Statistical Mechanics of Condensing Systems. III

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A general development of the Gibbs phase integral for a system of chemically saturated molecules gives equations for the thermodynamic properties of the system. The equations predict the usual condensation phenomenon of the gas to form a condensed phase with a surface tension at temperatures below a characteristic temperature T_m. At T_m the surface tension of the condensed phase is zero, and this phase undergoes a discontinuous change without heat of transition. Between T_m and the true critical temperature T_c, there exists a finite volume interval for which P and the Gibbs free energy F is independent of the volume. Above T_c the usual $P-V$ diagram predicted above the critical point is found, with no volume for which $(\partial P/\partial V)_T$ is zero.

THE GENERAL METHOD

IN a preceding paper[1] one of the authors has shown that the method commonly used in statistical mechanics to obtain the second virial coefficient, if followed through more completely, leads to equations predicting the existence of a condensed phase. In this paper we propose to develop a more concise method of handling the equations, and to show that the equations also predict the existence of some unexpected phenomena at the critical point. The method is a development, without arbitrary physical or mathematical assumptions, of the equations for the thermodynamic properties in terms of several series of integrals. In the temperature pressure range for which the liquid is stable the integral playing the predominant role cannot be numerically evaluated.

The system with which we wish to work must be limited to have certain properties if the development is to be applicable.

Three of these limitations are absolutely essential. They are: first, that the masses of the particles making up the system are large enough so that the classical laws of mechanics are applicable at the temperatures and volumes we wish to investigate; second, that the mutual potential between particle pairs falls off with the fourth or higher power of the distance between the pairs; and third, that the total potential energy of the system is representable as the sum of the potentials between pairs of particles which depend only on the differences of the coordinates of the pairs. The last limitation is equivalent to restricting the system to one composed of chemically saturated molecules incapable of forming true valence bonds with each other. It does not mean, of course, that we neglect higher than two-body collisions: on the contrary, we specifically treat multiple interactions, but we regard these as being made up of the sum of the interactions between all conceivable pairs of molecules.

Certain other unessential limitations are imposed on the system, limitations which are not necessary for the applicability of the general method, and which could be eliminated one by one at the cost of more complicated equations and a more complicated terminology and notation. These limitations are: that the system consist of N identical molecules; that N is large enough so that terms of the order of $N^{-\frac{1}{3}}$ or smaller can be neglected compared to unity; and that the individual molecules have three translational degrees of freedom only. This latter limitation means that internal degrees of freedom are absent or neglected, and that the mutual potential of a pair of molecules depends on their distance apart only, and not on mutual orientation angles.

The problem is attacked by means of the normalized phase integral, which is $1/N! \, h^{3N}$ times the integral (over the $3N$ momenta and $3N$ coordinates of N particles), of the exponent of minus the Hamiltonian divided by kT. The integration over the momentum space can be performed immediately if Cartesian coordinates are used. There remains the integration over the coordinate or configuration space. The integrand

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is the exponent of the negative of the potential energy divided by kT. Since this potential energy is the sum of the potential energies of the $N(N-1)/2$ possible pairs, the integrand can be written as the product of this number of terms. As in the usual method of obtaining the second virial coefficient, a function of the distance r_{ij} between molecules i and j, the quantity $f(r_{ij})+1$ (which defines the function f), is substituted for each exponential. The product is then expanded. The steps are indicated by the following equations.

$$Q = \frac{1}{N!h^{3N}} \int \int \cdots \int e^{-H(p, \, q)/kT} dp_1 \cdots dq_N$$

$$= \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \frac{Q_\tau}{N!}, \quad (1)$$

$$Q_\tau = \int \int \cdots \int e^{-V(q)/kT} d\tau_1 \cdots d\tau_N$$

$$= \int \int \cdots \int \prod_{N \geq i > j \geq 1} e^{-v(r_{ij})/kT} d\tau_1 \cdots d\tau_N$$

$$= \int \int \cdots \int \prod_{N \geq i > j \geq 1} [1+f(r_{ij})] d\tau_1 \cdots d\tau_N \quad (2)$$

$$= \int \int \cdots \int \left[1 + \sum_{i>j} f_{ij} + \sum f_{ij} f_{i'j'} + \cdots \right]$$

$$\times d\tau_1 \cdots d\tau_N,$$

with $\qquad d\tau_1 = dx_i dy_i dz_i, \qquad (3)$

$$f_{ij} = f(r_{ij}) = (e^{-v(r_{ij})/kT} - 1). \quad (4)$$

A plot of $f(r)$ for A/r^6 law of attraction and B/r^{12} repulsion potential at a temperature corresponding to the stable existence of a liquid is shown in Fig. 1. Since f drops rapidly to zero as the value of its argument r increases, the value of any term in the sum of Eq. (2) which involves a certain f_{ij}, is zero if the distance r_{ij} between the two molecules i and j is large. This term contributes to the total phase integral only in that part of configuration space for which the two molecules i and j are close together. For this reason we shall refer to the two molecules i and j as being "bound" to each other in any term containing the function f_{ij}. If, in any particular term, a molecule i is not bound to any other
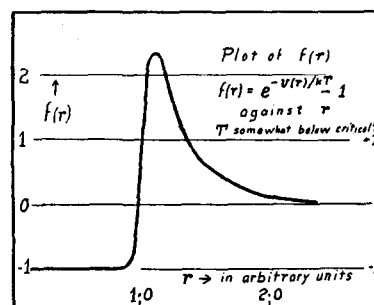

FIG. 1.

molecule (i.e., its index does not occur anywhere as a subscript in the product) we shall refer to it as a free molecule, or as being in a cluster consisting of one molecule. If, in a given term, the molecule i is bound to j, and neither i nor j is bound to any other molecule, we shall say that i and j are in a cluster of two molecules. If i is bound to j and j bound to k, whether or not i is bound to k we shall say i, j, k form a cluster of three, etc. Or in general, if l molecules are bound directly or indirectly to each other, but none of them is bound to any molecule not occurring in the group we shall say that they form a cluster of l molecules in that particular term.

We now propose to collect together all terms characterized by having the same number, m_1, of clusters of one molecule (free molecules), m_2 clusters of two molecules, . . ., m_l clusters of l molecules each. This method of collecting terms is purely arbitrary and by no means the only logical method of procedure from this point; it appears, however, to be justified, a posteriori, by the simplicity with which important results can be deduced from the procedure. Other equally logical procedures have failed so far to lead to interpretable results.

The physical significance of this particular grouping of terms is the following. All terms characterized by the same set of numbers, m_l, of clusters of size l, have in common the property that they contribute to the total phase integral Q only in that part of the configuration space where m_2 pairs of molecules are spatially close to their mates, . . ., m_l clusters of l molecules each are close to the other molecules of the clusters, etc., whereas the contribution to the integral is independent of the coordinates of the m_1 free molecules.

The quantity b_l, the integral over a cluster of size l, is defined by the following equation:

$$b_l = \frac{1}{Vl!} \int \int \cdots \int \sum_{l \geq i > j \geq 1} \prod f_{ij} d\tau_1 \cdots d\tau_l \quad (5)$$

(all products consistent with a single cluster).

The normalization factor $1/l!$ is merely for convenience. The integration is extended over the configuration volumes of all of the particles. The integrand is the sum of all possible products of the f's which are consistent with the existence of a single cluster. For small values of l, and for volumes of macroscopic dimensions, b_l is independent of the volume, due to the property of f that $f(\infty) = 0$. For values of l of the order of the number of particles in the system, the volume below which b_l becomes (significantly) volume dependent we shall later see is the volume of the condensed phase. It can be seen that in any term, the integration over the last particle, the l'th particle, in every cluster yields the volume, V, as a factor in the term, which is the reason we have defined b_l with V in the denominator. If b_1 is taken by definition to be unity this is also true of the m_1 clusters of single molecules.

It is then easily seen that the expression for $Q_\tau/N!$ becomes

$$\frac{Q_\tau}{N!} = \sum_{\substack{m_l \\ \Sigma\, lm_l = N}} \prod_l \frac{(Vb_l)^{m_l}}{m_l!} = \sum_{\substack{m_l \\ \Sigma\, lm_l = N}} \prod_l \frac{(Nvb_l)^{m_l}}{m_l!}, \quad (6)$$

with $\quad v = \dfrac{V}{N}$ (the volume per molecule). $\quad (7)$

The General Equations

The logarithm of the sum $Q_\tau/N!$ of Eq. (6) may be approximated with sufficient accuracy by the logarithm of the largest term,[1] giving Eq. (9). This method is only valid if all the b_l's are positive. Professor Born has pointed out to the authors that the function $Q_\tau/N!$, which can be seen to be the coefficient of Z^N in the expansion of the exponent $\sum vb_l Z^l$, can be expressed as a Cauchy integral and evaluated by means of the well-known method of steepest descents, leading also to Eq. (9). We believe that Professor Born will publish this proof shortly along with several other comments on the method of the present

article. Another method of obtaining the asymptotic Eq. (9) is discussed in the appendix of this article.

