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Citation: *J. Chem. Phys.* **15**, 187 (1947); doi: 10.1063/1.1746468

View online: <http://dx.doi.org/10.1063/1.1746468>

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are always equivalent amounts of Fe^{2+} and Fe^{3+} in the octahedral position, and there is no reason for a discontinuous increase of ϵ with increasing ZnCr_2O_4 content.

The corresponding $\log \sigma$ vs. $1/T$ curves are given in Fig. 4. At high temperatures the preparations containing large amounts of ZnCr_2O_4 show a break in the curves, suggesting that at these temperatures a second conduction mechanism covers the $\text{Fe}^{2+} - \text{Fe}^{3+}$ conduction prevailing for lower temperatures. The curves can be represented by

$$\sigma = \sigma_{\infty} \exp(-\epsilon/kT) + \sigma_{\infty}' \exp(-\epsilon'/kT).$$

As the specific conductivity of ZnCr_2O_4 is much

greater than that of MgCr_2O_4 this phenomenon is most probably caused by the conductivity of ZnCr_2O_4 itself, so that at higher temperatures the conduction is taken over by Zn (or by Zn and Cr ions jointly) as a consequence of the higher temperature coefficient of this conduction mechanism.

In Fig. 3, therefore, where ϵ has again been plotted against the composition, the value of ϵ corresponding to the low temperature part of the curves has been used. The plot shows a continuous increase of ϵ with increasing ZnCr_2O_4 content.

We wish to acknowledge the valuable assistance of Mr. A. Bol in the preparation of specimens and the measurements.

Integral Equations between Distribution Functions of Molecules

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(Received February 18, 1947)

Integral equations are derived that relate variations in the potentials of average force between molecules of a system at two different densities or activities. These permit the calculation of the change in thermodynamic properties, or of the change in the distribution of molecules in space, in a liquid or crystalline phase, if either the temperature is varied, or if the mutual potentials between the molecules is assumed to change. The equations are in a somewhat complex, but still distinguishable, matrix form. A matrix operates on the variations in potential occurring at one activity and transforms them into those occurring at a second activity. The matrix elements are combinations of the distribution functions at the second activity, to which the transformation is made, multiplied by powers of the difference of the two activities. The matrix approaches the unit matrix in value as this activity difference approaches zero. The product of the two matrices, one which transforms from activity α to activity β , with that which transforms from activity β to α , is the unit matrix. This leads to an integral (matrix) equation between the distribution functions at any two activities.

The calculation of one element of this matrix product leads to a cell type equation for the computation of the activity, or free energy, of a system in terms of the potential between a single molecule and the molecules that immediately surround it in the system.

The transformation matrices have solutions, at certain values of the activity difference y , corresponding to variations in the potentials of average force, which are transformed into zero variations at the new activity. The activities at which such variations can occur are those of the phase transitions in the systems. The solutions at these special values of the activity are differences of combinations of the distribution functions in the two pure phases that can coexist at these activities.

INTRODUCTION

ONE may define "distribution functions" for a given number, n , of molecules as being proportional to the probability density of finding n molecules in a certain configurational position,

averaged over all positions of the other molecules of the system. These functions are the exponent of minus the potential of average force between the molecules, divided by kT . The distribution functions of a given system at constant tem-

perature, but at two different densities, are then related to each other by equations which can be obtained by a simple extension of the concept of the Gibbs grand canonical ensemble. The special case of most general interest is that for which one of the two densities is the limit of zero density. At zero density the distribution function for a classical system is the exponent of minus the potential energy divided by kT , and may be regarded as known.

Although the equations relating the distribution functions of a liquid or solid to those at infinite dilution are rigorous and exact, they are not susceptible of numerical solution, since they involve integration over the coordinates of the number of molecules in a macroscopic portion of the system. It is, however, possible to consider a variational method which leads to certain integral equations involving integrations over fewer numbers of molecules.

The variational method discussed in this paper is essentially as follows: We consider the potentials of average force at one density, say those at infinite dilution, to be capable of some continuous variation. This, of course, causes a variation in the potentials at some other density, say that of the liquid. By assuming the variation in the potentials of zero density to be of the sort induced by a change in the mutual potentials between pairs, or between some relatively small number of molecules, the equations for the variation in the potentials of average force in the liquid can first be integrated over all but the molecules for which the change in potential is being computed, and the few with which these are interacting. One thus obtains a set of integral equations giving the variations in the liquid potentials as the sum of integrals of kernels times the variations in the potentials of zero density. The kernels are combinations of the unvaried distribution functions in the liquid.

One of the purposes of this paper is merely the formal attainment of these equations. Their use is not further discussed in the body of this article, but will be dealt with in a subsequent paper. By considering variations due to changes in temperature, or other physically meaningful changes, one has a tool for the calculation of the thermodynamic properties of the system in terms of the distribution functions.

However, certain formal mathematical relationships that follow from these equations appear to be of interest. The discussion of these relationships occupies the main body of the paper.

NOTATION

Owing to the relatively complex equations involved, it is desirable to use a special symbolism in order to attain some brevity of expression. The final equations are in no way more complicated if a system of many components is considered than if a single component system is handled. We deal with an infinite system containing σ types of molecular species, and use the subscript s (or r) to refer to a special species of type s (or r). Symbols ρ , z , without subscripts refer to a set of quantities:

$$\rho = \rho_1, \rho_2, \dots, \rho_s, \dots, \rho_\sigma, \quad (1)$$

$$z = z_1, z_2, \dots, z_s, \dots, z_\sigma. \quad (2)$$

The symbol ρ_s indicates the average concentration of molecules of species s , in molecules per unit volume, and z_s is the activity or fugacity, defined by the equation:

$$z_s = \lim_{\rho_0 \rightarrow 0} [\rho_{0s} \exp(\mu_s - \mu_{0s})/kT], \quad (3)$$

in which μ_s is the chemical potential of species s in the system, and the limit is taken as all concentrations, ρ_0 , approach zero, with μ_{0s} the chemical potential, and ρ_{0s} the concentration, of species s , in this limit at which the system approaches a perfect gas in properties. Thus z_s is proportional to the exponent of the chemical potential μ_s , divided by kT , with the proportionality constant so chosen that z_s/ρ_s becomes unity in the perfect gas at infinite dilution of the system:

$$\lim_{\rho \rightarrow 0} [z_s/\rho_s] = 1. \quad (4)$$

The letters k , m , n , κ , μ , ν , λ , etc., when written without subscripts, will be used to indicate sets of integers:

$$k = k_1, k_2, \dots, k_s, \dots, k_\sigma, \quad (5)$$

of k_s molecules of type s . The shorthand notation:

$$k! = k_1!k_2!\dots k_s!\dots k_\sigma!, \quad (6)$$

$$\rho^k = \rho_1^{k_1}\rho_2^{k_2}\dots \rho_s^{k_s}\dots \rho_\sigma^{k_\sigma}, \quad (7)$$

$$z^k = z_1^{k_1}z_2^{k_2}\dots z_s^{k_s}\dots z_\sigma^{k_\sigma},$$

will be employed. With this notation the equations for the σ component system become identical with those for a single component system of activity z , or concentration ρ , in which k, m, n , etc., is used to indicate the number of molecules of the single component. The reader will probably find the ensuing discussion simpler if the one component case only is kept in mind.

