ASSOCIATION THEORY AND LIQUID STRUCTURE

by

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ABSTRACT

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An approach to a theory of liquids is presented which discards earlier assumptions of association theory, especially that which assumed the presence in the liquid of clusters of every size. It is shown that this assumption leads to contradictions that may be resolved by abandoning it. Discussions of the nature and cause of the gas-liquid transition and of the critical state are given in light of the new approach. It is predicted that the postulated gap in cluster size disappears at the critical temperature and that the cluster size characteristic of the critical state should be five. Simple calculations show that for argon, nitrogen, oxygen, and water this value is indeed equal to 5.3, 5.2, 4.8, and 6.1, respectively. A discussion is presented of the reasons for the excellent results obtained for the atomic radii of the alkali metals using the now-discarded assumptions.

Appendices discuss the techniques of calculating compressibility parameters of the Tait-Tammann equation using a new approach, methods of gauging the reliability of compressibility data for liquids, and the range of applicability of the Tait-Tammann equation. A computer program for performing the calculations in the first appendix is included.

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Roman alphabet:

B_k = k-th virial coefficient.

$\underline{C}$ = number of clusters (in units of Avogadro's number) per unit volume.

C_j = number of clusters of size j ("j-mers"; in units of Avogadro's number) per unit volume.

E = integration constant of theoretical expression for J in Tait-Tammann equation.

H = integration constant of Tait-Tammann equation.

J = empirical constant in Tait-Tammann equation.

$K_{1,j}$ = equilibrium constant for the chemical reaction $X + X_j \rightleftarrows X_{j+1}$. $K_{1,j} = C_{j+1}/C_jC_1$.

K_j = equilibrium constant for overall net reaction $jX \rightleftarrows X_j$. $K_j = C_j/C_1^{\,j}$.

L = empirical constant in Tait-Tammann equation.

m = mass of sample, in grams; also used as size of largest cluster.

m_o = molecular weight of the 1-mer.

$\underline{N}$ = number of clusters of all sizes present in a sample. (In units of Avogadro's number.) $\underline{N} = \underline{C}v$.

N_j = number of clusters of size j present in a sample. $N_j = C_jv$.

N_s = number of formula weights of sample. $N_s = C_sv$.

P = pressure.

P^o = vapor pressure.

R = gas constant.

T = absolute temperature.

$u = 1 - \pi/v$.

v = volume.

Zn = number-average degree of association; $Zn = N_s/\underline{N} = C_s/\underline{C}$.

Z_w = weight-average degree of association; $Z_w = \Sigma_j^2 N_j / N_s = \Sigma_j^2 C_j / C_s$.

Greek alphabet:

α = smallest cluster size (other than 1) postulated to be present in the liquid.

ϵ = heat of 1-mer formation (calories/mole).

λ = $P\varphi Z_n$; defined by analogy to the theoretical expression for L/J except that α is held constant.

$\Phi = -d\ln C_1 / dv$.

$\varphi = -(\partial \ln C_1 / \partial v)_\alpha$.

Cyrillic alphabet:

В = total excluded volume of a sample.

$В_j$ = excluded volume per mole of j-mer.

I

Introductory and Historical

Introduction

The attempts to understand the varieties of macroscopic experience in terms of the "eternal" properties of atoms go back as far as Democritus in the fifth century before Christ. Atomism had no firm basis, however, until resurrected by Dalton to explain the Laws of Definite and Multiple Proportions. At roughly the same time, the caloric theory of heat gave way to the modern kinetic theory, and the ideas, generated thereby, of molecules in constant random motion, colliding with each other and with the walls of the containing vessel, led ultimately to a theoretical derivation of the ideal-gas law, $Pv = N_S RT$, which had been known experimentally years earlier (1). (N_S is the number of formula weights of the sample.)

The derivation of this simple law implicitly assumed two things which are true only at high temperatures and high dilution, namely (a) that the volume of the molecules themselves was negligible compared to the volume of the container, and (b) that the molecules exerted no force on each other except for elastic recoil on collision. Both of these assumptions are, in general, false, and the earliest attempts to correct them theoretically were carried out by Clausius and especially van der Waals, in 1873 (2).

Borrowing from Clausius, van der Waals assumed that the volume available to a molecule is actually less than the volume of the container by an amount b, the "excluded volume" or "covolume"

of the molecules themselves, and that therefore this term should be subtracted from v and the difference inserted into the ideal-gas law.

In addition, van der Waals corrected the pressure in the following way: There is a net force directed towards the interior exerted by the molecules in the bulk of the gas on those at the walls. If we imagine the gas divided into layers of molecules parallel to the walls, the total inward pull can be assumed proportional to the number of molecules in the layer near the wall (n), and to the number of molecules in the adjacent inner layer (also n), the other molecules being too far away from the walls to exert any influence. This pull has the effect of lowering the pressure from the ideal-gas value, and so the correction term must be added to the observed pressure.

The number of molecules, n, in any layer is proportional to the number density, N_S/v, of the gas. Hence the force inward is proportional to n^2 and therefore to $(N_S/v)^2$ or:

$$\text{correction term} = a(N_S/v)^2 \qquad (1)$$

where a is a proportionality constant.

Adding these two corrections to the ideal-gas law, we get

$$(P + aN_S^2/v^2)(v - b) = N_S RT \qquad (2)$$

for N_S moles of gas. This equation represented a substantial improvement over the ideal law. Since it is cubic in v, a graph of P vs. v will exhibit a loop ("van der Waals loop") implying the coexistence of two volumes at the same pressure (see Figure 1), the smaller of which is characteristic of the liquid phase. Above a

certain critical temperature, two of the roots become imaginary, and only a single fluid state is predicted. Thus van der Waals' equation was the first to include the peculiar phenomenon of the critical state.

Still other equations for gases have been proposed (3), but none of such general applicability as the virial equation first proposed by H. Kamerlingh Onnes (4). Originally presented simply as a curve-fitting device and written only in the first, second, fourth, and sixth powers of v, it is now generally employed in the more general form of the infinite series:

$$\frac{Pv}{N_s RT} = 1 + B_2\rho + B_3\rho^2 + \ldots\ldots \qquad (3)$$

where B_k is called the k-th virial coefficient, and ρ is the number density of the molecules, N_s/v. The coefficients are temperature-dependent, and can be given meaning from theoretical considerations, as is shown in the following sections.

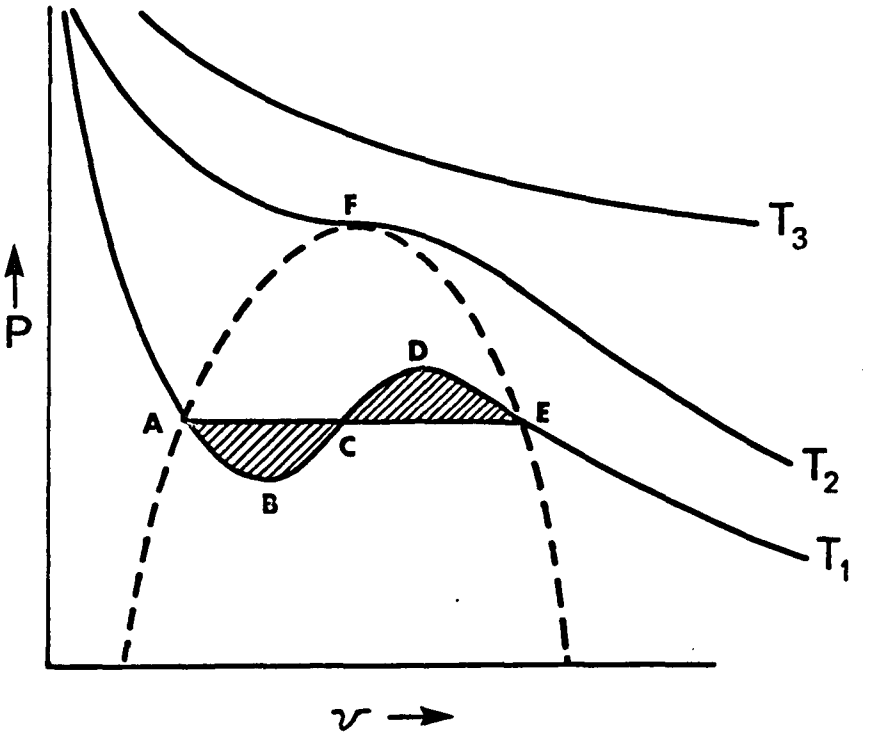


Figure 1. A plot of van der Waal's equation at three successively increasing temperatures, T_1, T_2, and T_3. T_1 exhibits the loop (ABCDE) described in the text. The areas ABC and CDE are equal. The volume at A is that of the liquid; that at E is the vapor. The line AE is the vapor pressure. T_2 is the critical temperature, exhibiting an inflection point ($dP/dv = d^2P/dv^2 = 0$) at F, the critical point. T_3 is well above the critical, and the material behaves much like an ideal gas. The dashed curve AFE is the locus of all points like A and E at temperatures less than the critical.

Statistical-Mechanical Derivation of the Virial Equation

It is most convenient, for this problem, to start with the grand partition function Ξ (5), defined by

$$\Xi(v, T, \mu) = e^{Pv/kT} = \sum_{j,N} \exp(\{N\mu - \epsilon_j\}/kT) \tag{4}$$

where μ is the chemical potential. Ξ is summed over the energy states j and the number of molecules N. It may also be written

$$\Xi = \sum_N e^{N\mu/kT} \sum_j e^{-\epsilon_j/kT}$$

$$= \sum_N Q_N \lambda^N \tag{5}$$

where $$Q_N = \sum_j \exp(-\epsilon_j/kT) \tag{6a}$$

and $$\lambda = \exp(\mu/kT). \tag{6b}$$

Then $$\Xi = \exp(Pv/kT) = 1 + \sum_{N\geq 1} Q_N \lambda^N \tag{7}$$

where we have set $Q_0 = 1$ since for $N = 0$ there is only one state, that with $E = 0$.

Let us define a new "activity", z, proportional to the "absolute activity", λ, and having the property that $z \to \rho$ as $\rho \to 0$.

To find the desired relation between z and λ, take the limit of Equation 7 as $\lambda \to 0$ so that $\Xi \to 1$:

$$\ln \Xi = Pv/kT = Q_1\lambda + \ldots. \tag{8}$$

Now, as $P \to 0$:

$$P/kT = N_s/v = \rho = Q_1\lambda/v. \tag{9}$$

Then clearly,

$$z = Q_1\lambda/v. \tag{10}$$

If we put zv/Q_1 in place of λ in Equation 7 we get

$$\Xi = 1 + \sum_{N\geq 1} (Q_N v^N/Q_1^N) z^N. \tag{11}$$

Let us define a new quantity Z_N by:

$$Z_N = N!Q_N v^N/Q_1^N. \tag{12}$$

Then Equation 11 may be written:

$$\Xi = \exp(Pv/kT) = 1 + \sum_{N\geq 1} (Z_N/N!) z^N. \tag{13}$$

Take the logarithm of both sides of Equation 13, expand the term on the right, divide by v, and get:

$$P/kT = \sum_{j\geq 1} b_j z^j \tag{14}$$

in which the b_j are given by:

$$\begin{aligned} 1!vb_1 &= Z_1 = v \\ 2!vb_2 &= Z_2 - Z_1^2 \\ 3!vb_3 &= Z_3 - 3Z_1Z_2 + 2Z_1^3 \\ &\text{etc.} \end{aligned} \tag{15}$$

Now, since the ensemble average number of particles in the system is (6):

$$N_s = \lambda(\partial \ln\Xi/\partial\lambda)_{T,v} \tag{16}$$

and since

$$\ln\Xi = Pv/kT \qquad \text{(from Equation 7)} \tag{17}$$

Then we may write

$$\rho = N_s/v = \lambda \left(\frac{\partial P/kT}{\partial \lambda}\right)_T = z \left(\frac{\partial P/kT}{\partial z}\right)_T \qquad (18)$$

since z is proportional to λ.

Taking the derivative of Equation 14 using the relationship in Equation 18, we get

$$\rho = \sum_{j \geq 1} j b_j z^j. \qquad (19)$$

To convert the z expansion (Equation 19) into a ρ expansion, we invert the series by substituting

$$z = \rho + a_2 \rho^2 + a_3 \rho^3 + \ldots \qquad (20)$$

into Equation 19 to obtain an identity in ρ. Equating the coefficients of like powers of ρ we find:

$$\begin{aligned} a_2 &= -2b_2 \\ a_3 &= -3b_3 - 4a_2 b_2 = -3b_3 + 8b_2^2 \\ &\text{etc.} \end{aligned} \qquad (21)$$

Finally, using the a's just deduced, put them into Equation 14 via Equation 20 and get:

$$Pv/N_s kT = 1 + B_2 \rho + B_3 \rho^2 + \ldots. \qquad (22)$$

where

$$\begin{aligned} B_2 &= -b_2 \\ B_3 &= 4b_2^2 - 2b_3 \\ &\text{etc.} \end{aligned} \qquad (23)$$

Note that to calculate B_2, we need only Q_1 and Q_2; for B_3 we need only Q_1, Q_2, and Q_3.

Let us examine the second virial coefficient. The Z_N above are in fact the classical configuration integrals $\int \ldots \int_V e^{-\sum u(r_{ij})/kT} d\tau_1 \ldots d\tau_N$.

Hence the first two are:

$$Z_1 = \int_V d\tau_1 = v$$
$$Z_2 = \iint_V e^{-u(r_{12})/kT} d\tau_1 d\tau_2 \tag{24}$$

The second virial coefficient is then:

$$B_2 = -b_2 = \frac{-1}{2v}(Z_2 - Z_1^2)$$
$$= \frac{-1}{2v}\iint_V (e^{-u(r_{12})/kT} - 1) d\tau_1 d\tau_2. \tag{25}$$

Changing the origin to molecule 1 so that $|\tau_2 - \tau_1| = \tau_{12}$ we may write:

$$B_2 = \frac{-1}{2v}\int_V d\tau_1 \int_V (e^{-u(r_{12})/kT} - 1) d\tau_{12}$$
$$= \frac{1}{2}\int_o^\infty (1 - e^{-u(r)/kT}) \cdot 4\pi r^2 dr \qquad (r \equiv r_{12})$$
$$= 2\pi \int_o^\infty (1 - e^{-u(r)/kT}) r^2 dr. \tag{26}$$

We will later show this last expression (Equation 26) to be identical to that obtained from association theory, which is described in the next section.

Theory of Association

The fundamental postulates of the theory of association are twofold (7). First, because of the attractive forces between molecules, they will tend to cluster; since under any steady-state conditions the numbers of clusters of various sizes will be constant with time, they may be treated as being in chemical equilibrium with each other. For a given molecule X, the growth and decay of a particular cluster, or j-mer, X_j, is presumed to occur via the addition or subtraction of single molecules (1-mers) according to the scheme:

$$X_{j-1} + X \rightleftarrows X_j \tag{27}$$

for which the equilibrium constant is

$$K_{1,j-1} = \frac{C_j}{C_{j-1}C_1} \tag{28}$$

where C_j is the concentration of j-mers in the system.

In considering the various possible equilibria (34), the question arises: is one justified in writing the equilibrium constants under the assumption that the addition and loss of 1-mers is the only process occurring, and totally neglecting the equilibria among larger species? Blatz (8) formulated a general principle which can be stated thus: the equilibrium equations are unique, no matter what the formal mechanisms by which they have been derived. The one-constant theory of Ginell (9), who neglects all the higher equilibria, and that of Blatz and Tobolsky (10) (also using one constant), who consider all of them to be present, lead to identical equations at

equilibrium (11). They differ, however, at times before equilibrium.

It is not self-evident from all this, however, that Blatz's principle also applies to cases where the equilibrium constants are <u>not</u> identical. That it does apply can be shown by the following proof.

The equilibria involved can be written thus:

$$\begin{array}{lll} X + X \rightleftarrows X_2 & & \\ X + X_2 \rightleftarrows X_3 & & \\ X + X_3 \rightleftarrows X_4; & X_2 + X_2 \rightleftarrows X_4 & \\ X + X_4 \rightleftarrows X_5; & X_2 + X_3 \rightleftarrows X_5 & \\ X + X_5 \rightleftarrows X_6; & X_2 + X_4 \rightleftarrows X_6; & X_3 + X_3 \rightleftarrows X_6 \\ \text{etc.} & \text{etc.} & \text{etc.} \end{array} \qquad (29)$$

Writing the equilibrium constants for the individual processes, we have:

$$\begin{array}{lll} K_{1,1} = C_2/C_1^2 & & \\ K_{1,2} = C_3/C_1C_2 & & \\ K_{1,3} = C_4/C_1C_3; & K_{2,2} = C_4/C_2^2 & \\ K_{1,4} = C_5/C_1C_4; & K_{2,3} = C_5/C_2C_3 & \\ K_{1,5} = C_6/C_1C_5; & K_{2,4} = C_6/C_2C_4; & K_{3,3} = C_6/C_3^2 \\ \text{etc.} & & \end{array} \qquad (30)$$

From the first column of Equation 30 we have

$$C_j = (K_{1,1}K_{1,2}K_{1,3}\cdots K_{1,j-1})C_1^j \qquad (31)$$

which is the recurrence equation given by Ginell (7) which neglects higher-order interactions. Since these are simultaneous equilibria, solving columns 1 and 2 of Equation 30 simultaneously gives:

$$K_{1,1}K_{1,1}K_{2,2} = K_{1,1}K_{1,2}K_{1,3}$$

or: $$K_{2,2} = K_{1,2}K_{1,3}/K_{1,1}$$

and $$K_{2,3} = K_{1,3}K_{1,4}/K_{1,1}$$

$$K_{2,j} = K_{1,j}K_{1,j+1}/K_{1,1} \qquad (32)$$

Similarly: $$K_{3,3} = K_{1,3}K_{1,4}K_{1,5}/K_{1,1}K_{1,2}$$

$$K_{3,4} = K_{1,4}K_{1,5}K_{1,6}/K_{1,1}K_{1,2}$$

and $$K_{4,4} = K_{1,4}K_{1,5}K_{1,6}K_{1,7}/K_{1,1}K_{1,2}K_{1,3}$$

the general expression for any $K_{n,m}$ being:

$$K_{n,m} = \prod_{i=m}^{m+n-1} K_{1,i} \Big/ \prod_{j=1}^{n-1} K_{1,j} \qquad (33)$$

This shows that all the higher equilibrium constants can be expressed in terms of the $K_{1,j}$'s and need not therefore enter into the equations unless it is convenient that they do so. The simplest relationship is the one already given in Equation 31, which is equivalent to that given by Woolley (12), if one states that

$$K_n^{(w)} = \prod_{x=1}^{n-1} K_{1,x} \qquad (34)$$

where $K_n^{(w)}$ is Woolley's constant.

In association theory, the string of constants in Equation 34 is also combined into a single constant, so that we have, in general:

$$C_j = K_j C_1^{\,j} \qquad (35)$$

where K_j is defined by the expression, analogous to Woolley's,

$$K_j = \prod_{x=1}^{j-1} K_{1,x} \qquad (36)$$

This is equivalent to the net chemical reaction

$$jX \rightleftarrows X_j \tag{37}$$

in which j 1-mers combine to form one j-mer. To avoid ambiguity, the term molecule is replaced by the term unimer; the unimer is either unassociated, in which case it is called a 1-mer, or it is bound with others in a cluster (or j-mer) of j unimers. Note the 1-mer may be considered a j-mer with j = 1. K_1, therefore, is unity.

In addition to clustering, the j-mers occupy a finite volume; however, the excluded volume of the j-mer is not j times the excluded volume of the 1-mer. A glance at Figure 2 shows the truth of this in the simple case of the 2-mer. Since the excluded volume in this treatment is different from that defined by van der Waals, it is represented by the cyrillic character Б (read "beth"), such that

$$Б = \sum Б_j N_j \tag{38}$$

where $Б_j$ is the excluded volume per mole of j-mer, and N_j is the number of moles of such j-mers.

We will now derive an equation of state incorporating the two basic ideas, association and excluded volume, of association theory (13). In the derivation we will follow in principle the classical kinetic derivation of the ideal gas law.

Let us imagine we have a cubical box of side a, containing a gas at equilibrium. As a consequence of the preceding discussion the particles in the box are of masses which are multiples of m_o,

the mass of the unimer. When a j-mer strikes the wall of the box, it undergoes a change in momentum on collision of $2m_j u_j$, where m_j is its mass and u_j its velocity component normal to the wall it is striking. The number of collisions it has in unit time with the two walls in this direction is $u_j/(a - \beta_j)$ where β_j is its diameter. This is obvious since if the particle has a volume, and for the moment we are imagining it to be a sphere, then its center cannot approach either wall closer than $\frac{1}{2}\beta_j$. The change in the component of momentum per unit time in this direction is then

$$2m_j u_j \times \frac{u_j}{a - \beta_j} = \frac{2m_j u_j^2}{a - \beta_j}. \tag{39}$$

The area of the walls against which this particle strikes in this direction is necessarily $2(a - \beta_j)^2$. Hence, the pressure exerted by the particle is:

$$P_j = m_j u_j^2/(a - \beta_j)^3. \tag{40}$$

Since the total pressure is the sum of the pressures exerted by each particle, the total pressure is

$$P = \sum_j n_j m_j \langle u_j^2 \rangle/(a - \beta_j)^3 \tag{41}$$

where n_j is the number of j-mers in the box and $\langle u_j^2 \rangle$ is the average of the squares of the u-component of the velocity of the particles of size j.

Now the prime condition of equilibrium requires that all the various species of particles be at the same temperature, and hence have the same average kinetic energy. Hence,

$$m_x \langle c_x^2 \rangle = m_y \langle c_y^2 \rangle \tag{42}$$

for all x and y, where $\langle c_x^2 \rangle$ is the mean square velocity of the x-mer. Since by definition $m_j = jm_o$, then, from Equation 42,

$$\langle c_j^2 \rangle = \langle c_1^2 \rangle / j \tag{43}$$

and since the component velocities along the three spatial axes are equal,

$$\langle u_j^2 \rangle = \langle c_j^2 \rangle / 3 = \langle c_1^2 \rangle / 3j \tag{44}$$

Hence $$m_j \langle u_j^2 \rangle = m_o \langle c_1^2 \rangle / 3 \tag{45}$$

and, from Equation 41:

$$P = \frac{m_o \langle c_1^2 \rangle}{3} \sum \frac{n_j}{(a - \beta_j)^3} \tag{46}$$

By the law of equipartition of energy,

$$m_o \langle c_1^2 \rangle / 3 = kT. \tag{47}$$

Hence

$$P = kT \sum \frac{n_j}{(a - \beta_j)^3}$$

or, $$P = RT \Sigma N_j / (a - \beta_j)^3 \tag{48}$$

where N_j is the number of j-mers in units of Avogadro's number.

The term a is the length of the box and the assumption was made that the particle must travel a distance $a-\beta_j$ before it could exert pressure on the wall. If we now consider that the box has a large number of particles in it and that the collisions with the wall are not instantaneous, there will then be particles between the one in question and the wall at collision. The distance that this particle must travel to exert its pressure is then less by the average thickness of particles between itself and the wall.

On the average this will be $a = (v - B)^{1/3}$ where v is the actual volume of the box and B is the excluded volume of all the particles, discussed earlier. This gives us the equivalent cube in free space of the particle.