If a function $Z(vb_1, vb_2, \cdots, vb_l, \cdots)$ is defined as the lowest positive real root of the equation ((A4) of the appendix),

$$G_1(vb_l) \equiv \sum_{l \geq 1} lvb_l Z^l = 1, \quad (8)$$

and the functions G_j are defined as

$$G_j(vb_l) = \sum_{l \geq 1} l^j vb_l Z^l, \quad (9)$$

so that $G_1 = 1$, then we find that, (Eq. (A57) of the appendix),

$$\frac{1}{N} \ln \frac{Q_\tau}{N!} = G_0(vb) - \ln Z, \quad (10)$$

plus terms of order of magnitude $1/N$, as long as Q_τ is positive and real for all large values of N, a condition which it obviously always fulfills.

The Helmholtz free energy A, the free energy at constant volume, or the work function of Lewis and Randall, is derived immediately from the phase integral as

$$A = -kT \ln Q$$

and from (1),

$$A = RT \left[\ln \left(\frac{h^2}{2\pi mkT} \right)^{\frac{3}{2}} - \frac{1}{N} \ln \frac{Q_\tau}{N!} \right],$$

which, with (10) becomes

$$A = RT[\ln (h^2/2\pi mkT)^{\frac{3}{2}} - G_0(vb_l) + \ln Z]. \quad (11)$$

The negative of the derivative of this with respect to the volume gives the pressure

$$P = -(\partial A/\partial V)_T = kT(\partial/\partial v)[G_0(vb_l) - \ln Z]$$
$$= (RT/V)[G_0(vb_l) + G_{0v}(vb_l)], \quad (12)$$

where

$$G_{jv}(vb_l) = \sum_{l \geq 1} l^j vb_l Z^l (\partial \ln b_l/\partial \ln v). \quad (13)$$

(the details of the differentiation are given in the appendix, preceding Eq. (A18)). The free energy at constant pressure, F, the Gibbs, and Lewis

and Randall, free energy, is given by

$$F = A + PV$$
$$= RT[\ln (h^2/2\pi mkT)^{\frac{3}{2}} + \ln Z + G_{0v}]. \quad (14)$$

We shall defer a more detailed discussion of the nature of these equations until the properties of the arguments b_l have been discussed more fully. However, one interpretation will be introduced at this point. The original Eq. (6) for Q_τ can be handled more simply than by the method of the appendix if all the b_l's are positive. In this case the logarithm of the total sum of $Q_\tau/N!$ can be shown to become asymptotically equal to the logarithm of the largest term as N increases indefinitely. Now the largest term is characterized by the set of numbers m_l^*, the number of clusters of size l, with lm_l^* the number of molecules in clusters of size l, and lm_l^*/N the fraction of material in clusters of size l. lm_l^*/N can be shown to be equal to lvb_lZ^l so that the l'th term in the sum G_1 of Eq. (8) is the (most probable) fraction of material in clusters of l molecules. The l'th term in G_0 is the number of clusters of l molecules each, divided by the total number of molecules, and from the Eq. (12) for the pressure it can be seen that each cluster contributes exactly as much to the pressure as a single molecule, (if G_{0v} is zero). For large values of v, $\partial \ln b_l/\partial \ln v$ is zero and G_{0v} must be zero. The volume below which G_{0v} differs from zero will be called v_f and later be shown to be that of the condensed phase.

EVALUATION OF THE b_l'S

We shall now investigate the integrals over the clusters, the b_l's of Eq. (5). It can be shown[1] that normalized irreducible integrals β_k can be so defined that the cluster integral b_l is the sum of coefficients times products of the β_k's raised to various powers.

The first three normalized irreducible integrals are

$$\beta_1 = (1/V) \int f_{21} d\tau_1 d\tau_2 = \int_0^\infty 4\pi r^2 f(r) dr, \quad (15)$$

$$\beta_2 = (1/V2!) \int \int f_{32} f_{31} f_{21} d\tau_1 d\tau_2 d\tau_3, \quad (16)$$

$$\beta_3 = (1/V3!) \int \int \int [3f_{43}f_{32}f_{21}f_{41} + 6f_{43}f_{32}f_{21}f_{41}f_{42}$$
$$+ f_{43}f_{32}f_{21}f_{41}f_{42}f_{31}]d\tau_1 d\tau_2 d\tau_3 d\tau_4. \quad (17)$$

The coefficients 3 and 6 in β_3 occur because permutation of the indices gives, respectively, 3 and 6 different products leading to the same integrals. The general k'th irreducible integral is an integral over the configuration space of $k+1$ particles. The integrand is the sum of all products of f between $k+1$ particles which connect every particle to every other particle by more than a single path,

$$\beta_k = (1/Vk!) \int \int \cdots \int \sum_{k+1 \geq i > j \geq 1} \prod f_{ij} d\tau_1 \cdots d\tau_{k+1}. \quad (18)$$

Products having all particles more than singly connected.

If n_k is the power to which β_k is raised in a certain term in b_l we have the condition that

$$\sum_k k n_k = l - 1.$$

The coefficient with which a term, defined by the powers n_k, occurs in b_l is very simple, namely

$$l^{-2} \prod_k l^{n_k}/n_k!.$$

The proof that this is the correct coefficient caused the authors a great deal of difficulty. They are greatly indebted to Dr. Goeppert Mayer for the final completion of the proof. An indication of the general method of this proof is given in the second part of the appendix. Due to its complicated nature the proof is not given in detail.

The equation for $l^2 b_l$ becomes

$$l^2 b_l = \sum_{\substack{n_k \\ \Sigma k n_k = l-1}} \prod_k (l\beta_k)^{n_k}/n_k!. \quad (19)$$

Comparison with (6) shows that it is similar in form to the equation for $Q_\tau/N!$, indeed it is identical in form with the Eqs. (A58) and (A36) of the appendix defining the function $F_1(M, x)$. We may use Eq. (A59) of the appendix which, with the arbitrary introduction of the function $p(l, \beta)$, is also an exact equation for b_l,

$$b_l = \frac{[b_0(\beta)]^l p(\beta)}{(2\pi G_2(\beta))^{\frac{1}{2}} l^{5/2}} \frac{1}{p(l, \beta)}, \quad (20)$$

where $p(l, \beta)$ is a function which takes erratic values for small values of l but which becomes asymptotically equal to unity as l becomes large. For $b_0(\beta)$ the equation, (A42),

$$\ln b_0(\beta) = G_0(\beta) - \ln \rho \qquad (21)$$

is obtained. ρ is determined by the β_k's in the same way that Z is determined by the vb_l's (Eq. 8), i.e.,

$$\sum_{k \geq 1} k \beta_k \rho^k = 1, \qquad (22)$$

and

$$G_0(\beta) = \sum_{k \geq 1} \beta_k \rho^k. \qquad (23)$$

For small values of l it is more convenient to use Eq. (19) to determine b_l, for large values of l the form (20) is of course preferable. The condition for Eq. (20) to be valid is that Eq. (22) has a real positive root of ρ, the lowest real positive root being the correct one to use.

DEVELOPMENTS FOR THE GAS

Returning now to Eq. (8), we see that at infinite volumes, since b_1 is unity, $Z = 1/v$, and $G_0 = 1$. Using these values in (11), (12) and (14) the equations of a perfect gas are obtained, remembering that G_{0v} is zero for large volumes.

As long as the sum G_1 is absolutely convergent, (see the discussion in the appendix), Z can be developed as a power series in $1/v$. Use of such a power series in (8) enables one to equate coefficients, and if b_l is expressed by (19), one obtains

$$Z = (1/v)\{1 - \beta_1 v^{-1} - [\beta_2 - (\beta_1{}^2/2)]v^{-2}$$
$$- [\beta_3 - \beta_1 \beta_2 + (\beta_1{}^3/6)]v^{-3} \cdots\}$$
$$= v^{-1} e^{-\sum \beta_k v^{-k}}. \qquad (24)$$

This may, in turn, be used in (9) to calculate $G_0(vb_l)$ as a power series in descending powers of v. The following simple equations are obtained:

$$G_0(vb_l) = \frac{PV}{RT} = 1 - \sum_k \frac{k}{k+1} \beta_k v^{-k}, \qquad (25)$$

$$A = RT\left[\ln\left(\frac{h^2}{2\pi m k T}\right)^{\frac{3}{2}} \frac{1}{ev} - \sum_k \frac{1}{k+1} \beta_k v^{-k}\right], \qquad (26)$$

$$F = RT\left[\ln\left(\frac{h^2}{2\pi m k T}\right)^{\frac{3}{2}} \frac{1}{v} - \sum_k \beta_k v^{-k}\right]. \qquad (27)$$

It is seen that $-k\beta_k/(k+1)$ is the $(k+1)$th virial coefficient.