The coordinates of the i th molecule of type s are indicated by

$$(i_s) = x_{is}, y_{is}, z_{is}, q_{1is}, \dots, q_{fis}, \quad (8)$$

including any internal coordinates, q , and the volume element, calculated in the Cartesian space of the constituent atoms by

$$d(i_s) = dx_{is} dy_{is} dz_{is} \left[\frac{q}{x} \right] dq_{1is} \dots dq_{fis}, \quad (9)$$

with $\left[\frac{q}{x} \right]$ the Jacobian transformation to the Cartesian volume. The introduction of the internal coordinates causes no change in the ensuing equations. The reader will probably find the visualization of the operations easier if the case that no internal coordinates are present is kept in mind. The coordinates of k_s molecules of type s are indicated by

$$\{k_s\} = (1_s), (2_s), \dots, (k_s), \quad (10)$$

and the volume element by

$$d\{k_s\} = d(1_s) d(2_s) \dots d(k_s), \quad (11)$$

whereas the coordinates of the set k of molecules are,

$$\{k\} = \{k_1\}, \{k_2\}, \dots, \{k_s\}, \dots, \{k_\sigma\}, \quad (12)$$

and the volume element is

$$d\{k\} = d\{k_1\} d\{k_2\} \dots d\{k_s\} \dots d\{k_\sigma\}. \quad (13)$$

A function, $\Psi_n\{n\}$, of the coordinates of the set $\{n\}$ of molecules may happen to be simply expressible as a sum of functions of the coordinates $\{\nu\}_n$ of small subsets of molecules out of

the set n . The typical component function, $\psi_\nu\{\nu\}_n$, composing a member of this sum, say for example, $\psi_2((i_s)(j_s))$, of the coordinates of the i_s th and j_s th molecule, will, if Ψ_n is symmetrical in permutations of identical molecules, have the same functional dependence on the coordinates that the function $\psi_2((j_s)(k_s))$ has upon the coordinates of the j_s th and k_s th molecule, but the two functions are distinct in the sum and have, in general, different values for some arbitrary value $\{n\}$ of the coordinates of the set n of molecules. The summation symbol, $(\sum\{\nu\}_n)$, will be used to indicate summation of functions of such subsets, $\{\nu\}_n$, over all subsets, for all values of ν , $0 \leq \nu_s \leq n_s$, including a single (constant) term for which all $\nu_s = 0$. It will be noted that there are $n!/(n-\nu)! \nu!$ different distinct subsets, $\{\nu\}_n$, for each value of the set of numbers, $\nu = \nu_1, \dots, \nu_s, \dots$, so that in the trivial case that the function is a constant, $(-1)^\nu$, for all ν s, then

$$(\sum\{\nu\}_n)(-1)^\nu = 0 \text{ if } n > 0, \quad (14)$$

$$(\sum\{\nu\}_n)(-1)^\nu = 1 \text{ if } n = 0. \quad (15)$$

Thus if Ψ_n is one of a set of functions of the coordinates $\{n\}$, symmetrical in permutations of identical molecules, defined for all values of n including $n=0$, for which the function, Ψ_0 , is a constant,

$$\Psi_n = \Psi_n\{n\}, \quad (16)$$

then we may define functions ψ_ν by

$$\psi_\nu = (\sum\{n\}_\nu)(-1)^{\nu-n} \Psi_n, \quad (17)$$

and, in view of (14) and (15) we have that,

$$\Psi_n = (\sum\{\nu\}_n) \psi_\nu, \quad (18)$$

since then on inserting (17) in (18) we obtain the identity:

$$\begin{aligned} \Psi_n &= (\sum\{\nu\}_n)(\sum\{\kappa\}_\nu)(-1)^{\nu-\kappa} \Psi_\kappa \\ &= (\sum\{\kappa\}_n)(\sum\{\nu-\kappa\}_{n-\kappa})(-1)^{\nu-\kappa} \Psi_\kappa \\ &= \Psi_n. \end{aligned}$$

THE DISTRIBUTION FUNCTION EQUATION

With this notation we now define distribution functions $F_n(\rho, T, \{n\})$, of the coordinates of a set n of molecules, by the statement that in a system of infinite extent ($V \gg n_s/\rho_s$ for all s) at the temperature T , and concentration ρ , the probability that there are an appropriate set n of molecules at the coordinates $\{n\}$ within the volume element $d\{n\}$ is equal to $\rho^n F_n(\rho, T, \{n\}) d\{n\}$. It is to be

noted that with this definition the functions F_n are so normalized that,

$$\lim_{V \rightarrow \infty} \left[\frac{1}{V^n} \int \int \cdots \int_V F_n d\{n\} \right] = 1. \quad (19)$$

We arbitrarily include $F_0 \equiv 1$ in the set of functions so defined.

In a previous paper¹ it has been shown that for two sets of concentrations ρ_α and ρ_β , for which the pressures are P_α and P_β , and for which the fugacity sets are z_α and z_β , respectively, the distribution functions are related by the equation set:

$$\begin{aligned} & [\exp(P_\alpha V/kT)] [\rho_\alpha/z_\alpha]^n F_n(\rho_\alpha, T, \{n\}) \\ &= \sum_{m \geq 0} \frac{(z_\alpha - z_\beta)^m}{m!} \int \int \cdots \int_V e^{P_\beta V/kT} \left[\frac{\rho_\beta}{z_\beta} \right]^{n+m} F_{n+m}(\rho_\beta, T, \{n+m\}) d\{m\}. \end{aligned} \quad (20)$$

This actually represents two sets of equations for each pair of concentrations ρ_α and ρ_β , since obviously the subscripts on the right and left can be interchanged. Thus if we define:

$$G_n = e^{P_\alpha V/kT} \left[\frac{\rho_\alpha}{z_\alpha} \right]^n F_n(\rho_\alpha, T, \{n\}), \quad (21)$$

$$G_n^* = e^{P_\beta V/kT} \left[\frac{\rho_\beta}{z_\beta} \right]^n F_n(\rho_\beta, T, \{n\}), \quad (21')$$

$$z = z_\alpha - z_\beta, \quad (22)$$

we may write (20) as,

$$G_n = \sum_{m \geq 0} \frac{z^m}{m!} \int \int \cdots \int_V G_{n+m}^* d\{m\}, \quad (23)$$

or as,

$$G_n^* = \sum_{m \geq 0} \frac{(-z)^m}{m!} \int \int \cdots \int_V G_{n+m} d\{m\}. \quad (23')$$

THE VARIATIONAL METHOD

Without regard, at first, to the physical interpretation of the functions G_n and G_n^* we shall now proceed to carry out some mathematical manipulations which lead us to a set of integral equations that are of considerable interest in interpreting the relationships between these two sets of functions. The only mathematical limitations which must be imposed upon the functions G_n and G_n^* are to require that they be symmetrical in permutations of identical molecules, and of such a form that the series (23) and (23') converge absolutely. These conditions are assuredly fulfilled for the physical case. The symmetry in permutations of the coordinates of identical molecules is obvious. In addition we have that G_n and G_n^* are positive definite, from their definitions in terms of probability functions, and for repelling molecules G_n and G_n^* approach zero in value for all values of the coordinates $\{n\}$ within a finite volume V as n/V approaches infinity.