Our equation then becomes

$$P/RT = \sum_j N_j / \{(v - B)^{1/3} - \beta_j\}^3 \qquad (49)$$

$$\text{or: } Pv/RT = \sum_j N_j \Big/ \left\{(1 - B/v)^{1/3} - \frac{\beta_j}{v^{1/3}}\right\}^3 \qquad (50)$$

If the volume that the gas occupies is comparatively large then β_j can be neglected; this assumption would be invalid if, for instance, the behavior in narrow capillaries were being considered. Consequently, Equation 50 becomes:

$$\begin{aligned} Pv/RT &= \underline{N}/u \\ \text{or: } P(v - B) &= \underline{N}RT \end{aligned} \qquad (51)$$

where the term $\underline{u}$ has been substituted for $(1 - B/v)$, and $\underline{N}$ is the total number of j-mers in the sample,

$$\underline{N} = \sum_j N_j. \qquad (52)$$

The number of unimers in a sample of mass m is given by the usual expression

$$N_s = m/m_o. \qquad (53)$$

Reflection will show that

$$N_s = \sum_j jN_j. \qquad (54)$$

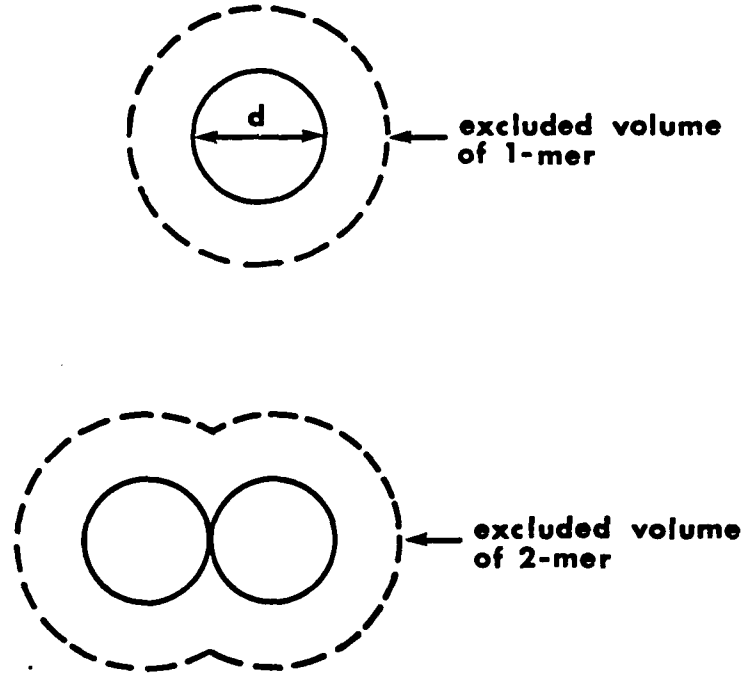


Figure 2. Excluded volumes of 1-mer and 2-mer. The dashed surface represents a volume whose interior is denied to the center of an approaching 1-mer. The radius of the sphere about the 1-mer is equal to the diameter of the 1-mer, hence $B_1 = \frac{4}{3}\pi d^3$. Because of the overlap of the covolumes of the two unimers making up the 2-mer, this excluded volume is only $\frac{9}{4}\pi d^3$, not twice that of the 1-mer.

Derivation of the Virial Equation from Association Theory

From the definition of C_j (Equation 35), we may define two important quantities. First, the total concentration of clusters, $\underline{C}$, is given by

$$\underline{C} = \underline{N}/v = \sum_j C_j = \sum_j K_j C_1^{\,j} \quad (K_1 = 1) \qquad (55)$$

and second, the classical concentration of formula weights per unit volume, C_s, is obtained by dividing Equations 53 and 54 by v:

$$C_s = N_s/v = \sum_j jC_j = \sum_j jK_j C_1^{\,j} = m/m_o v. \qquad (56)$$

Now Equation 56 can be inverted to give an infinite series

$$C_1 = \sum_k d_k C_s^{\,k} \qquad (57)$$

in which the d_k's may be evaluated as follows (14, 15a):

$$C_1 \equiv d_1(C_1 + 2K_2C_1^2 + \ldots) + d_2(C_1^2 + \ldots) + \ldots. \qquad (58)$$

Since this is an identity, like powers of C_1 can be equated, and the coefficients of all powers of C_1 greater than the first must vanish. Hence we get:

$$\begin{aligned} d_1 &= 1 \\ d_2 &= -2K_2 \\ d_3 &= 8K_2^2 - 3K_3 \\ d_4 &= -40K_2^3 + 30K_2K_3 - 4K_4 \\ d_5 &= 224K_2^4 - 252K_2^2K_3 + 48K_2K_4 + 27K_3^2 - 5K_5 \\ &\text{etc.} \end{aligned} \qquad (59)$$

Substituting the value of C_1 from Equation 57 into Equation 55 gives:

$$\underline{C} = \sum_k g_k C_s^{\,k} \tag{60}$$

where, by the same reasoning used to obtain the d_k's,

$$\begin{aligned} g_1 &= 1 \\ g_2 &= -K_2 \\ g_3 &= 4K_2^2 - 2K_3 \\ &\text{etc.} \end{aligned} \tag{61}$$

Dividing Equation 51 by v,

$$Pu = \underline{C}RT \tag{62}$$

We may therefore write

$$P/RT = \underline{C}/u = \sum_k g_k C_s^{\,k}/u. \tag{63}$$

Expanding 1/u (15b) and substituting in Equation 63 gives:

$$P/RT = (C_s + g_2 C_s^{\,2} + g_3 C_s^{\,3} + \ldots)(1 + B/v + \{B/v\}^2 + \ldots) \tag{64}$$

From Equation 38, we get

$$B/v = \sum_j B_j C_j = \sum_j B_j K_j C_1^{\,j}. \tag{65}$$

Substituting Equation 65 into Equation 64, carrying out the algebra and collecting terms, gives:

$$P/RT = \sum_{k=1}^{\infty} r_k C_s^{\,k}. \tag{66}$$

Finally, we may write, dividing Equation 66 by C_s,

$$Pv/N_sRT = 1 + r_2C_s + r_3C_s^2 + ... \qquad (67)$$

Comparison of Equation 67 with Equation 3, identifying C_s as N_s/v or ρ, immediately identifies each r_k with the corresponding B_k. The r_k, as calculated from association theory, are:

$$\begin{aligned} r_1 &= 1 \\ r_2 &= B_1 - K_2 \\ r_3 &= 4K_2^2 - 2K_3 + K_2(B_2 - 3B_1) + B_1^2 \\ &\text{etc.} \end{aligned} \qquad (68)$$

In the next section we will show, for r_2 at least, the equivalency of r_2 with the expression for the second virial coefficient in Equation 26, obtained from statistical mechanics.

Equivalency of the Second Virial Coefficients Calculated by Statistical Mechanics and by Association Theory

The equilibrium constant K_2 can be related to the partition functions for single and double molecules. From the Boltzmann distribution law the number of single molecules n_i with energy E_i is given by

$$n_i = g_i \exp(-E_i/kT)\exp(-a) \tag{69}$$

and for double molecules (primed quantities) by

$$n_j' = g_j' \exp(-E_j'/kT)\exp(-2a) \tag{70}$$

where g_i and g_j' are the degeneracies of states i and j, and $\underline{a}$ is a constant (16). Here we have assumed the same energy zero for both 1-mers and 2-mers; the factor 2 in the exponent of Equation 70 arises from the fact that the total number of unimers in the system must count the 2-mers twice.

Now the total numbers of 1-mers and 2-mers in the system are:

$$N_1 = \exp(-a)\sum_i g_i \exp(-E_i/kT) = Q_1 \exp(-a) \tag{71}$$

$$\text{and} \quad N_2 = \exp(-2a)\sum_j g_j' \exp(-E_j'/kT) = Q_2 \exp(-2a) \tag{72}$$

where Q_1 and Q_2 are the partition functions for 1-mers and 2-mers, respectively.

$$\text{Then} \qquad K_2 = C_2/C_1^2 = N_2 v/N_1^2 = vQ_2/Q_1^2. \tag{73}$$

Inserting the translational partition function yields:

$$K_2 = \frac{v^2(2\pi \cdot 2m_o kT/h^2)^{3/2}}{v^2(2\pi m_o kT/h^2)^3} \cdot Q_i = \left\{\frac{h^2}{\pi m_o kT}\right\}^{3/2} Q_i \quad (74)$$

where Q_i is the internal partition function of the 2-mer.

The phase integral form for Q_i is:

$$Q_i = (1/2h^3)\int \ldots \int \exp(-E\{p,q\}/kT)\, dq_1 \ldots dq_3 dp_1 \ldots dp_3 \quad (75)$$

where the factor 2 is the symmetry number of the 2-mer.

Now the internal energy of the 2-mer is

$$E(p,q) = (1/2\mu)(p_x^2 + p_y^2 + p_z^2) + u(r). \quad (76)$$

Here μ is the reduced mass, x, y, and z are the relative internal coordinates, and r is the internuclear separation.

Then each momentum integral is

$$\int \exp(-p^2/m_o kT)\, dp = (\pi m_o kT)^{\frac{1}{2}} \quad (77)$$

and therefore

$$Q_i = \tfrac{1}{2}(\pi m_o kT/h^2)^{3/2} \iiint \exp\{-u(r)/kT\}\, dq_1 dq_2 dq_3. \quad (78)$$

Shifting to spherical coordinates and integrating over the angles (giving the factor 4π):

$$Q_i = 2\pi(\pi m_o kT/h^2)^{3/2} \int_o^{r_o} \exp\{-u(r)/kT\} r^2 dr \quad (79)$$

where r_o is the diameter of the unimer, the internuclear distance at which the 2-mer is assumed to have been formed.

Combining this result with Equation 74,

$$K_2 = 2\pi \int_o^{r_o} \exp\{-u(r)/kT\} r^2 dr \quad (80)$$

and, from the definition of r_2 (Equation 68):

$$r_2 = B_2 = F_1 - K_2$$
$$= F_1 - 2\pi\int_o^{r_o} \exp\{-u(r)/kT\}r^2 dr. \qquad (81)$$

However, F_1 represents the volume excluded from a single molecule, and will be $\frac{1}{2}(4/3)\pi r_o^3$. The factor $\frac{1}{2}$ is introduced to avoid counting the members of the 2-mer twice.

Then

$$r_2 = (2/3)\pi r_o^3 - 2\pi\int_o^{r_o} \exp\{-u(r)/kT\}r^2 dr$$
$$= 2\pi\int_o^{r_o}\left\{ 1 - \exp\{-u(r)/kT\} \right\} r^2 dr. \qquad (82)$$

Finally, if u(r) is much less than kT, the expression in the exponential will be small, and if u(r) is proportional to r^{-6}, as is true for the London forces, the integral will converge rapidly with increasing r; one may therefore shift the upper limit to infinity, giving (Equation 83) an expression for r_2 identical to that for B_2, Equation 26:

$$r_2 = B_2 = 2\pi\int_o^{\infty}\left\{ 1 - \exp\{-u(r)/kT\} \right\} r^2 dr. \qquad (83)$$

From the foregoing discussion we may infer that association theory and statistical mechanics provide parallel approaches to chemical theory, and in general we can say that the choice of method on the part of the scientist becomes one of convenience, mathematical and/or conceptual, assuming, of course, that the choice made leads to agreement with experience. With this in mind, association theory was applied to liquids, and the Tait-Tamann

equation for their isothermal compressibilities was derived (17). This work is reviewed in the next section.

Derivation of the Tait-Tammann Equation

Tait (18) sought an equation to represent the isothermal compressibility of sea water, the density of which had been measured by the oceanographic research vessel H. M. S. Challenger, and proposed the relation

$$\frac{v_o - v}{v_o P} = \frac{A}{B + P} \tag{84}$$

where v_o is the volume at $P = 0$, and A and B are positive constants, which vary only with the temperature. The relationship was later erroneously reported by Tammann (19), and subsequently used by others, as a differential equation,

$$- dv/dP = \frac{A}{B + P} \tag{85}$$

in which we use the notation of the total derivative to signify a derivative taken at constant temperature. The reasons for this will become clear when we discuss the modifications needed in the theory of liquids; there can be no ambiguity since all discussions regarding Equation 85 involve isotherms.

It is Equation 85 or its integrated form

$$v_o - v = C \log \left[\frac{B + P}{B + P_o}\right] \tag{86}$$

where $C = 2.303A$, which is usually called "Tait's equation", but it makes more sense to call it the Tait-Tammann equation. The

substitution of Equations 85-86 for Equation 84 was detected in 1967 by Hayward (20), who pointed out that the fit of both equations as well as others depends heavily upon the quality of the data, and the uncertainties in even the best data make it impossible to discriminate among the better equations. Up to rather high pressures all good equations fit equally as well; hence the choice of equation depends upon other criteria. While simplicity is clearly one such criterion, a sound theoretical basis is at least as desirable.

If we differentiate Equation 62,

$$Pu = CRT \tag{62}$$

with respect to v, and divide by u, we may write

$$-\frac{dP}{dv} = \frac{RT}{u}\frac{dC}{dv} + \frac{P}{u}\frac{du}{dv} \tag{87}$$

Inverting and multiplying numerator and denominator of the right-hand side by 1/(dlnu/dv), we get

$$-\frac{dv}{dP} = \frac{u/(du/dv)}{\frac{-RT(dC/dv)}{(du/dv)} + P} \tag{88}$$

which is identical in form to Equation 85. If we write

$$\begin{aligned} J &= u/(du/dv) \\ L &= \frac{-RT(dC/dv)}{(du/dv)} \end{aligned} \tag{89}$$

we see that J may be equated with the empirical constant A, and L with B.

Since J is constant with P and v at a given temperature, the first of Equations 89 can be integrated with ease:

$$1/J = d\ln u/dv$$

$$\text{hence: } u = E \exp(v/J) \qquad (90)$$

where E is an integration constant which depends on the temperature. From Equations 90 and 62,

$$\underline{C} = \frac{PE}{RT} \exp(v/J) \qquad (91)$$

and the number-average degree of association, Zn, defined as

$$Zn = \Sigma j N_j / \Sigma N_j = N_s/\underline{N} = C_s/\underline{C} \qquad (92)$$

may therefore be written

$$Zn = \left(\frac{RT}{m_o E}\right)\frac{m \exp(-v/J)}{vP} . \qquad (93)$$

In addition to being able to derive Equation 85 theoretically, we have the knowledge of experience in its application to liquids other than water, for example, methyl, ethyl, propyl, isobutyl, and amyl alcohols (21), acetone (21), ethyl ether (21), ethyl chloride, bromide, and iodide (21), carbon disulfide (21), phosphorus trichloride (21), benzene (22), chloro-, bromo-, and nitrobenzene (23), aniline (23), ethylene glycol and its aqueous solutions (24), etc. Hirschfelder, Curtiss, and Bird (25) claim for the Tait-Tammann equation "almost perfect agreement with experimental observations."

MacDonald (26) has pointed out that the Tait-Tammann equation leads to negative volumes at high pressures; clearly this means that while J and L are constant over an extended pressure range (up to 100,000 atm.) they will vary if the pressure gets much

higher. High-pressure modifications have been proposed by Kirkwood and his co-workers (27) who proposed an "adiabatic" equation using pressure and entropy instead of pressure and temperature as the independent variables.

Writing Equation 86 in the form

$$\frac{v_o - v}{v_o} = \frac{1}{n} \log\{ 1 + P/B(T) \} \qquad (94)$$

where $1/n = C/v_o$ and is treated as a constant throughout, and $P_o = 0$, they modified it via thermodynamic arguments to

$$\log(v_1/v) = \frac{1}{H} \log\{ 1 + P/A(S) \} \qquad (95)$$

where instead of isotherms, v and v_1 are measured at the same entropy, so that

$$v = v(P,S) = v(P,T[P,S])$$

$$v_1 = v(0,S) \quad (\text{Cf. } v_o = v(0,T).)$$

$$\text{and } A(S) = B(T[0,S])$$

The ease of using Equation 95 is open to some question; it does extend Equation 94 over a greater pressure range, however.

Estimates of the range of validity of the Tait-Tammann equation are given in Appendix IV. At more normal pressures, though, its empirical utility coupled with its theoretical foundation enable one to use it with association theory to study liquids under applied pressures. It is clear, of course, that any progress in this direction will hinge on the success of the assumptions made in evaluating the constant E of Equations 90, 91, and 93.

One interesting point should be raised: from the point of view of many workers (28, 29) the essential difference between liquids and solids is one of symmetry, the latter being characterized by molecules in a space-filling symmetry (3-, 4-, or 6-fold), and the former by 5-fold symmetry, an arrangement unable to fill space without leaving void spaces. Thus the conversion between liquids and solids is one of symmetry. In view of this, we might suppose the compressibilities of the two states should obey the same laws, and it was shown by Ginell and Quigley (30) that the Tait-Tammann equation did in fact apply to at least one class of solids, the alkali metals. Thus we may conclude that the association equation of state, Equation 62, is valid for all three states of matter.

Understanding the detailed behavior of the derivatives in Equations 89 is needed to explore the intricacies of the structures of condensed phases, and the original attempt, along with the problems raised thereby, are discussed in the following section.

Evaluation of the Derivatives in the Tait-Tammann Constants

The original evaluation (17, 31) of the derivatives led to certain difficulties, the resolution of which is the principal subject of this thesis. Let us follow here the original scheme and see where it leads.

From Equations 89 we see:

$$J = u/(du/dv) = -u \Big/ \frac{d}{dv}\left(\frac{B}{v}\right)$$

$$L = \frac{-RT(d\underline{C}/dv)}{(du/dv)} = \frac{+ RT(d\underline{C}/dv)}{\frac{d}{dv}\left(\frac{B}{v}\right)} \qquad (96)$$

since $u = 1 - B/v$. From this we may write

$$\frac{d}{dv}\left(\frac{B}{v}\right) = -u/J = \frac{RT}{L}(d\underline{C}/dv)$$

$$\text{and} \quad d\underline{C}/dv = -Lu/JRT = -L\underline{C}/JP \qquad (97)$$

where the last expression incorporates Equation 62, $Pu = \underline{C}RT$.

The two derivatives in Equation 97 may be evaluated as follows:

$$\begin{aligned} \frac{d}{dv}\left(\frac{B}{v}\right) &= \frac{d}{dv}\sum_j B_j C_j \\ &= \frac{d}{dv}\sum_j B_j K_j C_1{}^j \\ &= \Sigma\, j B_j K_j C_1{}^{j-1}(dC_1/dv) \\ &= \Sigma\, j B_j C_j (d\ \ln C_1/dv) \end{aligned} \qquad (98)$$

By similar reasoning,

$$\begin{aligned} d\underline{C}/dv &= \frac{d}{dv} \Sigma\, C_j \\ &= \Sigma\, jK_j C_1^{\,j-1}(dC_1/dv) \\ &= \Sigma\, jC_j(d\ln C_1/dv) \\ &= C_s(d\ln C_1/dv) = \frac{m}{m_o v}(d\ln C_1/dv) \end{aligned} \quad (99)$$

To evaluate the derivative of C_1 on the right of Equations 98 and 99, it is helpful to go back to equation 57:

$$C_1 = \Sigma\, d_k C_s^{\,k} \quad (57)$$

From this, one gets:

$$dC_1/dv = \Sigma\, kd_k C_s^{\,k-1}(dC_s/dv) \quad (100)$$

and, since C_s is equal to $m/m_o v$,

$$dC_s/dv = -m/m_o v^2 = -C_s/v. \quad (101)$$

Putting this relation back into Equation 100 gives

$$dC_1/dv = \Sigma\, kd_k C_s^{\,k}(-1/v). \quad (102)$$

Let us go back to Equation 99, and using Equation 102 therein:

$$d\underline{C}/dv = -C_s\, \Sigma\, kd_k C_s^{\,k}/C_1 v \quad (103)$$

and, again inserting Equation 57 for C_1:

$$d\underline{C}/dv = -\frac{C_s}{v}\left[\frac{\Sigma\, kd_k C_s^{\,k}}{\Sigma\, d_k C_s^{\,k}}\right] \quad (104)$$

The two series, when divided, will yield a series of the form

$$\Sigma\, s_k(1/v)^{k-1}$$

This may be inserted into Equation 104, giving the result

$$d\underline{C}/dv = -C_s\, \Sigma\, s_k(1/v)^k \quad (105)$$

To evaluate the s_k's, differentiate Equation 60, obtaining:

$$\begin{aligned} d\underline{C}/dv &= \Sigma\, kg_k C_s^{k-1}(dC_s/dv) \\ &= (-1/v)\ \Sigma\, kg_k(m/m_o)^k(1/v)^k \\ &= (-m/m_o v)\ \Sigma\, kg_k(m/m_o)^{k-1}(1/v)^k \\ &= -C_s\ \Sigma\ \{kg_k(m/m_o)^{k-1}\}(1/v)^k \end{aligned} \tag{106}$$

Equating Equation 106 term-by-term with Equation 105 shows that

$$s_k = kg_k(m/m_o)^{k-1}. \tag{107}$$

For simplicity, let us introduce the symbol Φ, such that

$$\Phi = \Sigma\, s_k v^{-k}. \tag{108}$$

Then, from Equations 105 and 99,

$$d\ln C_1/dv = -\Phi \tag{109}$$

and Equations 98 and 99 become, respectively,

$$\frac{d}{dv}\left(\frac{F}{v}\right) = -\Phi\ \Sigma\ jF_jC_j \tag{110}$$

$$\text{and}\quad d\underline{C}/dv = -C_s\Phi. \tag{111}$$

Putting Equation 111 back into Equation 97, we see

$$C_s\Phi = Lu/JRT = L\underline{C}/JP \tag{112}$$

from which the number-average degree of association, Zn, is:

$$Zn = C_s/\underline{C} = L/JP\Phi. \tag{113}$$

Consequently, Φ may also be expressed in terms of the constant E of Equation 93 by equating that expression with Equation 113:

$$\Phi = (Lm_oE/JRT)(v/m)\exp(v/J) \tag{114}$$

or, more simply,

$$\Phi = D(v/m)\exp(v/J) \tag{115}$$

where D is the first expression in parentheses in Equation 114, Lm_oE/JRT.

It is found experimentally that as the pressure is increased, the quantity Zn, given by Equation 93, passes through a minimum. It is a simple process to find the condition for the minimum, as the following section demonstrates.

Using Equations 113 and 115, we may write:

$$Zn = \frac{(Lm/JD)}{Pv\ \exp(v/J)} \tag{116}$$

At the minimum, the derivative of Zn vanishes, so:

$$dZn/dP = 0 = -Zn_{min}\left\{ \frac{1}{P_{min}} + \left(\frac{1}{v_{min}} + \frac{1}{J}\right)\left(\frac{-J}{L + P_{min}}\right)\right\} \tag{117}$$

The term in braces must be the one that vanishes. Equate it to zero and cancel out the lowest common denominator, $P_{min}v_{min}(L+P_{min})$, giving:

$$0 = v_{min}(L + P_{min}) - JP_{min} - P_{min}v_{min} \tag{118}$$

or finally:

$$P_{min}/v_{min} = L/J. \tag{119}$$

Now the weight-average degree of association, Zw, is defined as:

$$Zw = \Sigma\ j^2C_j/C_s. \tag{120}$$

This quantity is simple to derive in terms of association theory, as follows:

$$dC_s/dv = -m/m_ov^2 = -C_s/v = \Sigma\ j^2K_jC_1^{j-1}(dC_1/dv)$$

$$-C_s/v = -\Phi\ \Sigma\ j^2C_j$$

$$\text{whence} \quad Zw = 1/v\Phi. \tag{121}$$

If, at any pressure P_e, Zn is equal to Zw, we can write:

$$L/JP_e\Phi_e = 1/v_e\Phi_e$$

$$\text{or: } P_e/v_e = L/J. \tag{122}$$

Since the ratio P/v increases monotonically with P, that ratio can equal the constant L/J at only one point. That point is the pressure P_e, which, by Equation 119, is also P_{min}. Hence, when Zn is at its minimum value, Zn = Zw.

But when Equation 115 is substituted into Equation 121, we find:

$$Zw = m/(Dv^2e^{v/J}). \tag{123}$$

Equation 123 does not exhibit any minimum, and the two terms, Zn and Zw, behave schematically as in Figure 3. This behavior is impossible, since mathematically Zw can never be less than Zn. To develop association theory properly, this difficulty must be removed.

A second problem arose in attempting to calculate the number of 1-mers present in a given system. Since Φ is $-d\ln C_1/dv$, one may integrate Equation 115 to get:

$$\ln C_1 = -(D/m)J^2e^{v/J}(v/J - 1) + Q \tag{124}$$

where Q is an integration constant. Now at P_{min}, Zn and Zw are assumed to be equal, according to the reasoning just given. The assumption made in the original work (32) was that at P_{min},

$$Zn = Zw = 1. \tag{125}$$

Given this assumption, we may write

$$C_{1_{min}} = m/m_o v_{min} = \underline{C}_{min} = C_{s_{min}} \qquad (126)$$

and, since Zw = 1 at this pressure, we may use Equation 123 to find:

$$D = \frac{m}{v_{min}^3 \exp(v_{min}/J)} \qquad (127)$$

Equation 124 may then be solved for Q at P_{min}:

$$Q = \ln(m/m_o v_{min}) + (J/v_{min})(1 - J/v_{min}). \qquad (128)$$

Substituting this into Equation 124, we get, after some rearrangement:

$$C_1 = (m/m_o v_{min}) \exp\left\{\frac{J}{v_{min}^3}\left[\exp\left(\frac{v-v_{min}}{J}\right)(J-v) - (J-v_{min})\right]\right\} \qquad (129)$$

Since D (Equation 127), and therefore E (Equation 114) are known, $\underline{C}$ may be readily calculated from Equation 91. A comparison of $\underline{N}$ and N_1 ($\underline{C}$ and C_1 multiplied by v) for water at 25 degrees based upon the above equations is presented in Figure 4. The data are from Adams (33). It is immediately clear that N_1 is greater than $\underline{N}$, an absurd conclusion. This same contradiction has been observed in all other systems studied.