The developments were first made by algebraic evaluation of the first few terms. They can however be proved by inserting the solution of Eq. (24) for Z in Eq. (8), and by manipulation of the sum obtained on expanding the exponential it can be shown that the coefficients of all powers of $1/v$ except the zeroth power are equal to zero. Professor Max Born has written to the authors that there exists a still simpler proof of the equations. The developments are, however, only valid if the sum $G_1(vb_l)$ converges absolutely, so that the last terms are negligible in their effect on the determination of Z.

From (25) we may evaluate $(\partial P/\partial V)_T$ as

$$(\partial P/\partial V)_T = -(RT/V^2)[1 - \sum k \beta_k v^{-k}], \qquad (28)$$

and if we define ρ as the reciprocal of the largest volume for which this becomes zero, it becomes the smallest positive root of the equation $g_1(\beta, \rho) - 1 = 0$, identically the Eq. (22) by which ρ was previously defined. We see, then, that the quantity ρ has the physical significance of being the reciprocal of the largest volume, v_s, for which $(\partial P/\partial V)_T = 0$,

$$v_s = 1/\rho \qquad (29)$$

From Eq. (24) for Z when $v = v_s = 1/\rho$, and (21) for b_0, we see that

$$Z_s = b_0{}^{-1}, \quad v = v_s = \rho^{-1}. \qquad (30)$$

By differentiating the logarithm of Z in (24) with respect to the logarithm of the volume, one obtains

$$\partial \ln Z / \partial \ln v = \sum k \beta_k v^{-k} - 1, \qquad (31)$$

which, in view of the definition of v_s as the largest root of this equation, is zero at $v = v_s$, and negative at all higher volumes. It follows that for $v > v_s$, $b_0 Z < 1$, and the sums $G_j(vb_l)$ converge absolutely (see the discussion of the second section of the appendix). In the range of volumes, $v_s \leqslant v \leqslant \infty$, then, the equations (24) to (31) are valid.

The quantity Z has the dimensions of the reciprocal of a volume. From the equation for F, (14), it can be seen that for large volumes when G_{0v} is zero, Z^{-1} is the volume per molecule of a perfect gas having the same free energy F as the

real gas in question. The quantity $(vZ) = \gamma_c$ may be called the concentration activity coefficient of the gas. It is the dimensionless quantity by which the concentration of the gas must be multiplied to obtain the concentration of an ideal gas having the same free energy F. From (24) this is seen to have the value

$$\gamma_c = vZ = e^{-\Sigma \beta_k v^{-k}}. \qquad (32)$$

CONDENSATION

For volumes lower than v_s the sums $G_j(vb_l)$ are not absolutely convergent, (see the discussion in the second section of the appendix), and the equations (24) to (32) will no longer be valid. In this range we may use (20) for b_l, which, inserted in (8) leads to the equation for the determination of Z,

$$\frac{v}{(2\pi)^{\frac{1}{2}}} \sum_{l \geq 1} \frac{(b_0 Z)^l \rho(\beta)}{l^{\frac{1}{2}}(G_2(\beta))^{\frac{1}{2}} p(l,\beta)} = 1. \qquad (33)^2$$

Since $p(l, \beta)$ becomes asymptotically unity for large values of l, it can be readily seen that $b_0 Z$ cannot become more than infinitesimally greater than unity. For values of the volume v equal to, or less than v_s, we can, to within terms of the order of magnitude of $1/N$, write

$$Z = 1/b_0, \quad \partial \ln Z / \partial v = 0, \quad v \leqslant v_s. \qquad (34)$$

By taking the derivative of $G_0(vb_l)/v$ with respect to v one obtains

$$\frac{\partial}{\partial v}\left[\frac{G_0(vb_l)}{v}\right] = \frac{1}{v}\left[\frac{\partial \ln Z}{\partial v} + G_{0v}(vb_l)\right]. \qquad (35)$$

If now v_f is defined as the volume above which G_{0v} is essentially zero, and since v_s is the volume below which $\partial \ln Z / \partial v$ is zero, in the volume range $v_f \leqslant v \leqslant v_s$ we find that G_0/v is a constant. From (12) for P we see that the pressure is a constant in this volume range. Since Z is inde-

pendent of v, and G_{0v} zero in this volume range, we see from (14) that the free energy, F, is also independent of the volume. This constancy of P and F for $v_f \leqslant v \leqslant v_s$ may be considered to be the thermodynamic criterion of a change of phase. v_f is seen to be the volume per molecule of the condensed phase, and v_s the volume per molecule of the saturated vapor.

The decrease of volume from v_s to v_f is accompanied by an increase of the fraction of material in the very large clusters, $l v b_l Z^l$, from zero to almost unity,[3] since the sum becomes divergent in this range (see the discussion in the appendix), but there is no corresponding increase in the fraction of material in the moderately large clusters; this remains essentially zero during the whole process. The fraction of material in the small clusters decreases proportionally with v in this range. Even at v_f the density of the small clusters, the number per unit volume, $b_l Z^l$, is the same as in the saturated vapor at v_s. Insofar as the clusters have a physical meaning this states that the number of free molecules in the liquid per unit volume is equal to the number per unit volume in the vapor in equilibrium with the liquid. This same relationship of equal densities in liquid and saturated vapor holds for all the small clusters.

With the knowledge that the volume of the saturated vapor per molecule is $v_s = 1/\rho$, and that Eq. (25) holds down to exactly this volume we may write the equation for the vapor pressure over the condensed phase as

$$P_s = kT\rho\left[1 - \sum_k (k/k+1)\beta_k \rho^k\right],$$

$$(v_f \leqslant v \leqslant v_s). \qquad (36)$$

Since $Z = b_0^{-1}$ for the range $v_f \leqslant v \leqslant v_s$, and $G_{0v}(vb_l)$ is zero, we may write from (14), for the free energy F of the saturated vapor, and of the

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[2] We have written $G_2(\beta)$ as though it were independent of l. In the case (A26) of the appendix for which the sums $G_j(\beta)$ are not absolutely convergent $G_2(\beta)$ will depend on l. For this reason we have written $G_2(\beta)$ under the summation sign.

Since we have previously found that $Zb_0 = 1$ at $v = 1/\rho$ it follows that $\sum 1/l^{3/2}(G_2(\beta))^{\frac{1}{2}} p(l, \beta) = (2\pi)^{\frac{1}{2}}$, an equation which we should be able to verify independently, but have been unable to do. Essentially this equation, however, has been carefully checked numerically for a wide variety of different values of the β_k's.

[3] The treatment of $F_0(M, x)$ in the appendix is not fully valid without further discussion if $G_1(x)$ diverges. The method of steepest descents is also invalid in this case. An extension of the method of the appendix shows that the equations used in the article are correct, in this case, to the degree of accuracy to which they are used. The method of using the logarithm of the largest term shows the difficulty most clearly. In the previous treatment the numbers m_l are treated as continuous, although they are obviously integers. If this simplification is not made, it becomes apparent that in the range of volumes $v_f \geqslant v \geqslant v_s$ for which condensation takes place, only one of the large clusters is present for which $l = N(v_s - v)/v_s$. The equations as used in this article are in no way affected.

liquid under its own vapor pressure,

$$F_s = RT[\ln (h^2/2\pi mkT)^{\frac{3}{2}} - \ln b_0]$$

$$= RT[\ln (h^2/2\pi mkT)^{\frac{3}{2}} - G_0(\beta) + \ln \rho],$$

$$(v_f \leqslant v \leqslant v_s). \quad (37)$$

THE CRITICAL POINT

The β_k's are all positive at very low temperatures. As the temperature increases the β_k's of higher k values tend to become negative. As discussed in the appendix, above a certain temperature, T_c, there exists no real root of equation (22) for ρ. Above this temperature Eq. (20) for b_l is invalid, and the complete argument that predicts the condensation phenomenon breaks down. One is immediately tempted to identify T_c with the critical temperature. This identification is made complete when we observe that ρ has also been defined as the reciprocal of the volume for which $(\partial P/\partial V)_T$, as given by Eq. (28), becomes zero. Above T_c, where no real root for ρ in Eq. (22) exists, there is no positive volume for which $(\partial P/\partial V)_T$ is equal to zero.

From Eq. (28) we may calculate $(\partial^2 P/\partial V^2)_T$, and find

$$(\partial^2 P/\partial V^2)_T = (RT/V^3)[2 - 2\sum k\beta_k v^{-k}$$
$$- \sum k^2\beta_k v^{-k}], \quad (v \geqslant v_s). \quad (38)$$

At $v_s = 1/\rho$ this becomes, since $G_1(\beta) = 1$,

$$(\partial^2 P/\partial V^2)_{T, \ v=v_s} = -(RT/V^3)G_2(\beta), \ (v=v_s). \quad (39)$$

As is shown (Eq. (A 60)), in the appendix $G_2(\beta)$ is zero at $T = T_c$.

