

The Statistical Mechanics of Condensing Systems. I*

JOSEPH E. MAYER, *Johns Hopkins University, Baltimore, Maryland*

(Received October 21, 1936)

It is shown that for a system composed of N identical molecules with mutual potential energy, the assumption that the total potential energy can be expressed as the sum of that between pairs of molecules allows the derivation of simple, accurate formal equations for the thermodynamic properties of the system. Under certain conditions, generally fulfilled at low temperatures, the equations predict a region where the pressure and Gibbs free energy are independent of volume, the characteristic of condensing systems. The equations permit calculation of the Gibbs free energy of the liquid in equilibrium with the vapor and all the properties of the saturated vapor, but not the volume or volume dependence of the condensed phase.

WE seek a theoretical equation of state for a system composed of N identical molecules. This can be done by calculating A , the work function, or Helmholtz free energy, a function of volume, V , and temperature, T , from Q , variously called the partition function, sum of states, or phase integral. The first partial derivative of A with respect to V gives the negative of the pressure, P . The equations are

$$A = -kT \ln Q, \quad (1)$$

$$P = -(\partial A / \partial V)_T, \quad (2)$$

$$Q = \frac{1}{N! h^f} \int \cdots \int e^{-H(p, q) / kT} dp_1 \cdots dp_f dq_1 \cdots dq_f. \quad (3)$$

In Eq. (3) f is the number of degrees of freedom of the complete system, and $H(p_1, \cdots, p_f, q_1, \cdots, q_f)$ is the Hamiltonian, or energy expressed as a function of the f momenta and f coordinates of the complete system. The integration extends over the complete phase space. The division by $N!$ times the f power of h , Planck's constant, leads to an absolute value of A consistent with quantum-mechanical equations. The Eq. (3) for Q holds only for systems for which the classical mechanical approximations are valid.

For a gas containing internal degrees of freedom Q may be expressed as a product, and A as a sum, of the contributions due to the cartesian coordinates of the center of gravity and those due to the internal coordinates of the molecule. For the multiplicative part of Q due to internal motion the form (3) can usually not be employed but the more general quantum-mechanical sum

over quantum states must be used. We shall be interested only in the factor of Q due to the $3N$ translational coordinates and momenta. Furthermore, we shall restrict ourselves to cases in which this part of the Hamiltonian can be written as

$$H(p, q) = \sum_{k=1}^{3N} \frac{1}{2m} p_k^2 + \sum_{i=1}^{i=N} \sum_{j=1}^{j=N-1} v_{ij}. \quad (4)$$

The expression for the part dependent on the momenta, the p 's, is quite general. The other part assumes that the total potential energy can be expressed as a sum of terms each due to the mutual potential energy of a pair of molecules, (i, j) , which is a function only of the differences of the coordinates of these molecules. This assumption would be unjustifiable in a gas composed of atoms or radicals which had a tendency to form valence bonds with each other (as monatomic hydrogen gas), but is presumably valid for all gases in which what are normally referred to as van der Waals forces only, occur. The v_{ij} 's are assumed to be functions of the coordinates of i and j alone. It is not necessary that they be functions of the coordinates of the centers of gravity alone, the mutual orientation angles may play a role, as they certainly do in all diatomic molecules. In the second paper of this series, in which numerical evaluations are made we shall assume spherically symmetrical molecules, essentially noble gases, but this assumption is nowhere needed in the more general discussion of this paper. Presumably the results of this paper may be considered to be applicable to all systems composed of chemically saturated molecules.

If we use the symbol $d\tau_i$ for the volume element of the i th particle (if spherically symmetrical

* Contribution from the Chemical Laboratory of The Johns Hopkins University.

atoms alone are considered $d\tau_i \equiv dx_i dy_i dz_i$) we can write

$$Q = \frac{1}{N! h^{3N}} \left\{ \int_{-\infty}^{+\infty} e^{-p^2/2mkT} dp \right\}^{3N} Q_\tau \quad (5)$$

$$= \left(\frac{2\pi mkT}{h^2} \right)^{3N} \frac{Q_\tau}{N!},$$

with

$$Q_\tau = \int \left\{ \prod_{i>j}^{N(N-1)/2 \text{ terms}} e^{-v_{ij}/kT} \right\} d\tau_1 \cdots d\tau_N. \quad (6)$$

In the event that if $v_{ij} \equiv 0$, Q_τ becomes equal to V^N and the complete equation is that for a perfect gas.