One final problem encountered was this: combining Equations 110 and 111 in Equation 96, we get:

$$L = \frac{-RTC_s\Phi}{-\Sigma_j B_j C_j \Phi} = \frac{RTm/m_o}{\Sigma_j F_j N_j} \qquad (130)$$

At P_{min}, if the only species present is the 1-mer, then

$$\Sigma_j B_j N_j = 1 \times B_1 N_1 = F_1 m/m_o \quad (P = P_{min}) \qquad (131)$$

and L reduces to:

$$L = RT/P_1. \tag{132}$$

Since L becomes negative at high temperatures, Equation 132 gives a negative excluded volume for the smallest species, again a disturbing result.

The difficulties discussed here can all be traced to the derivatives taken in Equations 98, 99, 100, 106, and 121, in which the equilibrium constants K_j were held constant during the differentiation. But if, during compression (or even at atmospheric pressure), a particular j-mer should have its concentration go to zero, not only would that imply a variable equilibrium constant, but it would lead to a singularity in Equation 36,

$$K_j = \prod_{x=1}^{j-1} K_{1,x} \tag{36}$$

since, if for some i less than j, $C_i = 0$, then $K_{1,i-1} = 0$ and all K_j for $j \geq i$ would vanish. In the next section a new model for liquids is proposed in which this approach is elaborated upon.

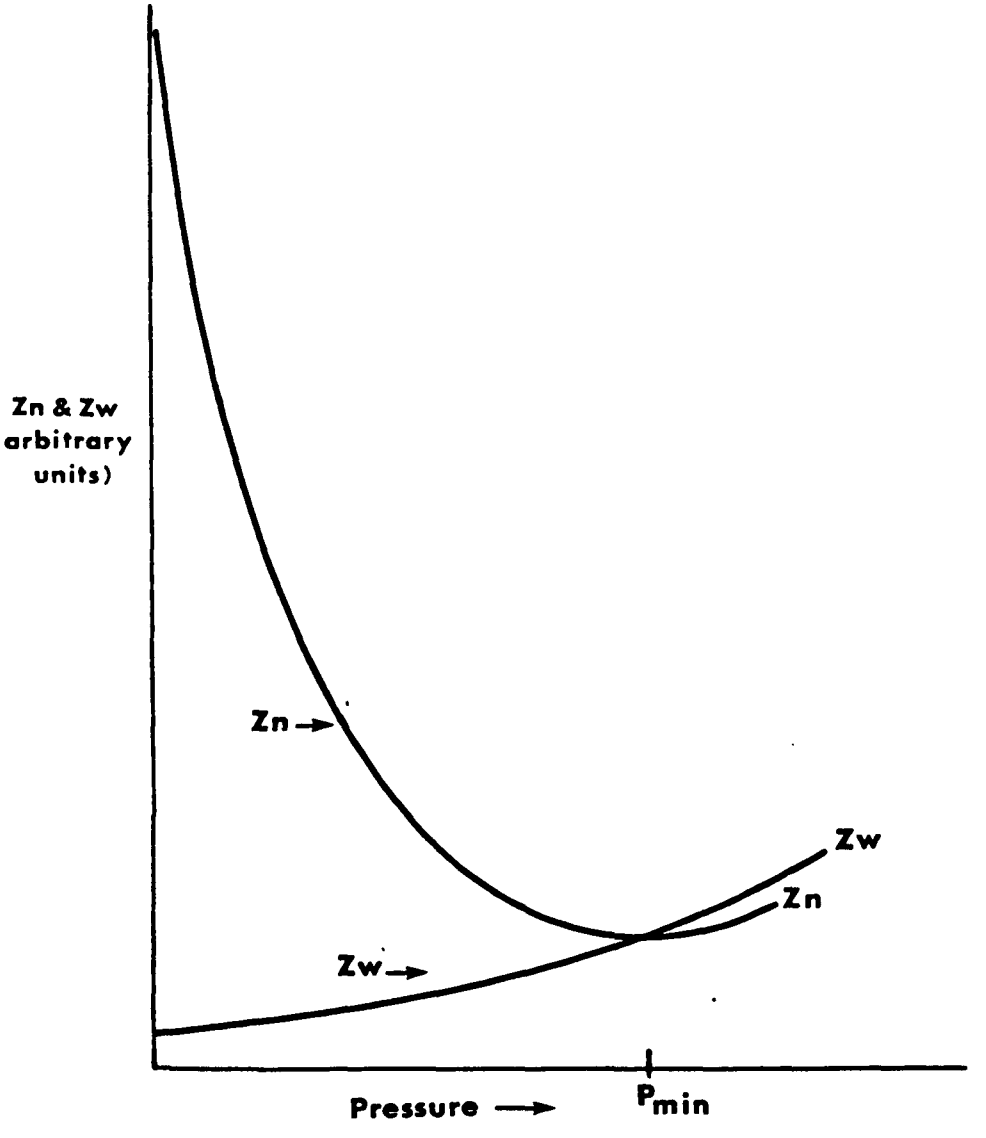


Figure 3. Calculated behavior of Zn and Zw with pressure.

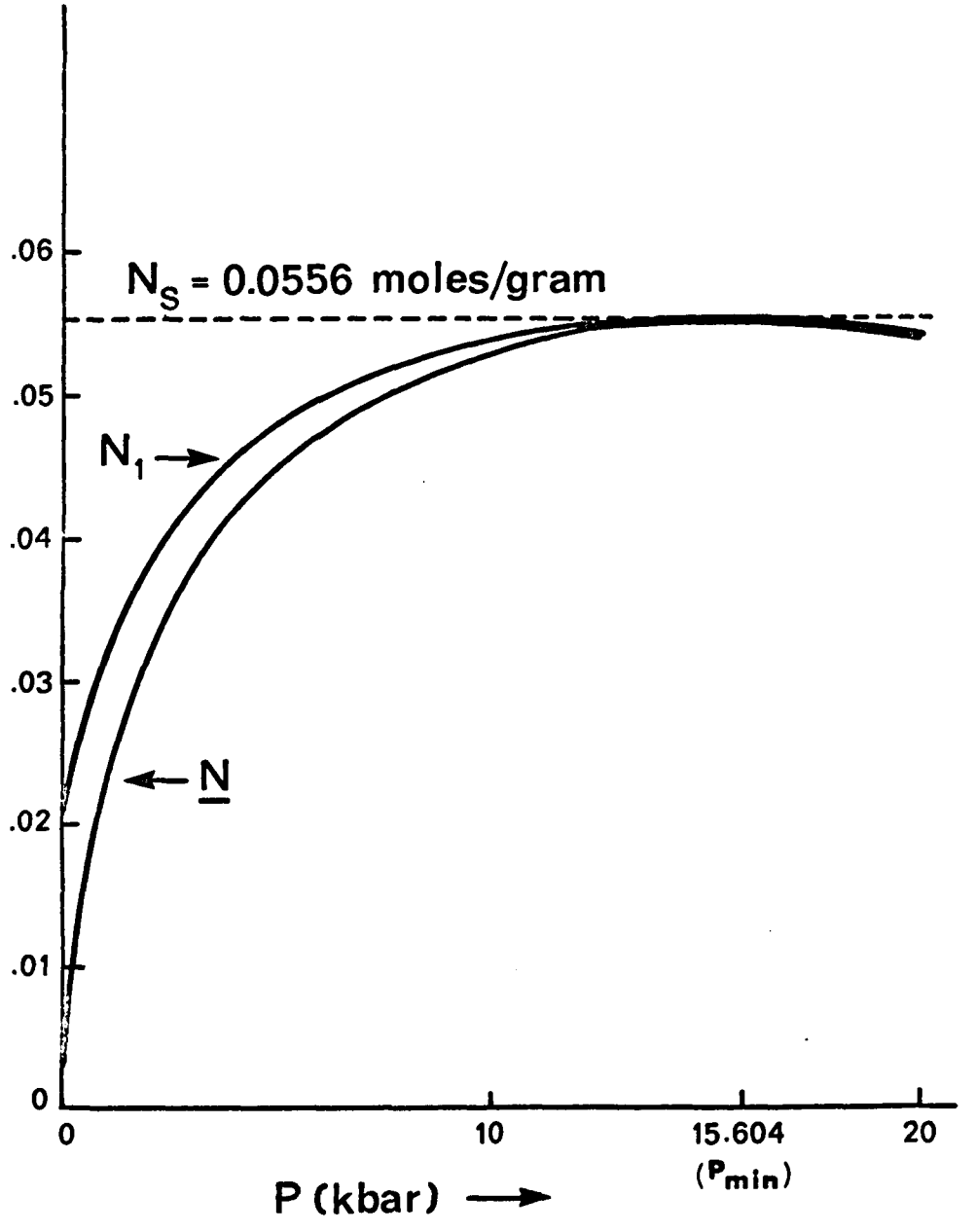


Figure 4. $\underline{N}$ and N_1 vs. pressure. Data from Adams (33).

II

The Discontinuous Case and the Structure of Liquids

Introductory

The origin of the assumption of a continuous distribution of cluster sizes lies in the kinetic derivation of the distribution equations (7), which assumes that we start with a hypothetical matrix of single molecules and from these we build an associated substance. This is equivalent to starting with a mass of matter at infinite volume where there are no collisions, and then compressing it to the volume, v, where the molecules will collide and associate. This is actually an unnecessary concept, since the same equations can be obtained by considering the equilibrium situation, as we have done in Section I (See also Ref. 34). The concept underlying this assumption was reinforced by the thought experiment (35) in which the individual frames of a hypothetical motion picture of a gas were examined one by one. In such an examination, 1-mers, 2-mers, 3-mers, etc., were seen. From the dynamic point of view, the 2-mers were static representations of binary collisions, the 3-mers of ternary collisions, and so on. This picture is the one presented by the kinetic-molecular theory and is true of a gas. Extrapolating this view to condensed phases led to the difficulties discussed in the previous section.

One must, therefore, look for an acceptable picture of liquids and solids within the framework of association theory. Part of this problem has been considered (28, 29) in connection with a discussion of close-packing in j-mers of large size, and

the suggestion has been made (28) that the essential difference between liquids and solids is one of symmetry. From this work it appears that higher j-mers packed in 3-, 4-, or 6-symmetry give rise to particles of regular form which are recognizable as prototypes of crystals, whereas higher j-mers packed in 5-symmetry form particles of irregular shape full of voids, corresponding to our current views of the structure of liquids, as mentioned briefly earlier in Section I.

This symmetry difference leads to an explanation of the mechanism of nucleation (28, 36). It seems, then, that we must consider a liquid to consist of an array of such 5-symmetric j-mers, separated by defects, all in equilibrium due to 1-mers breaking off one j-mer, crossing the defect volume, and joining another j-mer. The number of such 1-mers in the liquid is small, the bulk consisting of the larger j-mers. The equilibrium mechanism postulated is very similar to the mechanism proposed by Brown and Ginell (36) for the growth of crystals after heterogeneous nucleation.

If one views the liquid as a crowded aggregation of molecules, it is obvious that the vast majority of molecules, or unimers, exist as members of large 5-symmetric aggregates in equilibrium with each other. This equilibrium may be represented as an exchange of 1-mers, either "free":

$$\begin{aligned} X_r &\rightleftarrows X_{r-1} + X, \\ X + X_s &\rightleftarrows X_{s+1} \end{aligned} \tag{133}$$

or "bound":

$$X_p + X_q \rightleftarrows X_{p+1} + X_{q-1}. \qquad (134)$$

The question of whether 2-mers can exist in the liquid will depend upon the abundance of 1-mers; if N_1 is small then the probability of two 1-mers colliding with each other before either encounters a large j-mer is vanishingly small. The number of 3-mers is still smaller, and this leaves us with a substantial gap in cluster size between the 1-mer and the smallest large j-mer which exists in the liquid, which we call the α-mer.

This picture is substantially like that presented in Eyring's significant structures theory (37). That treatment represents the liquid as an equilibrium mixture of "gas-like" unbonded molecules (equivalent to 1-mers) and "solid-like" molecules bound in large aggregates (equivalent to large j-mers.) A partition function is then set up as a weighted combination of gas and solid partition functions, the weighting being done according to the excess volume, $v - v_s$, of the liquid. (v_s is the volume of the solid at the melting point.) In this treatment, the fraction of the molecules which are unbound (gas-like, 1-mers) is:

$$\text{fraction unbound} = (v - v_s)/v \qquad (135)$$

and the fraction of bound molecules (solid-like, members of large j-mers) is:

$$\text{fraction bound} = v_s/v. \qquad (136)$$

By this picture, about one molecule in every eight is unbound

at the melting point, the fraction increasing with the temperature. This seemed unreasonably large in light of the discussion in the preceding paragraph, so alternative approaches were sought.

Another difference between the theories is that association theory specifies the 5-symmetric nature of the large j-mers, while Eyring considers the molecules so situated to have the properties of the solid (extrapolated to the appropriate temperature), and of necessity that treatment contains some arbitrary parameters which have the effect of altering the coordination number of the solid-like molecules. In addition, because it ignores symmetry considerations, Eyring's theory is unable to account for nucleation, as does association theory (36).

Liquid-Gas Transition

The concept of a discontinuous distribution raises several questions, namely (a) how and why does such a distribution arise, and (b) why is it more applicable to liquids? Qualitatively, we may understand it in the following way (38, 39).

Let us imagine that we have a gas at some elevated temperature. The j-mers present will be 1-mers, 2-mers, 3-mers, and perhaps some 4-mers and 5-mers. Reducing the temperature would now have the effect of decreasing the energy, velocity, and momentum of the particles. Since every collision, except a direct-line collision (Figure 5), results in the transfer of some of the kinetic energy into rotational energy, there is time for additional bonds to form. From geometric considerations, the chance of a direct-line collision is small, hence extra bonds will be formed (Figure 6). This means that as the higher j-mers form, they tend to be more complex in terms of the number of bonds to each individual unimer. The situation in the case of the formation of a 4-mer from a 3-mer and a 1-mer is shown in Figure 7. Here the 4-mer ends up with each unimer bonded to three others (Figure 7-d). We refer to such a situation as three-hole (3-hole) bonding since the triangular array of the 3-mer forms a hole bounded by three unimers. The bonds in Figure 7 were formed one at a time; the breakup of the 4-mer may also proceed by sequential breaking of individual bonds.

As the temperature is lowered still further, higher j-mers have time to form. These clusters have 4-hole bonds, in which two bonds are formed simultaneously (Figure 8). The reverse process therefore demands the simultaneous breakup of two bonds, which is energetically more difficult than breaking bonds sequentially. Such stable structures, requiring the simultaneous breaking of two or more bonds, may be called "multiply-bonded" structures. When the temperature is low enough so that the multiply-bonded strucures persist, their stability will rapidly drain the gas of simply-bonded j-mers. As the multiply-bonded j-mers form, there is an extra release of energy due to their formation which is not used up in dissociating them because of their unusual stability; instead it will appear as kinetic energy, compensating for the drop in temperature. A halt in the temperature drop thus ensues while the multiply-bonded j-mers form a new (liquid) phase.

Clearly, if the temperature is too high for the 5-mer (the smallest multiply-bonded j-mer) to persist, no liquid will form. As the temperature is lowered, a temperature will be reached where the 5-mer will persist long enough to drain the vapor of molecules and form still larger clusters; this will be the critical temperature, T_c. Approaching T_c from below, the vapor phase, according to the model described earlier, will consist of simply-bonded j-mers (j = 1 through 4) and the liquid will consist of 1-mers and larger, multiply-bonded j-mers. When T_c is reached, α will be about 5, producing a distribution which overall is continuous (j = 1 to 4

in the former vapor, 5 and up in the former liquid) but with the heavier clusters concentrated at the bottom of the vessel. The overall continuous distribution accounts for the disappearance of the meniscus, but the density gradient will persist due to gravity. This phenomenon has been observed (40); the density difference persists above the critical temperature, though it may be removed by agitation.

The prediction that the 5-mer is characteristic of the critical state is reinforced below, in Section III.

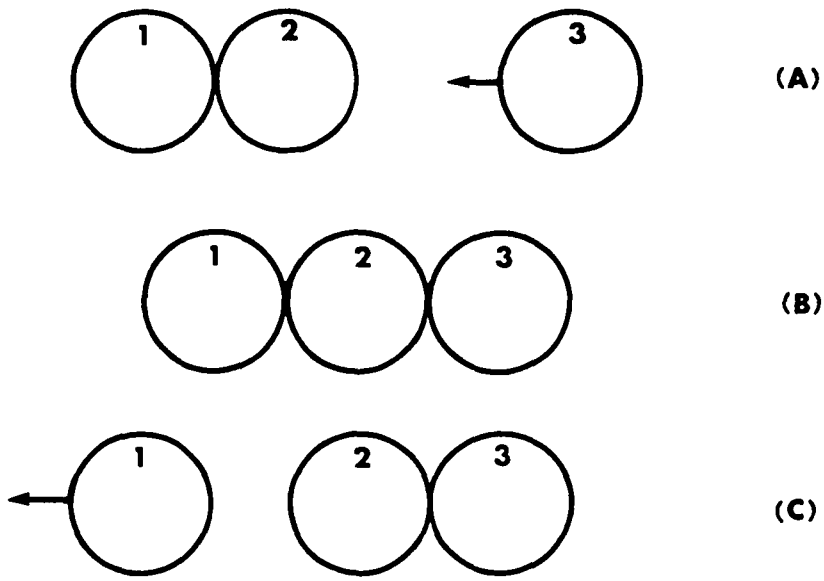


Figure 5. 1-mer and 2-mer; straight-line collision.

A) Approach.

B) Collision. During the lifetime of the 3-mer, the energy of the collision is stored as potential energy of distortion, although no distortion is shown in the figure.

C) Departure. The departing molecule will carry all the kinetic energy only in the case of collision precisely along the intermolecular axis, as shown here.

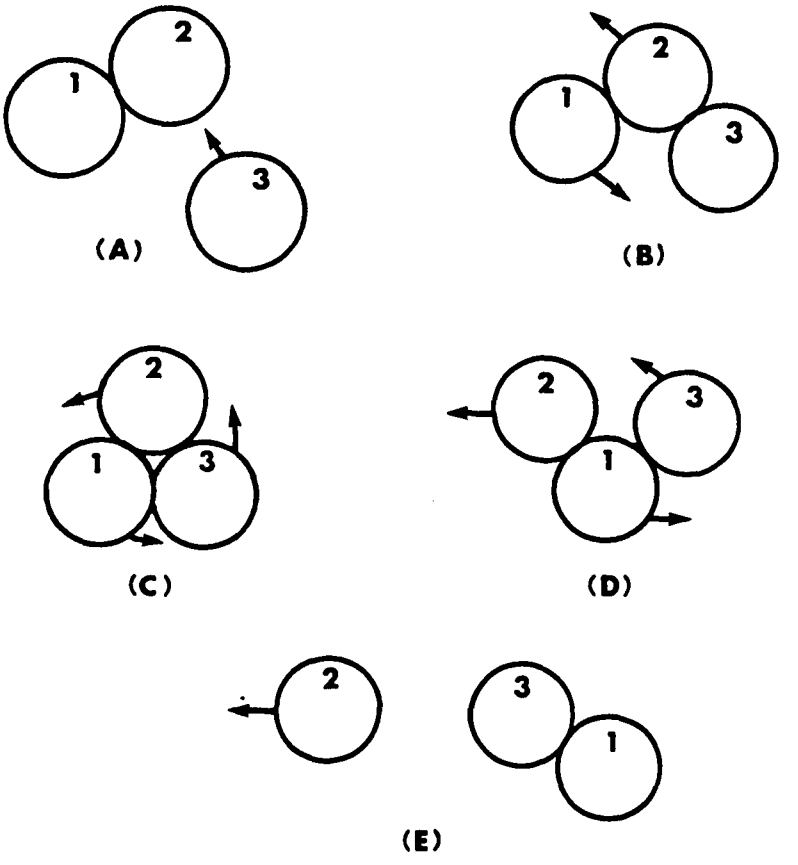


Figure 6. Collision between a 1-mer and a 2-mer. Partial transfer of kinetic to rotational energy. If the energy of impact is slight, a 3-mer may form at step C. At slightly higher energy, termination would be step D, a structure in equilibrium with C.

A) Approach.

B) Collision; formation of first bond.

C) Formation of second bond due to rotation.

D) Degradation; breaking of first bond.

E) Complete degradation; breaking of second bond.

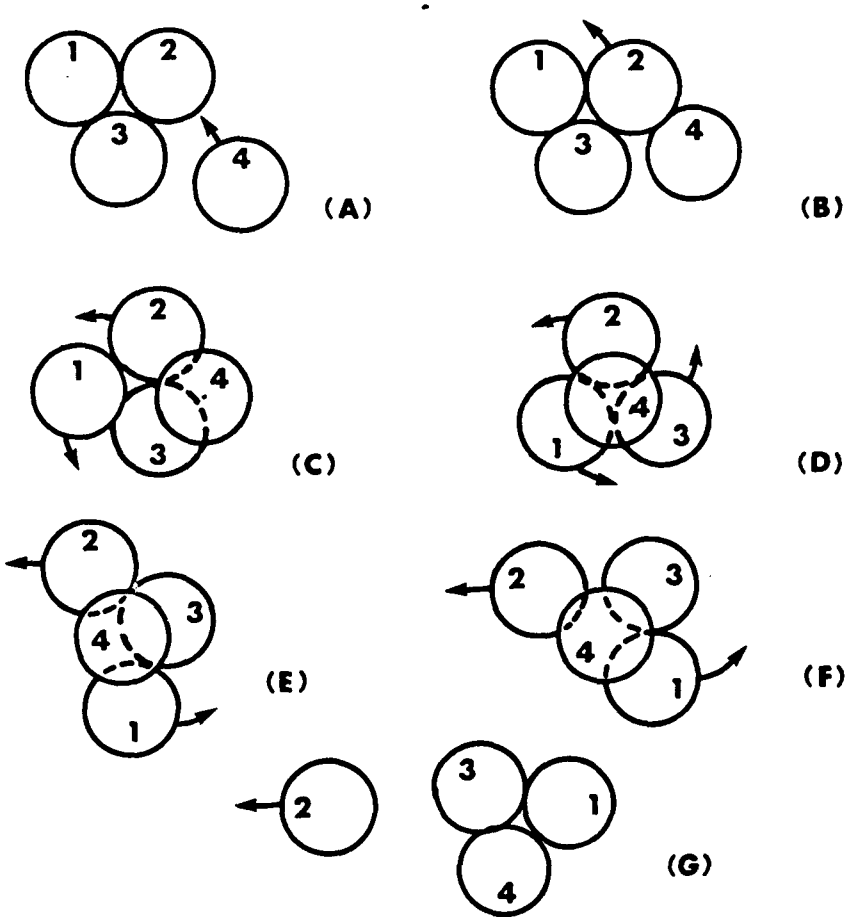


Figure 7. Bond formation in a 3-hole.

A) Approach. B) First bond forms.

C) Second bond forms. D) Third bond forms.

E) First bond breaks. F) Second bond breaks.

G) Third bond breaks (departure.)

The process may stop at any of several stages to form a 4-mer. The stages gone through and the amount of energy transferred depend on the impact energy and on the geometry of the collision. The most stable 4-mer (least energy) is D.