CONTINUITY OR DISCONTINUITY AT THE CONDENSATION POINT

For the sake of completeness we may return to the general Eq. (12) for the pressure P, and, limiting ourselves to $v \geqslant v_f$, for which G_{0v} is zero, calculate $(\partial P/\partial V)_T$ and $(\partial^2 P/\partial V^2)_T$ as

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{\partial}{\partial V} \frac{RT}{V} G_0(vb_l) = -\frac{RT}{V^2} \frac{1}{G_2(vb_l)},$$
$$(v \geqslant v_f), \quad (40)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = -\frac{RT}{V^3} \frac{G_3(vb_l) - 3G_2(vb_l)}{[G_2(vb_l)]^3}, \quad (v \geqslant v_f). \quad (41)$$

If $v > v_s$ all the sums in these expressions are finite, and the expressions are more readily calculated by the equivalent equations (28) and (38). For $v < v_s$, however, the sums diverge (in the sense discussed in the second section of the appendix) and $G_2(vb_l)$ becomes of order of magnitude N, and $G_3(vb_l)$ of order N^2; both $(\partial P/\partial V)_T$ and $(\partial^2 P/\partial V^2)_T$ are seen to be zero.

It is more difficult to ascertain from Eq. (42) whether $(\partial^2 P/\partial V^2)_T$ becomes "infinite" (i.e., of order of magnitude N), or not, as the volume v_s is crossed. Eq. (39), however, answers this question. If the sums $G_1(\beta)$ and $G_2(\beta)$ converge, $(\partial^2 P/\partial V^2)_T$ is seen to be finite at $v = v_s$; whereas if they diverge, this function becomes "infinite" as the volume crosses v_s.

It appears then that the question of whether $(\partial P/\partial V)_T$ goes continuously or discontinuously to zero at $v = v_s$ is determined by whether the sums $G_1(\beta)$ and $G_2(\beta)$ converge or diverge. If the sums are convergent $(\partial P/\partial V)_T$ goes continuously to zero as v decreases through v_s, and we must assume that the vapor cannot be supersaturated in the sense that a higher pressure than P_s could be observed. If, however, the sums are divergent, there is a sudden break in the shape of the P–V curve at v_s, and supersaturation of the vapor would be expected.

SURFACE TENSION AND THE TEMPERATURE T_m

For large values of k we have been unable to find a method of calculating the β_k's numerically. It is, however, fairly obvious that they must obey the relationship

$$(\lim k \to \infty) \ \ln \beta_k = k \ln \beta_0, \quad (42)$$

in which β_0, of the dimensions of a volume, represents the contribution as a factor to β_k of the integration over an average particle. It is also fairly obvious that in the important terms of the products of f_{ij}'s of Eq. (18) a number of molecules proportional to $k^{\frac{2}{3}}$ must have fewer "bonds" to neighbors than the average particles. These are the particles which are physically on the surface of the mechanical frame which may be associated to each product of f's. We may now amend (42) to

$$\ln \beta_k = k \ln \beta_0 - \gamma k^{\frac{2}{3}} + \ln \alpha(k, \beta_0) - n \ln k, \quad (43)$$

$$\beta_k = \beta_0^k e^{-\gamma k^{\frac{2}{3}}} \alpha(k, \beta_0)/k^n, \quad (44)$$

where β_0 is a positive quantity with the dimensions of volume, the dimensionless γ may be positive or negative, $\alpha(k, \beta_0)$ is presumed to be independent of k for large values of k, (a property which we shall not really use), and k^{-n} is introduced merely because it seems rather probable that some such term should be present. The only portions of (44) which are of importance are the already justified β_0 and γ.

Now for low values of the temperature, T, γ must be positive, the contribution of the "surface" molecules to β_k must be less than the contribution of the "inner" molecules, and we must expect that $d\gamma/dT < 0$. Let us assume $\gamma > 0$ for $T < T_m$, $d\gamma/dT < 0$, and $\gamma = 0$ at $T = T_m$. We now propose to show that, for $T < T_m$, $kT\gamma/(36\pi v_f^2)^{\frac{1}{3}}$ is the surface tension, S, or surface free energy of the condensed phase.

The case (44) is the same as the case II discussed in the appendix under the title "Convergence of the Auxiliary Functions." Below T_m with γ positive the sums $G_1(\beta)$ and $G_2(\beta)$ diverge in the sense used in that section. For temperatures above T_m the sums converge.[4] We have already seen in the preceding section that the cases of divergent and convergent $G_2(\beta)$ correspond respectively to discontinuous and continuous transitions of $(\partial P/\partial V)_T$ to zero at the volume v_s of the saturated vapor. The existence of a positive surface tension below T_m assures the instability of the small clusters; so an arbitrary restriction to integration over that region of phase space where no large numbers of molecules are close together (corresponding to the arbitrary assumption that the b_l's of large l values are zero or small) would result in a P-V curve showing higher values of P than P_s for $v < v_s$.

The proof that $kT\gamma/(36\pi v_f^2)^{\frac{1}{3}}$ is the surface tension is as follows. In the appendix it is shown that ρ, (the same as z of Eq. (A25II)) depends on

l, the upper limit of summation, if the sums are divergent, and indeed, (A29II),

$$\rho = \beta_0^{-1} e^{\gamma/l^{\frac{1}{3}}}. \tag{45}$$

If this value of ρ is inserted in Eq. (20) for b_l, with (21) for b_0, we find a multiplicative factor $e^{-\gamma l^{\frac{2}{3}}}$ in b_l. Now consider the chemical reaction in which clusters of size l dissociate to form clusters of size l/n. The concentration of clusters of size l is given by $c_l = b_l Z^l$, since $v b_l Z^l$ gives the number of such clusters divided by N. The concentration of clusters of size l/n is $b_{l/n} Z^{l/n}$. Inserting these values in the reaction constant $K = c_{l/n}^n/c_l$, and using the relationship $\Delta F^0 = -kT \ln K$ we find, upon neglecting lower order terms that

$$\Delta F^\circ = -kT\gamma l^{\frac{2}{3}}(1 - n^{\frac{1}{3}}), \tag{46}$$

where ΔF° is the difference in free energy (at hypothetical unit concentration) between n clusters of size l/n and one cluster of size l. This difference in free energy must be the product of the surface tension S multiplied by the increase of surface in the reaction. The area of the surface of a (spherical) drop of l molecules will be $(36\pi)^{\frac{1}{3}}(v_f l)^{\frac{2}{3}}$, since v_f is the volume per molecule of the condensed phase. The area increase is then seen to be $(36\pi v_f^2 l^2)^{\frac{1}{3}}(n^{\frac{1}{3}} - 1)$ and one obtains with (46) the equation for the surface tension in terms of γ,

$$S = kT\gamma/(36\pi v_f^2)^{\frac{1}{3}}. \tag{47}$$

In this section we have inserted the quantity γ into the equation for β_k as a reasonable assumption and have shown that its reality is in agreement with the experimental observation of the existence of a surface tension. For our equations to have a physical meaning, however, it is important that the quantity $\alpha(k, \beta_0)$ be positive for all large values of k, as long as γ is positive. In this case $G_2(\beta)$ must be very large and positive. At T_m the quantity γ is zero, and although it may and presumably does become negative for higher temperatures, because of the necessary convergence of the sums $G_1(\beta)$ and $G_2(\beta)$ above T_m, the quantity ρ does not depend on the upper limit of summation l, and $\ln b_l$ will contain no term proportional to $l^{\frac{2}{3}}$. Therefore, the surface tension S is zero for $T > T_m$. How-

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[4] Actually, although the sums certainly converge if γ is negative, it is not necessarily true that they diverge for all positive values of γ, and they would not if $\sum \alpha(k, \beta_0) k^{-n}$ were greater than unity. We should define T_m as the temperature at which the sums change from divergent to convergent, which could be at a finite positive value of γ. This would change nothing in the subsequent argument except that the surface tension S would extrapolate to a finite value at T_m and would become discontinuously zero at this temperature. This appears not to be the case experimentally.

ever, $G_2(\beta)$ is positive at $T = T_m$, and so the temperature T_c, the true critical temperature, at which $G_2(\beta) = 0$, must lie higher than T_m, $T_m < T_c$.

Thus T_m, the temperature at which the surface tension of the condensed phase becomes zero, and where the meniscus between liquid and gas disappears, is not identical with, but is lower than the true critical temperature T_c, the temperature at which the P–V curve has a horizontal tangent for only one volume. The two temperatures have been hitherto regarded as identical by most theoretical workers.

To recapitulate: we are forced to the conclusion that there exist two characteristic temperatures, T_c and T_m, with $T_c > T_m$. Above T_c the P–V curve is nowhere horizontal and there exists no difference between gas and liquid. Below T_m the condensed phase has a surface tension and the P–V curve shows (at least) one discontinuity in slope at the volume v_s, below which it is horizontal. Between T_m and T_c there is a finite temperature range in which the P–V curve is horizontal over a finite volume interval, but has no discontinuous change in slope. Between T_m and T_c, and of course also above T_c, there exists no surface tension.