We now assume that G_n , and therefore through (23') G_n^* , depend on a parameter y , defining:

$$\Psi_n = d \ln G_n / dy, \quad (24)$$

$$\Psi_n^* = d \ln G_n^* / dy. \quad (24')$$

For instance, we may take y to be the temperature T , in which case, from (21) and (24) one could relate the Ψ 's to the various temperature derivatives of the system. The function $F_n(0, T, \{n\})$, for $\rho \equiv 0$, is $\exp(-U_n/kT)$, with U_n the potential energy, if the system is classical. One might, for

¹ W. G. McMillan, Jr. and J. E. Mayer, J. Chem. Phys. **13**, 276 (1945) and for component systems, J. E. Mayer, J. Chem. Phys. **10**, 629 (1942).

instance, consider that U_n is $U_n^0 - yU_n^{(1)}$ with $U_n^{(1)}$ some sort of perturbation potential. In this case, if G_n^* referred to $\rho \equiv 0$, the functions Ψ_n^* would be $1/kT$ times the perturbation potential for the set n of molecules. The functions Ψ_n could then be related to the derivatives of the system with respect to this perturbation.

We may now define the functions ψ_ν and ψ_ν^* by (17) and by,

$$\psi_\nu^* = (\sum \{n\}_\nu) (-)^{\nu-n} \Psi_n^*, \quad (25)$$

so that (18), and,

$$\Psi_n^* = (\sum \{\nu\}_n) \psi_\nu^*, \quad (26)$$

are valid.

We now proceed to derive Eq. (29) by which the function ψ can be calculated as a sum of integrals of kernels multiplied by the functions ψ^* . The kernels are given by Eq. (30) as combinations of the functions G . A similar reciprocal set of equations, (29') and (30'), can be used to compute the functions ψ^* by integration over kernels formed from the G^* 's multiplied by the functions ψ . These equations are obtained by differentiation of both sides of (23) with respect to y , obtaining:

$$\begin{aligned} G_n \Psi_n &= \frac{d}{dy} G_n = \frac{d}{dy} \sum_{m \geq 0} \frac{z^m}{m!} \int \cdots \int G_{n+m}^* d\{m\} \\ &= \sum_{m \geq 0} \frac{z^m}{m!} (\sum \{\nu\}_n, \{\mu\}_m) \int \cdots \int \psi_{\nu+\mu}^* G_{n+m}^* d\{m\} \\ &= \sum_{\mu \geq 0} \frac{z^\mu}{\mu!} (\sum \{\nu\}_n) \int \cdots \int \psi_{\nu+\mu}^* \left[\sum_{k \geq 0} \frac{z^k}{k!} \int \cdots \int G_{n+\mu+k}^* d\{k\} \right] d\{\mu\} \\ &= \sum_{\mu \geq 0} \frac{z^\mu}{\mu!} (\sum \{\nu\}_n) \int \cdots \int \psi_{\nu+\mu}^* G_{n+\mu} d\{\mu\}. \end{aligned} \quad (27)$$

In this the second line follows from the first by the use of (24') and (26) and by considering that

$$(\sum \{\nu\}_{n+m}) = (\sum \{\nu\}_n) (\sum \{\mu\}_m) = (\sum \{\nu\}_n \{\mu\}_m),$$

where the last notation means summation over all subsets $\{\nu\}_n$ and $\{\mu\}_m$ including $\nu \equiv 0$, and $\mu \equiv 0$. For any given value of the set m one may arbitrarily call $m - \mu = k$, and, remembering that there are $m!/\mu!k!$ different subsets $\{\mu\}_m$ for any given value of the set m and μ , one may multiply by this and sum over μ and k rather than m and $\{\mu\}_m$. This leads to the third line. The fourth line follows by using equation (23).

We thus have:

$$\Psi_n = \sum_{\mu \geq 0} \frac{z^\mu}{\mu!} (\sum \{\nu\}_n) \int \cdots \int \psi_{\nu+\mu}^* \frac{G_{n+\mu}}{G_n} d\{\mu\}. \quad (28)$$

To this equation we apply the operation of equation (17) to both sides, and obtain,

$$\psi_k = \sum_{m \geq 0} \frac{z^m}{m!} (\sum \{\kappa\}_k) \int \cdots \int \psi_{\kappa+m}^* K_{k,\kappa,m} d\{m\}, \quad (29)$$

in which the kernels, $K_{k,\kappa,m}$, are defined by the equation:

$$K_{k+n, n, m} = (\sum \{\kappa\}_k) (-)^{k-\kappa} \frac{G_{\kappa+n+m}}{G_{\kappa+n}}. \quad (30)$$

The application of the equivalent series of operations to Eq. (23'), instead of (23), leads to the equations:

$$\psi_k^* = \sum_{m \geq 0} \frac{(-z)^m}{m!} (\sum \{\kappa\}_k) \int \cdots \int \psi_{\kappa+m} K_{k,\kappa,m}^* d\{m\}, \quad (29')$$

with,

$$K_{k+n, n, m}^* = (\sum \{\kappa\}_k) (-)^{k-n} \frac{G_{k+n+m}^*}{G_{k+n}^*}. \quad (30')$$

Special values of the kernels follow from (30) and (30') to be,

$$K_{0, 0, 0} = K_{0, 0, 0}^* = 1, \quad (31a)$$

$$K_{0, 0, m} = G_m/G_0; \quad K_{0, 0, m}^* = G_m^*/G_0^*, \quad (31b)$$

$$K_{k+n, n, 0} = K_{k+n, n, 0}^* = 0 \text{ if } k > 0, \quad (31c)$$

$$K_{n, n, 0} = K_{n, n, 0}^* = 1. \quad (31d)$$

AN OVERSIMPLIFICATION

Equations (29) and (29') apply for all values of $k \geq 0$. We may choose either the set ψ_k of functions or the set ψ_k^* as arbitrary, limited only by the condition that they be symmetrical in permutations of the coordinates of identical molecules.

A special case of the integral equation (29) (or (29') but not both) has been used by Kirkwood and Monroe² to determine distribution functions for liquids. The special case chosen by them may be constructed from our equations as follows. We use (23) with the asterisk, G_n^* , referring to infinite dilution of a one-component system, and G_n referring to the liquid state. Differentiation is then performed with respect to the coordinate of a molecule at a particular position over which the integration is not extended, that is, one of the coordinates of one of the molecules, (i), of the set n in (23). The functions $\Psi_n^* kT$ are then the true forces, and are zero unless n contains the molecule (i). They are symmetrical in the coordinates of all identical molecules except the molecule i . The ψ_n^* are assumed to be zero unless $n=2$. The functions $\Psi_n kT$ are the average forces in the liquid, which are related, by a well-known relationship to the unknown distribution functions G_n , in the liquid. Equation (29) then has unknown ψ_n and kernel K , but a subsidiary relationship between them is known. It then represents a non-linear integral equation, which Kirkwood and Monroe solved approximately with certain assumptions.

The form (29') for their problem would have presented them with a linear (non-homogeneous)

integral equation with known kernel K^* and known function ψ^* , but unknown average force ψ . The possible advantages of this form have not been investigated.

The standard form of a non-homogeneous linear integral equation of the Fredholm type may be written as

$$\psi(x) = \psi^*(x) - z \int K(x, y) \psi^*(y) dy, \quad (32)$$

in which ψ and the kernel $K(x, y)$ are known functions, and ψ^* is the unknown function to be determined from the equation. There exists a reciprocal kernel $K_z^*(x, y)$ depending on the value of the parameter z , such that, independent of ψ ,

$$\psi^*(x) = \psi(x) - z \int K_z^*(x, y) \psi(y) dy. \quad (32')$$

It is, of course, quite unimportant whether the variables x and y are one dimensional or a set of coordinates in multidimensional space.

