrium between the solution and the pure solvent.

† It is tacitly assumed that the density function (96) increases monotonically in the fugacity, and vice versa.

and

$$\left(\frac{\partial^2 \pi}{\partial c^2}\right)_{z, T} = -kT[G''(c, B_{on}) + cG'''(c, B_{on})]. \quad (102)$$

From the shape of the osmotic pressure curve *vs.* solute density at the phase transitions in a temperature region far from the critical mixing temperature, particularly its discontinuity in slope, we can only conclude that the singularity in the function  $G(a, b_{om})$  corresponds to a singularity in  $G(c, B_{on})$  since otherwise, if  $\bar{c}$  were determined as the root of (100),  $(\partial\pi/\partial c)_{z, T}$  would approach zero continuously as  $c$  approached  $\bar{c}$  from either side.

In the idealized two-component case for which  $w_n = 0$  for  $n > 2$ , the irreducible integrals with which we are concerned are defined as

$$B^*_{on} = \frac{1}{Vn!} \int \int \cdots \int_V \sum \Pi [\exp(-u_{aa}(z, 0; r_{kl})/kT) - 1] d\tau_1 \cdots d\tau_n \quad (103)^{14}$$

(sum over all products with all molecules more than singly connected)

in which  $u_{aa}(z, 0; r_{kl})$  is the potential of average force between two molecules of type  $a$  (in an infinitely dilute solution of solvent fugacity  $z$ ) as a function of their distance of separation  $r_{kl}$ . The presence of the solvent at fugacity  $z$  serves only to modify the potential energy function from its value at  $z=0$  and not the character of the behavior of the integrals with temperature.

Although little is known about the behavior of the actual irreducible integrals  $B_{on}(z, 0)$ , there is no apparent reason why their qualitative behavior with temperature should be radically different from that of  $B_{on}(0, 0)$ , used for the gas. If, as seems probable, this is the case, the arguments of Mayer<sup>17</sup> regarding the nature of the critical region of an imperfect gas may be analogously applied to the critical mixing region of two partly miscible liquids.

Let us then investigate the temperature dependence of certain properties of the osmotic pressure function, particularly its first and second derivatives with respect to  $c$ , as that variable is increased. At the (lower) critical mixing temperature,\*  $T_c$ , defined as the lowest temperature at which the first derivative is zero, in order to have a critical point of the "van der Waals" type both first and second derivatives (Eqs. (101) and (102)) must be zero.

If, for all values of  $T > T_c$ , the series  $cG''(c, B_{on})$  approaches a value less than unity as  $c$  approaches  $\bar{c}$ , then  $\bar{c}(T)$  will be the density at which a second phase appears, and  $T_c$  will be the (lower) limiting temperature at which a second phase may be obtained. If it happens that

$$\lim_{c \rightarrow \bar{c}} c(T_c)G''[c(T_c), B_{on}(T_c)] < 1, \quad (104)$$

the slope given by (101) will not be zero at the critical mixing point—a type of critical point which is never observed. Furthermore, since it seems unlikely that the values of the  $B_{on}$ 's for a particular system should be such that at the critical mixing point we should have fulfilled simultaneously both the conditions (for  $c = \bar{c}$ ):

$$cG''(c, B_{on}) = 1 \quad (105)$$

and

$$c^2G'''(c, B_{on}) = -1, \quad (106)$$

which presumably may be accomplished only by very special types of attractive forces, it appears highly improbable that *all* critical mixing points are of this type. For the case in which the limit (104)

<sup>17</sup> Reference 1, pp. 308–314; reference 10, pp. 639–640.

\* In liquid systems some confusion may arise due to the fact that both "upper" and "lower" critical mixing points may occur, and even in the same system. In what follows we shall consistently speak of the lower critical point, but what is said will be equally true for the upper critical point with only slight changes, such as the order of certain temperatures:  $T_c < T_m$  (lower);  $T_c > T_m$  (upper). The subscripts  $c$  and  $m$  are those used in reference 1, and should not be confused with concentration  $c$ , which never occurs as a subscript, or the running index  $m$ .