By a trick which is commonly employed Q_τ may be expanded into a sum. The trick is to write

$$e^{-v_{ij}/kT} = 1 + e^{-v_{ij}/kT} - 1 = 1 + f_{ij}, \quad (7)$$

$$f_{ij} = e^{-v_{ij}/kT} - 1, \quad (8)$$

$$Q_\tau = \int \cdots \int \left[1 + \sum_{i=j+1}^N \sum_{j=1}^{N-1} f_{ij} + \sum_{i'>j'} \sum_i f_{ij} f_{i'j'} + \cdots \right] d\tau_1 \cdots d\tau_N. \quad (9)$$

This trick makes possible an easy numerical evaluation of a first-order approximation to Q_τ .¹ However, although an entirely arbitrary mathematical decomposition of Q_τ into a sum of terms, it also aids in a qualitative discussion of the phenomena of condensation into liquid or crystalline phases.

Consider a general term of the sum in which P pairs f_{ij} occur, and L ($L/2 \leq P \leq L(L-1)/2$) different indices (molecules) occur in these P pairs. (Whereas no single pair, (ij) , may occur more than once in a single term, any one index i may occur frequently, paired with different indices j' and j'' etc.) The L indices may be grouped into "clusters," such that all the indices occurring in one cluster are directly or indirectly connected with each other through a series of pairs, but no index occurring in one cluster occurs paired with an index occurring in any other

¹ The usual method of treating the first term of the sum of Eq. (9) as small compared to unity, but as the only important term is unjustifiable. It is neither small, nor the most important term. A satisfactory treatment is given in Fowler's book *Statistical Mechanics* (Cambridge University Press, 1929), p. 168.

cluster. Now let us collect all these terms together in which the same identical indices occur grouped together in the same clusters, and call the sum of these terms a constituent T of the sum. The significance of this particular grouping is the following. Suppose the indices 1 to 10 inclusive are connected together in one cluster. Integration of any or all of these terms contributes nothing in that part of the phase space where any of the molecules numbered 1 to 10 are far removed from any other of the cluster, since the function f_{ij} becomes zero for large values of its variable, r_{ij} . The complete value of the term can be obtained by limiting our integration to that part of the phase space where the molecules 1 to 10 are "reasonably" close to each other. This is connected with the fact that in a system of N molecules of which the stable configuration corresponds to M molecules in the liquid phase and $N-M$ in the gas phase, integration of the phase integral over that part of the phase space in which M molecules are "near" to each other contributes practically the whole of the phase integral, integration over the remainder giving only the vanishingly small contribution of the unstable supersaturated vapor to the complete free energy.

Integration over the volume element of any of the particles not occurring in the term contributes exactly V as a factor to the integral. Integration over the volume elements of $l-1$ indices of a cluster of l indices gives a value independent of the volume V , provided only that V is reasonably large compared to the "size" of the cluster. Integration over the l th index of the cluster contributes V (as a factor) to the integral. We wish now to define b_l as $1/l!$ times the integral over $l-1$ of the l indices occurring in the sum of all the terms which can be written as products of at least $l-1$ of the $l(l-1)/2$ functions f_{ij} between l definitely selected indices, consistent with the condition that the product correspond to a single cluster.

$$b_l = \frac{1}{l!} \int \cdots \int \sum_{l \leq i > j} [\prod f_{ij}] d\tau_1 \cdots d\tau_{l-1}. \quad (10)$$

(Sum over all products consistent with a single cluster.)

The condition that the product is consistent with the existence of a single cluster means that there exists no single index or group of indices that is

not at least indirectly connected to all the other indices, so that the integral (10) is independent of the volume of the system.