The reciprocal kernel, K^* , varies continuously with the parameter z between the value $z=0$ (where $K^*=K$) and the first eigenvalue, z_γ , for which the homogeneous equation,

$$\psi^*(x) = z_\gamma \int K(xy) \psi^*(y) dy, \quad (33)$$

has a solution. For values of z between z_γ and z_i , the second eigenvalue, K^* again varies continuously with z . In general the functions which K^* approach as z approaches z_γ from above and below are different.

Now let us consider a special case of (29), namely that there is only one component kind of molecule, and that ψ_k^* , which we can choose arbitrarily, is identically zero except for $k=1$.

² John G. Kirkwood and Elizabeth Monroe, J. Chem. Phys. 9, 514 (1941).

There are, then, only two non-zero terms in the sum on the right, that with $\kappa=1, m=0$, and that with $\kappa=0, m=1$. We consider the case $k=1$, for which the kernel $K_{1,1,0}$ when $\kappa=1, m=0$ is unity from (31d). The equation for this case is,

$$\psi_1(i) = \psi_1^*(i) + z \int K_{1,0,1}((i), (j)) \psi_1^*(j) d(j), \quad (34)$$

identical in form to (32). Were we justified in assuming that $\psi_k=0$ for all values of k except $k=1$ then (29') for $k=1$ would be,

$$\psi_1^*(i) = \psi_1(i) - z \int K_{1,0,1}^*((i), (j)) \psi_1(j) d(j) \quad (34')$$

of the same form as (32'). That is were the assumption correct then $K_{1,0,1}$ and $K_{1,0,1}^*$ would be simple reciprocal kernels for the parameter z .

We may now examine more closely what the kernels $K_{1,0,1}$ and $K_{1,0,1}^*$ are. Choosing $\rho_\beta=0, z_\beta/\rho_\beta=1$, in Eqs. (21) and (21') defining G and G^* , so that $z_\alpha=z$ from (22), and using (30) and (30') defining the kernels we have,

$$K_{1,0,1}^*((i), (j)) = \frac{F_2^*((i), (j))}{F_1^*(i)} - F_1^*(j), \quad (35)$$

$$K_{1,0,1}((i), (j)) = \frac{\rho}{z} \left[\frac{F_2((i), (j))}{F_2(i)} - F_1(j) \right], \quad (35')$$

where the asterisks refer to infinite dilution and the functions F are the distribution functions at concentration ρ . Now if there are no internal coordinates then $F_1^* \equiv 1$, so that,

$$K_{1,0,1}^* = F_2^* - 1, \quad (36)$$

which is a function symmetrical in permutations of the coordinates of the two molecules, approaching zero in value as the distance between them becomes large.

At least in the gaseous and liquid phases we also have $F_1=1$, so that for these phases,

$$K_{1,0,1} = \frac{\rho}{z} [F_2 - 1], \quad (36')$$

which is also symmetrical and approaches zeros for large distances.

The simplicity of the result obtained from this unjustified assumption of identifying $\psi_k=0$ for $k>1$ when $\psi_k^*=0$ for $k>1$ is made particularly

intriguing when we consider that the function (36') will show discontinuities in form as z changes through the eigenvalues of the kernel (36), so that these eigenvalues would be identified with the values of the activity at which phase transitions occur.

The actual situation is far more complicated due to the occurrence of the summations in the original Eqs. (29) and (29'). We have discussed this simple case at some length because of its suggestiveness, and because it appears to represent a simplified caricature of the true case.

THE KERNELS AS OPERATORS

We shall show that Eq. (29) may be regarded as a generalized matrix equation, in which a matrix, of which combinations of the kernels, K , constitute the elements, operate on the set of functions ψ_k^* to transform them to the set ψ_k . The equation (29') is the reciprocal equation, in which the reciprocal matrix, of elements formed from the kernels K^* , operate on the set of functions ψ_k , transforming them to the set ψ_k^* .

These matrices, which transform from the activity z_β to the activity z_α , are functions of the distribution functions at the activity z_α , and of the difference, $z=z_\alpha-z_\beta$, Eq. (22), in the activity. We can thus consider the matrices, $A_z(y)$, as depending on two parameters, z and y , the matrix consisting of elements composed of the distribution functions at activity z , and transforming the set of functions ψ_k^* corresponding to the activity $z-y$ into the set ψ_k at z . We then obtain the matrix Eqs. (46) between the matrices for different values of z and y .

Let us use the symbol $a(\{k\}, \{m\})$ for a function of the coordinates $\{k\}$ and $\{m\}$, defined by,

$$a(\{k\}, \{m\}) = (\sum \{\kappa\}_k \{\mu\}_m) \delta(\{\kappa\}_k, \{\mu\}_m) \frac{z^{m-\mu}}{(m-\mu)!} K_{k,\kappa,m-\mu}, \quad (37)$$

where the summation runs over all subsets, $\{\kappa\}_k$, of the set $\{k\}$, and all subsets, $\{\mu\}_m$, of $\{m\}$, but $\delta(\{\kappa\}_k, \{\mu\}_m) = 0$ unless the two subsets contain the same numbers of the same types of molecules, and unless the coordinates of all corresponding molecules of the two sets are identical; and in the latter case the integral of $\delta(\{\kappa\}_k, \{\mu\}_m)$ about the position of identity of the coordinates

is unity. We similarly define:

$$a^*({k}, {m}) = (\sum \{k\}_k, \{m\}_m) \delta(\{k\}_k, \{m\}_m) \frac{(-z)^{m-\mu}}{(m-\mu)!} K_{k, \kappa, m-\mu}^* \quad (37')$$

With these two quantities we may write Eqs. (29) and (29') as,

$$\psi_k = \sum_{m \geq 0} \int a({k}, {m}) \psi_m^* d{m}, \quad (38)$$

$$\psi_k^* = \sum_{m \geq 0} \int a^*({k}, {m}) \psi_m d{m}. \quad (38')$$

These equations are now in a more conventional form than that of (29) and (29'). If Φ and Φ^* are the sets of functions:

$$\Phi = \psi_0, \psi_1, \dots, \psi_k, \dots, \quad (39)$$

$$\Phi^* = \psi_0^*, \psi_1^*, \dots, \psi_k^*, \dots; \quad (39')$$

and A and A^* are the matrices of elements $a({k}, {m})$ and $a^*({k}, {m})$, respectively; then (38) and (38') may be written as:

$$\Phi = A\Phi^*, \quad \Phi^* = A^*\Phi, \quad (40)$$

$$AA^* = A^*A = E, \quad (41)$$

With E the unit matrix. The matrix multiplication of the two elements involves *both* summation over the middle index m and integration over the coordinates $\{m\}$ for each value of the index m . The matrix A is thus a generalized type of matrix with continuous and discrete ranges. Thus we see that the Eqs. (29) and (29') do correspond to the equations for two reciprocal commutative linear operators whose matrix elements can be represented by the a and a^* of Eqs. (37) and (37').

Written in terms of these matrix elements equation (41) takes the form:

$$\begin{aligned} \sum_{m \geq 0} \int \int \dots \int a({k}, {m}) a^*({m}, {n}) d{m} \\ = \sum_{m \geq 0} \int \int \dots \int a^*({k}, {m}) a({m}, {n}) d{m} \\ = \delta({k}\{n}). \end{aligned} \quad (42)$$

This equation could be used, in principle at least, as a means of determination of the functions G from known functions G^* .