is greater than unity the Jacobian (69), changes sign; the expansion (94) is no longer valid, and Eq. (101) would indicate a (physically ridiculous) osmotic pressure which *decreases* with increasing solute density. The only other apparent alternative is that the sum in (105) becomes unity at some value of the temperature,  $T_m$ , which is higher than the true critical temperature, and that for temperatures between  $T_c$  and  $T_m$  the singularity in  $G(a, b_{om})$  is determined by condition (100) rather than by a singularity in  $G(c, B_{on})$ . The solution of (105) satisfies the condition (106) at  $T = T_c$ . An anomalous first-order transition,<sup>18</sup> in which the  $\pi$ - $c$  curve is horizontal over a finite range of density but has no discontinuity in slope, thus occurs between the temperatures  $T_m$  and  $T_c$ . An analysis strictly analogous to that used by Mayer for the imperfect gas<sup>19</sup> shows that, under the hypothesis that the  $B_{on}$  have the same sort of temperature dependence as the  $\beta_k$ , the separation into two conjugate phases occurs only at temperatures greater than  $T_m$ , at which point the surface tensions of the two phases are identical. The argument will not be repeated here, but it should be noted that it is the mutual surface tension between the two phases which should be considered.

Probably because of the extremely high osmotic pressures involved in all but the most dilute solutions, there are no such measurements of osmotic pressure with which to compare the foregoing theoretical description of the region of the critical mixing point. However, constancy of the osmotic pressure requires constancy of the partial vapor pressures of the two components over the solution, since the vapor pressure,  $p$ , of the solvent in the solution is uniquely expressed in terms of the osmotic pressure as the solution of the equation:

$$\int_p^{p_0} \bar{v}(p) dp = v_o \left\{ \pi + (p_o - p) \left[ 1 + \frac{\beta}{2} (p_o - p) \right] - \frac{\beta}{2} \pi (\pi - 2p) \right\}, \quad (107)^{20}$$

in which  $v_o$  is the molar volume,  $p_o$  the vapor pressure, and  $\beta$  the compressibility of the pure solvent; and  $\bar{v}(p)$  is the partial molar volume of the solvent in the vapor phase above the solution. The region of anomalous first-order transition is thus characterized by a finite concentration range in which the plot of the partial vapor pressure of either component (or, for that matter, the total pressure of the solution) against concentration is horizontal but has no discontinuities in slope.

There is much experimental evidence supporting this conclusion.\* As early as 1900 van der Lee<sup>21</sup> remarked on the flatness of these curves for the system: phenol-water. The same characteristic of the system: cyclohexane-aniline was noted and briefly discussed by Mme. H. Schlegel.<sup>22</sup> Measurements by Dr. L. D. Roberts<sup>23</sup> in this laboratory showed that over a wide range of composition the partial pressure of triethylamine in triethylamine-water mixtures, at temperatures a few degrees below the (lower) critical mixing temperature, was constant to within approximately 0.1 percent.

## 11. SUMMARY

The method of the grand-canonical ensemble has been generalized for multicomponent systems, and equations have been obtained for the calculation of the thermodynamic properties and distribution functions of such systems at any particular set of fugacities in terms of those functions at any other fugacity set. The theory is thus applicable to liquid solutions, for which the osmotic pressure has been shown to play a role analogous to that of the total pressure of a gaseous system. It has further been shown that the existence of an anomalous first-order transition near the critical mixing temperature of a binary mixture is probable.

<sup>18</sup> Cf. J. E. Mayer and S. F. Streeter, J. Chem. Phys. **7**, 1019 (1939).

<sup>19</sup> See reference 1, pp. 310 ff; reference 5, pp. 93-94.

<sup>20</sup> Cf. for example, A. A. Noyes and M. S. Sherrill, *Chemical Principles* (The Macmillan Company, New York, 1938), second edition, paragraph IV, 25.

\* The anomalous behavior of imperfect gases, with experimental comparisons, in the critical region has been thoroughly discussed by S. F. Harrison and J. E. Mayer, J. Chem. Phys. **6**, 101 (1938).

<sup>21</sup> Zeits. f. physik. Chemie **33**, 628 (1900).

<sup>22</sup> H. Schlegel, J. Chem. Phys. **32**, 215 (1935).

<sup>23</sup> L. D. Roberts and J. E. Mayer, J. Chem. Phys. **9**, 852 (1941).