Temperature Derivatives

In order to obtain equations for the thermodynamic quantities S, E, H, and $(\partial P/\partial T)_V$, etc., it will be necessary to express the functions β_k as functions of T and to differentiate them. Although this might be done formally without any special assumption as to the form of β_k for large values of k, certain relationships become more obvious if Eqs. (43) and (44) are used for β_k. Using the definitions

$$-d \ln \beta_0 / d \ln T = B_0, \qquad (48)$$

$$-d\gamma / d \ln T = C_0, \qquad (49)$$

$$d \ln \alpha(k, \beta_0) / d \ln T = B_k, \qquad (50)$$

we may write

$$d \ln \beta_k / d \ln T = -kB_0 + k^{\frac{2}{3}}C_0 + B_k. \qquad (51)$$

By the use of (51) in Eq. (26) for A with $v \geqslant v_s$ one obtains

$$\left(\frac{\partial A}{\partial T}\right)_V = -S = \frac{A}{T} - \tfrac{3}{2}R + R\left[B_0 \sum_k \frac{k}{k+1}\beta_k v^{-k}\right.$$
$$\left. - C_0 \sum_k \frac{k^{\frac{2}{3}}}{k+1}\beta_k v^{-k} - \sum_k \frac{B_k \beta_k}{k+1}v^{-k}\right], \qquad (52)$$

or

$$S = R\left[\ln\left(\frac{2\pi mkTe}{h^2}\right)^{\frac{3}{2}}ev + \sum_k \frac{\beta_k}{k+1}v^{-k}\right.$$
$$\left. - B_0 \sum_k \frac{k\beta_k}{k+1}v^{-k} + C_0 \sum_k \frac{k^{\frac{2}{3}}\beta_k}{k+1}v^{-k} + \sum_k \frac{B_k\beta_k}{k+1}v^{-k}\right]. \qquad (53)$$

Using $E = A + TS = A - T(\partial A/\partial T)_V$, and $H = E + PV$, with (25) for PV one obtains

$$E = RT\left[\frac{3}{2} - B_0 \sum_k \frac{k\beta_k}{k+1}v^{-k} + C_0 \sum_k \frac{k^{\frac{2}{3}}\beta_k}{k+1}v^{-k}\right.$$
$$\left. + \sum_k \frac{B_k\beta_k}{k+1}v^{-k}\right], \qquad (54)$$

$$H = RT\left[\frac{5}{2} - (B_0+1) \sum_k \frac{k\beta_k}{k+1}v^{-k} + C_0 \sum_k \frac{k^{\frac{2}{3}}\beta_k}{k+1}v^{-k}\right.$$
$$\left. + \sum_k \frac{B_k\beta_k}{k+1}v^{-k}\right]. \qquad (55)$$

Similarly (25), if differentiated, yields

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}\left[1 - \sum_k \frac{k\beta_k}{k+1}v^{-k} + B_0 \sum_k \frac{k^2\beta_k}{k+1}v^{-k}\right.$$
$$\left. - C_0 \sum_k \frac{k^{5/3}\beta_k}{k+1}v^{-k} - \sum_k \frac{kB_k\beta_k}{k+1}v^{-k}\right]. \qquad (56)$$

For dP_s/dT we may use

$$dP_s/dT = (\partial P/\partial T)_{v=v_s} + (\partial P/\partial V)_{T,\,v=v_s}(\partial V_s/\partial T)$$

but since $(\partial P/\partial V)_{T,\,v=v_s}$ is zero, we find that dP_s/dT is equal to $(\partial P/\partial T)_V$ when $v = v_s$.[5]

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[5] This apparently high-handed neglect of the "infinite" value of $(\partial^2 P/\partial V^2)_T$ when the sum $G_2(\beta)$ diverges is justified by the fact that $G_2(\beta)$, and hence $(\partial^2 P/\partial V^2)_T$, is actually finite in a mathematical sense, although very large. We have used the expression "discontinuous" for $(\partial P/\partial V)_T$ at $v = v_s$ in the physical sense since magnitudes of order N are pretty big. This is, of course, mathematically unjustifiable, and all our equations are strictly speaking continuous. The equation (56) for $(\partial P/\partial T)_V$ and (57) for dP_s/dT lead to different values for these two quantities if v is infinitesimally greater than v_s. We shall discuss the values of the thermodynamic properties of the super-saturated vapor in the neighborhood of $v = v_s$ in the following section.

Using the condition that $G_1(\beta) = 1$ at $v = v_s = \rho^{-1}$, and that $k^2/(k+1) = k - k/(k+1)$ we obtain

$$\frac{dP_s}{dT} = \frac{R}{V_s}\left[(1+B_0)\left(1 - \sum_k \frac{k\beta_k}{k+1}\rho^k\right) - C_0\sum_k \frac{k^{5/3}\beta_k}{k+1}\rho^k - \sum_k \frac{kB_k\beta_k}{k+1}\rho^k\right]. \quad (57)$$

Finally, by noting that $G_1(\beta) = 1$ at $v = v_s = \rho^{-1}$ so that $dG_1/dT = 0$, we obtain for $d \ln v_s/d \ln T$,

$$d \ln v_s/d \ln T = -B_0 + [G_2(\beta)]^{-1}$$
$$\times [C_0\sum k^{5/3}\beta_k\rho^k + \sum kB_k\beta_k\rho^k], \quad (58)$$

or, since $G_2(\beta)$ is "infinite" when $T < T_m$

$$d \ln v_s/d \ln T = -B_0, \quad (T < T_m). \quad (59)$$

It is seen from Eq. (58) for $d \ln v_s/d \ln T$ that this quantity increases discontinuously as T is increased through the value $T = T_m$. dP_s/dT is, however, seen to be continuous at $T = T_m$. Further differentiation shows that d^2P_s/dT^2 is discontinuous at T_m. Since dP_s/dT is continuous at T_m there is no discontinuous change in the heat content of the condensed phase at this temperature; therefore no true change of phase occurs at T_m.

At $T = T_c$ since $G_2(\beta)$ is zero it is seen from (58) that $d \ln v_s/d \ln T$ is infinity. Numerical calculations of the β_k's at this temperature have shown that the derivative approaches infinity from the negative side as is to be expected.

Equations of the Supersaturated Vapor

Equation (28) for $(\partial P/\partial V)_T$ and (56) for $(\partial P/\partial T)_V$ show discontinuities at $v = v_s$ if $T < T_m$ and the sums $G_1(\beta)$ and $G_2(\beta)$ are divergent. The point $v = \beta_0^{-1}$, $\beta_0/v = 1$ lies on the circle of convergence of the sum $G_1(\beta)$ if that sum is regarded as having an infinite upper limit of summation. The value of v_s is infinitesimally smaller than β_0 so that β_0/v_s is actually larger than unity by a very small amount. If we set β_0/v exactly equal to unity (a value which it has when v is negligibly larger than v_s) we obtain a value of $G_j(\beta)$ which may be used in (28) and (56) for the supersaturated vapor in the neighborhood of the volume v_s. Using (44) for β_k, this leads to

$$g_j(\beta, v^{-1}) = \sum_{\substack{k \\ \beta_0/v=1}} k^j\beta_k v^{-k}$$
$$= \sum_k \alpha(k, \beta_0)e^{-\gamma k^{\frac{2}{3}}}k^{j-n} = G_j{}^0(\beta). \quad (60)$$

The symbol $G_j{}^0(\beta)$ has been used to indicate the sum $g_j(\beta, v^{-1})$ when $\beta_0/v = 1$, $G_j(\beta)$ being the value when $G_1 = 1$ which for divergent sums, $T < T_m$, gives $\beta_0/v = 1 + \epsilon$. It is obvious that $G_0(\beta) = G_0{}^0(\beta)$ always, but $G_1{}^0(\beta) < 1$ if $T < T_m$. Since $\partial \ln g_j(\beta, v^{-1})/\partial \ln v = -g_{j+1}(\beta, v^{-1})$ we may develop $g_j(\beta, v^{-1})$ in terms of a semi-convergent Taylor's series as

$$g_j(\beta, v^{-1}) = \sum_{\nu \geq 0} [\ln v - \ln v_s]^\nu$$
$$\times (\partial^\nu/\partial \ln v^\nu)g_j(\beta, v^{-1})_{v=v_s}$$
$$= \sum_{\nu \geq 0} [(-\ln v\rho)^\nu G^0{}_{j+\nu}(\beta)]/\nu!. \quad (61)$$

This equation could be used for values of $v < v_s = \rho^{-1}$ with any of the equations (25) to (32) or (52) to (59) to calculate the thermodynamic functions of the supersaturated vapor. We shall not carry out the obvious operations.