The matrices A and A^* which we have defined by means of their elements in Eqs. (37) and (37') depend both on the activity set z at which the kernels are determined (z_α for A and z_β for A^* in Eqs. (21) and (21')), and upon the difference of activity, $z = z_\alpha - z_\beta$, between the two systems. Let us change our nomenclature at this place, and write the matrices as $A_z(y)$ of element,

$$a_z(y, {k}, {m}) = (\sum \{k\}_k, \{m\}_m) \delta(\{k\}_k, \{m\}_m) \frac{y^{m-\mu}}{(m-\mu)!} K_{k, \kappa, m-\mu}(z), \quad (43)$$

in which the kernels are made up according to (30) from the distribution functions at the activity set z .

If y becomes identically zero there remain in (43) only the terms for which $\mu = m$, and from (31c) and (31d) these are zero unless $k = \kappa = \mu = m$, and are then unity. We thus have,

$$\lim_{y \rightarrow 0} [A_z(y)] = E, \quad (44)$$

is the unit operator.

Now let $\Phi(z)$ represent the set of functions $\psi_0(z), \psi_1(z), \dots, \psi_k(z)$ giving the variations in the potentials at the activity z . The transformation equations, (40), then take the form:

$$\Phi(z) = A_z(y) \Phi(z-y). \quad (45)$$

If we operate on this with $A_{z+x}(x)$ we find:

$$\begin{aligned} \Phi(z+x) &= A_{z+x}(x) \Phi(z) = A_{z+x}(x) A_z(y) \Phi(z-y) \\ &= A_{z+x}(x+y) \Phi(z-y), \end{aligned}$$

or

$$A_{z+x}(x+y) = A_{z+x}(x) A_z(y). \quad (46)$$

Equation (41) is seen to be a special case of (46), namely that for which $x = -y$, in which, from (44), $A_{z+x}(0) = E$, and,

$$A_{z+x}(x) A_z(-x) = E. \quad (46')$$

A SPECIAL EQUATION

Equation (42), which represents a set of equations, one for each value of k and n , is comparatively awkward to handle for the case of general values of k and n . It can be seen that the equation is trivially satisfied if $n \equiv 0$, as we shall show in this section. If $k \equiv 0$ and $n = 1$, one obtains an expression which leads to an equation

for the activity, z_s , of the single molecule represented in the set $n=1$.

We use the symbol i_s or j_s to represent a single molecule of type s , and (i_s) or (j_s) to represent its coordinates, but use the subscript s to indicate a kernel in which the corresponding set n is a set consisting of one molecule of type s , and $m-s$ when the set is some general set, m , ($m_s \geq 1$) less one molecule of type s . If n represents a set consisting of a single molecule of type s then $z^n = z_s$ in our notation. Using (37) and (37'), and Eqs. (31a) to (31d) inclusive, for special values of the kernels, we may write:

$$\left. \begin{aligned} a(0, \{m\}) &= (z^m/m!) K_{0,0,m} \\ &= (z^m/m!) G_m/G_0, \\ a^*(\{m\}, 0) &= a(\{m\}, 0) = \delta(m, 0), \\ a^*(\{m\}, (i_s)) &= -z_s K_{m,0,s}^* + \delta(\{m\}, (i_s)). \end{aligned} \right\} (47)$$

Using these, the sum $\sum a(0, \{m\}) a^*(\{m\}, 0)$ has only the single term $G_0/G_0=1$ when $m \equiv 0$, so that Eq. (42) for the case $k \equiv 0$, $n \equiv 0$, is trivially satisfied. Similarly, all sums

$$\sum a(\{k\} \{m\}) a^*(\{m\}, 0)$$

contain no non-zero terms if $k > 0$, from the second of these equations, so that (42) for this case is also trivially satisfied.

The sum $\sum a(0, \{m\}) a^*(\{m\}, (i_s)) = 0$, leads to the equation:

$$\begin{aligned} -\frac{1}{G_0} \sum_{m \geq 0} \frac{z^m}{m!} \int \int \cdots \int G_m K_{m,0,s}^* d\{m\} \\ + \frac{G_s}{G_0} = 0. \end{aligned} \quad (48)$$

If, in this, one sets the special case that the functions with asterisks refer to infinite dilution, see Eqs. (21), (21') and (22), then $z \equiv z_a$, and

$$z^m G_m/G_0 = \rho^m F_m(\rho, T, \{m\}),$$

is the probability density that the set m of molecules will occur at the position $\{m\}$. The functions $K_{m,0,s}^*$ are now, from (30'),

$$K_{m,0,s}^* = (\sum \{\mu\}_m) (-)^{m-\mu} \frac{F_{\mu+s}^*(0, T, \{\{\mu\}_m + (i_s)\})}{F_\mu^*(0, T, \{\mu\}_m)},$$

where the distribution function at zero concen-

tration is:

$$F_\mu^*(0, T, \{\mu\}) = \exp - (U_\mu \{\mu\} / kT), \quad (49)$$

and U_μ is the potential energy of the μ molecules, if the system is classical.

Equation (48) now becomes,

$$\begin{aligned} (\rho_s/z_s) F_s(\rho, T, (i_s)) \\ = \sum_{m \geq 0} \frac{\rho^m}{m!} \int \int \cdots \int F_m(\rho, T, \{m\}) \\ \times \{ \exp [(-1/kT)(U_{\mu+s} \{\mu\} + (i_s)) \\ - U_\mu \{\mu\}] \} d\{\mu\}, \end{aligned} \quad (50)$$

as a general equation for any system, if U is understood to be defined by (49) when the system is non-classical, in which case it is not a potential energy.

If Eq. (50) is divided by V , and integrated over the coordinates $d(i_s)$, due to the normalization condition (19), one obtains ρ_s/z_s , the inverse of the activity coefficient, on the left-hand side.

Let us assume a more specialized case, and one that is particularly simple. We assume that there are no internal coordinates, or that they have been integrated out of the distribution functions at zero density so that the potential U_μ is a function of the centers of mass, averaged over the internal coordinates. We further consider a single component system, and one existing in the liquid state so that F_s is unity. If, now, it is legitimate to express U_μ as a sum of terms, u_{jk} , each dependent only on the coordinates of the pair of molecules, j and k , then if,

$$f_{ij} = [\exp - (u_{ij}/kT)] - 1, \quad (51)$$

we have that,

$$K_{m,0,s}^* = \prod_{j=1}^{j=m} f_{ij}. \quad (52)$$

The functions f_{ij} approach zero in value if the distance between the molecules i and j become large, since their mutual potential is then zero. Equation (50) now takes the form,

$$\begin{aligned} \frac{\rho}{z} = \sum_{m \geq 0} \frac{\rho^m}{m!} \int \int \cdots \int F_m(\rho, T, \{m\}) \\ \times \prod_{j=1}^{j=m} f_{ij} d\{m\}. \end{aligned} \quad (53)$$

The distribution functions F_m become zero if too many molecules are crowded into too small a space. The product of f_{ij} 's is zero unless *all* of the m molecules are within interacting distance of the molecule i . As m becomes large there are no positions of the coordinates for which the integrand is non-zero, so the sum converges, and, indeed, terms with $m > 13$ must be very small.

This equation is essentially a cell type equation in that one computes the activity, and therefore the free energy, by considering only the interactions of one molecule with those others that can approach it at any one time. The equation is exact in the form (50). It is not essentially different from that derived previously by the author with Montroll,³ although it is cast in an entirely different appearing form.

EQUATIONS BETWEEN THE KERNELS

To use Eq. (42) in the case of general values of k and n , and convert it to a direct summation of integrals of products of the kernels K and K^* is comparatively difficult. One runs into rather awkward summations, which then simplify with considerable labor. The simplest form of these equations can be found more readily by another method. However, we wish to emphasize that the equations derived in this section are actually another form of (42).