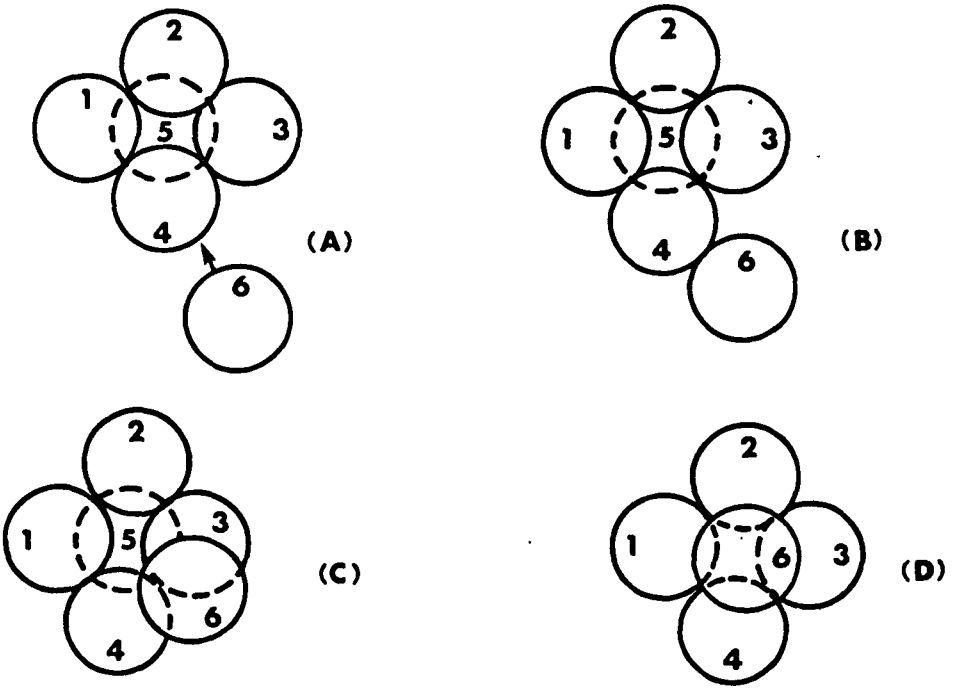


Figure 8. Bond formation in a 4-hole.

A) Approach.

B) First bond forms.

C) Second bond forms.

D) Third and fourth bonds form simultaneously.

Degradation takes place in the reverse order; two bonds break simultaneously in the first step. The example in the figure is a 1-mer and a 5-mer; atom 5 is necessary since the 4-mer would be more stable in a tetrahedral arrangement, rather than a square planar.

Mathematical Development

Let us define the α-mer as the next largest cluster size present in the system after the 1-mer, so that:

$$N_2 = N_3 = \ldots N_{\alpha-1} = 0.$$

The chemical equations and the corresponding equilibrium constants are then:

$$\begin{aligned} X + X_\alpha &\rightleftharpoons X_{\alpha+1} & K_{1,\alpha} &= C_{\alpha+1}/C_1C_\alpha \\ X + X_{\alpha+1} &\rightleftharpoons X_{\alpha+2} & K_{1,\alpha+1} &= C_{\alpha+2}/C_1C_{\alpha+1} \\ &\vdots & &\vdots \\ X + X_{m-1} &\rightleftharpoons X_m & K_{1,m-1} &= C_m/C_1C_{m-1} \end{aligned} \tag{137}$$

where the m-mer is the largest species present. Consequently,

$$\begin{aligned} N_1 &= N_1 \\ N_j &= 0 \quad (2 \le j < \alpha) \\ N_j &= N_j \quad (\alpha \le j \le m) \\ N_j &= 0 \quad (j > m). \end{aligned} \tag{138}$$

In Table I are presented the equations and definitions for both the continuous (Section I) and discontinuous cases; the continuous case is readily seen to be the case in which $\alpha = 1$.

The equation of state (Equation 62) will not change, but the derivatives evaluated for the Tait-Tammann constants were all taken assuming $dK_j/dv = 0$. Since, however, α will vary with the applied pressure, this assumption must be discarded, since

$K_j = 0$ for $j < \alpha$, but is finite for $j \geq \alpha$; obviously, as α changes, the value of a particular K_j will shift sharply as the value of α passes the fixed value of j in question.

We may hold the K_j constant under one condition, namely that the derivatives evaluated in Section I be partials at constant α. The following equations result; note again the use of the notation d/dv for isothermal derivatives $(\partial/\partial v)_T$ and the partial notation $(\partial/\partial v)_\alpha$ for isothermal derivatives with α held fixed, $(\partial/\partial v)_{\alpha,T}$.

The equations used in deriving the Tait-Tammann equation are the same (Equations 87 to 93), as is the condition for the minimum in Zn, Equation 119. However, the derivation of Zw (Equations 120 and 121) assumed the K_j constant; this can be true only if α is held fixed, hence:

$$m/m_o v = C_s = \sum_j jC_j = \sum_j jK_j C_1{}^j$$

$$(\partial C_s/\partial v)_\alpha = -m/m_o v^2 = -C_s/v = \sum_j j^2 K_j C_1{}^j (\partial \ln C_1/\partial v)_\alpha$$

$$\text{or: } C_s/v = \varphi \Sigma j^2 C_j \qquad (139)$$

$$\text{where} \qquad \varphi = -(\partial \ln C_1/\partial v)_\alpha \qquad (140)$$

by analogy with Φ (Equation 109).

Rearranging Equation 139,

$$Zw = 1/v\varphi. \qquad (141)$$

This term φ cannot be easily integrated, since the integration must be carried out at constant α, and we do not know the

dependence of α on v. But the problem posed in which Zw was less than Zn may be qualitatively resolved as follows:

From Equation 62, we may obtain a "Tait-Tammann-like" equation using partials:

$$-(\partial v/\partial P)_\alpha = \frac{u/(\partial u/\partial v)_\alpha}{\frac{-RT(\partial \underline{C}/\partial v)_\alpha}{(\partial u/\partial v)_\alpha} + P} \tag{142a}$$

$$\text{Letting } J_V = u/(\partial u/\partial v)_\alpha \tag{142b}$$

$$\text{and} \qquad L_V = \frac{-RT(\partial \underline{C}/\partial v)_\alpha}{(\partial u/\partial v)_\alpha}. \tag{142c}$$

These equations are precisely analogous in form to Equations 88 and 89, except that while J and L, by definition, are empirical constants, the behavior of J_V and L_V with applied pressure is not known.

The partial derivatives may be evaluated as the total derivatives were in Section I, giving:

$$(\partial \underline{C}/\partial v)_\alpha = -\alpha C_s \tag{143}$$

and, from Equations 142,

$$L_V/J_V = \lambda = RT\varphi C_s/u. \tag{144}$$

Inserting Equation 62,

$$\lambda = P\varphi Zn$$

$$\text{or,} \quad Zn = \lambda/P\varphi. \tag{145}$$

Note the difference between Equation 145 and Equation 113. If, now, a point (P_e, v_e) exists such that at that point Zn = Zw, then from Equations 141 and 145,

$$P_e/v_e = \lambda. \tag{146}$$

This is not the same point as P_{min}, v_{min}, unless $\lambda = L/J$, which it need not. Indeed, it is conceivable that a point given by Equation 146 may not exist at all, depending on the behavior of λ.

The relevant equations for the continuous and discontinuous cases are summarized in Table II. It can be seen that the definitions of Zn and Zw have changed due to the appearance of a new variable, λ, which will prevent Zw from falling below Zn. It has so far proved impossible to evaluate λ unambiguously. Progress has been made in evaluating α for liquids in equilibrium with their vapors, and some interesting results have been obtained. This discussion follows immediately, in Section III.

TABLE I

Association Equations for

Continuous and Discontinuous Cases

Continuous Case	Discontinuous Case
$C_1 = C_1$	$C_1 = C_1$
$C_j = C_j \quad (2 \leq j \leq m)$	$C_j = 0 \quad (2 \leq j < \alpha)$
$C_j = 0 \quad (j > m)$	$C_j = C_j \quad (\alpha \leq j \leq m)$
	$C_j = 0 \quad (j > m)$
Equilibrium constants (double index)	
$K_{1,j} = C_{j+1}/C_1C_j \quad (j \geq 1)$	$K_{1,j} = C_{j+1}/C_1C_j \quad (j \geq \alpha)$
Equilibrium constants (single index)	
$K_1 = 1$	$K_1 = 1$
	$K_j = 0 \quad (2 \leq j < \alpha)$
$K_j = C_j/C_1{}^j \quad (1 < j \leq m)$	$K_j = C_j/C_1{}^j \quad (\alpha \leq j \leq m)$
$= \prod_{x=1}^{j-1} K_{1,x}$	$= K_\alpha \prod_{x=\alpha}^{j-1} K_{1,x}$
$K_j = 0 \quad (j > m)$	$K_j = 0 \quad (j > m)$
$\underline{C} = \sum_{j=1}^{m} K_jC_1{}^j$	$\underline{C} = C_1 + \sum_{j=\alpha}^{m} K_jC_1{}^j$

Considering the definitions of the K_j's and C_j's above, the continuous definition can be used in either case.

TABLE II

Comparison of Equations for Degrees of Association,

Zn and Zw,

for the Continuous and Discontinuous Cases

Continuous Case	Discontinuous Case
$\Phi = -d\ln C_1/dv$ $= (Em_o/RT)(L/J)(v/m)e^{v/J}$	$\varphi = -(\partial \ln C_1/\partial v)_\alpha$ $= (Em_o/RT)(\lambda)(v/m)e^{v/J}$
$Zn = L/JP\Phi$ $= (RT/m_oEP)(m/v)e^{-v/J}$	$Zn = \lambda/P\varphi$ $= (RT/m_oEP)(m/v)e^{-v/J}$
$Zw = 1/v\Phi$ $= (RT/m_oE)(m/v^2)e^{-v/J}(J/L)$	$Zw = 1/v\varphi$ $= (RT/m_oE)(m/v^2)e^{-v/J}(1/\lambda)$

III

Cluster Sizes in the Saturated Liquid

Assumptions

For the sake of simplicity in calculation and of obtaining useful results, approximations must be made, to be justified by their reasonableness and by the results deduced therefrom. The first assumption made here is that the range of cluster sizes from α to m is small, and that α may therefore be redefined as an average quantity intermediate in value between the smallest and largest cluster sizes (excluding the 1-mer) and close in magnitude to both. This changes none of the foregoing discussion, but simplifies the calculations in this section while still preserving the basic concepts of the theory.

Accordingly, we may write the usual parameters as follows:

$$\begin{aligned} \underline{N} &= N_1 + N_\alpha \\ N_s &= N_1 + \alpha N_\alpha \end{aligned} \tag{147}$$

From the two equations above it follows immediately that

$$\alpha = \frac{N_s - N_1}{\underline{N} - N_1} \tag{148}$$

There are two unknowns on the right of Equation 148, $\underline{N}$ and N_1, and to solve the equation we must make further assumptions.

Let us therefore assume that only the 1-mers contribute to the vapor pressure in the two-phase system along the saturation line. This is consistent with the model proposed in Section II, in which the liquid is presumed to consist of 1-mers and very large α-mers, and since the α-mers are much larger than any

clusters in the vapor phase, they are non-volatile, and the 1-mers will be the only species that can escape. While the essence of this assumption is not true at the critical point, the liquid-vapor equilibrium below that point may be assumed to obey this model; even at T_c this argument may still be valid, inasmuch as association theory treats cluster equilibria as an exchange of 1-mers. The liquid-solid nucleation problem has been successfully quantitatively considered this way (36); it makes sense to extend the idea to other phase equilibria as well. The excellent results at the critical point obtained in this work would seem to bear this out.

From kinetic theory we know (41) that the number of molecules vaporizing from unit surface per unit time is proportional to the product of their vibration frequency and the probability that one possesses sufficient energy to break away from its neighbors; a molecule meeting that energy criterion clearly qualifies as a 1-mer. Thus we can say that the number of molecules entering the vapor phase is proportional to the number of 1-mers in the liquid, and the pressure exerted by the vapor is proportional to the number of molecules in that phase. Association of vapor-phase molecules at the higher temperatures and vapor pressures will muddle this simple picture, and it is probably this tendency more than any other which will counteract the growing volatility of the α-mer in the critical region, suggested in the previous paragraph.

Keeping these ideas in their simplest form, then, yields:

$$N_1 = kP^\circ$$

$$\text{or, } \ln N_1 = \ln k + \ln P^\circ \qquad (149)$$

where k is an unknown constant and P° is the vapor pressure. The vapor pressure can conveniently be expressed as a function of temperature by the well-known empirical equation (42):

$$\ln P^\circ = A - B/T. \qquad (150)$$

The accuracy of this simple equation may be improved by adding additional parameters. For example, the Antoine equation (43),

$$\ln P^\circ = a - b/(T + c) \qquad (151)$$

has been proposed, and represents an improvement, especially for polar liquids. An example of the extremes to which one can go in improving the accuracy of vapor-pressure equations is the one for water by Osborne and Meyers (44):

$$\log_{10} P^\circ = A + \frac{B}{T} + \frac{Cx}{T}(10^{Dx^2} - 1) + E \cdot 10^{Fy^{5/4}} \qquad (152)$$

in which P° is in atmospheres, and

$x = T^2 - K$	$C = 1.3869 \times 10^{-4}$
$K = 293{,}700$	$D = 1.1965 \times 10^{-11}$
$y = 647.27 - T$	$E = -0.0044$
$A = 5.4266514$	$F = -0.0057148$
$B = -2005.1$	

Equation 152 is said to be good to one part in 2000 for all temperatures.

For theoretical purposes, however, the simplest equation

(Equation 150) is sufficient, even preferable for the utility it offers. Even a complex liquid such as water exhibits only a 7.8% standard deviation in the vapor pressure from Equation 150, which for this work is acceptable. (See under "Calculations".)

If, then, we substitute Equation 150 into Equation 149, we get:

$$\ln N_1 = \text{constant} - B/T. \qquad (153)$$

To evaluate this constant, we note that as T goes to infinity, the extrapolated "vapor pressure" stays finite. We may imagine this to be an infinitely expanded system of two phases, the liquid phase being vanishingly small, and the likelihood of intermolecular collision in the vapor phase being likewise negligible. In that case the entire system can be considered to consist only of 1-mers and therefore:

$$\text{constant} = \ln N_s. \qquad (154)$$

The usual interpretation of B is that it is equal to $\Delta H/R$, where ΔH is the heat of vaporization. This assumption (the Clausius-Clapeyron equation) is not correct, since, as is well known, ΔH drops off at high temperatures, reaching zero at the critical point. From the point of view of association theory, however, ΔH is the difference between the net heat of the processes in the liquid represented by

$$X_{\alpha+1} \rightleftarrows X + X_\alpha \qquad \text{Heat} = \epsilon \qquad (155)$$

and the net heat of the processes in the vapor,

$$X + X_j \rightleftharpoons X_{j+1} \qquad \text{Heat} = \epsilon' \tag{156}$$

so that

$$\Delta H = \epsilon - \epsilon' \tag{157}$$

As the liquid and vapor cluster sizes become more alike towards the critical point, ΔH will fall to zero, as observed. The term ϵ corresponds to the formation of the 1-mer in the liquid phase; since small clusters have been ruled out in that phase by this theory, processes analogous to Equation 156 are not involved, so that a better representation of B is as ϵ/R. At low vapor pressures, of course, there is virtually no cluster formation in the vapor phase, and ΔH at those temperatures is about equal to ϵ.

Values of ϵ for liquids considered in this study are shown in Table III.

TABLE III

Calculated Values of ϵ (Calories per Mole)

Argon	1590
Nitrogen	1400
Oxygen	1720
Water	9720

Calculations

Calculations were carried out on data readily available on oxygen (45), nitrogen (45), argon (45), and water (46). Calculation of $\underline{N}$ from the equation of state, $P(v - B) = \underline{N}RT$, requires an estimate of the excluded volume, B. If we assume the void space of the solid to be negligible in comparison to the total volume, v_s, then the excluded volume may be approximated by

$$B = v_s \tag{158}$$

where v_s is the volume of the solid at the melting point. This is the same approximation Eyring makes (37); however, expansion of the "solid-like" lattice into the liquid region is not necessary since, as a first approximation, any expansion represents a contribution to the free volume, v - B, and not to B itself.

In the case of ice, the void spaces are certainly not negligible, as evidenced by its contraction on melting. To obviate this problem, B for water was taken to be 11% below the volume of the liquid at freezing. This is the relative volume change characteristic of simple liquids like argon, nitrogen, etc., and it seems logical to suppose that the covolume of water is similarly smaller than the liquid volume. The large voids in ice are, of course, due to the geometric requirements of forming four hydrogen bonds around each water molecule, giving ice its unusual tetrahedral arrangement (coordination number = 4) as opposed to more

conventional solids with coordination numbers of 6 or more.

P^o-v-T data were taken every five degrees from the triple point to the critical point (every ten degrees for water); the constant B in Equation 150 was evaluated by linear least-squares treatment of $\ln P^o$ vs. $1/T$. The relative standard deviation, σ, of the observed vapor pressures from the calculated ones was computed as:

$$\sigma = \sqrt{\frac{1}{n}\sum\left[\frac{P^o - P^o(\text{calc.})}{P^o}\right]^2} \qquad (159)$$

where n is the number of data points in the calculation. The data are shown in Table IV, and the values of α calculated are plotted in Figure 9.

TABLE IV, PAGE 1

CALCULATION OF MOLAR PARAMETERS FOR SATURATED LIQUIDS.

WATER - V IN CC/GM. DORSEY DATA. P IN ATMOSPHERES.

BETH TAKEN AS 0.8914

T KELVIN	VAP PRESSURE	CALC. V. P.	PCT. DEV.	VOLUME
273.15	0.60273E-02	0.75188E-02	24.746	1.00021
283.15	0.12102E-01	0.14154E-01	16.957	1.00035
293.15	0.23042E-01	0.25520E-01	10.753	1.00184
303.15	0.41831E-01	0.44257E-01	5.798	1.00442
313.15	0.72748E-01	0.74098E-01	1.856	1.00789
323.15	0.12170E 00	0.12017E 00	-1.258	1.01210
333.15	0.19656E 00	0.18930E 00	-3.692	1.01710
343.15	0.30752E 00	0.29042E 00	-5.560	1.02280
353.15	0.46740E 00	0.43488E 00	-6.956	1.02900
363.15	0.69192E 00	0.63688E 00	-7.955	1.03590
373.15	0.10000E 01	0.91383E 00	-8.617	1.04350
383.15	0.14139E 01	0.12867E 01	-8.994	1.05150
393.15	0.19594E 01	0.17805E 01	-9.129	1.06030
403.15	0.26658E 01	0.24244E 01	-9.056	1.06970
413.15	0.35663E 01	0.32522E 01	-8.807	1.07980
423.15	0.46975E 01	0.43025E 01	-8.408	1.09060
433.15	0.60996E 01	0.56189E 01	-7.881	1.10210
443.15	0.78167E 01	0.72502E 01	-7.247	1.11440
453.15	0.98960E 01	0.92505E 01	-6.523	1.12750
463.15	0.12388E 02	0.11679E 02	-5.723	1.14150
473.15	0.15347E 02	0.14601E 02	-4.864	1.15650
483.15	0.18830E 02	0.18085E 02	-3.957	1.17260
493.15	0.22898E 02	0.22208E 02	-3.014	1.19000
503.15	0.27613E 02	0.27048E 02	-2.045	1.20870
513.15	0.33042E 02	0.32692E 02	-1.061	1.22910
523.15	0.39256E 02	0.39227E 02	-0.072	1.25120
533.15	0.46326E 02	0.46749E 02	0.912	1.27550
543.15	0.54331E 02	0.55354E 02	1.882	1.30230
553.15	0.63352E 02	0.65144E 02	2.828	1.33210
563.15	0.73475E 02	0.76223E 02	3.740	1.36550
573.15	0.84793E 02	0.88699E 02	4.606	1.40360
583.15	0.97406E 02	0.10268E 03	5.416	1.44750
593.15	0.11142E 03	0.11828E 03	6.158	1.49920
603.15	0.12696E 03	0.13562E 03	6.817	1.56200
613.15	0.14417E 03	0.15480E 03	7.376	1.64000
623.15	0.16320E 03	0.17595E 03	7.809	1.74100
633.15	0.18429E 03	0.19918E 03	8.077	1.89400
643.15	0.20777E 03	0.22461E 03	8.103	2.22500
647.30	0.21798E 03	0.23583E 03	8.191	3.10000

STANDARD PERCENT DEVIATION IN P = 7.84 PERCENT.

TABLE IV, PAGE 2

SUBROUTINE P502, CALC. OF MOLAR PARAMETERS FROM VAPOR PRESSURES.

T KELVIN	N (MOLES)	N1 (MOLES)	N ALPHA	ALPHA
273.15	0.52725E-06	0.16630E-07	0.51062E-06	0.19584E 07
283.15	0.10226E-05	0.31305E-07	0.99127E-06	0.10088E 07
293.15	0.19063E-05	0.56443E-07	0.18498E-05	0.54059E 06
303.15	0.34247E-05	0.97884E-07	0.33258E-05	0.30059E 06
313.15	0.59426E-05	0.16389E-06	0.57787E-05	0.17305E 06
323.15	0.99817E-05	0.26578E-06	0.97159E-05	0.10292E 06
333.15	0.16286E-04	0.41869E-06	0.15857E-04	0.63024E 05
343.15	0.25858E-04	0.64234E-06	0.25216E-04	0.39658E 05
353.15	0.39990E-04	0.96185E-06	0.39028E-04	0.25623E 05
363.15	0.60456E-04	0.14086E-05	0.59048E-04	0.16935E 05
373.15	0.89505E-04	0.20212E-05	0.87484E-04	0.11431E 05
383.15	0.12973E-03	0.28459E-05	0.12688E-03	0.78313E 04
393.15	0.18483E-03	0.39380E-05	0.18090E-03	0.55280E 04
403.15	0.25888E-03	0.53622E-05	0.25352E-03	0.39444E 04
413.15	0.35709E-03	0.71931E-05	0.34990E-03	0.28580E 04
423.15	0.48556E-03	0.95161E-05	0.47604E-03	0.21006E 04
433.15	0.65149E-03	0.12428E-04	0.63906E-03	0.15648E 04
443.15	0.86368E-03	0.16036E-04	0.84755E-03	0.11797E 04
453.15	0.11321E-02	0.20460E-04	0.11116E-02	0.89955E 03
463.15	0.14688E-02	0.25831E-04	0.14430E-02	0.69299E 03
473.15	0.18880E-02	0.32293E-04	0.18557E-02	0.53885E 03
483.15	0.24064E-02	0.40000E-04	0.23664E-02	0.42257E 03
493.15	0.30442E-02	0.49118E-04	0.29951E-02	0.33387E 03
503.15	0.38234E-02	0.59824E-04	0.37636E-02	0.26569E 03
513.15	0.47744E-02	0.72306E-04	0.47021E-02	0.21266E 03
523.15	0.59278E-02	0.86761E-04	0.58411E-02	0.17119E 03
533.15	0.73279E-02	0.10340E-03	0.72245E-02	0.13840E 03
543.15	0.90244E-02	0.12243E-03	0.89020E-02	0.11232E 03
553.15	0.11082E-01	0.14408E-03	0.10938E-01	0.91413E 02
563.15	0.13581E-01	0.16859E-03	0.13413E-01	0.74544E 02
573.15	0.16637E-01	0.19618E-03	0.16441E-01	0.60811E 02
583.15	0.20394E-01	0.22711E-03	0.20167E-01	0.49575E 02
593.15	0.25068E-01	0.26161E-03	0.24806E-01	0.40302E 02
603.15	0.30993E-01	0.29995E-03	0.30693E-01	0.32571E 02
613.15	0.38645E-01	0.34238E-03	0.38303E-01	0.26099E 02
623.15	0.48854E-01	0.38915E-03	0.48464E-01	0.20626E 02
633.15	0.64072E-01	0.44053E-03	0.63632E-01	0.15708E 02
643.15	0.94588E-01	0.49677E-03	0.94091E-01	0.10523E 02
647.30	0.16329E 00	0.52160E-03	0.16277E 00	0.61405E 01

EPSILON = 9721.76 CAL/MOLE

WATER - V IN CC/GM. DORSEY DATA. P IN ATMOSPHERES.

CALCULATION OF MOLAR PARAMETERS FOR SATURATED LIQUIDS.

ARGON. RODER DATA JAN 1968 NBS 361. P IN ATM, V IN CC/MOLE.

BETH TAKEN AS 24.9800

T KELVIN	VAP PRESSURE	CALC. V. P.	PCT. DEV.	VOLUME
83.80	0.67979E 00	0.68125E 00	0.214	28.23900
90.00	0.13213E 01	0.13142E 01	-0.539	29.00699
95.00	0.21110E 01	0.20973E 01	-0.650	29.69800
100.00	0.32097E 01	0.31942E 01	-0.485	30.45599
105.00	0.46812E 01	0.46737E 01	-0.161	31.29199
110.00	0.65910E 01	0.66058E 01	0.225	32.21999
115.00	0.90965E 01	0.90601E 01	0.595	33.26199
120.00	0.11997E 02	0.12103E 02	0.882	34.45000
125.00	0.15637E 02	0.15798E 02	1.030	35.83499
130.00	0.20006E 02	0.20203E 02	0.986	37.49699
135.00	0.25192E 02	0.25370E 02	0.707	39.58299
140.00	0.31297E 02	0.31343E 02	0.150	42.39999
145.00	0.38442E 02	0.38163E 02	-0.724	46.81000
150.86	0.48340E 02	0.47276E 02	-2.202	74.55800

STANDARD PERCENT DEVIATION IN P = 0.85 PERCENT.