It is interesting to note that the sum $g_1(\beta, v^{-1})$ is itself semi-convergent for values of v smaller than v_s, that is the first terms of $g_1(\beta, v^{-1})$ converge, and it is only after a comparatively large value of the index of summation of k has been reached that the terms commence to grow larger again. Using (44) for β_k and differentiating $\beta_k(v_s/v)^k$ with respect to k, we find that the term of minimum value is given by the equation

$$\frac{1}{k}\frac{\partial \ln \alpha(\beta_0, k)}{\partial \ln k} - \frac{n}{k} - \frac{2}{3}\frac{\gamma}{k^{\frac{1}{3}}} + \ln \frac{v_s}{v} = 0. \quad (62)$$

For large values of k this is approximately

$$k = \frac{8}{27}\frac{\gamma^3}{[\ln (v_s/v)]^3}, \quad (63)$$

which should give approximately the size of droplet which forms least easily at a volume $v < v_s$. After a droplet of this size has once been formed in a supersaturated vapor of volume v, the drop should increase rapidly in size until the pressure attains the value P_s.

CONCLUSION

Except for Eq. (44) assuming a special form for β_k no assumptions have been introduced into the general deductions other than those listed in the third and fourth paragraphs of the introduction. The assumption in (44) that $\ln \beta_k$ varies linearly with k for large k values can scarcely be questioned. The addition of a term proportional to $k^{\frac{2}{3}}$ appears, *a priori*, to be reasonable, and is later justified by its appearance in the final equations as the surface free energy.

We conclude that a liquid-saturated vapor system has two characteristic temperatures, T_m and T_c, instead of one critical temperature as usually assumed. Above T_c and below T_m the properties correspond to those predicted classically above and below the critical point, but between T_m and T_c for a certain volume range we predict properties which are not given by any classical description of the critical phenomenon.

The authors will show in a subsequent paper that published experimental results amply confirm this conclusion.

Numerical evaluation of the first few β_k's shows that the experimental properties of the critical point, especially its relative position with respect to the temperature for which the second virial coefficient is zero (the Boyle point), and the value of PV/RT, are in agreement with the assumption that only β_1 and β_2 play a role at these temperatures and pressures. It is probable that a calculation of β_1, β_2 and β_3, which is not impracticable, would suffice to cover the range above T_m. As yet no theoretical calculation of β_0 appears to be practicable. Until this is accomplished, no numerical values below T_m can be theoretically calculated.

It is possible, by means of the formal introduction of new quantities, to extend the equations to volumes below v_f. This appears to be unfruitful at the present time.

APPENDIX

The auxiliary functions

We shall first investigate the properties of a set of functions which occur repeatedly in the article. The functions g_j of the variables $x_1, x_2, \cdots, x_\nu \cdots, q$ will be defined as

$$g_j(x_1, \cdots, x_\nu, \cdots, q) = \sum_{\nu \geq 1} \nu^j x_\nu q^\nu, \tag{A1}$$

so that

$$q \partial g_j / \partial q = g_{j+1}. \tag{A2}$$

If the value of the lowest real root of the equation for q, $g_1 = 1$, be designated as z, then this z is a function of the arguments x_ν; and if this z replaces q in the functions g_j they then become new functions G_j of the arguments x_ν alone.

$$G_j(x) = \sum_{\nu \geq 1} \nu^j x_\nu z^\nu, \tag{A3}$$

$$G_1(x) = \sum_{\nu \geq 1} \nu x_\nu z^\nu = 1 \quad \text{defines } z, \tag{A4}$$

where the symbol x is used to represent all the x_ν's together. Now

$$\partial G_j / \partial x_\nu = \partial g_j / \partial x_\nu + (\partial \ln z / \partial x_\nu) \cdot q (\partial g_j / \partial q)_{q=z}, \tag{A5}$$
$$= \nu^j z^\nu + G_{j+1}(\partial \ln z / \partial x_\nu).$$

Since

$$\partial G_1 / \partial x_\nu = 0 = \nu z^\nu + G_2 \partial \ln z / \partial x_\nu, \tag{A6}$$

it follows that

$$\partial \ln z / \partial x_\nu = -\nu z^\nu / G_2, \tag{A7}$$

and from (A5) that

$$\partial G_j / \partial x_\nu = \nu z^\nu (\nu^{j-1} - G_{j+1} / G_2), \tag{A8}$$

$$\partial^2 \ln z / \partial x_\nu^2 = (\nu z^\nu)^2 (2 \nu G_2 - G_3) / G_2^3. \tag{A9}$$

Also

$$\partial (G_0 - \ln z) / \partial x_\nu = z^\nu, \tag{A10}$$

$$\partial^2 (G_0 - \ln z) / \partial x_\nu^2 = -(\nu z^\nu)^2 / G_2. \tag{A11}$$

If the x_ν's are all functions of one variable y, $x_\nu = x_\nu(y)$ from (A8)

$$\partial G_j / \partial y = \sum_\nu x_\nu \partial G_j / \partial x_\nu (\partial \ln x_\nu / \partial y)$$

$$= \sum_\nu \nu^j x_\nu z^\nu (\partial \ln x_\nu / \partial y)$$
$$- (G_{j+1} / G_2) \sum_\nu \nu x_\nu z^\nu (\partial \ln x_\nu / \partial y), \tag{A12}$$

$$\partial \ln z / \partial y = -\left[\sum_\nu \nu x_\nu z^\nu (\partial \ln x_\nu / \partial y) \right] / G_2. \tag{A13}$$

It is seen from (A12) that $\partial G_1 / \partial y$ is identically zero.

We shall have use for the special case that the x_ν's are explicitly written in the form $x_\nu = v b_\nu$, but the b_ν's may also be functions of v. If $x_\nu = v b_\nu$,

$$\partial \ln x_\nu / \partial \ln v = 1 + \partial \ln b_\nu / \partial \ln v, \tag{A14}$$

and we define

$$G_{jv} = \sum_\nu \nu^j v b_\nu z^\nu (\partial \ln b_\nu / \partial \ln v), \tag{A15}$$

then from (A12) and (A13)

$$\partial G_j / \partial \ln v = G_j - G_{j+1} / G_2 + G_{jv} - G_{j+1} / G_2 G_{1v}, \tag{A16}$$

$$\partial \ln z / \partial \ln v = -(1 + G_{1v}) / G_2, \tag{A17}$$

$$\partial (G_0 - \ln z) / \partial \ln v = G_0 + G_{0v}. \tag{A18}$$

In the special case that all x_ν's are proportionatl to u, i.e., if

$$\partial \ln x_\nu / \partial \ln u = 1 \qquad (A19)$$

$$\partial G_j / \partial \ln u = G_j - G_{j+1}/G_2, \qquad (A20)$$

$$\partial \ln z / \partial \ln u = -1/G_2. \qquad (A21)$$

These functions play a role in handling the properties of the function $F_0(M, x)$ which will be defined later.

Convergence of the auxiliary functions

In the definitions (A3) and (A4) of G_j and z, the sums were written as if ν varied from unity to infinity. We shall, however, be interested in cases in which the summation is explicitly limited to $1 \leqslant \nu \leqslant M$ with M an extremely large number, although the x_ν's are defined to $\nu = \infty$. Actually we shall only be interested in cases for which

$$\left(\lim_{\nu \to \infty} \right) \ln x_\nu = \nu \ln x_0, \qquad (A22)$$

and in two different modifications of this dependence of x_ν on ν, namely

$$x_\nu = \alpha(x_0, \nu) x_0^\nu / \nu^n, \qquad (A23\mathrm{I})$$

and

$$x_\nu = \alpha(x_0, \nu) x_0^\nu a^{\nu^{\frac{2}{3}}} / \nu^n, \qquad (A23\mathrm{II})$$

in which x_0, α and a are positive, n need not necessarily be an integer, and $\partial \alpha(x_0, \nu) / \partial \nu$ approaches zero for very large values of ν.

We shall refer to the cases (A23I) and (A23II) as cases I and II, respectively.

Now if

$$\sum_{\nu=1}^{\nu=M} \alpha(x_0, \nu) / \nu^{n-1} > 1, \qquad (A24\mathrm{I})$$

or

$$\sum_{\nu=1}^{\nu=M} \alpha(x_0, \nu) a^{\nu^{\frac{2}{3}}} / \nu^{n-1} > 1, \qquad (A24\mathrm{II})$$

respectively, the equation determining z, namely

$$G_1 = 1 = \sum_{\nu=1}^{\nu=M} \alpha(x_0, \nu) (x_0 z)^\nu / \nu^{n-1}, \qquad (A25\mathrm{I})$$

or

$$G_1 = 1 = \sum_{\nu=1}^{\nu=M} \alpha(x_0, \nu) a^{\nu^{\frac{2}{3}}} (x_0 z)^\nu / \nu^{n-1}, \qquad (A25\mathrm{II})$$

can only be satisfied by $(x_0 z) < 1$, and the sum G_1 as well as all the other sums G_2 and G_3, etc., will be absolutely convergent; so that if the upper limit of summation, M, is sufficiently large, their values, and that of z will be independent of M. This case will be referred to as the case of convergent sums.