A single constituent T , as it has been defined, is characterized by having m_2 clusters, each of two definitely numbered particles; m_3 clusters each of three numbered particles; \dots ; m_l clusters each of l numbered particles; with $M = \sum m_l$, the total number of clusters, and $L = \sum l m_l$ the total number of particles involved in clusters. The additive contribution of this constituent to Q_τ will be.

$$T = \prod_{l \geq 2} l! b_l V^{N-L+M}. \quad (11)$$

The numerical value of the integrals b_l depend only on l , the number of particles in the cluster, and not on the particular particles involved. Therefore the same contribution T will occur several times, arising from all the terms characterized by the same set of numbers of the different size clusters $t \equiv (m_2, m_3, \dots, m_l, \dots)$ but differing from each other by the molecules involved. The sum of the contributions of all the constituents of the type t we shall call a term T_t , its numerical value will be

$$T_t = \frac{N!}{(N-L)! \prod_l m_l!} \\ = \frac{N!}{(N-L)! \prod_l m_l!} \prod_{l \geq 2} b_l^{m_l} V^{N-L+M}, \quad (12)$$

and the total phase integral Q_τ will be the sum of these terms,²

$$Q_\tau = \sum_t T_t. \quad (13)$$

By this grouping the number of terms P_N occurring in the sum Q has shrunk considerably, it is, namely, the "partitio numerorum" of N , the number of ways that N can be expressed as a sum of numbers irrespective of the order of writ-

ing the numbers in the sum. This follows from the fact that N is the sum of $(N-L)1$'s, plus m_2 2's + \dots + m_l l 's + \dots . The logarithm of P_N is known³ to approach $\Pi(2N/3)^{\frac{1}{2}}$.

Were all the terms of the sum (13) positive we could call the largest single term of the sum T_{t^*} , and write

$$\ln T_{t^*} \leq \ln Q_\tau \leq \ln T_{t^*} + \Pi(2N/3)^{\frac{1}{2}}, \quad (14)$$

and since $\Pi(2N/3)^{\frac{1}{2}}$ is negligible compared to $\ln T_{t^*}$ which increases linearly with N we may write

$$\ln Q_\tau = \ln T_{t^*}. \quad (15)$$

We shall not wish to limit ourselves to the case that all the terms are positive. Nevertheless the derivation of the equation for $\ln Q_\tau$ on this assumption of equating it to the logarithm of the largest single term is so simple, and leads to such valuable intuitive results that we shall follow it here. In the appendix it is shown that a more careful derivation of the value of Q_τ independent of the assumption of only positive terms leads to identical equations.

We will find it convenient to introduce the Stirling approximation for the factorials in Eq. (12) and to introduce some new symbols, for quantities which do not depend on N , the total number of particles,

$$\mu_l = m_l/N, \quad (16)$$

$$\lambda = L/N = \sum_{l \geq 2} l \mu_l, \quad (17)$$

$$\mu = M/N = \sum_{l \geq 2} \mu_l, \quad (18)$$

$$v = V/N, \quad (19)$$

in which case we can rewrite Eq. (12) as

$$\frac{T_t}{N!} = \left\{ \frac{v^{1-\lambda+\mu} e^{1-\lambda+\mu}}{(1-\lambda)^{(1-\lambda)}} \prod_{l \geq 2} \left(\frac{b_l}{\mu_l} \right)^{\mu_l} \right\}^N. \quad (20)$$

We define $\tau(\mu_2, \dots, \mu_l, \dots, b_2, \dots, b_l, v) = (1/N) \ln (T_t/N!)$

$$= \sum_{l \geq 2} \mu_l [\ln b_l - \ln \mu_l - (l-1)(\ln v + 1)] - (1-\lambda) \ln (1-\lambda) + \ln v + 1, \quad (21)$$

and also define the convenient quantity q_τ ,

$$q_\tau = (1/N) \ln (Q_\tau/N!) = \tau(\mu_2^*, \dots, \mu_l^*, \dots, b_2, \dots, v) \quad (22)$$

² Up to about this point the treatment is not original; identical equations are derived, for instance, by Ursell, Proc. Camb. Phil. Soc. **23**, 685 (1927).