TABLE IV, PAGE 4

SUBROUTINE P602, CALC. OF MOLAR PARAMETERS FROM VAPOR PRESSURES.

T KELVIN	N (MOLES)	N1 (MOLES)	N ALPHA	ALPHA
83.80	0.32219E-03	0.72059E-04	0.25013E-03	0.39977E 04
90.00	0.72050E-03	0.13901E-03	0.58149E-03	0.17195E 04
95.00	0.12777E-02	0.22184E-03	0.10558E-02	0.94693E 03
100.00	0.21420E-02	0.33787E-03	0.18041E-02	0.55410E 03
105.00	0.34294E-02	0.49436E-03	0.29351E-02	0.34054E 03
110.00	0.52867E-02	0.69874E-03	0.45880E-02	0.21781E 03
115.00	0.79046E-02	0.95833E-03	0.69463E-02	0.14382E 03
120.00	0.11538E-01	0.12802E-02	0.10258E-01	0.97359E 02
125.00	0.16549E-01	0.16711E-02	0.14878E-01	0.67102E 02
130.00	0.23475E-01	0.21370E-02	0.21338E-01	0.46765E 02
135.00	0.33209E-01	0.26835E-02	0.30525E-01	0.32672E 02
140.00	0.47457E-01	0.33154E-02	0.44142E-01	0.22579E 02
145.00	0.70530E-01	0.40367E-02	0.66493E-01	0.14978E 02
150.86	0.19360E 00	0.50006E-02	0.18850E 00	0.52757E 01

EPSILON = 1598.18 CAL/MOLE

ARGON, RODE? DATA JAN 1968 NBS 361. P IN ATM, V IN CC/MOLE.

CALCULATION OF MOLAR PARAMETERS FOR SATURATED LIQUIDS.

NITROGEN, RODER DATA JAN 1968 NBS 361. P IN ATM, V IN CC/MOLE.

BETH TAKEN AS 28.5371

T KELVIN	VAP PRESSURE	CALC. V. P.	PCT. DEV.	VOLUME
63.15	0.12300E 00	0.12678E 00	3.070	32.25999
70.00	0.38300E 00	0.37740E 00	-0.685	33.34799
75.00	0.75000E 00	0.73785E 00	-1.620	34.24300
80.00	0.13490E 01	0.13266E 01	-1.660	35.23399
85.00	0.22540E 01	0.22261E 01	-1.238	36.33400
90.00	0.35510E 01	0.35267E 01	-0.685	37.57100
95.00	0.53270E 01	0.53230E 01	-0.076	38.98199
100.00	0.76760E 01	0.77102E 01	0.445	40.62399
105.00	0.10694E 02	0.10781E 02	0.811	42.59299
110.00	0.14480E 02	0.14622E 02	0.979	45.05699
115.00	0.19140E 02	0.19313E 02	0.902	48.35399
120.00	0.24800E 02	0.24924E 02	0.499	53.36699
126.26	0.33556E 02	0.33337E 02	-0.652	89.04599

STANDARD PERCENT DEVIATION IN P = 1.26 PERCENT.

SUBROUTINE P612, CALC. OF MOLAR PARAMETERS FROM VAPOR PRESSURES.

T KELVIN	N (MOLES)	N1 (MOLES)	N ALPHA	ALPHA
63.15	0.88371E-04	0.14411E-04	0.73961E-04	0.13520E 05
70.00	0.31828E-03	0.42898E-04	0.27539E-03	0.36312E 04
75.00	0.69537E-03	0.83871E-04	0.61150E-03	0.16352E 04
80.00	0.13762E-02	0.15079E-03	0.12254E-02	0.81592E 03
85.00	0.25197E-02	0.25304E-03	0.22667E-02	0.44107E 03
90.00	0.43438E-02	0.40088E-03	0.39430E-02	0.25351E 03
95.00	0.71376E-02	0.60506E-03	0.65326E-02	0.15299E 03
100.00	0.11307E-01	0.87641E-03	0.10430E-01	0.95790E 02
105.00	0.17446E-01	0.12254E-02	0.16221E-01	0.61574E 02
110.00	0.26502E-01	0.16621E-02	0.24840E-01	0.40191E 02
115.00	0.40195E-01	0.21953E-02	0.37999E-01	0.26258E 02
120.00	0.62536E-01	0.28331E-02	0.59703E-01	0.16702E 02
126.26	0.19598E 00	0.37894E-02	0.19219E 00	0.51935E 01

EPSILON = 1398.78 CAL/MOLE

NITROGEN, POWER DATA JAN 1968 NBS 361. P IN ATM, V IN CC/MOLE.

CALCULATION OF MOLAR PARAMETERS FOR SATURATED LIQUIDS.

OXYGEN BOOER DATA NBS 361 JAN 1969. P IN ATM, V IN CC/MOLE.

BETH TAKEN AS 21.6630

T KELVIN	VAP PRESSURE	CALC. V. P.	PCT. DEV.	VOLUME
54.35	0.15000E-02	0.16930E-02	12.869	24.48900
60.00	0.72000E-02	0.75683E-02	5.116	24.96599
65.00	0.22900E-01	0.22935E-01	0.154	25.43500
70.00	0.61400E-01	0.59323E-01	-3.383	25.91599
75.00	0.14300E 00	0.13518E 00	-5.469	26.40199
80.00	0.29700E 00	0.27790E 00	-6.431	26.90900
85.00	0.56100E 00	0.52486E 00	-6.442	27.45000
90.00	0.98100E 00	0.92367E 00	-5.844	28.03099
95.00	0.16110E 01	0.15316E 01	-4.928	28.65900
100.00	0.25090E 01	0.24145E 01	-3.768	29.34299
105.00	0.37380E 01	0.36447E 01	-2.496	30.09299
110.00	0.53630E 01	0.52997E 01	-1.181	30.92099
115.00	0.74540E 01	0.74593E 01	0.071	31.84499
120.00	0.10082E 02	0.10204E 02	1.211	32.88899
125.00	0.13321E 02	0.13613E 02	2.194	34.09099
130.00	0.17249E 02	0.17763E 02	2.982	35.50299
135.00	0.21947E 02	0.22726E 02	3.550	37.21799
140.00	0.27501E 02	0.28568E 02	3.881	39.40199
145.00	0.34018E 02	0.35350E 02	3.915	42.41399
150.00	0.41638E 02	0.43125E 02	3.571	47.31400
154.77	0.50140E 02	0.51510E 02	2.733	75.00000

STANDARD PERCENT DEVIATION IN P = 4.75 PERCENT.

SUBROUTINE B602, CALC. OF MOLAR PARAMETERS FROM VAPOR PRESSURES.

T KELVIN	N (MOLES)	N1 (MOLES)	N ALPHA	ALPHA
54.35	0.94698E-06	0.12306E-06	0.82392E-06	0.12137E 07
60.00	0.48127E-05	0.55012E-06	0.42626E-05	0.23460E 06
65.00	0.16136E-04	0.16671E-05	0.14469E-04	0.69114E 05
70.00	0.45297E-04	0.43120E-05	0.40985E-04	0.24399E 05
75.00	0.10971E-03	0.98257E-05	0.99888E-04	0.10011E 05
80.00	0.23648E-03	0.20200E-04	0.21628E-03	0.46235E 04
85.00	0.46377E-03	0.38150E-04	0.42562E-03	0.23494E 04
90.00	0.84281E-03	0.67138E-04	0.77557E-03	0.12891E 04
95.00	0.14405E-02	0.11133E-03	0.13292E-02	0.75225E 03
100.00	0.23397E-02	0.17550E-03	0.21642E-02	0.46198E 03
105.00	0.36440E-02	0.26492E-03	0.33791E-02	0.29586E 03
110.00	0.54807E-02	0.38522E-03	0.50954E-02	0.19618E 03
115.00	0.80136E-02	0.54219E-03	0.74714E-02	0.13377E 03
120.00	0.11452E-01	0.74170E-03	0.10711E-01	0.93296E 02
125.00	0.16082E-01	0.98951E-03	0.15092E-01	0.66194E 02
130.00	0.22298E-01	0.12912E-02	0.21006E-01	0.47543E 02
135.00	0.30705E-01	0.16519E-02	0.29053E-01	0.34363E 02
140.00	0.42311E-01	0.20765E-02	0.40234E-01	0.24803E 02
145.00	0.59113E-01	0.25695E-02	0.56543E-01	0.17640E 02
150.00	0.86458E-01	0.31346E-02	0.83323E-01	0.11964E 02
154.77	0.20981E 00	0.37441E-02	0.20607E 00	0.48346E 01

EPSILON = 1718.33 CAL/MOLE

OXYGEN BOOER DATA NBS 361 JAN 1969. P IN ATM, V IN CC/MOLE.

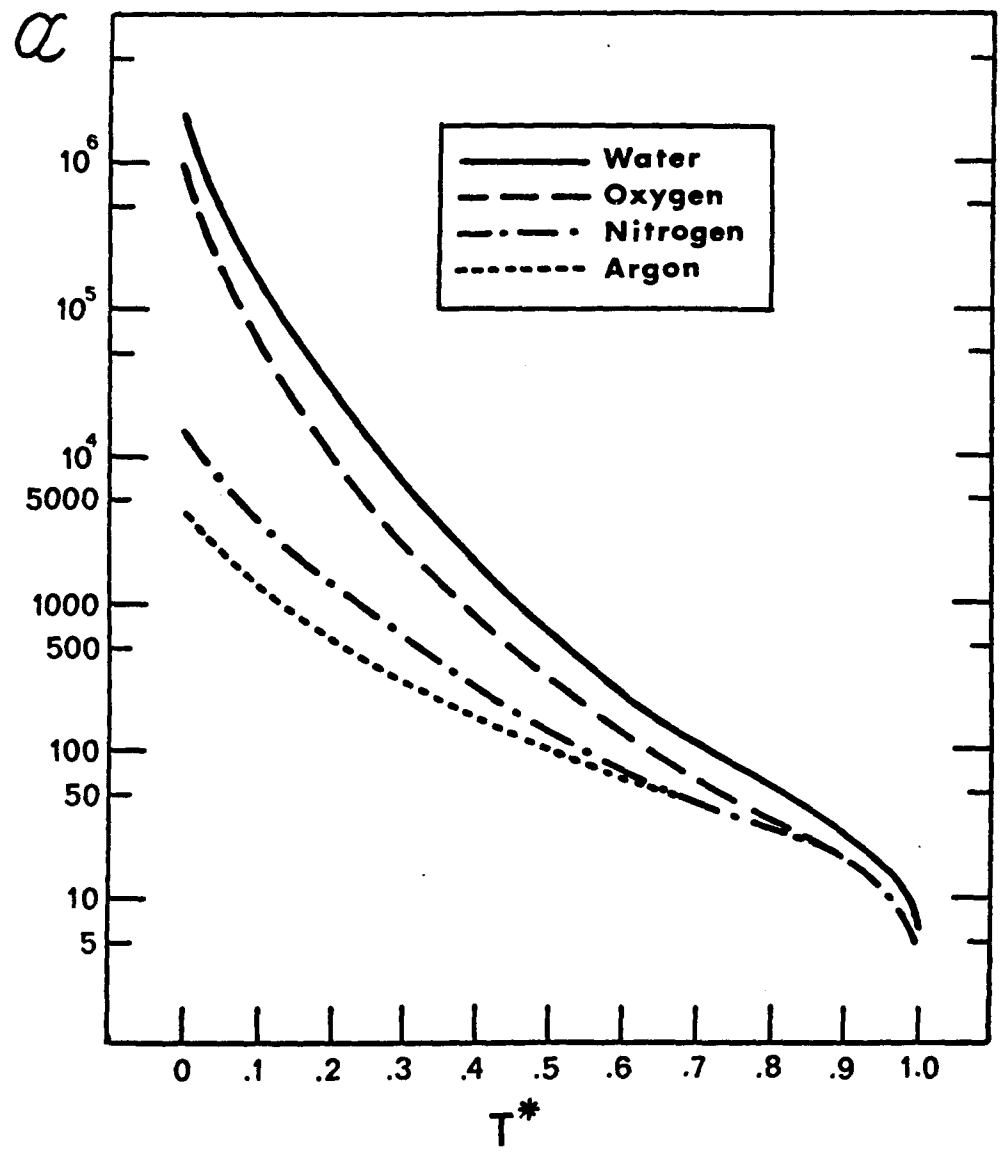


Figure 9. Saturated liquids, α vs. T*, where:

$$T^* = (T - T_{tp})/(T_c - T_{tp}).$$

T* is thus a reduced temperature such that T* = 0 at the triple point, and T* = 1 at the critical point for all liquids.

Discussion

The number of 1-mers in all cases is low compared to the treatments of Eyring and (for water) of Nemethy and Scheraga (47). Substitution of their values into Equation 62 gives negative values for B, an unreasonable result from our point of view. However, the numbers may be reconciled in the following way: the numbers these authors get are characteristic of short-lived "flickering" clusters (48) of lifetime less than 10^{-11} sec. These are the 1-mers participating in exchanges like those represented by Equation 134, and one would expect large numbers of these. In this type of process, though, the 1-mers are never really free to leave the liquid, if indeed they are ever free at all. Their short lifetimes are sufficient to account for relaxation phenomena, as Nemethy and Scheraga point out, but from the point of view of this theory only those 1-mers generated by processes such as that represented in Equation 133 could properly be said to exist free long enough to leave the liquid phase.

Hence the other models, in which as many as one molecule in three (47) is unbonded to any other, are in effect snapshots taken during diffusion over at most one molecular diameter, a picture Eisenberg and Kauzmann (49) call a "vibrationally-averaged" structure. These authors go on to state: "Thermodynamic properties measured by the usual methods are characteristic of the [diffusionally-

averaged] structure of the liquid" with lifetime long compared to the former. In effect, this picture is more blurred than the other. Consequently, since we are looking at only those 1-mers which are free for a comparatively long time, there will be fewer of them, and by the same reasoning the molecules will, on the average, be clustered in much larger aggregates than those calculated by these other workers.

The much larger values of α for water vis-a-vis argon and nitrogen are expected because of the strong intermolecular forces in water. These values give quantitative meaning to often-heard statements like "water is a highly associated substance." Oxygen, too, presents an interesting case; at the triple point its cluster size is of the same order of magnitude as that for water, and some 100 times that for argon and nitrogen, although both of the latter are non-polar, like oxygen, and nitrogen is a homonuclear diatomic as well. The cluster size of liquid oxygen drops off more rapidly than does water's as the temperature is raised, until at about 9/10 of the way from the triple point to the critical point it exhibits substantially identical behavior with argon and nitrogen. (See Figure 9.)

What is undoubtedly at work here is an intermolecular π-bond between the singly occupied antibonding orbitals of adjacent oxygen molecules. This is similar to the "back-bonding" in complex ions in which the two electrons of a filled metal d-orbital enter an empty π^* orbital of the ligand, providing additional stability to the aggregate; here the molecules contribute one electron apiece. The

orbitals are said to be antibonding because they exhibit a nodal plane midway along the interatomic axis; Figure 10 demonstrates that there is no such node between two adjacent molecules, and hence overlap may occur. Such a bond will be weak, as there can be no intermolecular σ-bond. Hence it comes as no surprise that it is easily overcome at higher temperatures where oxygen reverts to exhibiting corresponding-states behavior with simpler substances like argon and nitrogen.

The values of α at the critical point are especially noteworthy. Keeping in mind the caveats mentioned at the beginning of this section, we find that α for all three non-polar liquids is approximately 5 at the critical point. The 5-mer is the smallest multiply-bonded structure predicted by association theory, and in Section II of this work it was predicted that this cluster size should be characteristic of the critical state.

This sort of corresponding-states behavior has been observed also in the critical ratio RT_c/P_cv_c. (See Table V.) Water is anomalous here as it is in its value of α_c. While the anomaly in α may well be due to the many approximations made in calculation, the consistency of the α values at T_c for the other liquids, along with the data in Table V, hint that it may indeed be real. In any case, the results for water should not be put forth with the same force as those for the other three substances. There are too many complicating factors in that molecule to be adequately covered by a treatment which made its predictions on the basis of the geometries of

clusters of spherical molecules. These results do demonstrate that reasonable (if not correct) values for water can be obtained even treating it as a simple substance. They indicate that refinements which take into account the detailed structure of the molecule should be expected to improve them greatly.

There is no easy way at present to check the values of α or to calculate any thermodynamic functions from them. This check will undoubtedly involve a marriage of association theory with statistical mechanics, creating a partition function based on that work and comparing the calculated thermodynamic properties with the observed ones. Such a project is unfortunately beyond the scope of the present work.

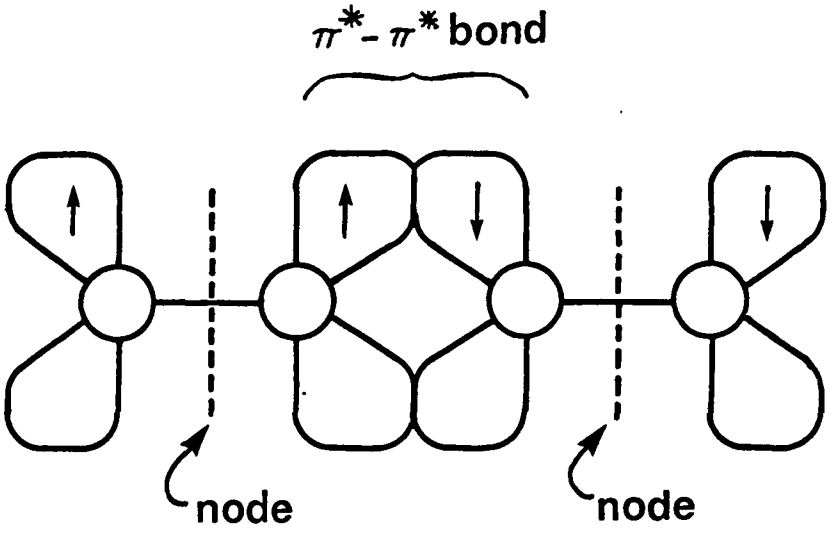


Figure 10. O_2 - O_2 π - bond.

TABLE V

Values of the Critical Ratio RT_c/P_cv_c

Calculated from Experimental Data

Argon	3.434	(a)
	3.435	(b)
Nitrogen	3.422	(a)
	3.467	(b)
Oxygen	3.424	(a)
	3.377	(b)
Water	4.385	(a)
	4.367	(c)

(a) Moelwyn-Hughes, Ref. 41, page 536

(b) Roder et al., Ref. 45

(c) Dorsey, Ref. 46

IV

The Atomic Radii of the Alkali Metals

One of the more striking successes of association theory was the calculation from compressibility data of the atomic radii of the alkali metals by Ginell and Quigley (32). The calculation, however, was based on the assumption that at the minimum in Zn, Zn was equal to Zw and that both were equal to unity. (See Equations 119, 122, and 125.) The difficulties in this idea were discussed in Section I and resolved in Section II of this work, but the question remains: why are such good results obtained?

To understand this situation, rearrange Equation 93 to read:

$$E = \left(\frac{RT}{m_o}\right)\left(\frac{m}{v}\right)\frac{\exp(-v/J)}{P\ Zn}. \qquad (160)$$

Assuming E can be found, one can obtain B at any pressure (at the same temperature) from Equation 90:

$$B = v(1 - Ee^{v/J}). \qquad (161)$$

The radii of the alkali metals were calculated from the known geometry of their crystals (body-centered cubic) and the compressibility data of Bridgman (50), giving:

$$r = \sqrt[3]{\frac{3\sqrt{3}}{32N_o}\frac{Bm_o}{m}} \qquad (162)$$

where N_o is Avogadro's number.

Clearly, then, the value of r obtained depends on the estimate of B, and the success of the earlier work lies in the fact that the void space, v-B, of the solid is comparatively small, so that

when widely differing values are calculated for the void space, B is still close to v, and the sensitivity of Equation 162 is reduced.

Let us examine the behavior of these numbers in the case of sodium, for example. Setting Zn = 1 at P_{min} in Equation 160, Ginell and Quigley calculated a value of 0.868 cm^3 for B per gram of sodium at 1 atm. The specific volume of sodium at that pressure and at room temperature is 1.030 cm^3/gm, giving a free volume of 0.162 cm^3/gm. Substituting B into Equation 162 gives the result,

$$r = 1.75 \text{ Å}. \qquad (163)$$

This compares extremely favorably with the x-ray work of Slater (51), Bragg (52), and Aruja and Perlitz (53), which are presented in Table VI.

In attempting to find alternative assumptions for the calculation of E, the following idea was tried on a purely intuitive basis.

Let the crystal of mass m at the lowest pressures be regarded as a single crystal, hence a single cluster of the N_s atoms in the sample. That is, there are presumed to be no 1-mers, and

$$\alpha^o = Zn^o = Zw^o = N_s = N_o m/m_o \qquad (164)$$

at the vapor pressure P^o, the lowest pressure at which the crystal is stable.

Application of higher pressure would presumably deform the lattice, producing 1-mers, raising N, and lowering α, Zn, and Zw.

Then in the single crystal, Equation 160 becomes

$$E = \frac{RT}{N_o} \frac{\exp(-v^o/J)}{P^o v^o}. \qquad (165)$$

Taking the vapor pressure at room temperature from Millar (54),

$$u^o = E\exp(v^o/J) = 1.20 \times 10^{-9} \qquad (166)$$

so that we may set

$$B^o = v^o = 1.030 \text{ cm}^3/\text{gm}. \qquad (167)$$

From Equation 162, then,

$$r = 1.85 \text{ Å}. \qquad (168)$$

This value is included in Table VI for easy comparison. We may conclude that the extreme insensitivity of this calculation makes it useless for deciding the correctness of a model, since the void space of a solid is so small compared to the total volume. As can be seen from the table, the two calculations of the void space differ by a factor of 10^8, yet the resulting calculations of the atomic radius each differ by 2.8% from Slater's value. This accounts for the good results obtained by Ginell and Quigley using assumptions now known to be logically incorrect.

TABLE VI

Calculated Crystal Data and Atomic Radii for Sodium

(Room Temperature, 1 Atm. Volume = 1.030 cm^3/gram.)

	B (cm^3/gm)	v - B (cm^3/gm)	r (Å)
Ginell & Quigley (32)	0.868	0.162	1.75
This work	1.030	1.24×10^{-9}	1.85
Slater (51)	(0.941)	(0.089)	1.80
Bragg (52)	(0.895)	(0.135)	1.77
Aruja & Perlitz (53)	(1.021)	(0.009)	1.85

The values in parentheses are back-calculated using Equation 162, and are presented for complete comparison.

APPENDIX I

CALCULATION OF TAIT-TAMMANN CONSTANTS

The constants J and L of the Tait-Tammann equation were evaluated in the following way. The equation itself may be inverted to give:

$$-dP/dv = L/J + P/J. \tag{169}$$

Thus a plot of -dP/dv vs. P will give a straight line with slope 1/J and intercept L/J (55). The derivative may be obtained from P-v data by the Lagrangian method (56, 57) for equal intervals of the independent variable:

$$(dv/dP)_{\text{kth point}} = \sum_{j=0}^{n} A_{kj} v_j / \Delta P \tag{170}$$

where ΔP is the interval between any two points, n is 6 (usually), and the coefficients A_{kj} are given by:

$$A_{kj} = \frac{(-1)^{k+j}\, k!(n-k)!}{j!(n-j)!(k-j)!} \tag{171a}$$

where $k \neq j$. If $k = j$, the relation becomes

$$A_{kk} = -\sum_{i=k+1}^{n-k} (1/i) \qquad (2k \leq n-1)$$

$$\text{or} \quad A_{kk} = +\sum_{i=n-k+1}^{k} (1/i) \qquad (n-1 < 2k) \tag{171b}$$

These coefficients arise from the differentiation of the Lagrangian interpolation formula, which is used explicitly if the data are unequally spaced. The formula is (57):

$$v_k = \sum_{j=1}^{n} \left\{ \prod_{i=1}^{n} \frac{(P_k - P_i)}{(P_j - P_i)} \right\}_{i \neq j} \cdot v_j \tag{172}$$

in which n is usually taken as 7, and P_4 is the observed pressure closest to the desired P_k. It is possible to take the derivative at unequally spaced points, but in that case the A_{kj} would have to be calculated individually for each data set. From the point of view of computer programming, it is clearly simpler to use the A_{kj} calculated from Equations 171 and tabulate them (See reference 56) and interpolate if necessary.