If, however,

$$\sum_{\nu=1}^{\nu=M} \alpha(x_0, \nu) / \nu^{n-1} < 1, \qquad (A26\mathrm{I})$$

or

$$\sum_{\nu=1}^{\nu=M} \alpha(x_0, \nu) a^{\nu^{\frac{2}{3}}} / \nu^{n-1} < 1, \qquad (A26\mathrm{II})$$

which can only be satisfied in case I if $n > 2$, and in case II if $a < 1$, we find that the solution of (A25) will be $x_0 z = 1 + \epsilon$ where ϵ is an extremely small quantity. We may estimate the value of ϵ in the following manner. The order of magnitude of the last term, the term $\nu = M$ in (A25), may be

expected to lie between $1/M^2$ and unity (actually it seems probable that it will be of order $1/M \ln M$). Using this inequality, and inserting e^ϵ for $x_0 z$ in the last term of (A25) we obtain

$$1/M^2 < \alpha(x_0, M) e^{M\epsilon} / M^{n-1} < 1, \qquad (A27\mathrm{I})$$

or

$$1/M^2 < \alpha(x_0, M) a^{M^{\frac{2}{3}}} e^{M\epsilon} / M^{n-1} < 1, \qquad (A27\mathrm{II})$$

resulting in

$$(1/M)[(n-3) \ln M - \ln \alpha] < \epsilon \\ < (1/M)[(n-1) \ln M - \ln \alpha], \qquad (A28\mathrm{I})$$

$$(1/M)[(n-3) \ln M - \ln \alpha] - (1/M^{\frac{1}{3}}) \ln a < \epsilon \\ < (1/M)[(n-1) \ln M - \ln \alpha] - (1/M^{\frac{1}{3}}) \ln a. \qquad (A28\mathrm{II})$$

In case I we see that ϵ is of the order of magnitude $1/M$, which will be sufficient for the purposes of our investigation. In case II, however, we find that, to within terms of definitely smaller order of magnitude, we may write

$$\epsilon = (-\ln a)/M^{\frac{1}{3}} = \gamma/M^{\frac{1}{3}}, \qquad (A29\mathrm{II})$$

where $\gamma = -\ln a$ is positive because the case of divergent sums can occur only if a is less than unity.

The condition of Eq. (A26) will always lead to the equation $z = x_0^{-1}$ to within terms of order of magnitude M^{-1} in I, and $M^{-\frac{1}{3}}$ in II. This will be referred to as the case of divergent sums.

If the sums are divergent in the sense discussed in the previous paragraph, the values of the individual terms of the sum G_1 will not decrease rapidly with increasing values of ν. It is obvious that the sum G_0, the individual terms of which have $1/\nu$ times the value of the terms of G_1, must be smaller than G_1 and independent of the value of M. The terms of G_2 and G_3, which are ν, and ν^2 fold greater, respectively, than the corresponding terms of G_1 will certainly not converge. The values of the sums will be expected to be dependent on the value of M. Various methods of estimation lead to the same qualitative result for the order of magnitude of the sums G_j, namely

$$G_j \cong M^{j-1}, \qquad (j > 1). \qquad (A30)$$

The equation (A30) is nowhere of great importance to the argument of the article. It is of importance, but fairly obvious, that G_2 and G_3 are extremely large and dependent on the limit of summation M, in the case of divergent sums.

The case that

$$\sum_{\nu=1}^{M} \alpha(x_0, \nu) / \nu^{n-1} = 1, \qquad (A31\mathrm{I})$$

is used once in the article. In this case the solution of (A25I) is obviously that $x_0 z$ is exactly equal to unity. In this case the summation of G_2 and G_3 offers no difficulties. If $n = 5/2$ we obtain

$$G_2 \cong \sum_{\nu=1}^{\nu=M} 1/\nu^{\frac{1}{2}} \cong M^{\frac{1}{2}}, \qquad (n = 5/2), \qquad (A32\mathrm{I})$$

$$G_3 \cong \sum_{\nu=1}^{\nu=M} \nu^{\frac{1}{2}} \cong M^{\frac{3}{2}}, \qquad (n = 5/2), \qquad (A33\mathrm{I})$$

whereas if $n = 3$:

$$G_2 \lessgtr \sum_{\nu=1}^{M} 1/\nu \lessgtr \ln M, \quad (n = 3), \qquad \text{(A34I)}$$

$$G_3 \lessgtr \sum_{\nu=1}^{M} 1 \lessgtr M, \quad (n = 3). \qquad \text{(A35I)}$$

The function $F_0(Mx)$

The function $F(M, J, x_1, \cdots, x_\nu, \cdots)$ of the variable M, a very large integer, J, a parameter, and of the x_ν's, is defined as

$$F(M, J, x) = \sum_{\substack{\mu_\nu \\ \Sigma \nu \mu_\nu = M}} \prod_\nu (Jx_\nu)^{\mu_\nu}/\mu_\nu !, \qquad \text{(A36)}$$

where, as before, x is taken to represent all the x_ν's together. If J is set equal to M we shall call

$$F(M, M, x) = F_0(M, x). \qquad \text{(A37)}$$

Direct differentiation of (A36) with respect to x_ν leads to

$$\frac{1}{J} \frac{\partial F(M, J, x)}{\partial x_\nu} = F(M - \nu, J, x) = \frac{1}{J^\nu} \frac{\partial^\nu F(M, J, x)}{\partial x_1^\nu}, \quad \text{(A38)}$$

which, upon setting $J = M$, gives the equation for F_0

$$\frac{1}{M} \frac{1}{F_0} \frac{\partial F_0}{\partial x_\nu} = \frac{\partial}{\partial x_\nu}\left(\frac{\ln F_0}{M}\right) = \frac{1}{M^\nu} \frac{1}{F_0} \frac{\partial^\nu F_0}{\partial x_1^\nu}. \qquad \text{(A39)}$$

Since F_0 is a homogeneous function of degree M in the variables $y_\nu = x_\nu^{1/\nu}$ it follows from Euler's theorem that

$$\sum_\nu y_\nu \frac{1}{M} \frac{1}{F_0} \frac{\partial F_0}{\partial y_\nu} = \sum_\nu \nu x_\nu \frac{\partial}{\partial x_\nu}\left(\frac{\ln F_0}{M}\right) = 1. \qquad \text{(A40)}$$

We now propose to show that we can write approximately[6]

$$\ln F_0(M, x) = M \ln f(x) + \ln h(x) + \ln g(M), \quad \text{(A41)}$$

and that

$$\ln f(x) = G_0(x) - \ln z(x), \qquad \text{(A42)}$$

$$\ln h(x) = -[\ln G_2(x)]/2, \qquad \text{(A43)}$$

$$\ln g(M) = -[\ln 2\pi M]/2. \qquad \text{(A44)}$$

The approximation of Eq. (A42) holds as long as there is a real positive root to Eq. (A4) for $z(x)$, and as long as $z(x)$ is independent of M as discussed in the section under convergence of the auxiliary functions.

The combination of the assumption (A41) with (A40) shows that

$$\sum_\nu \nu x_\nu \partial \ln f(x)/\partial x_\nu = 1, \qquad \text{(A45)}$$

$$\sum_\nu \nu x_\nu \partial \ln h(x)/\partial x_\nu = 0, \qquad \text{(A46)}$$

since $f(x)$ and $h(x)$ are assumed to be independent of M. We shall use the symbols

$$z(x) = \partial \ln f(x)/\partial x_1, \qquad \text{(A47)}$$

$$z_1(x) = \partial z(x)/\partial x_1, \qquad \text{(A48)}$$

$$\sigma(x) = \partial \ln h(x)/\partial x_1, \qquad \text{(A49)}$$

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[6] Professor M. Born of Edinburgh has kindly communicated to the authors that this theorem may be proved by using a Cauchy integral and the method of steepest descents.

and later identify $z(x)$ with the $z(x)$ defined by (A4).