³ Hardy and Ramanujan, Proc. London Math. Soc. **16**, 130 (1917).

in which the $\mu_i^* = \mu_i$ (maximum), are determined by the equations

$$\partial \tau / \partial \mu_i = 0 \text{ (at all } \mu_i = \mu_i^*) = \ln b_i - \ln \mu_i^* - (l-1) \ln v + l \ln (1-\lambda^*), \quad (23)$$

with

$$\lambda^* = \sum_{l \geq 2} l \mu_l^*. \quad (24)$$

Then

$$\mu_i^* = b_i (1-\lambda^*)^l / v^{l-1}, \quad (25)$$

and

$$q_\tau = 1 - \lambda^* + \mu^* - \ln (1-\lambda^*) + \ln v, \quad (26)$$

with,

$$\mu^* = \sum_{l \geq 2} \mu_l^*. \quad (27)$$

Using Eq. (22) we find, for the derivative of q_τ with respect to the logarithm of v ,

$$v(\partial q_\tau / \partial v) = v(\partial \tau / \partial v)_{\mu_i = \mu_i^*} + \sum_l (\partial \tau / \partial \mu_l)_{\mu_l = \mu_l^*} (\partial \mu_l^* / \partial v), \quad (28)$$

but since $\partial \tau / \partial \mu_i = 0$ at $\mu_i = \mu_i^*$.

$$v(\partial q_\tau / \partial v) = v(\partial \tau / \partial v)_{\mu_i = \mu_i^*} = 1 - \lambda^* + \mu^*. \quad (29)$$

For the second derivative one obtains

$$v^2(\partial^2 q_\tau / \partial v^2) = -[1 - \lambda^* + \mu^* + v(\partial \lambda^* / \partial v) - v(\partial \mu^* / \partial v)]. \quad (30)$$

If now both sides of Eq. (25) are differentiated with respect to $\ln v$, multiplied by l , or by unity, and summed over l .

$$\begin{aligned} v(\partial \lambda^* / \partial v) &= \sum_l l v(\partial \mu_l^* / \partial v) = -\sum_l l^2 \mu_l^* - l \mu_l^* + [v/(1-\lambda^*)](\partial \lambda^* / \partial v) l^2 \mu_l^* \\ &= -\{h^* - \lambda^* + [h^*/(1-\lambda^*)](\partial \lambda^* / \partial v)\}, \end{aligned} \quad (31)$$

with

$$h^* = \sum_l l^2 \mu_l^*, \quad (32)$$

$$\text{from which } v(\partial \lambda^* / \partial v) = -(1-\lambda^*)(h^* - \lambda^*) / (1 + h^* - \lambda^*). \quad (33)$$

$$\begin{aligned} \text{Also } v(\partial \mu^* / \partial v) &= \sum_l v(\partial \mu_l^* / \partial v) = -\sum_l l \mu_l^* - \mu_l^* + [v/(1-\lambda^*)](\partial \lambda^* / \partial v) l \mu_l^* \\ &= -\lambda^* + \mu^* - [\lambda^*/(1-\lambda^*)]v(\partial \lambda^* / \partial v) \\ &= -(\lambda^* - \mu^* - \mu^*(h^* - \lambda^*) / (1 + h^* - \lambda^*)). \end{aligned} \quad (34)$$

Substitution of (33) and (34) in (30) leads to

$$v^2(\partial^2 q_\tau / \partial v^2) = -(1 - h^* - \lambda^*)^{-1}. \quad (35)$$

Returning now to Eqs. (1), (2), (5) and (22); and using (26), (29) and (35) we can write, for one mole of gas.

$$A = RT[\ln (h^2 / (2\pi m k T))^{3/2} (N_0 / V e) + \lambda^* - \mu^* + \ln (1-\lambda^*)], \quad (36)$$

$$P = (RT/V)(1 - \lambda^* + \mu^*), \quad (37)$$

$$(\partial P / \partial V)_T = -(RT/V^2)[1/(1 + h^* - \lambda^*)], \quad (38)$$

$$((\partial \ln P) / (\partial \ln V))_T = (V/P)(\partial P / \partial V)_T = -1/((1 - \lambda^* + \mu^*)(1 + h^* - \lambda^*)). \quad (39)$$