However, this method has certain disadvantages, principally (a) the use of interpolated points in the original data, and (b) the exaggeration of small errors in the P-v data into larger fluctuations in the derivative. Hence it was decided to use the J and L determined in this way as initial approximations in a least-squares iteration procedure which uses only the experimental points and does not depend on interpolated points or derivatives beyond this first step; in fact, the computer program has been written (Appendix II) to allow the investigator to supply his own initial approximations.

To carry out this procedure, one first integrates the Tait-Tammann equation:

$$dv = \frac{-J\, dP}{P + L}$$

$$v = J \ln \frac{H}{P + L} \qquad (173a)$$

$$\text{and} \quad H = (P + L)\exp(v/J) \qquad (173b)$$

where H is the constant of integration. To get a suitable initial approximation for H, use the initial J and L to calculate a term like Equation 173b for each experimental point and average the

H-values thus obtained.

In a least-squares procedure, the object is to minimize a function S (ideally zero) with respect to the adjustable parameters. S is the sum of the squares of the function

$$F_o(P, v, J, L, H) = 0. \tag{174}$$

Since F_o does not, in general, equal zero, we must minimize

$$S = \Sigma F_o^2. \tag{175}$$

From Equation 173b, we see

$$F_o = (P + L)\exp(v/J) - H. \tag{176}$$

The iteration is carried out according to the method outlined by Deming (58):

1. Calculate values of F_o at each pressure, using the most recent approximations of J, L, and H.

2. Calculate values for the derivatives of F_o with respect to each parameter J, L, H, and v. (P is assumed relatively error-free.) Note that for the parameter x (where x is J, L, H, or v) we define our notation such that:

$$F_x = dF_o/dx. \tag{177}$$

The differentiation is done algebraically, from Equation 176, not numerically.

3. Divide F_J, F_L, and F_H by F_v at each experimental point.

4. Sum the squares and cross-products, so:

$$F_{xx} = \Sigma(F_x/F_v)^2$$
$$\text{and} \quad F_{xy} = \Sigma(F_xF_y/F_v^2). \tag{178}$$

These lead to the normal equations:

$$\begin{bmatrix} F_{LL} & F_{LJ} & F_{LH} \\ F_{LJ} & F_{JJ} & F_{JH} \\ F_{LH} & F_{JH} & F_{HH} \end{bmatrix} \times \begin{bmatrix} \Delta L \\ \Delta J \\ \Delta H \end{bmatrix} = \begin{bmatrix} F_{OL} \\ F_{OJ} \\ F_{OH} \end{bmatrix} \tag{179}$$

Equations 179 are three equations in three unknowns, ΔJ, ΔL, and ΔH. They may be solved by determinants or shortcuts; the latter method was chosen, using the Gauss-Doolittle (or Gauss-Jordan) method (59) which, in matrix notation, is the following:

Premultiply both sides of Equation 179 by a matrix $\underline{M}$, such that the 3 x 3 matrix resulting on the left-hand side is triangular:

$$\begin{bmatrix} 1 & u_1 & u_2 \\ 0 & 1 & u_3 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} \Delta L \\ \Delta J \\ \Delta H \end{bmatrix} = \begin{bmatrix} u_4 \\ u_5 \\ u_6 \end{bmatrix} \tag{180}$$

where the u_k's are complicated functions, yielding the results:

$$\Delta H = \frac{F_{OH} - \dfrac{(F_{JH} - F_{LJ}F_{LH}/F_{LL})(F_{OJ} - F_{LJ}F_{OL}/F_{LL})}{F_{JJ} - F_{LJ}^2/F_{LL}} - \dfrac{F_{LH}F_{OL}}{F_{LL}}}{F_{HH} - \dfrac{(F_{JH} - F_{LJ}F_{LH}/F_{LL})^2}{F_{JJ} - F_{LJ}^2/F_{LL}} - \dfrac{F_{LH}^2}{F_{LL}}}$$

$$\Delta J = \frac{F_{OJ} - F_{LJ}F_{OL}/F_{LL} - \Delta H(F_{JH} - F_{LJ}F_{LH}/F_{LL})}{F_{JJ} - F_{LJ}^2/F_{LL}} \tag{181}$$

$$\Delta L = (F_{OL} - F_{LJ}\Delta J - F_{LH}\Delta H)/F_{LL}.$$

While the derivation is formidable, only the results (Equations 181) need be programmed into the computer, at a considerable saving in time. The new estimate of the Tait-Tammann constant is obtained by subtracting the residual calculated by Equations 181 from the

previous estimate. The entire process is repeated (step 1 above) with the new estimates until the successive values of J, L, and H are within the desired relative tolerances (10^{-10}). More than one iteration is needed since the basic assumption of this least-squares technique is based on a Taylor expansion and neglects terms beyond the square. Where these higher-order terms are small, the iterations converge quickly, otherwise many are needed. With data deviating widely from the Tait-Tammann equation, the iterations may not converge at all.

As an aid in speeding up the iterations, a "rapid convergence" technique (60) was used, viz:

For a converging sequence of numbers, a_i, the kth term a_k may be "improved" to the value a_k^* via the equation:

$$a_k^* = a_k - (a_k - a_{k-1})^2/(a_{k-2} + a_k - 2a_{k-1}). \qquad (182)$$

This has the effect of projecting ahead several iterations, but does so for J, L, and H separately, without regard for their mutual interrelationship or for the requirement that S in Equation 175 be a minimum. Hence the process used in the computer program is to conduct eight least-squares iterations followed by the rapid-convergence treatment and then repeating the whole procedure until convergence is reached. If the iterations diverge after a long enough time the process is abandoned and only the initial approximations of J, L, and H are retained.

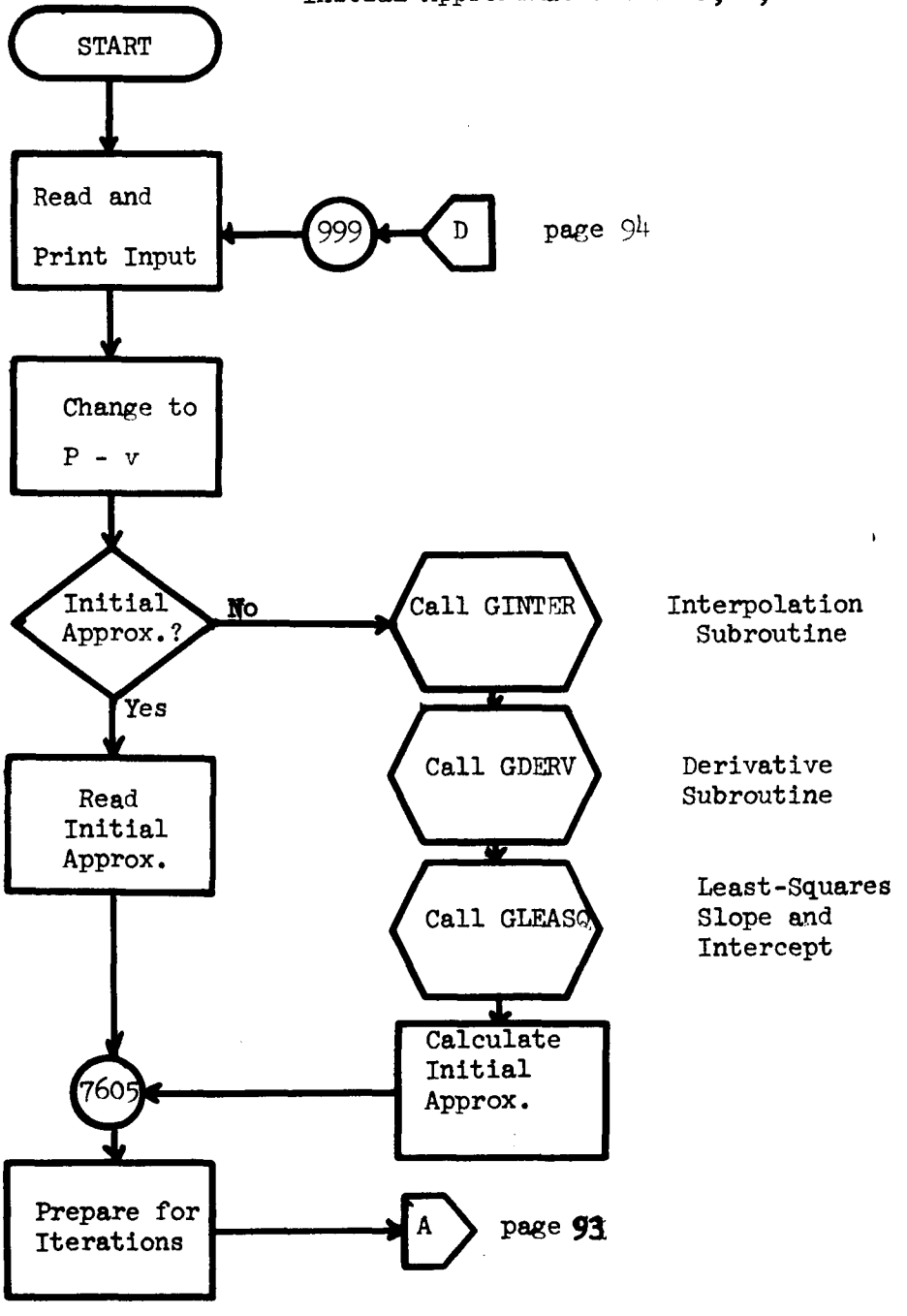
The program for these calculations and some samples of output are found in Appendix II.

APPENDIX II

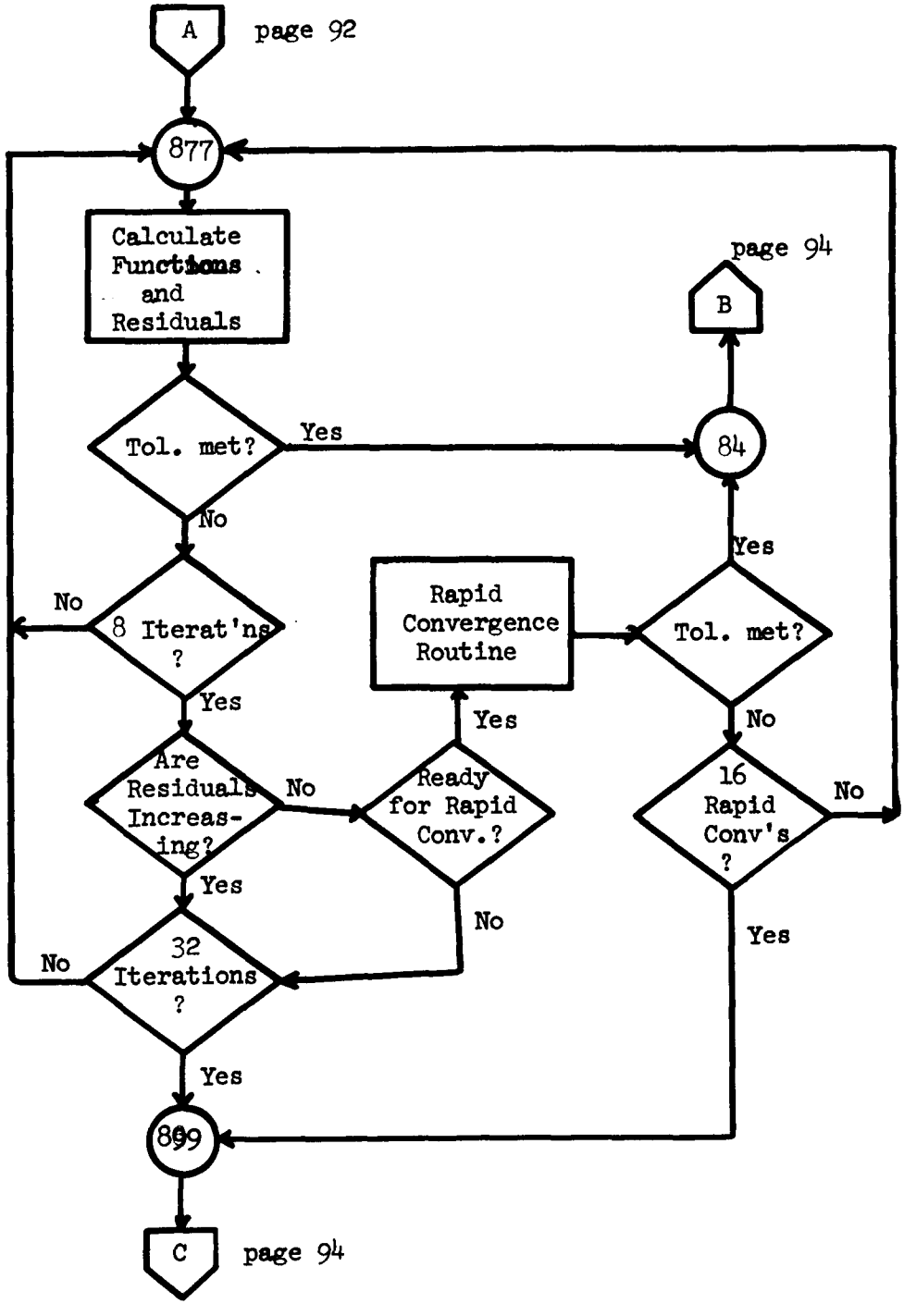
COMPUTER PROGRAM (#500)

AND SAMPLE OUTPUT

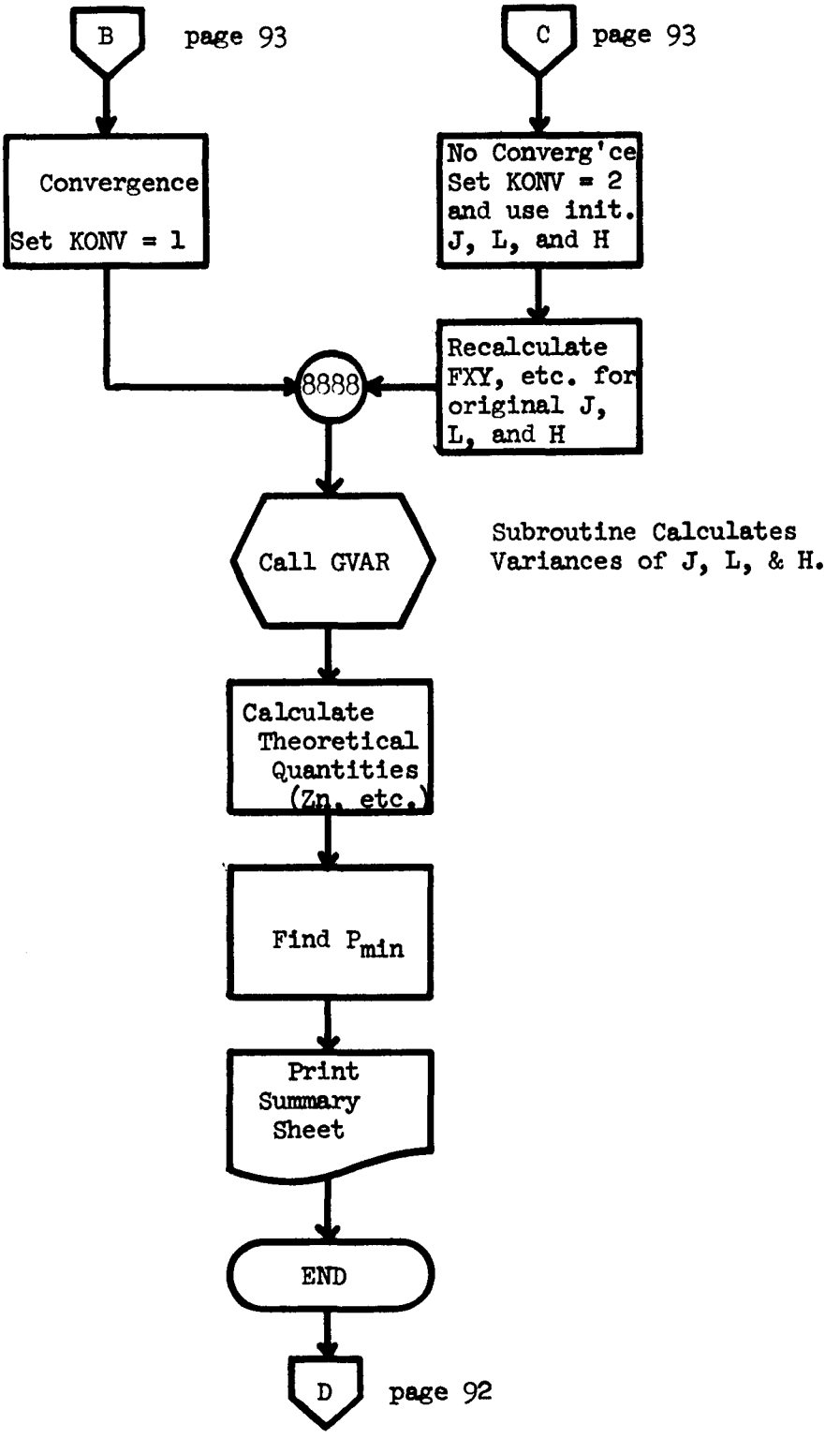
Flowchart for Program 500 - Input and Calculations of Initial Approximations of J, L, and H.