We use Eq. (23'), write it for a set $k+n$ of numbers, sum over μ , and divide and multiply each term in the sum by $G_{k+\mu}$, using, however, (23) for $G_{k+\mu}$ in the numerator:

$$\begin{aligned} G_{k+n}^* &= \sum_{\mu \geq 0} \frac{(-z)^\mu}{\mu!} \int \int \cdots \int_{\mathcal{V}} G_{k+n+\mu} d\{\mu\} \\ &= \sum_{\mu \geq 0} \frac{(-z)^\mu}{\mu!} \int \int \cdots \int_{\mathcal{V}} \frac{G_{k+n+\mu}}{G_{k+\mu}} \left[\sum_{\nu \geq 0} \frac{z^\nu}{\nu!} \int \int \cdots \int G_{k+\mu+\nu}^* d\{\nu\} \right] d\{\mu\} \\ &= \sum_{\mu \geq 0} \sum_{\nu \geq 0} \frac{z^{\nu+\mu}}{\nu! \mu!} (-)^\mu \int \int \cdots \int \frac{G_{k+n+\mu} G_{k+\mu+\nu}^*}{G_{k+\mu}} d\{\nu\} d\{\mu\}. \end{aligned}$$

In this equation we write $\nu + \mu = m$, and sum over all sets of numbers m . Since there are $m!/(\nu! \mu!)$ different subsets, $\{\mu\}_m$, for every value of the set of numbers m and μ , we may divide by this and sum over all $\{\mu\}_m$. One obtains,

$$G_{k+n}^* = \sum_{m \geq 0} \frac{(-z)^m}{m!} \int \int \cdots \int_{\mathcal{V}} G_{k+m}^* \left[(\sum \{\mu\}_m) (-)^{m-\mu} \frac{G_{k+\mu+n}}{G_{k+\mu}} \right] d\{m\},$$

or with Eq. (30),

$$G_{k+n}^* = \sum_{m \geq 0} \frac{(-z)^m}{m!} \int \int \cdots \int_{\mathcal{V}} G_{k+m}^* K_{m+k, k, n} d\{m\}. \quad (54)$$

If instead we start with (23), the equation,

$$G_{k+n} = \sum_{m \geq 0} \frac{z^m}{m!} \int \int \cdots \int G_{k+m} K_{m+k, k, n}^* d\{m\}, \quad (54')$$

may be obtained by the corresponding manipulations.

At first sight Eqs. (54) and (54') appear to be only complications of the relatively simple forms (23) and (23'), but the forms (54) and (54') have one enormous advantage, namely that the summations converge far more rapidly in these equations than in (23) and (23'). This superiority of convergence will be discussed in greater detail later, and is merely remarked here in passing.

³ J. E. Mayer and E. Montroll, J. Chem. Phys. 9, 2 (1941), Eq. (70).

We now use (54) to obtain an equation for $K_{k,0,m}^*$, using (30') defining this kernel as:

$$K_{k,0,n}^* = (\sum \{\kappa\}_k) (-)^{k-\kappa} G_{\kappa+n}^* / G_k^* = \sum_{m \geq 0} \frac{(-z)^m}{m!} \int \int \cdots \int (\sum \{\kappa\}_k) (-)^{k-\kappa} K_{\kappa, \kappa, m}^* K_{m+\kappa, \kappa, n} d\{m\}.$$

However from (30') we may write,

$$K_{\kappa, \kappa, m}^* = (\sum \{\lambda\}_{\kappa-\mu}) K_{\lambda+\mu, \mu, m}^*,$$

where $\mu = \{\mu\}_\kappa$ is any subset of κ , and from (30),

$$K_{m+\kappa, \kappa, n} = (\sum \{\mu\}_\kappa) K_{m+\mu, 0, n},$$

so that,

$$\begin{aligned} (\sum \{\kappa\}_k) (-)^{k-\kappa} K_{\kappa, \kappa, m}^* K_{m+\kappa, \kappa, n} &= (\sum \{\kappa\}_k \{\mu\}_\kappa \{\lambda\}_{\kappa-\mu}) (-)^{k-\kappa} K_{\lambda+\mu, \mu, m}^* K_{m+\mu, 0, n} \\ &= (\sum \{\mu\}_\kappa \{\lambda\}_{\kappa-\mu}) (-)^{k-\mu-\lambda} (\sum \{\kappa-\mu-\lambda\}_{\kappa-\lambda-\mu}) (-)^{\kappa-\mu-\lambda} K_{\lambda+\mu, \mu, m}^* K_{m+\mu, 0, n} \\ &= (\sum \{\mu\}_\kappa) K_{k, \mu, m}^* K_{m+\mu, 0, n}, \end{aligned}$$

where the last line follows from the fact that the summation in the brackets of the preceding expression is zero unless $\lambda+\mu=k$. One therefore has,

$$K_{k,0,n}^* = \sum \frac{(-z)^m}{m!} (\sum \{\kappa\}_k) \int \int \cdots \int K_{k, \kappa, m} K_{m+\kappa, 0, n} d\{m\}. \quad (55')$$

If, instead, (54') is used, one finds,

$$K_{k,0,n} = \sum_{m \geq 0} \frac{z^m}{m!} (\sum \{\kappa\}_k) \int \int \cdots \int K_{k, \kappa, m} K_{m+\kappa, 0, n}^* d\{m\}. \quad (55)$$

Now for fixed values of the coordinates $\{n\}$ the kernels $K_{k,0,n}^*$ and $K_{k,0,n}$ are functions of the coordinates $\{k\}$, symmetrical in permutations of the coordinates of identical molecules. It is seen that Eqs. (55) and (55') are identical to Eqs. (29) and (29') with $K_{k,0,n}^*$ replaces ψ_k^* and $K_{k,0,n}$ replacing ψ_k . That is, the functions $K_{k,0,n}$ and $K_{k,0,n}^*$ for any set of numbers n and any value of the coordinates $\{n\}$, regarded as functions of the coordinates $\{k\}$, form a suitable set ψ_k and the corresponding solutions ψ_k^* , respectively, to Eqs. (29) and (29') or (38) and (38').

THE CONVERGENCE OF THE EQUATIONS

Whether or not the sum in Eqs. (29) or (29') converge depend on the variation functions ψ_k and ψ_k^* . We shall assume that the functions ψ_k^* are of the type which one might actually wish to handle if one considers variations in the potential energy of the molecules, or variations in temperature. In particular we assume that ψ_k^* approaches zero if the coordinates of any pair of the molecules composing the set k are sufficiently distant in the three-dimensional space of their mass centers, and that this approach to zero is more rapid than r^{-2} , so that,

$$\lim_{V \rightarrow \infty} \left[V^{-1} \int \int \cdots \int \psi_k^* d\{k\} \right] = \text{finite}. \quad (56)$$

We shall also assume that the functions ψ_k approach zero in value as $k \rightarrow \infty$, or at least that the integral of Eq. (56) approaches zero as $k \rightarrow \infty$.

We shall show that the form of the Eq. (30) defining the kernels is such, that, if the functions ψ_k^* obey the conditions above, then if the kernels are formed at an activity for which the system can only exist in one phase, the Eq. (29) will converge and the functions ψ_k will also obey the above conditions. If, however, the kernels are formed at an activity for which two phases are stable no such convergence can be expected.