## APPENDICES

## A. Thermodynamic Excursion

Since the independent variable  $z_s$ , which we call fugacity,\* is not a common one, it may be well to discuss briefly its properties. As in Eq. (18), we may write

$$\mu_s = kT \ln z_s + \mu_{os}(T), \quad (\text{A1})$$

where  $\mu_{os}(T)$ , a function of the temperature alone, is the chemical potential of a perfect gas of pure constituent  $s$  at a density of one molecule per unit volume. The total derivative of  $\mu_{os}(T)$  with respect to  $T$  may be calculated as

$$\begin{aligned} d\mu_{os}/dT &= \{(\partial\mu_s/\partial T)_P + (\partial\mu_s/\partial P)_T(dP/dT)\}_{\text{pure } s, \rho_s=1} \\ &= -S_{os} + k, \end{aligned} \quad (\text{A2})$$

where  $S_{os}$  is the entropy per molecule of pure perfect gas of species  $s$  at unit density, and  $k$  is the Boltzmann constant, the latter following from the fact that the perfect gas equations are to be employed for  $\mu_{os}$ .

From (A1) we then have

$$(\partial\mu_s/\partial z_s)_T = kT/z_s \quad (\text{A3})$$

and

$$\begin{aligned} (\partial\mu_s/\partial T)_{z_s} &= k \ln z_s + d\mu_{os}/dT \\ &= \frac{1}{T} [\mu_s - \mu_{os} + kT - TS_{os}] \\ &= \frac{1}{T} \{ \mu_s + [-\mu + Pv - TS]_{\rho_s=1, \text{ pure gas}} \} \\ &= \frac{1}{T} [\mu_s - E_{os}(T)], \end{aligned} \quad (\text{A4})$$

where  $v$  is the volume per molecule and  $E_{os}$  is the energy of a perfect gas of molecules of type  $s$  at unit density, which is, of course, a function of temperature alone. We also have that  $\mu_s$  is a function of  $z_s$  and  $T$  alone, or,

$$(\partial\mu_s/\partial z_r)_T, z_s=0, \quad r \neq s. \quad (\text{A5})$$

Let us now consider the extensive thermodynamic potential:

$$PV = F - A = \sum_s N_s \mu_s - A, \quad (\text{A6})$$

for which:

$$\begin{aligned} d(PV) &= \sum_s N_s d\mu_s + \sum_s \mu_s dN_s - \sum_s \mu_s dN_s + PdV + SdT \\ &= \sum_s N_s d\mu_s + PdV + SdT, \end{aligned}$$

from which it is seen that  $PV$  is a "natural" function of  $\mathbf{y}$ ,  $V$ , and  $T$ , namely that

$$[\partial(PV)/\partial\mu_s]_{V, T, \mu_r} = N_s, \quad (\text{A7})$$

and

$$[\partial(PV)/\partial V]_{T, \mu} = P \quad (\text{A8})$$

$$[\partial(PV)/\partial T]_{V, \mu} = S. \quad (\text{A9})$$

Corresponding to this, the grand partition function for a grand ensemble of fixed  $V$ ,  $T$ , and  $\mathbf{y}$  is equal to the exponential of  $PV/kT$  (Section 4).

\* The fugacity of Lewis and Randall is proportional to  $z_s$ , the former becoming equal to the pressure at infinite dilution instead of to the number of molecules per unit volume. The Lewis and Randall fugacity is thus  $kTz_s$ .

From (A7, 8, and 9) it is seen that the intensive property  $P = (PV)/V$ , if expressed as a function of the intensive variables  $T, \mathbf{y}$  has the partial derivatives

$$(\partial P / \partial T)_\mu = S/V, \quad (\text{A10})$$

$$(\partial P / \partial \mu_s)_{T, \mu_r} = N_s/V = \rho_s, \quad (\text{A11})$$

and, of course,  $(\partial P / \partial V)_{T, \mu} = 0$ .