Iteration Procedure



Calculations



```
C     PROGRAMME 500.8 BY ASK. REVISED JULY 1970.
C     ** LEAD CARD BEFORE ALL DATA = DATE. (COLUMN 1 BLANK.)
C     ** CARD 1 = TITLE AND OTHER INFORMATION. (COL. 1 BLANK.)
C     ** CARD 2 = INDEX (FORMAT I4). INDEX = 1 IF NO INITIAL APPROXIMA-
C                  TIONS ARE SUBMITTED, = 2 IF THEY ARE.
C     ** CARD 3 = M, D, IJK, KI, PI(1), HH, & PN.
C                 FORMAT IS I3,F12,2I2,3F12.
C                 M = NUMBER OF DATA POINTS.
C                 D = DENSITY IN GM/CC.
C                 IJK = 1 FOR COMPRESSION DATA (VO-V)/VO.
C                     = 2 FOR RELATIVE VOLUME DATA, V/VO.
C                     = 3 FOR PLAIN OLD VOLUME VS. PRESSURE.
C                     = 4 FOR DENSITY DATA.
C                     = 5 FOR COMPRESSIBILITY Z = PV/RT.
C                     = 6 FOR PV VS. P DATA.
C                 KI = ORDER OF INTERPOLATION = 3, 5, OR (USUALLY) 7.
C                 PI(1) = LOWEST OF INTERPOLATED PRESSURES.
C                 HH = INTERPOLATION INTERVAL.
C                 PN = HIGHEST OF INTERPOLATED PRESSURES.
C                 THESE LAST THREE SHOULD CORRESPOND AS CLOSELY AS
C                 POSSIBLE WITH THE EXPERIMENTAL RANGE AND INTERVAL.
C     ** CARDS 4FF = PRESSURE AND DEPENDENT VARIABLE, FORMAT 2F12.
C     ** CARD 5 = NAME OF ABOVE DEPENDENT VARIABLE, IN FIRST 16 COLUMNS.
C     ** CARD 6 = R (GAS CONSTANT) AND T (KELVIN). CARD 6 BELONGS IN
C                 DECK ONLY IF IJK = 5.
C     ** CARD 7 = J, L, & H AS INITIAL APPROXIMATIONS. CARD 7 BELONGS IN
C                 DECK ONLY IF INDEX = 2.
C
C     ITERATION METHOD DUE TO DEMING, CHAPTERS 6 & 9.
C     RAPID-CONVERGENCE PROCEDURE FROM ZAGUSKIN, PAGE 133.
C
C     ***************************************************************
C     *                                                             *
C     *     EXPLANATION OF SUNDRY VARIABLES IN PROGRAMME            *
C     *                                                             *
C     *     NOUT = NUMBER OF INTERPOLATED POINTS.                   *
C     *     PEX = EXPERIMENTAL PRESSURE.                            *
C     *     VEX = EXPERIMENTAL DEPENDENT VARIABLE. CONVERTED TO     *
C     *           VOLUME IF NECESSARY.                              *
C     *     PI = INTERPOLATED PRESSURES.                            *
C     *     V = INTERPOLATED VOLUMES (EARLY PART OF PROGRAM),       *
C     *       = VOLUMES CALCULATED FROM TAIT CONSTANTS (LATTER PART *
C     *         OF PROGRAM.)                                        *
C     *     DVDP, DPDV = DERIVATIVES DV/DP & DP/DV, RESPECTIVELY.   *
C     *     SLOPE = SLOPE OF LINE DP/DV VS. P.                      *
C     *     AIN = INTERCEPT OF THAT LINE.                           *
C     *     SIGMA = STANDARD DEVIATION.                             *
C     *     VAR = VARIANCE.                                         *
C     *     HVAL = INDIVIDUAL H-VALUE CALCULATED AT EACH PRESSURE.  *
C     *           THEY ARE AVERAGED TO GET INITIAL APPROXIMATION FOR*
C     *           H.                                                *
C     *     FXY = SUM(FX*FY/FV**2)                    SEE DEMING.   *
C     *     F0 = ABS(P+L)*EXP(V/J) - H.                  DITTO.     *
C     *     FX = D(F0)/DX.                               DITTO.     *
```

```
C      *     RESX = RESIDUAL OF X (DELTA X) = OLDX - NEW X.                *
C      *     VARX = VARIANCE OF X. CALCULATED BY SUBROUTINE GVAR.          *
C      *     SIGX = STANDARD ERROR OF X = SQRT(VARX).                      *
C      *     KONV = 1 IF ITERATIONS CONVERGE, =2 IF NOT.                   *
C      *     C = J/VO WITH PO TAKEN AS LOWEST EXPERIMENTAL PRESSURE.       *
C      *     PMIN = PRESSURE WHERE ZN (Q. V.) IS A MINIMUM AND WHERE       *
C      *           P/V = L/J.                                              *
C      *     VMIN = VOLUME AT PMIN.                                        *
C      *     ZN = NUMBER-AVERAGE DEGREE OF ASSOCIATION.                    *
C      *     ZNA = ZN*E*MO/M*R*T.                                          *
C      *           E IS AN UNDETERMINED CONSTANT,                          *
C      *           M IS THE MASS OF THE SAMPLE, AND                        *
C      *           MO IS THE MOLECULAR WEIGHT OF THE UNIMER.               *
C      *                                                                   *
C      *********************************************************************
C
      DOUBLE PRECISION D,PI(50),HH,PN,PEX(50),VEX(50),R,T,  RT,J,L,H,V(5
     10),DVDP(50),DPDV(50),DCALC(50),DEV(50),SLOPE,AIN,SIGMA,SUM,HVAL(50
     2),FM,VAR,OLDJ,OLDL,OLDH,FLL,FLJ,FLH,FJJ,FJH,FHH,FOL,FOJ,FOH,ZONK,I
     3V,FO,FJ,FL,FINK,D4,D3,D2,E3,E4,RESH,RESL,RESJ,XJ,XL,XH,GNUH(8),GNU
     4L(8),GNUJ(8),VARL,VARJ,VARH,SIGL,SIGJ,SIGH,RAPIDJ,RAPIDL,RAPIDH,C,
     5ZNA(50),PMIN(50),PMOR,X1,X2,ZN1,ZN2,PX(11),VP(50),PP(50),AJL(50),V
     6MIN
      DIMENSION VARBL(4)
  101 FORMAT(80H
     1                                )
  102 FORMAT(80H
     1                                )
  103 FORMAT(1H1'PROGRAM 500.8 BY ASK. CALCULATION OF TAIT PARAMETERS.'
  104 FORMAT(I3,F12.0,2I2,3F12.0)
  105 FORMAT(2F12.0)
  106 FORMAT('0ORIGINAL DATA'/)
  108 FORMAT(2(1XD16.9))
  110 FORMAT('0PRESSURE'8X'VOLUME'/)
  111 FORMAT('0PRESSURE'8X'VOLUME'11X'DV/DP'12X'DP/DV'/)
  112 FORMAT(/'0EXP PRESSURE'4X'EXP VOLUME'7X'H-VALUE'10X'DEVIATION'/)
  114 FORMAT('0AVERAGE H-VALUE = 'D16.9)
  116 FORMAT('0PRESSURE'8X'THEOR VOL'8X'EXP VOL'10X'ZN*EMO/MRT'/)
  118 FORMAT('0 V MIN = 'D16.9)
  122 FORMAT('0 R = 'D16.9,', T = 'D16.9,' DEG KELVIN')
  611 FORMAT('0CONVERGENCE O.K.'/)
 1000 FORMAT('0VARIANCE OF L= 'D16.9,', STD ERR = 'D16.9)
 1050 FORMAT(I4)
 1051 FORMAT(3F12.0)
 1060 FORMAT(4A4)
 1061 FORMAT('0PRESSURE'8X,4A4 /)
 1080 FORMAT(4(1XD16.9))
 2000 FORMAT('0VARIANCE OF J= 'D16.9,', STD ERR = 'D16.9)
 3000 FORMAT('0VARIANCE OF H= 'D16.9,', STD ERR = 'D16.9)
 6005 FORMAT('0NO CONVERGENCE. INITIAL APPROXIMATIONS USED.'/)
 6999 FORMAT('0 P MIN = 'D16.9)
 7500 FORMAT(1H1)
 7501 FORMAT(1H0)10X'SUMMARY SHEET.'/)
 7502 FORMAT('0 J = 'D16.9/)
```

```
 7503 FORMAT('0 L = 'D16.9/)
 7504 FORMAT('0 H = 'D16.9/)
 7511 FORMAT('0 CONVERGENCE CODE (KONV) ='I3/)
 7604 FORMAT('0INITIAL APPROXIMATIONS SUBMITTED ON CARD.'/)
 8001 FORMAT('0C = J/V0 = 'D16.9,' WITH P0 TAKEN AS 'D16.9,'.')
 8100 FORMAT('0INITIAL APPROXIMATIONS FOR ITERATION='/)
 8101 FORMAT('0J= 'D16.9,' L= 'D16.9,' H= 'D16.9 )
 8102 FORMAT('0ITERATION NUMBER'I4)
 8201 FORMAT('0DELTA J INCREASING, = 'D16.9,' VS. 'D16.9)
 8202 FORMAT('0DELTA L INCREASING, = 'D16.9,' VS. 'D16.9)
 8203 FORMAT('0DELTA H INCREASING, = 'D16.9,' VS. 'D16.9)
 8301 FORMAT(/'0RAPID CONVERGENCE VALUES, SERIES'I4)
 9000 FORMAT('0PRESSURE'8X'DP/DV EXP'8X'DP/DV THEOR'6X'DEV'/)
 9001 FORMAT('0SLOPE = 'D16.9,' INTERCEPT = 'D16.9)
 9002 FORMAT('0STANDARD DEVIATION = 'D16.9)
      CALL SETCLK (15)
      READ(1,101)
  999 READ(1,102)
      WRITE(3,103)
      WRITE(3,102)
      WRITE(3,101)
      READ(1,1050) INDEX
      READ(1,104)M,D,IJK,KI,PI(1),HH,PN
      READ(1,105)(PEX(I),VEX(I),I=1,M)
      WRITE(3,106)
      READ(1,1060) VARBL
      WRITE(3,1061) VARBL
      WRITE(3,109)(PEX(I),VEX(I),I=1,M)
      GO TO (1,2,33,4,5,6),IJK
C
C     CHANGE DATA TO P-V.
C
    1 DO 51 I = 1,M
   51 VEX(I)=(1.-VEX(I))/D
      GO TO 3
    2 DO 52 I=1,M
   52 VEX(I)=VEX(I)/D
      GO TO 3
    5 READ(1,105)R,T
      RT=R*T
      WRITE(3,122)R,T
      DO 56 I=1,M
   56 VEX(I) = RT*VEX(I)/PEX(I)
      GO TO 3
    4 DO 55 I=1,M
   55 VEX(I)=1./VEX(I)
      GO TO 3
    6 DO 54 I=1,M
   54 VEX(I)=VEX(I)/PEX(I)
C
    3 WRITE(3,110)
      WRITE(3,108)(PEX(I),VEX(I),I=1,M)
   33 NOUT = (PN-PI(1))/HH + 1.
      DO 955 I=2,NOUT
```

```
  955 PI(I)=PI(I-1) + HH
      GO TO (7601,7602),INDEX
 7602 READ(1,1051)J,L,H
      WRITE(3,7604)
      GO TO 7605
 7601 CALL GINTER(KI,M,NOUT,PEX,VEX,PI,V)
      CALL GDERV(HH,V,NOUT,DVDP,DPDV,2)
C
C     INTERPOLATION PERFORMED AND DERIVATIVES CALCULATED.
C
      WRITE(3,111)
      WRITE(3,1080)(PI(I),V(I),DVDP(I),DPDV(I),I=1,NOUT)
C
C     PERFORM LEAST-SQUARES ON DP/DV VS. P.
C
      CALL GLEASQ(PI,DPDV,DCALC,DEV,NOUT,SLOPE,AIN,SIGMA)
      WRITE(3,9000)
      WRITE(3,1080)(PI(I),DPDV(I),DCALC(I),DEV(I),I=1,NOUT)
      WRITE(3,9001)SLOPE,AIN
      WRITE(3,9002)SIGMA
      J = -1./SLOPE
      L = AIN/SLOPE
C
C     CALCULATE INITIAL VALUE FOR H.
C
      SUM = 0.
      DO 501 I = 1,M
      HVAL(I)=DEXP(VEX(I)/J)*DABS(PEX(I)+L)
  501 SUM = SUM + HVAL(I)
      FM=M
      H=SUM/FM
      VAR=0.
      DO 502 I=1,M
      DEV(I)=HVAL(I)-H
  502 VAR=VAR+DEV(I)*DEV(I)
      SIGMA = DSQRT(VAR/(FM-1.))
      WRITE(3,112)
      WRITE(3,1080)(PEX(I),VEX(I),HVAL(I),DEV(I),I=1,M)
      WRITE(3,114)H
      WRITE(3,9002)SIGMA
C
C     BEGIN ITERATION PROCEDURE.
C
 7605 WRITE(3,8100)
      WRITE(3,8101)J,L,H
      OLDJ=J
      OLDL=L
      OLDH=H
      KONV=1
      ITER=1
      IRAPID=1
      KTER=1
      KRAUT=1
  877 FLL=0.
```

```
      FLJ=0.
      FLH=0.
      FJJ=0.
      FJH=0.
      FHH=0.
      FOL=0.
      FOJ=0.
      FOH=0.
      DO 8500 I=1,M
      ZONK = DABS(PEX(I) +L)*DEXP(VEX(I)/J)
      FV=ZONK/J
      FO=(ZONK-H)/FV
      FJ= -VEX(I)/J
      FL= J/DABS(PEX(I)+L)
C
C     NOTE EACH OF THE ABOVE HAS ALREADY BEEN DIVIDED BY FV.
C     NOTE ALSO FH = -1, SO FH/FV = -1/FV, AS BELOW.
C
      FLL=FLL+FL*FL
      FLJ=FLJ+FL*FJ
      FLH=FLH-FL/FV
      FJJ=FJJ+FJ*FJ
      FJH=FJH-FJ/FV
      FHH=FHH+1./(FV*FV)
      FOL=FOL+FO*FL
      FOJ=FOJ+FO*FJ
 8500 FOH=FOH-FO/FV
      GO TO (8501,8888), KONV
 8501 FINK=FLJ/FLL
      D4=FOJ-FINK*FOL
      D3=FJH-FINK*FLH
      D2=FJJ-FINK*FLJ
      E3=FHH-D3*D3/D2 - FLH*FLH/FLL
      E4=FOH-D3*D4/D2 - FLH*FOL/FLL
      RESH=E4/E3
      RESJ = (D4 - RESH*D3)/D2
      RESL=(FOL-RESH*FLH-RESJ*FLJ)/FLL
      NORK=1
      NJ=1
      NL=1
      NH=1
      WRITE(3,8102)ITER
      IF(ITER-1)88,88,89
   89 IF(DABS(RESJ)-DABS(XJ))810,8110,811
 8110 NJ=2
  811 WRITE(3,8201)RESJ,XJ
      NORK=2
  810 IF(DABS(RESL)-DABS(XL))812,8130,813
 8130 NL=2
  813 WRITE(3,8202)RESL,XL
      NORK=2
  812 IF(DABS(RESH)-DABS(XH))88,8150,815
 8150 NH=2
  815 WRITE(3,8203)RESH,XH
```

```
      NORK=2
   88 XJ=RESJ
      XL=RESL
      XH=RESH
      GNUH(KTER)=H-RESH
      GNUL(KTER)=L-RESL
      GNUJ(KTER)=J-RESJ
      H=GNUH(KTER)
      L=GNUL(KTER)
      J=GNUJ(KTER)
      WRITE(3,8101)J,L,H
      IF(DABS(RESH/H)-1.0D-10)860,861,861
  860 IF(DABS(RESJ/J)-1.0D-10)862,861,861
  862 IF(DABS(RESL/L)-1.0D-10)84,861,861
  861 IF(KTER-7)823,8240,824
 8240 GO TO (8241,823),NORK
 8241 KRAUT=KRAUT+1
  823 KTER=KTER+1
      ITER=ITER+1
      GO TO 877
  824 GO TO (825,826),NORK
  826 IF(ITER-32)827,899,899
  899 J=OLDJ
      L=OLDL
      H=OLDH
      KONV=2
      WRITE(3,6005)
      GO TO 877
C
C     NO CONVERGENCE IF HERE.
C
 8888 CALL GVAR(FLL,FLJ,FLH,FJJ,FJH,FHH,PEX,VEX,M,L,J,H,VARL,VARJ,VARH,
     1 SIGL,SIGJ,SIGH)
      WRITE(3,2000)VARJ,SIGJ
      WRITE(3,1000)VARL,SIGL
      WRITE(3,3000)VARH,SIGH
      GO TO 1101
  827 KTER=1
      ITER=ITER+1
      KRAUT=1
      GO TO 877
C
C     RAPID-CONVERGENCE ROUTINE.
C
  825 KRAUT=KRAUT+1
      IF(KRAUT-3)826,828,828
  828 IF(RESJ)829,830,829
  830 RAPIDJ=J
      GO TO 833
  829 GO TO (831,832), NJ
  832 RAPIDJ=2.*J-GNUJ(7)
      GO TO 833
  831 RAPIDJ= J - ((J-GNUJ(7))**2)/(J+GNUJ(6)-2.*GNUJ(7))
  833 IF(RESL)834,835,834
```

```
  835 RAPIDL=L
      GO TO 836
  834 GO TO (837,838), NL
  838 RAPIDL=2.*L-GNUL(7)
      GO TO 836
  837 RAPIDL= L - ((L-GNUL(7))**2)/(L+GNUL(6)-2.*GNUL(7))
  836 IF(RESH)839,840,839
  840 RAPIDH=H
      GO TO 841
  839 GO TO(842,843),NH
  843 RAPIDH=2.*H-GNUH(7)
      GO TO 841
  842 RAPIDH= H - ((H-GNUH(7))**2)/(H+GNUH(6)-2.*GNUH(7))
  841 WRITE(3,8301) IRAPID
      H=RAPIDH
      J=RAPIDJ
      L=RAPIDL
      WRITE(3,8101)J,L,H
      IF(DABS((J-GNUJ(8))/GNUJ(8))-1.0D-10)81,82,82
   81 IF(DABS((L-GNUL(8))/GNUL(8))-1.0D-10)83,82,82
   83 IF(DABS((H-GNUH(8))/GNUH(8))-1.0D-10)84,82,82
   82 IF(IRAPID-16)850,899,899
  850 IRAPID=IRAPID+1
      KTER=1
      ITER=1
      KRAUT=1
      GO TO 877
   84 KONV=1
      WRITE (3,611)
C
C     ITERATIONS CONVERGE. WHOOPEE.....
C
      GO TO 8888
 1101 C = 1./DLOG(H/DABS(PEX(1)+L))
      WRITE(3,8001)C,PEX(1)
C
C     CALCULATE THEORETICAL QUANTITIES.
C
      DO 508 I=1,M
      V(I)=J*DLOG(H/DABS(PEX(I)+L))
  508 ZNA(I)=DEXP(-V(I)/J)/(PEX(I)*V(I))
      WRITE(3,116)
      WRITE(3,1080)(PEX(I),V(I),VEX(I),ZNA(I),I=1,M)
      DO 514 I =2,M
C
C     SEARCH FOR MINIMUM IN ZN AMONG EXPERIMENTAL POINTS.
C
      IF(ZNA(I)-ZNA(I-1))514,515,515
  515 PMIN(1)=PEX(I)
      GO TO 516
  514 CONTINUE
      PMIN(1)=PEX(M)
C
C     IF HERE, MINIMUM BEYOND EXPERIMENTAL RANGE.
```

```
C
  519 PMOR=PMIN(1)+5.*HH
      X1=H/DABS(PMIN(1)+L)
      X2=H/DABS(PMOR   +L)
      ZN1=1./(X1*PMIN(1)*J*DLOG(X1))
      ZN2=1./(X2*PMOR   *J*DLOG(X2))
      IF(ZN2-ZN1)517,518,518
  517 PMIN(1)=PMOR
      GO TO 519
  518 PMIN(1)=PMOR
  516 PX(1)=PMIN(1)-5.*HH
      IF(PX(1))520,520,521
  520 HH=(PMIN(1)-1.)/5.
      GO TO 516
  521 DO 707 I=2,11
  707 PX(I)=PX(I-1)+HH
      DO 602 I=1,11
      II=12-I
      VP(II)=J*DLOG(H/DABS(PX(I)+L))/PX(I)
  602 PP(II)=PX(I)
      AJL(1)=J/L
      CALL GINTER(7,11,1,VP,PP,AJL,PMIN)
C
C     INTERPOLATES FOR POINT WHERE V/P = J/L.
C
      VMIN=AJL(1)*PMIN(1)
      WRITE(3,6999)PMIN(1)
      WRITE(3,118)VMIN
C
C     PRINT SUMMARY SHEET.
C
      WRITE(3,7500)
      WRITE(3,103)
      WRITE(3,102)
      WRITE(3,101)
      WRITE(3,7501)
      WRITE(3,7511)KONV
      GO TO (7606,7607),INDEX
 7607 WRITE(3,7604)
 7606 GO TO (61,62),KONV
   61 WRITE (3,611)
      GO TO 67
   62 WRITE(3,6005)
   67 WRITE(3,7502)J
      WRITE(3,7503)L
      WRITE(3,7504)H
      WRITE(3,8001)C,PEX(1)
      WRITE(3,6999)PMIN(1)
      WRITE(3,118)VMIN
      WRITE (3,7500)
      GO TO 999
      END
```

```
      SUBROUTINE GINTER (KI,MX,NNA,XIN,YIN,XOUT,YOUT)
C     KI = ORDER OF INTERPOLATION, 3, 5, OR 7.
C     MX = NUMBER OF DATA POINTS.
C     NNA = NO. POINTS OUTPUT.
C     XIN = INDEPENDENT VARIABLE DATA INPUT.
C     YIN =   DEPENDENT VARIABLE DATA INPUT.
C     XOUT = INDEPENDENT VARIABLE OUTPUT.
C     YOUT =   DEPENDENT VARIABLE OUTPUT.
      DOUBLE PRECISION XIN(50),YIN(50),XOUT(50),YOUT(50),S(11),G(11,11),
     1SB(11),RR(50),TTA(50),XX,SA,SU,PR
      KJ=((KI-1)/2)+1
      DO 606 I=1,NNA
      IQ=0
      MA=MX-KJ+1
      KZ=KJ-1
      DO 605 MN=KJ,MA
      IF(XIN(MN)-XOUT(I))604,608,660
  604 IF((MX-KZ)-MN)607,608,605
  605 CONTINUE
  606 CONTINUE
      GO TO 626
  607 WRITE(3,683)
  683 FORMAT('0INTERP SNAFU...NEG. QUANTITY STATEMENT 604, GINTER.')
      STOP
  660 XX=(XIN(MN)+XIN(MN-1))/2.
      IF(XX-XOUT(I))608,608,661
  661 J=MN-1
      IQ=J
      IF(IQ-KJ)663,662,662
  663 J=KJ
      GO TO 662
  608 J=MN
  662 DO 639 JJ=1,MX
      IF(XIN(JJ)-XOUT(I)) 639,637,639
  637 YOUT(I)=YIN(JJ)
      IQ=1
  639 CONTINUE
      IF(IQ)607,609,605
  609 IQ=I
      DO 630 IX=1,KI
       KY=J+IX-KJ
  630 S(IX)=XIN(KY)
      SA=XOUT(I)
      DO 610 LX=1,KI
      G(LX,LX)=SA-S(LX)
      LL=LX+1
      IF(LL-KI) 613,613,614
  613 DO 611 L=LL,KI
      G(L,LX)=S(L)-S(LX)
  611 G(LX,L)=-G(L,LX)
  610 CONTINUE
  614 DO 615 IX=1,KI
      KY=J+IX-KJ
  615 SB(IX)=YIN(KY)
```

```
      DO 622 L=1,KI
      RR(L)=1.
      DO 621 K=1,KI
      IF(G(L,K))635,621,635
635   RR(L)=RR(L)*G(L,K)
621   CONTINUE
622   TTA(L)=SB(L)/RR(L)
634   SU=0.
      DO 624K=1,KI
624   SU=SU+TTA(K)
      PR=1.
      DO 625 K=1,KI
625   PR=PR*G(K,K)
      YOUT(I)=PR*SU
651   WRITE(3,681)I,J
681   FORMAT('0      I='I3,',  J='I3)
      GO TO 605
626   WRITE(3,682)KI
682   FORMAT('0END INTERPOLATION, ORDER ='I3)
      RETURN
      END
```

```
      SUBROUTINE GDERV (H,AV,NN,AT,AR,IND)
C     EQUALLY SPACED POINTS, INTERVAL = H.
C     AV = DEPENDENT VARIABLE.
C     NN = NO. OF POINTS, MAXIMUM 50.
C     AT = DERIVATIVE DAV/D(INDEP.).
C     AR = 1/AT
C     ALLOWS SKIPPING 1ST AND LAST 3 POINTS. IND = 1 FOR SKIP, =2 FOR
C     NO SKIP.
      DOUBLE PRECISION AV(50),AT(50),AR(50),H,AA(49),AZ
      AA( 1)=-1764.
      AA( 2)=4320.
      AA( 3)=-5400.
      AA( 4)=4800.
      AA( 5)=-2700.
      AA( 6)=864.
      AA( 7)=-120.
      AA( 8)=-120.
      AA( 9)=-924.
      AA(10)=1800.
      AA(11)=-1200.
      AA(12)=600.
      AA(13)=-180.
      AA(14)=24.
      AA(15)=24.
      AA(16)=-288.
      AA(17)=-420.
      AA(18)=960.
      AA(19)=-360.
      AA(20)=96.
      AA(21)=-12.
      AA(22)=-12.
      AA(23)=108.
      AA(24)=-540.
      AA(25)=0.
      DO 500 I = 26,49
      J = 50-I
  500 AA(I)=-AA(J)
      AZ=720.*H
      DO 540 I = 1,NN
      AR(I)=0.
  540 AT(I)=0.
      GO TO (562,561),IND
  561 DO 545 N=1,3
      DO 544 I=1,7
      K=I+N*7 -7
  544 AT(N)=AT(N)+AA(K)*AV(I)
  545 AT(N)=AT(N)/AZ
  562 K=NN-6
      DO 547 J=1,K
      L=J+3
      DO 548 I=1,7
      KK=I+21
      JJ=J-1+I
  548 AT(L)=AT(L) + AA(KK)*AV(JJ)
```

```
547 AT(L)=AT(L)/AZ
    GO TO (564,563),IND
563 N=NN-2
    NM=0
    DO 550 L=N,NN
    DO 551 I = 1,7
    KK=I+28+NM*7
    JJ=NN-7+I
551 AT(L)=AT(L) + AA(KK)*AV(JJ)
    AT(L)=AT(L)/AZ
550 NM=NM+1
    IN=1
    INN=NN
    GO TO 565
564 IN=4
    INN=NN-3
565 DO 552 I=IN,INN
552  AR(I)=1./AT(I)
    RETURN
    END
```

```
      SUBROUTINE GLEASQ(X,Y,CALCY,DEV,N,SLOPE,AIN,SIGMA)
      DOUBLE PRECISION X(50), Y(50),SLOPE,AIN,SUMX,SUMX2,SUMY,SUMXY,FM,V
     1AR,SIGMA,CALCY(50),DEV(50)
      SUMX =0.
      SUMX2=0.
      SUMY =0.
      SUMXY=0.
      DO 51 I = 1,N
      SUMX=SUMX+X(I)
      SUMX2=SUMX2+X(I)*X(I)
      SUMY=SUMY+Y(I)
   51 SUMXY=SUMXY+X(I)*Y(I)
      FM=N
      SLOPE=(SUMX*SUMY-SUMXY*FM)/(SUMX*SUMX-FM*SUMX2)
      AIN=(SUMY-SLOPE*SUMX)/FM
      DO 52 I=1,N
      CALCY(I)=SLOPE*X(I)+AIN
   52 DEV(I)=Y(I)-CALCY(I)
      VAR=0.
      DO 53 I=1,N
   53 VAR = VAR + DEV(I)*DEV(I)
      SIGMA=DSQRT(VAR/(FM-2.))
      RETURN
      END
```

```
      SUBROUTINE GVAR(AA,AB,AC,BB,BC,CC,X,Y,M,A,B,C,VARA,VARB,VARC,SIGA,
     1SIGB,SIGC)
C     CALCULATES VARIANCE AND STANDARD ERRORS OF 3 PARAMETERS A, B, &
C     C, OF THE FORM Y = B*LOG(C/(X+A)).
C     REF. DEMING PAGE 167, SECTION 62.
C
      DOUBLE PRECISION AA,AB,AC,BB,BC,CC,X(50),Y(50),A,B,C,VARA,VARB,VAR
     1C,SIGA,SIGB,SIGC,DELTA,COFAA,COFBB,COFCC,SSS,CLOT,FM
      COFAA = BB*CC-BC*BC
      COFBB = AA*CC-AC*AC
      COFCC = AA*BB-AB*AB
      DELTA = AA*COFAA-AB*(AB*CC-AC*BC)+AC*(AB*BC-AC*BB)
      SSS=0.
      DO 50 I=1,M
   5) SSS=SSS+(Y(I)-B*DLOG(C/DABS(X(I)+A)))**2
      FM=M
      CLOT=SSS/(DELTA*(FM-3.))
      VARA=DABS(COFAA*CLOT)
      VARB=DABS(COFBB*CLOT)
      VARC=DABS(COFCC*CLOT)
      SIGA=DSQRT(VARA)
      SIGB=DSQRT(VARB)
      SIGC=DSQRT(VARC)
      RETURN
      END
```

PROGRAM 501.8 BY ASK. CALCULATION OF TAIT PARAMETERS.
ADAMS. COMPRESSION OF WATER. D = 0.99704. T = 25 C. P IN BARS.
SAMPLE DATA FOR THESIS.