The Gibb's free energy F is $A + PV$, adding V times Eq. (37) to (36) after eliminating V from (36) by means of (37), one obtains

$$F = RT \left\{ \ln \left(\frac{h^2}{2\pi m k T} \right)^{3/2} \frac{P}{kT} - \ln \left(1 + \frac{\mu^*}{1 - \lambda^*} \right) \right\}. \quad (40)$$

Substitution of (37) for $v = V/N$ in (25) leads to

$$\mu_l^* = \frac{b_l(1-\lambda^*)^l}{v^{l-1}} = \frac{b_l(1-\lambda^*)^l P^{l-1}}{(kT)^{l-1}(1-\lambda^*+\mu^*)^{l-1}}. \quad (41)$$

Between h^* , λ^* and μ^* the relationship holds

$$h^* = \sum_{l \geq 2} l^2 \mu_l^* > \lambda^* = \sum_{l \geq 2} l \mu_l^* > \mu^* = \sum_{l \geq 2} \mu_l^*, \quad \text{and also} \quad \lambda^* \leq 1. \quad (42)$$

With the definition of b_l , Eq. (10) the Eqs. (36) to (42) form a perfectly general and sufficient set from which the thermodynamical properties of any pure substances could, in principle, be calculated, provided: firstly, that the condition of Eq. (4) that the total potential energy be expressible as a sum of the potential between pairs of molecules be fulfilled; and secondly, that the volume of the system be greater than that of the condensed phases. This second requirement is needed because of the use of the condition that b_l be independent of the volume. Were the total system restricted to a volume comparable with the "natural" size of the cluster⁴ this condition would not be fulfilled. The equations hold only for the condensed phases in equilibrium with their vapor, and cannot be used for the condensed phases under greater external pressure. Such cases might, however, be handled by the integral inclusion into the system of molecules of a second kind (an inert gas) with appropriate potentials between pairs of the two kinds of molecules.

The differences between the values of A , P , $(\partial P/\partial V)_T$ and F , in Eqs. (36) to (40), and the values of these quantities for a perfect gas, are all simple functions of the three quantities h^* , λ^* and μ^* . The results of the appendix show that the Eqs. (41) and (42) can be used for these quantities even if any of the b_l 's have a value less than zero. In this event it is difficult to find a simple physical interpretation for these quantities. If all the b_l 's happen to be positive, as they will at low temperatures (below the critical point), their

physical significance is easy to see. λ^* is the (most probable) fraction of the material existing in clusters, that is, it is the fraction of the material, in excess of that expected from a random space distribution, which is spacially concentrated so that the molecules are close to each other.

μ^* is the number of these clusters divided by the total number of molecules, and h^* the product, number of molecules per cluster times fraction of material in the clusters, summed over all clusters. Perhaps $\lambda^* - \mu^*$ is of more significance than either λ^* or μ^* alone, it is the fraction of material which has been constrained to a dependent motion, so that $1 - \lambda^* + \mu^*$ may be regarded as the number of independent entities in the system divided by the total number of molecules. Similarly $h^* - \lambda^*$ is the number of constrained molecules per cluster (since one, so to speak, is free) multiplied by the fraction of material in the clusters, summed over all clusters. The ratio which occurs in the expression for F is the ratio of the number of clusters to the number of completely independent molecules. It appears that if any of the b_l 's are negative these quantities are to be interpreted in the opposite sense, that is λ^* as the fraction of the material which is not in clusters of size l compared to a certain amount which would be expected from considerations of random space orientation.

The phenomenon of condensation is easily explained by means of these equations. For small values of l the values of b_l can be individually calculated, or at least estimated. For very large values of l , $\ln b_l$ becomes asymptotically equal to $(l-1) \ln b_0$, in which b_0 is a constant, dependent on the temperature but independent of l or v , whose value can, in some cases at least, be estimated. The value of b_l for any value of l can always, then, be written as $b_l = b_0^{l-1}/f(l)$ in which $\ln f(l) \ll l-1$ for large values of l .