Now let us examine  $P$  as a function of  $T$  and  $\mathbf{z}$ , using (A4, 5, and 10) to obtain

$$\begin{aligned} (\partial P / \partial T)_z &= (\partial P / \partial T)_\mu + \sum_s (\partial P / \partial \mu_s)_{T, \mu_r} (\partial \mu_s / \partial T)_z \\ &= \frac{1}{TV} [(TS + \sum_s N_s (\mu_s - E_{os})] \\ &= (TS + F - E_o) / TV \\ &= (H - E_o) / TV = (PV + E - E_o) / TV, \end{aligned} \quad (\text{A12})$$

where  $E_o = \sum_s N_s E_{os}$  is the energy of the constituent molecules of the system at unit density, and  $H = E + PV$  is the enthalpy. Using (A3, 5, and 11) one arrives at

$$(\partial P / \partial z_s)_{T, z_r} = (\partial P / \partial \mu_s)_{T, \mu_r} (\partial \mu_s / \partial z_s)_{T, z_r} = kT \rho_s / z_s. \quad (\text{A13})$$

We may regard  $z_s$  as a function of the intensive variables  $P, T$ , and  $z_r$  for all  $r \neq s$ . By inversion of (A13) we find

$$(\partial \ln z_s / \partial P)_{T, z_r} = 1 / kT \rho_s \quad (\text{A14})$$

while the negative ratio of (A12) to (A13) gives

$$(\partial \ln z_s / \partial T)_{P, z_r} = -(PV + E - E_o) / (kT^2 V \rho_s), \quad (\text{A15})$$

and the negative ratio of two equations of the type (A13) shows that

$$(\partial \ln z_s / \partial \ln z_r)_{T, P, z_r} = -\rho_r / \rho_s = -N_r / N_s. \quad (\text{A16})$$

The second derivative  $(\partial^2 P / \partial T \partial z_s)_{z_r}$  may be calculated by differentiating (A12) with respect to  $z_s$ , or (A13) with respect to  $T$ . Equating the two results leads to the equation

$$(\partial \rho_s / \partial T)_z = (z_s / V k T^2) [\partial E(\mathbf{z}) / \partial z_s]_{T, z_r}. \quad (\text{A17})$$

If  $z_s$  is regarded as a function of  $P, T$ , and  $N_s$ , Eq. (A1) permits us to write all derivatives from common forms, leading to the familiar Gibbs-Duhem relationship for all changes at constant  $T$  and  $P$ :

$$(\sum_s N_s d \ln z_s)_{T, P} = (\sum_s \rho_s d \ln z_s)_{T, P} = 0, \quad (\text{A18})$$

showing that  $z_s$  depends only on  $N_s/N$ , of which Eq. (A16) is seen to be a special case; furthermore,

$$(\partial \ln z_s / \partial P)_{T, N_s} = \bar{v}_s / kT, \quad (\text{A19})$$

where  $\bar{v}_s = (\partial V / \partial N_s)_{P, T, N_s}$  is the partial molecular volume. The derivative with respect to temperature requires a little computation, and is found to be

$$\begin{aligned} (\partial \ln z_s / \partial T)_{P, N_s} &= (-T \bar{S}_s + T S_{os} - \mu_s + \mu_{os}) / kT^2 \\ &= -(\bar{H}_s - H_{os}) / kT^2 \end{aligned} \quad (\text{A20})$$

where  $\bar{H}_s$  is the partial molecular enthalpy of species  $s$ ,  $\bar{H}_s = (\partial H / \partial N_s)_{P, T, N_r}$ , and  $H_{os}$  is the enthalpy per molecule of a perfect gas composed of molecules of species  $s$  at unity density.

### B. Reversion of the Expansion of the Potentials of Average Force

We wish to solve the set of equations

$$W_N(\mathbf{z}, \{\mathbf{N}\}) = \sum \{\mathbf{n}\}_N w_n(\mathbf{z}, \{\mathbf{n}\}_N), \quad N=1, 2, \dots \quad (\text{B1})$$

discussed in Section 6 (Eq. (47)) for the component potentials of average force  $w_n(\mathbf{z}, \{\mathbf{n}\})$ . Let us first note that each molecule is assigned a number, so that they are all distinguishable; if we associate with each molecule a second number denoting species it makes them none the more distinguishable (except, of course, when we perform integrations, in which case coordinate *interchanges* are limited to pairs of molecules of the same species). Therefore, for the purposes of this and the following section we may simply consider a set of numbered molecules without regard to species, and not write the symbols in bold-face; also, since all the quantities are functions of  $\mathbf{z}$ , this will be omitted for convenience in writing.