For such values of the activity set z that the system exists in a single phase, we may expect the distribution functions to show certain characteristics. These functions may be written

$F_n = \exp(-W_n/kT)$ where W_n is the potential of average force. We would expect W_n in single phase systems to have no terms corresponding to long range forces. That is, we expect that for two sets of molecules, k and m , if the distances, $r_{k,m}$, between all molecules of the set k and all of the set m are large, then $W_{k+n} = W_k + W_m$. This means that:

$$\lim_{r_{k,m} \rightarrow \infty} [F_{k+m}] = F_k F_m. \quad (57)$$

Let us assume that Eq. (57) applies, and that the difference $F_{k+m} - F_k F_m$ approaches zero more rapidly than $r_{k,m}^{-2}$, an assumption that corresponds to having all forces approach zero more rapidly than r^{-3} .

Now let us examine the kernels,

$$K_{k+n, n, m} = \left(\frac{\rho}{z}\right)^m (\sum \{\kappa\}_k) (-)^{k-\kappa} \frac{F_{\kappa+n+m}}{F_{\kappa+n}}, \quad (58)$$

which equation is equivalent to (30) when ρ and z refer to the concentration and activity set for the functions without asterisks, see Eq. (21). Suppose the distances, $r_{k, n+m}$, between all molecules of the set k , and all molecules of $n+m$ are large. Then from (57)

$$F_{\kappa+n+m} = F_\kappa F_{n+m}, \quad F_{\kappa+n} = F_\kappa F_n,$$

and

$$F_{\kappa+n+m}/F_{\kappa+n} = F_{n+m}/F_n.$$

But the sum $(\sum \{\kappa\}_k) (-)^{k-\kappa}$ is zero if $k > 0$, Eq. (15). It follows that,

$$\lim_{r_{k, n+m} \rightarrow \infty} [K_{k+n, n, m}] = 0, \quad k > 0, \quad (59)$$

and the approach to zero is more rapid than $r_{k, n+m}^{-2}$ according to our assumptions.

Let us now look at the product:

$$K_{k+n, n, m} \psi_{n+m}^* \quad (60)$$

which composes the integrand in the general term of the sum (29). If ψ_{n+m}^* approaches zero as any of the distances of the set $n+m$ becomes large, that is it obeys (56), then the integrand is zero unless all molecules of the set $n+m$ are close together. But if the set $n+m$ is far from the set k , then from (59) the kernel is zero, and the integrand is zero. Furthermore, the argument leading to Eq. (59) applies if *any one* of the molecules of the set k is far from all of the set

$n+m$. It follows that, within our assumptions, the integrand (60) is zero unless *all* of the molecules of the complete set $k+n+m$ are reasonably close together (within range of molecular forces one to the other) in the three-dimensional space of their centers of mass. It also follows, since we have assumed conditions leading to a sufficiently rapid approach to zero, that the integral of (60) over the coordinates $\{m\}$ leads to a finite result independent of the volume V over which the range of integration is extended.

If we also assume that $\psi_k^* \rightarrow 0$ as $k \rightarrow \infty$, then we have assured the convergence of (29) since only a finite number of terms have non-zero integrands, and these each converge upon integration. But we have also shown that, within our assumptions, each integrand is zero in (29) unless all the molecules of the set k are close together, so the ψ_k 's also obey the condition (56).

Now at such values of the activity set, z , that two phases can coexist in the system, Eq. (57) is not correct. For instance, in the absence of a gravitational field (which would make z a function of position in the system) the distribution function for the system would be:

$$\rho^n F_n = x \rho_a^n F_n^{(a)} + (1-x) \rho_b^n F_n^{(b)},$$

where ρ_a, ρ_b are the densities of the two phases, and $F_n^{(a)}$ and $F_n^{(b)}$ the distribution functions in the pure phases. The number x is the volume fraction of the system in phase a , and is variable at the given z . Functions constructed according to this equation do not obey (57) even if $F_n^{(a)}$ and $F_n^{(b)}$ do satisfy it singly. We may conclude that, in general, solutions to (29) are not obtainable at such values of the set z that two phases can coexist in the system at the activities at which the kernels are determined. However, satisfactory solutions should be obtainable as z is varied to approach the value of the transition, but the solutions will, in general, be different as this value is approached from the side of one phase or the other.

EIGENVALUES AS THE ACTIVITIES OF PHASE TRANSITION

The first terms in Eqs. (29) and (29') are those for which $m=0$. From (31c) and (31d) we see that only the term with $\kappa=k$ in those of $m=0$ has a non-zero kernel, and for this term the

kernel is unity. We may consequently write:

$$\psi_k = \psi_k^* + \sum_{m \geq 1} \frac{z^m}{m!} (\sum \{\kappa\}_k) \times \int \int \cdots \int_V K_{k, \kappa, m} \psi_{\kappa+m}^* d\{m\}, \quad (61)$$

$$\psi_k^* = \psi_k + \sum_{m \geq 1} \frac{(-z)^m}{m!} (\sum \{\kappa\}_k) \int \int \cdots \int_V K_{k, \kappa, m}^* \psi_{\kappa+m} d\{m\}, \quad (61')$$

as modified forms of (29) and (29'). The fact that the terms independent of z in the matrix element were $\delta(\{k\}\{m\})$ has already been noted in the discussion under Eq. (43), and Eq. (61) and (61') merely repeat this.

If we define a matrix $B_z(y)$ by the equation:

$$B_z(y) = A_z(y) - E, \quad (62)$$

so that, from (44),

$$\lim_{y \rightarrow 0} [B_z(y)] = 0, \quad (63)$$

then the transformation equation (45) becomes:

$$\Phi(z) = \Phi(z-y) + B_z(y)\Phi(z-y). \quad (64)$$

Let us write this for $z \equiv y$,

$$\Phi(z) = \Phi(0) + B_z(z)\Phi(0), \quad (65)$$

and the reciprocal equation,

$$\Phi(0) = \Phi(z) + B_0(-z)\Phi(z). \quad (65')$$

Suppose that there exists a value of the set z , namely z_γ , for which there is a solution, Φ_γ , to the homogeneous equation obtained by setting $\Phi(0) = 0$ in (65'), namely:

$$\Phi_\gamma + B_0(-z_\gamma)\Phi_\gamma = 0. \quad (66)$$

This would mean that there would exist a possible variation of the potentials of average force at the activity z_γ which would not be reflected in a change of the distribution functions at zero density. Without regard to the physical interpretation of this let us first examine its implication in our equations. With this Φ_γ for $\Phi(z_\gamma)$ in (65') we find $\Phi(0) = 0$. However, if we insert $\Phi(0) = 0$ in (65) we cannot obtain $\Phi(z_\gamma) = \Phi_\gamma \neq 0$ if the matrix Eqs. (61) (or (38)) converge.

Now at such values of the activity set z that

the system exists in a single phase only, one expects that the distribution functions be uniquely determined, and that no stable variations would exist that did not require alterations in the potentials at zero density. One also expects that no long range average forces be present, and that, therefore, as discussed in the preceding section, the matrix Eq. (61) would converge.

However, at values of the activity set for which two or more phases are present the situation is entirely altered. The distribution functions are *not* uniquely determined by the activity, since the relative fractions of the different phases vary at the constant activity. There *are*, then, variations possible which do not require changes in the potentials at zero density. But also the existence of more than one phase introduces a pseudo long range average force which completely spoils the convergence of the matrix Eq. (61), corresponding to (65).

We may therefore identify the values of z for which the homogeneous Eq. (66) has a solution with the values of the activity set for which more than one phase can coexist in the system.