Upon using the assumption of (A42) in Eq. (A39), then developing according to powers of $1/M$, and inserting the above symbols, one obtains

$$\frac{\partial}{\partial x_\nu}\left(\frac{\ln F_0}{M}\right) = \frac{\partial \ln f(x)}{\partial x_\nu} + \frac{1}{M} \frac{\partial \ln h(x)}{\partial x_\nu} = \frac{1}{M^\nu} \frac{1}{F_0} \frac{\partial^\nu F_0}{\partial x_1^\nu}$$

$$= \sum_{\substack{n_k \\ \Sigma k n_k = \nu}} \prod_k \frac{\nu!}{n_k!(k!)^{n_k}} M^{-\Sigma_k (k-1) n_k} \left[\frac{\partial^k}{\partial x_1^k} \frac{\ln F_0}{M}\right]^{n_k}$$

$$= z^\nu + \frac{1}{M}\left[\nu z^\nu\left(\frac{\sigma}{z} - \frac{z_1}{2z^2}\right) + \nu^2 z^\nu \frac{z_1}{2z^2}\right] + \cdots. \quad \text{(A50)}$$

Equating powers of $1/M$ leads to

$$\partial \ln f(x)/\partial x_\nu = z^\nu, \qquad \text{(A51)}$$

$$\partial \ln h(x)/\partial x_\nu = \nu z^\nu(\sigma/z - z_1/2z^2) + \nu^2 z^\nu z_1/2z^2. \quad \text{(A52)}$$

The use of (A51) in (A45) gives us Eq. (A4) which identifies $z(x)$ as defined by (A47) with $z(x)$ defined by (A4). Comparison of (A51) with (A10) shows that Eq. (A42) holds to an additive constant which we shall later show to be zero. Having identified $z(x)$ we may now use (A7) to show that $z_1/2z^2 = -1/2G_2$ and inserting this value in (A52), and (A52) in (A46) one obtains

$$\sum_\nu \nu^2 x_\nu z^\nu(\sigma/z + 1/2G_2) - \sum_\nu \nu^3 x_\nu z^\nu(1/2G_2)$$

$$= G_2(\sigma/z + 1/2G_2) - G_3/2G_2 = 0, \quad \text{(A53)}$$

or

$$\sigma/z = (G_3 - G_2)/2G_2^2. \qquad \text{(A54)}$$

Using (A54) and the equation z_1 in (A52) finally yields

$$\partial \ln h(x)/\partial x_\nu = \nu z^\nu G_3/2G_2^2 - \nu^2 z^\nu(1/2G_2). \quad \text{(A55)}$$

Comparison of this equation with (A8) shows that (A43) holds to within a constant of integration, which we shall now show can be taken as zero.

We shall consider the special case that $x_1 > 0$ and $x_\nu = 0$, $\nu \neq 1$. In this case we may evaluate Eq. (A36) with $J = M$ directly by the use of the Stirling approximation obtaining, since only the term $\mu_1 = M$ occurs,

$$\ln F_0(M, x) = M(\ln x_1 + 1) - (\ln 2\pi M)/2,$$
$$(x_1 > 0; x_\nu = 0, \nu \neq 1). \quad \text{(A56)}$$

In this special case G_0 and G_2 are both unity and $z = 1/x_1$, so that the equations (A42) and (A44) inclusive lead to the same value for $\ln F_0(M, x)$.[7] This suffices to show that the integration constants properly present in deriving (A42) and (A43) for $\ln f(x)$ and $\ln h(x)$ from (A51) and (A55) are zero and the $\ln g(M)$ of (A44) respectively.

Validity of the asymptotic expressions for F

Combining equations (A41) to (A44) inclusive we obtain the final asymptotic expression for $F_0(M, x)$ which is

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[7] This special case $x_k > 0$, $x_\nu = 0$ if $\nu \neq k$, may also be readily evaluated by both using (A37) directly and (A42) to (A45). In this case $\ln z = -(\ln kx_k)/k$ and $G_0 = 1/k$, $G_2 = k$. Evaluation by means of (A42) to (A45) leads to $\ln F_0(M, x) = (M/k)(1 - \ln kx_k) - (\ln 2\pi kM)/2$. Direct evaluation of (A37) with $J = M$ using the Stirling approximation for the factorial gives the above expression plus $\ln k$ if M/k is an integer. If M/k is not an integer $F_0(M, x)$ is zero. It is obvious that this extreme case is not covered by Eqs. (A42) to (A45), but it is of interest to note that if the F_0 is averaged over a range of M's the above expression is obtained; since only every k'th M leads to F_0 other than zero, and if this value for M/k an integer is divided by k we obtain agreement with the above.

correct for very large values of M,

$$F_0(M, x) = e^{MG_0(x)}/[z(x)]^M(2\pi MG_2(x))^{\frac{1}{2}},$$
$$\ln F_0(M, x) = M[G_0(x) - \ln z(x)]$$
$$- [\ln 2\pi MG_2(x)]/2. \quad (A57)$$

If the function $F_1(M, x)$ is defined as

$$F_1(M, x) = F(M-1, M, x) = (1/M)\partial F_0(M, x)/\partial x_1, \quad (A58)$$

then by direct differentiation

$$F_1(M, x) = e^{MG_0(x)}/[z(x)]^{M-1}(2\pi MG_2(x))^{\frac{1}{2}},$$
$$\ln F_1(M, x) = MG_0(x) - (M-1) \ln z(x)$$
$$- [\ln 2\pi MG_2(x)]/2. \quad (A59)$$

The function $F_0(M, x)$ is the same as $Q_T/N!$ if the x_ν's are the νb_l's of the article and M is N, the total number of particles. The function $F_1(M, x)$ is the same as $l^2 b_l$ if l replaces M and the x_ν's are the irreducible integrals β_k.

The expressions (A57) for $F_0(M, x)$ and (A59) for $F_1(M, x)$ are correct asymptotic expressions for these functions as long as they can be approximated in the general form of (A41). We have already discussed the case that one of the x_ν's alone is different from zero. Unless ν is unity, the approximation (A41) is invalid. Even then (A57) and (A59) give correct average values for a range of M values. It appears to be sufficient for the validity of (A57) and (A59) that two x_ν's alone be different from zero, and that the ratio of the smaller to the greater x_ν be larger than $\nu/M\nu'$.

One other case that (A57) and (A59) as well as the expression (A41) are invalid is that $G_2(x) < 0$. If all the x_ν's are positive the equation $G_1 - 1 = 0$ has only one positive root for z. If the x_ν's are all functions of one variable, say the temperature T, and are all positive at low values of T, it may be that some of them become increasingly negative with increasing T's. Because $G_1 - 1$ is a finite polynomial in z with its zeroth coefficient minus unity, the single positive root of the equation at low T's cannot become zero or infinity, but may, and does, disappear into the complex plane with increasing values of T. At this temperature $T = T_c$, z must be a double root, and

$$\partial(G_1 - 1)/\partial \ln z = G_2 = 0. \quad (A60)$$

At $T = T_c$ the real root z disappears, G_2 becomes zero, and the expressions (A41), (A57) and (A59) become invalid. This temperature T_c is shown in the article to be the critical temperature.

The coefficients of $\Pi\beta_\nu{}^{n_\nu}$ in b_l

It can be shown that there is a one to one correspondence between the coefficient of the term characterized by the n_ν's, the powers of the ν'th normalized irreducible integral in a term of b_l, $(\sum \nu n_\nu = l-1)$, and the answer to the problem discussed in the following paragraph.

Suppose we have n_1 identical mechanical frames of type 1, n_2 of type 2, $\cdots$, n_ν of type ν. The frame of type ν has $\nu + 1$ holes into which bolts can be inserted, the frames being so built that every one of the $\nu + 1$ holes is exactly equivalently situated with respect to every other one of the holes (a geometrical impossibility in three dimensions for most large values of ν). Suppose we have l numbered bolts with $l = \sum_\nu \nu n_\nu + 1$. The problem is to determine how many ways we can insert the l bolts into the $l - 1 + \sum n_\nu$ holes so that the frames are all singly connected to each other by common bolts.

Each bolted arrangement can be broken down into l different dissociated arrangements consisting of n frames and one free bolt, where each frame has ν bolts in it and one free hole, and no frames are connected by a common bolt. We can dissociate in exactly l ways because we can choose from the bolted arrangement any one of the bolts as the free bolt, and the dissociation process is then uniquely determined. The number of ways that we can make a dissociated arrangement is

$$l!/\prod_\nu n_\nu!(\nu!)^{n_\nu}.$$

If D is the number of bolted arrangements we can make make from one dissociated arrangement then the desired answer is $Dl!/\prod_\nu n_\nu!(\nu!)^{n_\nu}l$.

For the small values of $n = \sum n_\nu$ we know by counting that $D = l^{n-1}$. We now prove that if the equation $D = l^{n-1}$ holds for n it also holds for $n + 1$. To do this we add a frame ν to a system of n frames and bolts and show that the new D becomes $(l+\nu)^n$, (method of complete induction). We consider that the old frames are first bolted together into $\nu + 1$ (or fewer) groups, knowing how many ways that can be done, and then these groups are bolted to the new frame. The resulting complicated sum can be shown to be equal to $(l+\nu)^n$. Use must be made of the fact that

$$\sum_{\nu=0}^{\nu=m} \binom{m}{\nu} (-1)^\nu(a+\nu)^P = 0 \quad \text{if } P < m.$$

The final answer then becomes $l!l^n/\prod_\nu n_\nu!(\nu!)^{n_\nu}l^2$, which is the same as Eq. (19) if it is remembered that $\nu!$ is included in the definition of β_ν as a normalization factor. this proof is primarily due to Dr. M. Goeppert Mayer to whom the authors are greatly indebted. The original equation was deduced by Dr. P. G. Ackermann from a numerical calculation of the first several members. Without this hint as to the correct solution, the proof would have been impossible.