Let us consider, then, the set of equations

$$W_n\{n\} = \sum [1]_n w_1 + \sum [2]_n w_2 + \dots + \sum [n-1]_n w_{n-1} + w_n, \quad (\text{B2})$$

$$W_{n-1}\{n-1\} = \sum [1]_{n-1} w_1 + \sum [2]_{n-1} w_2 + \dots + \sum [n-2]_{n-1} w_{n-2} + w_{n-1}, \quad (\text{B3})$$

$$\dots \dots \dots$$

$$W_{n-i}\{n-i\} = \sum [1]_{n-i} w_1 + \sum [2]_{n-i} w_2 + \dots + \sum [n-i-1]_{n-i} w_{n-i-1} + w_{n-i}, \quad (\text{B4})$$

$$W_1(1) = w_1(1), \quad (\text{B5})$$

where the symbol  $\sum [n-i]_n$  indicates summation over only those subsets of  $n$  which are  $n-i$  in size. Evidently there will be one equation of type (B2);  $n$ -equations of type (B3), depending upon the choice of the unique molecule included in the set  $\{n\}$  but not in the subset  $\{n-1\}_n$ ; and in general,  $n!/(n-i)!$ -equations of type (B4).

If we were to sum over all the  $n$ -Eqs. (B3) and subtract (B2), the terms  $w_{n-1}$  would cancel. We propose now to generalize this procedure so that all terms on the right cancel except  $w_n$ .

In the set of Eqs. (B4), the number of equations having the term  $w_{n-j}$  for  $\{n-j\}_{n-i}$  particular molecules (of the set  $n-i$ ) is just the number of ways in which we can choose  $i$ -molecules from the set  $\{n\}$  without including any of the set  $\{n-j\}$ —or, the number of ways in which we can choose the set  $\{i\}$  of molecules from the set  $\{j\}$ ; this is simply  $j!/(j-i)!$ . Again employing the symbol  $\sum [n-j]_n$  to indicate summation over only those subsets of  $n$  which are  $n-j$  in size,

$$\sum [n-i]_n W_{n-i}\{n-i\} = \sum_{j=i}^{n-1} [j!/(j-i)!i!] \sum [n-j]_n w_{n-j}\{n-j\}. \quad (\text{B6})$$

Now we form the sum

$$\begin{aligned} \sum_{i=0}^{n-1} (-)^i \sum [n-i]_n W_{n-i} &= \sum_{n-1 \geq j \geq i \geq 1} \sum [j!(-)^i/(j-i)!i!] \sum [n-j]_n w_{n-j} \\ &= \sum_{j=1}^{n-1} \sum_{i=1}^j [j!(-)^i/(j-i)!i!] \sum [n-j]_n w_{n-j} \\ &= \sum_{j=1}^{n-1} (1-1)^j \sum [n-j]_n w_{n-j} \end{aligned} \quad (\text{B7})$$

or

$$w_n(\mathbf{z}, \{\mathbf{n}\}) = \sum \{\mathbf{N}\}_n (-)^{n-N} W_N(\mathbf{z}, \{\mathbf{N}\}_n), \quad (\text{B8})$$

which is Eq. (48).

### C. Reversion of the Expansion of the Distribution Functions

In Section 7 (Eq. (49)) we wrote

$$F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}\}) = \sum \{k\{\mathbf{m}_i\}_{\mathbf{M}}\}_u \prod_{i=1}^k g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}_i\}_{\mathbf{M}}). \quad (\text{C1})$$

As in Appendix B we may omit the variable  $\mathbf{z}$  and the bold-face without loss of generality. This device aids the understanding of the proof as well as the explanation.

By writing out the series (C1) for  $M=1$ , to 5, it is possible to guess the solution for the functions  $g_{\mu}$  in the form

$$g_{\mu}\{\mu\} = \sum \{l\{M_j\}_{\mu}\}_u (-)^{l-1} (l-1)! \prod_{j=1}^l F_M\{M\}_{\mu}. \quad (\text{C2})$$