⁴ Integration over $l-1$ volume elements of a cluster of l particles leads to b_l independent of the volume provided the integrand product, (Πf_{ij}) , is zero before the boundary of the vessel is reached. Integration over the l th element leads to something like $V - v_l$ where v_l is the "natural" volume of a cluster of l particles. This correction, however, is entirely negligible since if V is greater than the volume of the condensed phase, which is about the natural volume of a cluster of N particles, then $v_l \ll V$ except for a very few (few compared with N) of the largest clusters. We are really interested in $(1/N) \ln Q_r$, and an error in Q_r of a good many fair size factors can be safely neglected.

Now from Eq. (41), using this form for b_l , the equation determining λ^* can be written in the form

$$\frac{\lambda^*}{1-\lambda^*} = \sum_{l=2}^{l=N} \frac{l}{f(l)} \left\{ \frac{b_0(1-\lambda^*)}{v} \right\}^{l-1}. \quad (43)$$

This equation, with b_0 and all $f(l)$'s positive, has obviously a solution with $0 \leq \lambda^*/(1-\lambda^*) \leq +\infty$, or $0 \leq \lambda^* \leq 1$, for all positive values of v . We shall define as v_s that value of v for which $b_0(1-\lambda^*)/v$ becomes exactly equal to unity. At $v=v_s$ from (43) $\lambda^*/(1-\lambda^*) = \sum l/f(l)$, and since the number of terms is finite this sum will have a finite, although possibly very large, value.

Anticipating the results of the following article, we find that, at low temperatures at least, $l/f(l)$ decreases with increasing l more rapidly than $l^{-\frac{1}{2}}$, so that the sum of $l/f(l)$ which we shall call σ has a relatively small value. Under these conditions, at $v=v_s$, the value of λ^* , which we shall call λ_s^* is appreciably smaller than unity.

For values of v equal to, or smaller than v_s the quantities μ_i^* and $l\mu_i^*$ decrease with increasing values of l . However, if v becomes even slightly smaller than v_s , so that $b_0(1-\lambda^*)/v$ becomes even very slightly larger than unity, say equal to $1+\epsilon$, the last terms in the sum (43) tend to become enormous. If $\epsilon = (1/N)[\ln(f(N)/N) + 23]$ (for $N=10^{23}$) the last term alone would be 10^{10} and $1-\lambda^* = 10^{-10}$. Now $\ln(f(N)/N)$ is a number very much smaller than N , so that we can say that for values of λ^* between $\sigma/(1+\sigma)$ and unity, $b_0(1-\lambda^*)/v$ is equal to unity and $(1-\lambda^*)/v$ remains constant. In this range the very large clusters, corresponding to the condensed phase, appear with increasing probability as v decreases.

Now the additive contribution μ_i^* of the large clusters to μ^* , as can be seen from the fact that we must always have μ_i^* less than $1/l$, is negligible. For small values of l we can say that $[(1-\lambda^*)/v]^l$ is constant (although not for $l \geq 10^{23}$) so that, from Eq. (41), for $l \ll N$, μ_i^* and therefore μ^* is proportional to v . With both μ^* and $1-\lambda^*$ proportional to v we see from Eq. (37) that P , and from (40) that F remain constant during the condensation process. h^* very rapidly becomes large compared to unity and $\partial P/\partial V$ becomes zero, as of course must be the case if P is to be constant.

The volume of condensation, that is, the

volume of the saturated vapor per molecule is v_s , determined by the condition that $b_0(1-\lambda^*)/v = 1$ when $\lambda_s^*/(1-\lambda_s^*) = \sum l/f(l)$. Indicating all values corresponding to the saturated vapor by a subscript s , and defining the two sums

$$\sigma = \sum_{l=2} l/f(l) \quad (44)$$

with $f(l)$ and b_0 defined by

$$f(l) = b_0^{l-1}/b_l; \quad (l-1) \ln b_0 = \ln b_l (l \rightarrow \infty) \quad (45)$$

and

$$\phi = \sum_{l=2} 1/f(l), \quad (46)$$

we have for λ_s^* and v_s the equations

$$\lambda_s^* = \sigma/(1+\sigma); \quad 1-\lambda_s^* = (1+\sigma)^{-1}, \quad (47)$$

$$v_s = b_0(1-\lambda_s^*) = b_0/(1+\sigma). \quad (48)$$

Substitution of these values in (41) leads to

$$\mu_s^* = \phi/(1+\sigma). \quad (49)$$

Using the above values in Eqs. (36), (37) and (40), one obtains, for one mole of the saturated vapor.