We have previously¹ identified the occurrence of a phase transition with the divergence of a power series in the activity. That is, one could start with a system of any activity, say activity z , and compute the thermodynamic properties such as pressure, density, or the distribution functions, F_n , at some other activity, say $z+y$, in terms of the same property at z and a power series in y . If y were sufficiently small the power series converges, but if, as y increases, the activity $z+y$ approaches the activity, z_γ , at which a phase transition occurs, the power series diverges.

Now the kernel, reciprocal to that in a Fredholm type integral equation, can be calculated by an iterative process as a power series in the characteristic parameter, y , of the equation, provided the value of y is less than the first eigenvalue of the corresponding homogeneous equation. As y approaches this value, the series diverges.

One may regard Eq. (61') as an equation for unknown functions ψ_k , and attempt to solve it by using $\psi_k^* = \psi_k$ under the integral as a first approximation, and use the resulting equation as a

second approximation. By reiterating this process one obtains an equation involving integrations of products of the kernels K^* multiplied by ψ^* , and by comparison with (61) one obtains an equation for K as a sum of integrals of products of the kernels K^* . The sum is a power series in z . These equations, so obtained, can be transformed into the equations formerly obtained for the thermodynamic properties and distribution functions as a power series in z .

But the iterative process can only lead to a convergent series for those values of the parameter z which are less than the first eigenvalue of the corresponding homogeneous equation. The two methods of obtaining the phase transitions are thus formally equivalent.

THE SOLUTIONS OF THE HOMOGENEOUS EQUATIONS

It is possible to find the significance of the solutions of the homogeneous Eq. (66) at the values, z_γ , of the activity coefficient for which two phases coexist.

We know, from experience, that the solutions G_n , to Eq. (23), for $n > 0$, undergo discontinuous changes as z crosses the values at which phase transitions occur. It is possible to disentangle the mathematical reason for this, and to see that the value of m for the term of maximum value undergoes discontinuous transitions at these values of z . In general, then, there exist two values, $G_n^{(a)}$, and $G_n^{(b)}$, which the sum (23) approaches as z approaches z_γ , depending on whether the approach to the activity of the phase transition occurs from the activities for which phase (a) or phase (b) are stable. At $z = z_\gamma$ any value, $G_n = xG_n^{(a)} + (1-x)G_n^{(b)}$ for $0 \leq x \leq 1$ is a physically meaningful solution to (23), corresponding to having the volume fraction x of the system in the volume V in the form of phase (1). We might expect to use this for G_n in (24) and take derivatives with respect to x to determine the functions Ψ_n for which no change in G_n^* is required. This procedure bogs down in mathematical difficulties.

Let us instead turn to equations (55'). We again interpret the functions with asterisks to refer to infinite dilution. As z approaches z_γ from the two sides there are two solutions, $K_{m,0,n}^{(a)}$, and $K_{m,0,n}^{(b)}$, for every m and n , that satisfy (55') with

the same values of K^* . It follows that:

$$\sum_{m \geq 0} \frac{(-z)^m}{m!} (\sum \{ \kappa \}_k) \int \int \cdots \int_V K_{k,\kappa,m}^* \times [K_{m+\kappa,0,n}^{(a)} - K_{m+\kappa,0,n}^{(b)}] d\{m\} = 0. \quad (67)$$

The functions,

$$\psi_k(\gamma, \{n\}) = K_{k,0,n}^{(a)} - K_{k,0,n}^{(b)}, \quad (68)$$

and the sets;

$$\Phi_\gamma(\{n\}) = \psi_0(\gamma, \{n\}), \dots, \psi_k(\gamma, \{n\}), \quad (69)$$

for any $\{n\}$ are therefore solutions to the homogeneous Eq. (66) at the activity z_γ at which phases (1) and (2) can coexist in the system.

CONCLUSION

The essential results may be summarized as follows. One may define distribution functions, F_n , as being proportional to the probability density that a set, n , of molecules are found at the coordinate position $\{n\}$. The logarithms of these functions are $-W_n\{n\}/kT$, in which $W_n\{n\}$ is the potential of average force between the molecules at the position $\{n\}$. These potentials depend on the activity set z of the different molecular species present, and vary with z continuously from the true potential energy, at zero activity, but with discontinuities at the phase transitions.

The function, $W_n(z, \{n\})$ may be represented as a sum of terms, each depending on the coordinates, $\{\nu\}_n$, of a subset ν of molecules of the set n , summed over all subsets:

$$W_n = (\sum \{\nu\}_n) w_\nu(z, \{\nu\}_n). \quad (70)$$

At zero density, at least, one usually assumes that only the functions w_ν for $\nu \leq 2$, are non zero, corresponding to having the forces between molecules the sum of those between pairs only.

One considers a possible variation in the various functions, $w_k(z, \{k\})/kT$. A set, $\Phi(z)$, of functions, $\psi_0(z)$, $\psi_1(z, \{i\})$, \dots , $\psi_k(z, \{k\})$, \dots , may be defined by

$$\psi_k(z, \{k\}) = \delta[w_k(z, \{k\})/kT], \quad (71)$$

where $\delta(w_k/kT)$ is the variation in w_k/kT . This set of functions, depending on the activity parameter z , represents a self-consistent set of

variations of w_k/kT , of which the set at one particular activity, most naturally that at zero activity, may be regarded as arbitrary.

In order to compute the set $\Phi(z)$, from a knowledge of the functions at some other activity, say $\Phi(z-y)$, a transformation matrix $A_z(y)$ may be employed which transforms $\Phi(z-y)$ into $\Phi(z)$. The elements, $a_z(y, \{k\}, \{m\})$, of this matrix, given by Eqs. (43), (30), and (21), consist of combinations of the distribution functions at the activity z , to which the transformation is made, multiplied by powers of y , the difference of activities. The limit of the transformation matrix, as the activity difference y becomes zero, is, of course, the unit matrix. The matrix multiplication involves both summation over all sets of molecules, and integration over the coordinates of each set.

The product of the two matrices $A_z(y)$ and $A_{z-y}(-y)$ is the unit matrix. This is a special case of the more general relation that

$$A_z(y)A_{z+x}(x) = A_{z+x}(x+y).$$

These matrix equations are equivalent to a set of sums of integral equations, (55) and (55'), relating the distribution functions at different activities of the system. The equations are convergent if the activities are such that only single

phases are present in the system, even if the activity pairs are those at which different phases are stable.

One member of these equations, (53), permits a computation of the activity or free energy of the system in terms of the interactions of one molecule with its neighbors in the system.

If z is an activity for which the system exists in a single phase only, and z_γ an activity at which two phases, (*a*), and (*b*), can coexist, then there are function sets Φ_γ characteristic of z_γ which satisfy the transformation equation

$$A_z(z-z_\gamma)\Phi_\gamma = 0.$$

In particular if $z=0$, $A_0(-z_\gamma)\Phi_\gamma=0$, Eqs. (66) and (62), show that there exist a set, Φ_γ , of variations of the potential of average force in the two phase system which can occur without variations in the temperature or potentials between the molecules at infinite dilution. The transformation matrix, $A_{z_\gamma}(y)$, to this activity, z_γ , of the phase transition, has elements such that the summations and integrations diverge. The solutions, Φ_γ , to the homogeneous equation, $A_0(-z_\gamma)\Phi_\gamma=0$, are differences of certain combinations of the distribution functions of the two phases (*a*) and (*b*) which are at equilibrium at the activity z_γ , Eqs. (68), (30), and (21).