This step is straightforward but lengthy, and we shall not include it here. We shall prove the correctness of (C2) by substitution with (C1) and reduction to an identity. This substitution gives

$$\begin{aligned} g_{\mu}\{\mu\} &= \sum \{l\{M_j\}_{\mu}\}_u (-)^{l-1} (l-1)! \prod_{j=1}^l \sum \{k\{m_i\} M_j\}_u \prod_{i=1}^k g_{\mathbf{m}}\{m_i\} M_j \\ &= \sum \{K\{m_i\}_{\mu}\}_u \left[ \sum_{l=1}^K (-)^{l-1} (l-1)! P_l^K \right] \prod_{i=1}^K g_{\mathbf{m}}\{m_i\}_{\mu}, \end{aligned} \quad (\text{C3})$$

in which  $P_l^K$  is the number of ways in which  $K$ -particular subsets  $\{m_i\}$  may be grouped together in exactly  $l$ -sets—or, the number of ways of putting  $K$ -distinguishable objects into  $l$ -numbered boxes with at least one to each box. We have found no closed form for the general quantity  $P_l^K$ , but the following recursion formula, valid for  $K > 2$ , is easily obtained:

$$P_l^K = P_{l-1}^{K-1} + l P_l^{K-1}, \quad (\text{C4})$$

in which the first term on the right corresponds to putting the  $K$ th-subset alone in the  $l$ th-box, and the second term, to putting it into any one of the  $l$  boxes which already contain  $K-1$  subsets. Now the coefficient in (C3) becomes (for  $K \geq 2$ )

$$\begin{aligned} \sum_{l=1}^K (-)^{l-1} (l-1)! P_l^K &= \sum_{l=1}^K (-)^{l-1} (l-1)! P_{l-1}^{K-1} - \sum_{l=1}^{K-1} (-)^l l! P_l^{K-1} \\ &= \sum_{l'=1}^{K-1} (-)^{l'} l'! P_{l'}^{K-1} - \sum_{l=1}^{K-1} (-)^l l! P_l^{K-1} \\ &= 0 \quad (K \geq 2), \end{aligned}$$

since  $P_l^K$  is zero for  $l=0$  or  $l > K$ .  $P_1^1$  is obviously unity, and consequently the coefficient is given by

$$\sum_{l=1}^K (-)^{l-1} (l-1)! P_l^K = \delta_{K1}, \quad (\text{C5})$$

and Eq. (C3) thus reduces to an identity, since for  $K=1$ ,  $\{m_j\} \equiv \mu$ . Reverting to the bold-face notation, we obtain

$$g_{\mathbf{m}}(\mathbf{z}, \{\mathbf{m}\}) = \sum \{l\{\mathbf{M}_j\}_{\mathbf{m}}\}_u (-)^{l-1} (l-1)! \prod_{j=1}^l F_{\mathbf{M}}(\mathbf{z}, \{\mathbf{M}_j\}_{\mathbf{m}}), \quad (\text{C6})$$

which is Eq. (50).

The inverse, (C2), has been previously reported<sup>7</sup> but this appears to be the first published proof.

## D. Glossary

For easy reference the following compilation of symbols is appended (the numbers in parentheses refer to the defining equations):