$$A_s = RT \left[\ln \left(\frac{h^2}{2\pi m k T} \right)^{\frac{1}{2}} \frac{1}{e} - \ln b_0 + \frac{\sigma - \phi}{1 + \sigma} \right]. \quad (50)$$

$$P_s = kT((1+\phi)/b_0), \quad (51)$$

$$(PV)_s = RT((1+\phi)/(1+\sigma)), \quad (52)$$

$$F_s = F_{liq} = RT[\ln(h^2/2\pi m k T)^{\frac{1}{2}} - \ln b_0]. \quad (53)$$

In Eq. (53), F_s , the Gibb's free energy of the saturated vapor is equal to that of the liquid (or solid) in equilibrium with it. For other conditions of pressure our equations tell us nothing about the thermodynamic properties of the liquid. Indeed, in the discussion of the condensation process it appeared, according to our equations, that $(1-\lambda^*)/v$, μ^*/v , and therefore P and F remain constant down to zero volume. This is due to the oft reiterated fact that we have assumed b_l to have a value independent of the volume. There is nothing in our equations to show us the volume of the liquid.

One can, however, calculate $\partial P/\partial T$ for the liquid vapor equilibrium, and, under the assumption that the volume of the liquid is negligibly small compared with that of the saturated vapor, from this the value of ΔH and ΔS for the condensation process. One obtains, for one mole,

$$\Delta H = T \Delta V \frac{\partial P}{\partial T} = T N v_s \frac{\partial P}{\partial T}$$

$$= \frac{RT}{1+\sigma} \left[(1+\phi) \left(1 - \frac{\partial \ln b_0}{\partial \ln T} \right) + \phi \frac{\partial \ln \phi}{\partial \ln T} \right], \quad (54)$$

$$\Delta S = \Delta H/T$$

$$= \frac{R}{1+\sigma} \left[(1+\phi) \left(1 - \frac{\partial \ln b_0}{\partial \ln T} \right) + \phi \frac{\partial \ln \phi}{\partial \ln T} \right]. \quad (55)$$

The above equations are, of course, only approximate, due to the neglect of the volume of the liquid. At low temperatures they become asymptotically exact.

Eq. (48) enables us to calculate the volume of the saturated vapor, v_s , provided b_0 can be calculated, and provided the sum σ converges rapidly enough to allow it to be evaluated. This is actually the case for temperatures somewhat below the critical point. Such a value of v_s will presumably correspond to the experimental value of the volume per molecule of the saturated vapor provided it is larger than v_l , the volume per molecule of the liquid at the same temperature and pressure. This is obviously not the case at the critical point. We cannot expect the equations of this article, then, without further extension, to give us correct values at the critical point. The behavior of the system in the neighborhood of this temperature will be discussed in a later paper.

In the following paper it will be shown that b_0 , σ and ϕ can be estimated, and that the observable values of v_s , $(PV)_s$ and P_s so calculated are in reasonable agreement with experimental values, at least over a short temperature range.

APPENDIX.⁵

We wish to calculate the function $Q_\tau/N!$ defined by Eqs. (13) and (12) of the text,

$$\frac{Q_\tau}{N!} = \sum_{m_l=0}^{\sum m_l=N} \frac{\prod_i b_i^{m_i} V^{N-L+M}}{(N-L)! \prod_i m_i!}. \quad (1)$$

We define $v = V/N$, and $B_l = b_l v$,

$$\frac{Q_\tau}{N!} = \sum_{m_l=0}^{\sum m_l=N} \frac{\prod_i B_i^{m_i} v^{N-L+M}}{(N-L)! \prod_i m_i!} \quad (2)$$

and notice that

⁵ The treatment here was suggested by that of Fowler (reference 1), which in turn apparently originated from Ursell (reference 2). The discussion in Fowler's book is more complete than given here.

$$\frac{\partial}{\partial B_k} \left(\frac{Q_\tau}{N!} \right) = \frac{1}{N^{k-1}} \left(\frac{\partial}{\partial v} \right)_k \left(\frac{Q_\tau}{N!} \right). \quad (3)$$

If now we define

$$q = \frac{1}{N} \ln \frac{Q_\tau}{N!}, \quad (4)$$

then

$$\frac{\partial}{\partial B_k} \left(\frac{Q_\tau}{N!} \right) = \frac{Q_\tau}{N!} N \frac{\partial q}{\partial B_k} \quad (5)$$

$$\text{and} \quad \left(\frac{\partial}{\partial v} \right)^k \left(\frac{Q_\tau}{N!} \right) = \frac{Q_\tau}{N!} N^k \left(\frac{\partial q}{\partial v} \right)^k \left(1 + \frac{1}{N} \times \dots + \dots \right) \quad (6)$$

in which we can neglect the terms divided by N . Combining (5), (6) and (3) we obtain

$$(\partial q / \partial B_k)_{v, B_l} = (\partial q / \partial v)_k B_l. \quad (7)$$

Now independently of all this we can write

$$\frac{Q_\tau}{N!} = v^N f(B_2/v^2, \dots, B_l/v^l, \dots), \quad (8)$$

from which we can derive that

$$v(\partial q / \partial v)_{B_l} = [1 - \sum l B_l (\partial q / \partial B_l)_{v, B_m}], \quad (9)$$

and substitution of this in (7) leads to

$$(\partial q / \partial B_k)_{v, B_l} = [1 - \sum l B_l (\partial q / \partial B_l)_{v, B_m}]^k v^{-k}. \quad (10)$$

We now reintroduce our old variables $b_l = B_l/v$, so that

$$(\partial q / \partial B_k)_{v, B_l} = (\partial q / \partial b_k)_{v, b_l/v}, \quad (11)$$

$$(\partial q / \partial v)_{B_l} = (\partial q / \partial v)_{b_l} - v^{-1} \sum l b_l (\partial q / \partial b_l)_{v, b_m}. \quad (12)$$

Eq. (7) now becomes

$$\frac{1}{v} \frac{\partial q}{\partial b_k} = \left[\frac{\partial q}{\partial v} - \frac{1}{v} \sum_{l \geq 2} b_l \frac{\partial q}{\partial b_l} \right]^k, \quad (13)$$

in which case we can now safely drop the subscript indications of what is kept constant during the partial differentiation, and (10) becomes

$$\frac{1}{v} \frac{\partial q}{\partial b_k} = \frac{1}{v} \left[1 - \sum_{l \geq 2} l b_l \frac{\partial q}{\partial b_l} \right]^k. \quad (14)$$

Equating (13) and (14) and taking the k th root,

$$\frac{\partial q}{\partial v} = \frac{1}{v} \left[1 - \sum_{l \geq 2} (l-1) b_l \frac{\partial q}{\partial b_l} \right]. \quad (15)$$

We now define

$$\mu_l^* = b_l (\partial q / \partial b_l), \quad (16)$$

$$\mu^* = \sum_{l \geq 2} l \mu_l^* \quad (17)$$

$$\lambda^* = \sum l \mu_l^*, \quad (18)$$

in which case (14) becomes

$$\mu_l^* = (b_l (1 - \lambda^*)^l) / v^{l-1}, \quad (19)$$

$$\text{and (15)} \quad v(\partial q / \partial v) = (1 - \lambda^* + \mu^*). \quad (20)$$

Eqs. (17), (18) and (19) are identical with (27), (24) and (25) of the text, respectively, and Eq. (20) is identical (29) of the text. In the above derivation no use was made of any assumption that the b 's were positive quantities. The above equations are sufficient to determine q completely since the integration constant at infinite volume is $\ln V$.