$a$	Activity of the solute in a two-component system (94).	$m, M$	Numbers of systems (Section 4).
$a_s$	Activity of the solute species $s$ (78c).	$P, P(\mathbf{z})$	Pressure.
$A$	Helmholtz free energy (Appendix A).	$\Phi_{INV}, \Phi_{NV}$	Defined in Eqs. (25), (28).
$b_m$	The cluster integrals of the first kind (52); $b_0 = 0$ .	$P_l^K$	Appendix C.
$b_m^0$	Cluster integral evaluated at zero fugacities (76).	$\{\mathbf{P}_N\}$	The momenta of $N$ molecules (39).
$b_{\mu m}^*$	Cluster integral evaluated at fugacity set $\mathbf{z}^*$ (80, ff.).	$q_{is}$	Coordinate $q$ of molecule $i_s$ (42), (7).
$b_{nm}$	Cluster integral of the second kind (53); employed in Section 7 only.	$Q$	Canonical partition function (Eq. (3) and Section 4).
$c$	Concentration of the solute in a two-component system (Section 10).	$Q_s$	Single particle partition function (1).
$c_s$	Concentration of solute species $s$ (Section 9).	$Q_{is}$	Single particle internal partition function (1'').
$E$	Thermodynamic "internal energy" (Appendix A).	$r_{ij}$	Distance between the centers of mass of two particles (Section 6).
$E_l$	The energy of the $l$ th quantum state of a canonical system.	$r, s, t$	Designation of species of molecules. (Subscripts.)
$f$	The number of degrees of freedom (39).	$S$	Entropy (Section 4, Appendix A).
$f_{qis}$	The force on molecule $i_s$ along coordinate $q$ (Section 6).	$T$	Absolute temperature.
$F$	The Gibbs free energy (Appendix A).	$u_{ij}$	Component potential energy (Section 6).
$F_N(\mathbf{z}, \{\mathbf{n}\})$	The distribution function (Section 2b).	$u$	Designates "unconnected" subsets (Eq. 49 etc.).
$g_m$	Correction term for $m$ proximate molecules (49, 50).	$U_N$	The potential energy (Section 6), (40).
$g_{nm}$	Second type of correction term (51).	$V$	Volume.
$G, G_s$	Defined by (62).	$\bar{v}$	Partial molar or molecular volume (A18), (107).
$h$	Planck's constant.	$w_n$	Component potentials of average force (Eqs. (47), (48)).
$i$	"Internal," as on $Q_{is}$ (1').	$W_N$	The potential of average force (Section 6).
$i, j, k, l$	Running indices.	$x_{is}, y_{is}, z_{is}$	Cartesian coordinates of the center of mass (Section 2a), (7).
$I_N$	An auxiliary function (Section 5), (36).	$y_s$	The fugacity or fugacity increment of component $s$ .
$J[x/q]$	The Jacobian between the coordinate frames $q$ and $x$ (11).	$Y$	Equation (67).
$k$	Boltzmann's constant.	$z_s$	The fugacity of component $s$ .
$k, K, l$	The total number of subsets for a particular subdivision (49, 50, C3)	$Z$	Equation (66).
$m, \mathbf{M}, \mathbf{n}, \mathbf{N}$	Sets of molecules. $\sum_{m \geq 0}$ indicates summation over all sets for $m \geq 0$ .	$\alpha$	Solvent activity (Section 9).
$\{\mathbf{M}_z\}$	The spatial coordinates of $\mathbf{M}$ molecules.	$\beta_k$	The irreducible integrals used in reference 5.
		$B_N$	The irreducible integrals, implicitly defined by (60); $B_0 = 0$ .
		$B_{0n}$	The irreducible integral (Section 9); $B_{00} = 0$ .
		$\gamma(\mathbf{z})$	The activity coefficient (19).
		$\gamma$	Solvent activity coefficient (77d).
		$\delta_{ij}$	Kronecker's delta. $=0$ for $i \neq j$ and $=1$ for $i = j$ .

$\epsilon$	The energy of a single molecule (Section 1).	$\omega, \Omega$	Number of quantum states (Section 4).
$\mu$	Set or subset of molecules, Appendix C; also a running index, Section 9.	<b>Special symbols</b>	
$\mathfrak{u}$	A chemical potential set (16); it never appears in brackets as independent variable as does the subset $\mu$ of molecules.		
$\mu_{os}$	The chemical potential of species $s$ at density $\rho_{os}$ (18).	A <b>bold-face</b> symbol indicates a <i>set</i> , one for each species (Eq. (9)).	
$\prod_s$	Indicates a product over all $s$ .	$\{\mathbf{n}\}$	The coordinates of the set $\mathbf{n}$ of molecules (Eq. (10)).
$\varrho$	A density set (14).	$\mathbf{n} \cdot \mathfrak{u}$	A kind of dot product (Eq. (20)).
$\rho$	Solvent density (Sections 9, 10).	$\{k\{\mathbf{m}\}\mathbf{M}\}_u$	A set of $k$ unconnected subsets $\{\mathbf{m}\}$ of the set $\mathbf{M}$ of molecules.
$\sigma$	The total number of components.	$  \cdot  _\sigma$	$\sigma$ th-order determinant (Section 8).
$\sum$	Summation.	$\langle \cdot \rangle$	Average value of (Section 6).
$d\tau$	A volume element in configuration space (Eq. 103).	$*$	Superscript, refers to the standard state, $\mathbf{z}^*$ (Section 9).
$\psi_l$	The eigenfunction corresponding to quantum state $l$ (Section 4).	$^0$	Superscript, refers to the state $\mathbf{z}=\mathbf{0}$ (Section 9).