ORIGINAL DATA

PRESSURE	COMPRESSION
0.1000000000D 01	0.0
0.5000000000D 03	0.2120000000D-01
0.1000000000D 04	0.3930000000D-01
0.1500000000D 04	0.5550000000D-01
0.2000000000D 04	0.6990000000D-01
0.2500000000D 04	0.8450000000D-01
0.3000000000D 04	0.9945000000D-01
0.4000000000D 04	0.1152000000D 00
0.5000000000D 04	0.1330000000D 00
0.6000000000D 04	0.1485000000D 00
0.7000000000D 04	0.1622000000D 00
0.8000000000D 04	0.1746000000D 00
0.9000000000D 04	0.1858000000D 00
0.1000000000D 05	0.1964000000D 00
0.1100000000D 05	0.2059000000D 00
0.1200000000D 05	0.2147000000D 00

PRESSURE	VOLUME
0.1000000000D 01	0.1002968790D 01
0.5000000000D 03	0.9817058490D 00
0.1000000000D 04	0.9635521140D 00
0.1500000000D 04	0.9473040200D 00
0.2000000000D 04	0.9328612690D 00
0.2500000000D 04	0.9081882370D 00
0.3000000000D 04	0.8874267830D 00
0.4000000000D 04	0.8695739390D 00
0.5000000000D 04	0.8540279230D 00
0.6000000000D 04	0.8402872500D 00
0.7000000000D 04	0.8278504370D 00
0.8000000000D 04	0.8166171870D 00
0.9000000000D 04	0.8059857180D 00
0.1000000000D 05	0.7964575140D 00
0.1100000000D 05	0.7876313890D 00

I= 1, J= 4

END INTERPOLATION, ORDER = 7

PRESSURE	VOLUME	DV/DP	DP/DV
0.0	0.1003016770D 01	-0.4464936670-04	-0.2239673430 05
0.1000000000D 04	0.9635521140D 00	-0.3462546450-04	-0.2888047900 05
0.2000000000D 04	0.9328612690D 00	-0.2724237610-04	-0.3670751750 05
0.3000000000D 04	0.9081882370D 00	-0.2246228570-04	-0.4451906700 05
0.4000000000D 04	0.8874267830D 00	-0.1919013610-04	-0.5211010450 05
0.5000000000D 04	0.8695739390D 00	-0.1661417800-04	-0.6018955630 05
0.6000000000D 04	0.8540279230D 00	-0.1455474870-04	-0.6870609850 05
0.7000000000D 04	0.8402872500D 00	-0.1304695230-04	-0.7664625240 05
0.8000000000D 04	0.8278504370D 00	-0.1176482390-04	-0.8499914750 05
0.9000000000D 04	0.8166171870D 00	-0.1093068820-04	-0.9148554820 05
0.1000000000D 05	0.8059857180D 00	-0.1021523710-04	-0.9789297990 05
0.1100000000D 05	0.7964575140D 00	-0.8814424030-05	-0.1134504080 06
0.1200000000D 05	0.7876313890D 00	-0.9837452190-05	-0.1016523360 06

PRESSURE	DP/DV EXP	DP/DV THEOR	DEV
0.0	-0.2239673430 05	-0.2262280890 05	0.2260746350 03
0.1000000000 04	-0.2888047900 05	-0.3012972830 05	0.1249249290 04
0.2000000000 04	-0.3670751750 05	-0.3763664770 05	0.9291301740 03
0.3000000000 04	-0.4451906710 05	-0.4514356710 05	0.6245001540 03
0.4000000000 04	-0.5211010450 05	-0.5265048650 05	0.5403819890 03
0.5000000000 04	-0.6018955630 05	-0.6015740590 05	-0.3215036830 02
0.6000000000 04	-0.6870609850 05	-0.6766432530 05	-0.1041773210 04
0.7000000000 04	-0.7664625240 05	-0.7517124470 05	-0.1475007660 04
0.8000000000 04	-0.8499914750 05	-0.8267816410 05	-0.2320983340 04
0.9000000000 04	-0.9148554820 05	-0.9018508360 05	-0.1300464700 04
0.1000000000 05	-0.9789297990 05	-0.9769200300 05	-0.2009769130 03
0.1100000000 05	-0.1134504080 06	-0.1051999220 06	-0.8251485370 04
0.1200000000 05	-0.1016523360 06	-0.1127058420 06	0.1105350530 05

SLOPE = -0.7506919410 01 INTERCEPT = -0.2262280890 05

STANDARD DEVIATION = 0.4304379980 04

EXP PRESSURE	EXP VOLUME	H-VALUE	DEVIATION
0.1000000000 01	0.1002968790 01	0.5612048530 07	0.8727155070 05
0.5000000000 03	0.9817058490 00	0.5575995790 07	0.5121881750 05
0.1000000000 04	0.9635521140 00	0.5558008940 07	0.3323196230 05
0.1500000000 04	0.9473040230 00	0.5532686110 07	0.7909131930 04
0.2000000000 04	0.9328612630 00	0.5514120430 07	-0.1065654350 05
0.3000000000 04	0.9081882370 00	0.5495684970 07	-0.2909201170 05
0.4000000000 04	0.8874267330 00	0.5484557190 07	-0.4021978950 05
0.5000000000 04	0.8695739390 00	0.5480550620 07	-0.4422635350 05
0.6000000000 04	0.8540279230 00	0.5485440570 07	-0.3933640520 05
0.7000000000 04	0.8402872500 00	0.5496749840 07	-0.2802714150 05
0.8000000000 04	0.8278504370 00	0.5506788380 07	-0.1798859670 05
0.9000000000 04	0.8166171870 00	0.5521022000 07	-0.3754972450 04
0.1000000000 05	0.8059357130 00	0.5521828560 07	-0.2948413590 04
0.1100000000 05	0.7964575140 00	0.5535683060 07	0.1090607880 05
0.1200000000 05	0.7876313890 00	0.5550489660 07	0.2571268640 05

AVERAGE H-VALUE = 0.5524776980 07

STANDARD DEVIATION = 0.3722466370 05

INITIAL APPROXIMATIONS FOR ITERATION=

J= 0.1332104350 00 L= 0.3013594210 04 H= 0.5524776980 07

ITERATION NUMBER 1

J= 0.1250395290 00 L= 0.2564644030 04 H= 0.7383332660 07

ITERATION NUMBER 2

J= 0.1273048750 00 L= 0.2690243170 04 H= 0.7073970580 07

ITERATION NUMBER 3

J= 0.1276918040 00 L= 0.2712091470 04 H= 0.7007013760 07

ITERATION NUMBER 4

J= 0.1277006660 00 L= 0.2712600990 04 H= 0.7005708710 07

ITERATION NUMBER 5

```
J=  0.127700646D 00 L=  0.2712599850 04 H=  0.7005716010 07

ITERATION NUMBER   6

J=  0.127700646D 00 L=  0.2712599850 04 H=  0.7005716000 07

ITERATION NUMBER   7

J=  0.127700646D 00 L=  0.2712599850 04 H=  0.7005716000 07

CONVERGENCE O.K.

VARIANCE OF J=  0.2170310640-06, STD ERR =  0.4658659290-03

VARIANCE OF L=  0.4577193370 03, STD ERR =  0.2139437630 02

VARIANCE OF H=  0.2324259320 11, STD ERR =  0.1524552170 06

C = J/VO =  0.127287912D 00 WITH PO TAKEN AS  0.1000000000 01.

PRESSURE          THEOR VOL          EXP VOL          ZN*EMO/MRT

 0.1000010000D 01  0.1003242520 01  0.1002968790 01  0.3860889280-03
 0.5000000000D 03  0.9816850830 00  0.9817058490 00  0.9342464710-06
 0.1000000000D 04  0.9632139520 00  0.9635521140 00  0.5501775320-06
 0.1500000000D 04  0.9470792820 00  0.9473040200 00  0.4232725310-06
 0.2000000000D 04  0.9327564100 00  0.9328612690 00  0.3605867790-06
 0.3000000000D 04  0.9081824010 00  0.9081882370 00  0.2992863710-06
 0.4000000000D 04  0.8875827420 00  0.8874267830 00  0.2698791860-06
 0.5000000000D 04  0.8698490810 00  0.8695739390 00  0.2531246030-06
 0.6000000000D 04  0.8542804690 00  0.8540279230 00  0.2426294500-06
 0.7000000000D 04  0.8404053140 00  0.8402872500 00  0.2356655710-06
 0.8000000000D 04  0.8278910840 00  0.8278504370 00  0.2308761990-06
 0.9000000000D 04  0.8164944950 00  0.8166171870 00  0.2275123670-06
 0.1000000000D 05  0.8060321830 00  0.8059857180 00  0.2251279770-06
 0.1100000000D 05  0.7963624960 00  0.7964575140 00  0.2234414760-06
 0.1200000000D 05  0.7873737560 00  0.7876313890 00  0.2222668600-06

     I=  1, J=  8

END INTERPOLATION, ORDER =  7

 P MIN =  0.1606416700 05

 V MIN =  0.7562503180 00
```

PROGRAM 501.8 BY ASK. CALCULATION OF TAIT PARAMETERS.
ADAMS. COMPRESSION OF WATER. D = 0.99704. T = 25 C. P IN BARS.
SAMPLE DATA FOR THESIS.

SUMMARY SHEET.

CONVERGENCE CODE (KONV) = 1

CONVERGENCE O.K.

J = 0.1277006460 00

L = 0.2712599850 04

H = 0.7005716000 07

C = J/VO = 0.1272879120 00 WITH PO TAKEN AS 0.1000000000 01.

P MIN = 0.1606416700 05

V MIN = 0.7562503180 00

PROGRAM 500.8 BY ASK. CALCULATION OF TAIT PARAMETERS.
KENNEDY WATER DATA FOR 40 DEGREES. PRESSURE IN BARS.
SAMPLE DATA FOR THESIS.

ORIGINAL DATA

PRESSURE	VOLUME
0.1000000000D 01	0.1007800000D 01
0.1000000000D 03	0.1003400000D 01
0.2000000000D 03	0.9990000000D 00
0.3000000000D 03	0.9948000000D 00
0.4000000000D 03	0.9908000000D 00
0.5000000000D 03	0.9869000000D 00
0.6000000000D 03	0.9830000000D 00
0.7000000000D 03	0.9792000000D 00
0.8000000000D 03	0.9755000000D 00
0.9000000000D 03	0.9720000000D 00
0.1000000000D 04	0.9686000000D 00
0.1100000000D 04	0.9652000000D 00
0.1200000000D 04	0.9619000000D 00
0.1300000000D 04	0.9587000000D 00
0.1400000000D 04	0.9555000000D 00

INITIAL APPROXIMATIONS SUBMITTED ON CARD.

INITIAL APPROXIMATIONS FOR ITERATION=

J= 0.1000000000D 00 L= 0.3000000000D 04 H= 0.3000000000D 07

ITERATION NUMBER 1

J= 0.1082812750D 00 L= 0.3118262480D 04 H= 0.1463515610D 08

ITERATION NUMBER 2

DELTA J INCREASING, = -0.8870629080D-02 VS. -0.8281275020D-02

J= 0.1171519040D 00 L= 0.3209842990D 04 H= 0.9073475730D 07

ITERATION NUMBER 3

DELTA J INCREASING, = -0.8873997810D-02 VS. -0.8870629080D-02

J= 0.1260309020D 00 L= 0.3229194300D 04 H= 0.6220747420D 07

ITERATION NUMBER 4

DELTA L INCREASING, = 0.3249130780D 02 VS. -0.2821000970D 02

J= 0.1337191630D 00 L= 0.3196702990D 04 H= 0.4817297690D 07

ITERATION NUMBER 5

DELTA L INCREASING, = 0.5793134640D 02 VS. 0.3249130780D 02

J= 0.1386630800D 00 L= 0.3138771640D 04 H= 0.4217019060D 07

ITERATION NUMBER 6

J= 0.140546374D 00 L= 0.311361899D 04 H= 0.402009239D 07

ITERATION NUMBER 7

J= 0.140930447D 00 L= 0.311473440D 04 H= 0.397208455D 07

ITERATION NUMBER 8

DELTA L INCREASING, = -0.135707609D 01 VS. -0.111541137D 01

J= 0.140989285D 00 L= 0.311609148D 04 H= 0.396289446D 07

ITERATION NUMBER 9

J= 0.140998498D 00 L= 0.311633508D 04 H= 0.396136798D 07

ITERATION NUMBER 10

J= 0.140999946D 00 L= 0.311637349D 04 H= 0.396112590D 07

ITERATION NUMBER 11

J= 0.141000174D 00 L= 0.311637952D 04 H= 0.396108785D 07

ITERATION NUMBER 12

J= 0.141000209D 00 L= 0.311638047D 04 H= 0.396108188D 07

ITERATION NUMBER 13

J= 0.141000215D 00 L= 0.311638062D 04 H= 0.396108094D 07

ITERATION NUMBER 14

J= 0.141000216D 00 L= 0.311638064D 04 H= 0.396108080D 07

ITERATION NUMBER 15

J= 0.141000216D 00 L= 0.311638064D 04 H= 0.396108077D 07

ITERATION NUMBER 16

J= 0.141000216D 00 L= 0.311638064D 04 H= 0.396108077D 07

RAPID CONVERGENCE VALUES, SERIES 1

J= 0.141000216D 00 L= 0.311638064D 04 H= 0.396108077D 07

ITERATION NUMBER 1

J= 0.141000216D 00 L= 0.311638064D 04 H= 0.396108077D 07

CONVERGENCE O.K.

VARIANCE OF J= 0.536360994D-05, STD ERR = 0.231594688D-02

VARIANCE OF L= 0.377839993D 04, STD ERR = 0.614686907D 02

VARIANCE OF H= 0.150326033D 12, STD ERR = 0.387719013D 06

C = J/VO = 0.139913384D 00 WITH PO TAKEN AS 0.100000000D 01.

PRESSURE THEOR VOL EXP VOL ZN*EMO/MRT

```
 0.1000000000D 01   0.1007767890D 01   0.1007800000D 01   0.7809363160-03
 0.1000000000D 03   0.1003359720 01   0.1003400000D 01   0.8092767810-05
 0.2000000000 03    0.9990426710 00    0.9990000000D 00   0.4190218210-05
 0.3000000000 03    0.9948538820 00    0.9948000000D 00   0.2889828040-05
 0.4000000000 03    0.9907859530 00    0.9908000000D 00   0.2239970780-05
 0.5000000000 03    0.9868320970 00    0.9869000000D 00   0.1850321380-05
 0.6000000000 03    0.9829860930 00    0.9830000000D 00   0.1590771730-05
 0.7000000000D 03   0.9792422250 00    0.9792000000D 00   0.1405561380-05
 0.8000000000 03    0.9755951950 00    0.9755000000D 00   0.1266810220-05
 0.9000000000 03    0.9720401230 00    0.9720000000D 00   0.1159029440-05
 0.1000000000D 04   0.9685724860 00    0.9686000000D 00   0.1072925830-05
 0.1100000000 04    0.9651880860 00    0.9652000000D 00   0.1002585630-05
 0.1200000000 04    0.9618830210 00    0.9619000000D 00   0.9440663850-06
 0.1300000000D 04   0.9586536550 00    0.9587000000D 00   0.8946387710-06
 0.1400000000 04    0.9554966000 00    0.9555000000D 00   0.8523533220-06

      I=   1, J=   8

END INTERPOLATION, ORDER =   7

 P MIN =   0.1653578020 05

 V MIN =   0.7481591140 01
```

PROGRAM 500.8 BY ASK. CALCULATION OF TAIT PARAMETERS.
KENNEDY WATER DATA FOR 40 DEGREES. PRESSURE IN BARS.
SAMPLE DATA FOR THESIS.

SUMMARY SHEET.

CONVERGENCE CODE (KONV) = 1

INITIAL APPROXIMATIONS SUBMITTED ON CARD.

CONVERGENCE O.K.

J = 0.1410002160 00

L = 0.3116380640 04

H = 0.3961080770 07

C = J/V0 = 0.1399133840 00 WITH P0 TAKEN AS 0.1000000000 01.

P MIN = 0.1653578020 05

V MIN = 0.7481591140 00

APPENDIX III

THE CRITERIA FOR GOOD COMPRESSIBILITY DATA IN LIQUIDS

Now that we have, hopefully, the best set of constants for a set of data, calculated by the methods of Appendix I, how can we judge the quality of the original data? Offhand, we may say that if the iterations failed to converge, we would be justified in presuming that the data did not conform to the Tait-Tammann equation, which we know to be a widely applicable empirical standard. In any case, we can calculate the standard errors of J, L, and H from the relations given in Deming (58):

$$\sigma_x^2 = \sigma^2 \mathrm{cof}(F_{xx})/\det(\underline{F}) \qquad (183)$$

where:

x represents J, L, or H, as the case may be,

σ_x is the standard error in the constant x,

$\mathrm{cof}(F_{xx})$ is the cofactor of F_{xx} in the matrix $\underline{F}$,

$\underline{F}$ is the matrix on the left-hand side of Equation 179,

$\det(\underline{F})$ is the determinant of $\underline{F}$,

and σ^2 is given by:

$$\sigma^2 = \sum_{k=1}^{n} \frac{[v_k - v_k(\mathrm{calc.})]^2}{(n-3)} \qquad (184)$$

where n is the number of data points.

The subroutine GVAR for performing this calculation is included in Appendix II.

However, although this may give an estimate of the precision of the data, there is no way to judge the accuracy of a single set. But if data are taken over an extended range of temperatures, especially

towards the critical, we may make use of a simple relationship, namely that L descends linearly as the temperature is raised (61, 62). This relation does not hold at lower temperatures, where L goes through a maximum before beginning its descent (62). By way of example, the linear region of L for water is approximately that from the boiling point to the critical point (63).

Note that at the critical point, $dP/dv = 0$, and hence, from Equation 169,

$$L_c = -P_c. \tag{185}$$

If the critical temperature is known, the critical pressure can be predicted by extrapolating the linear portion of the L versus T curve to T_c (62). Very few compressibility data have been carried to these elevated temperatures; some of those examined in this work are shown in Table VII. While the data may be checked for accuracy this way in the high-temperature region, there is no guarantee that work by the same authors will be as reliable at lower temperatures. For example, the data of Smith and Keyes (64) on water are very well-behaved at high temperatures, but the iterations failed to converge for any temperature below 250 degrees. Unfortunately, it is their data which is currently used to derive the steam tables. The work of Kennedy and his co-workers (65, 66) was found by the criteria outlined here to be generally superior throughout the entire liquid range of water; their work was undertaken expressly "with the hope of resolving this conflict [among the investigators of water's compressibility]." Some more detailed comments on the reliability of water data by many other investigators (not including Kennedy's),

published before the iteration process could be accomodated by the Brooklyn College computer (although the conclusions are unchanged), may be found in the work of the Ginells (63).

TABLE VII

Critical Pressures Calculated by Extrapolation of L to T_c

Substance	Crit. Temp.	Crit. Press.	$-L_c$(atm)	Error
Helium I (67)	5.2°K	2.26 atm.	2.3 (62)	2%
Water (64, Series I)	374.15°C	217.7 atm.	320	47%
Water (64, Series II)	"	"	242	11%
Water (64, Series III)	"	"	214	2%
Water (66)	"	"	239	9%
Water (68)	"	"	59	73%

Note: Among the water values, the "bad" values may be forgiven; Series I data of Smith and Keyes (64) do not go above 300°, Series II goes in 10° steps from 300° to 360°, while the Tammann and Rühembeck data (68) are reported only at 300° and 400°. At supercritical temperatures it is not meningful to apply the Tait-Tammann equation in any case.

APPENDIX IV

THE RANGE OF APPLICABILITY OF THE TAIT-TAMMANN EQUATION

At elevated temperatures, L becomes negative. The immediate implication of this is that, at pressures less than the absolute value of L, the derivative dv/dP is positive. However, the pressure given by the absolute value of L is below the vapor pressure of the liquid, P^o, as can be seen from the following discussion.

The integrated Tait-Tammann equation, Equation 173b, may be rearranged to give:

$$P = H \exp(-v/J) - L. \qquad (186)$$

A graph of P against v exhibits a decreasing pressure until P = -L. (This is a positive pressure, since L is negative; at lower temperatures where L is positive, this discussion applies to negative pressures and can be ignored.) At P = -L, the volume is infinite, by Equation 186.

Recalling Equation 173a,

$$v = J \ln \frac{H}{P + L} \qquad (173a)$$

so at pressures less than -L we may still draw a "low-pressure" branch of the P-v curve. (The logarithm is real since the denominator takes the absolute value on integration of the Tait-Tammann equation.) As can be seen from Figure 11, the Tait-Tammann equation is meaningless in this region and the peculiar behavior of dv/dP described here is seen to be a mathematical fiction.

While the extrapolation of L to the critical temperature does give the critical pressure, as discussed in Appendix III, it is clear from the above discussion that the Tait-Tammann equation

incorrectly gives an infinite critical volume. Since the Tait-Tammann isotherm passes the observed critical volume above the critical pressure, a discontinuity is implied, since ordinarily the isotherm passes through the observed points to the vapor pressure, and the extrapolated isotherm becomes infinite below the lowest experimental pressure; see Figure 12. That is, as long as the temperature lies below the critical, the Tait-Tammann equation will give the correct P-v relations at pressures down to the equilibrium vapor pressure. At the critical temperature, however, the isotherm misses the boundary of the two-phase region. This suggests at least two intriguing possibilities.

One possibility is suggested by the Mayers (69); they predicted, from statistical-mechanical arguments, the existence of a "bubble" in the phase diagram, like that shown in Figure 13. While they place the critical pressure at the top of the bubble, our work suggests it may be at the bottom.

A second suggestion was made privately by Ginell, who raised the possibility that the Law of Rectilinear Diameters (70) may not lead to equal densities at the critical point, in which case a discontinuity might appear as in Figure 14. (The density difference has already been discussed in Section II; see also reference 40.) The precise meaning of the critical pressure, and the detailed behavior of the fluid at that point, must be examined with these possibilities in mind.

In any case, the meaning of the critical pressure must be

refined. Using the Mayers' picture, we might suppose that the meniscus would disappear at the bottom of the bubble, and the density difference at the top. This would be in accord with the discussion in Section II, where it was pointed out that these two phenomena do occur at different temperatures; further experimental work is needed to look for pressure changes on moving from the meniscus loss to the liquid-vapor isochore.

A common criticism of the Tait-Tammann equation is its prediction of negative volumes at high pressures (26). It has already been mentioned that at very high pressures J and L, which are composite terms involving derivatives, will not be constant under such extreme conditions, and that modifications have been proposed (27). It would be appropriate here to ask just how extreme the pressure must be for v to become negative, assuming J and L stay constant.

It can be seen from Equation 173a that v will be negative if the denominator, P + L, becomes greater than H, or, equivalently,

$$H - L < P. \qquad (187)$$

However, our calculations show that H is consistently on the order of 10^6 - 10^8 atmospheres. Since L is much smaller than H (typically 0 to 5000 atm.) it can be neglected in Equation 187. Where are pressures of millions of atmospheres encountered? They are found in the interiors of stars and planets; a pressure of 10^7 or 10^8 atmospheres is thought to represent a limit to the size of cooled, planetary bodies, a limit approached by Jupiter. Above these

pressures, presumably, atoms would be crushed to plasmas, as in the interior of stars (71).

It is clear, then, that the Tait-Tammann equation does not yield physically unreasonable results for any pressures encountered in laboratory work. Of course, data may be produced at pressures higher than 100,000 atmospheres, the highest to date (50), at which the Tait-Tammann "constants" may change, but the equation is excellent for pressures studied until now.

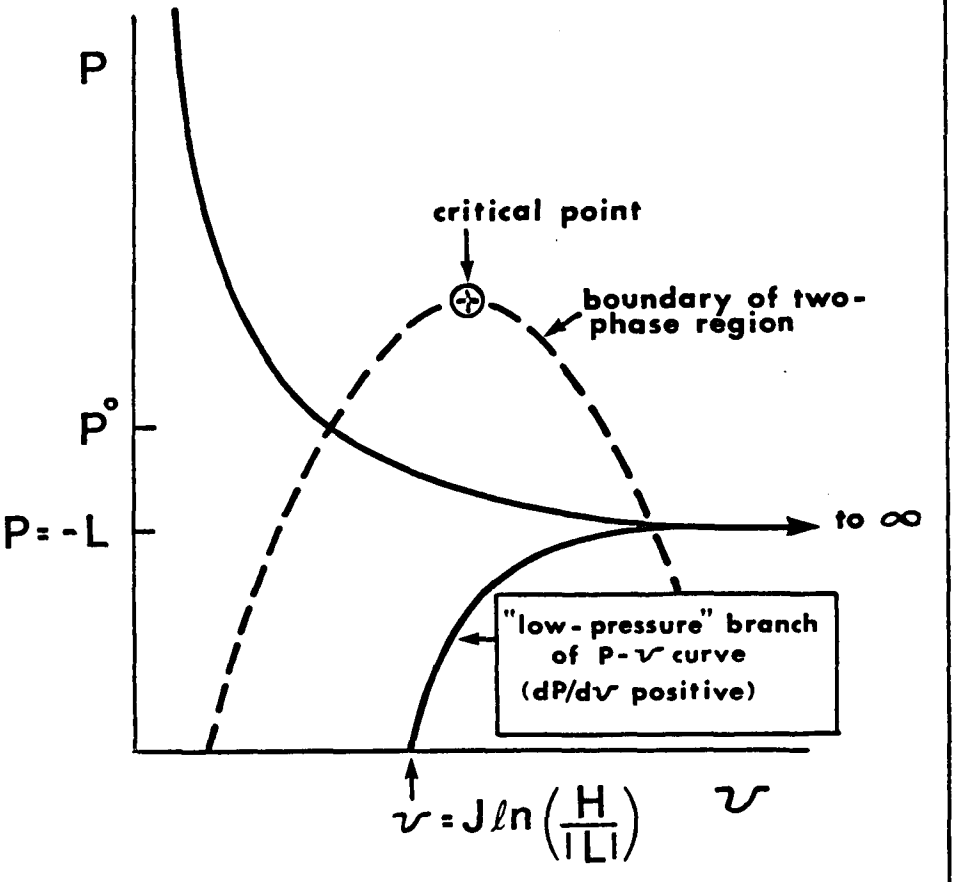


Figure 11. Graph of the integrated Tait-Tammann equation superimposed on a P-v phase diagram. Only that portion of the curve above the vapor pressure P° is physically real.

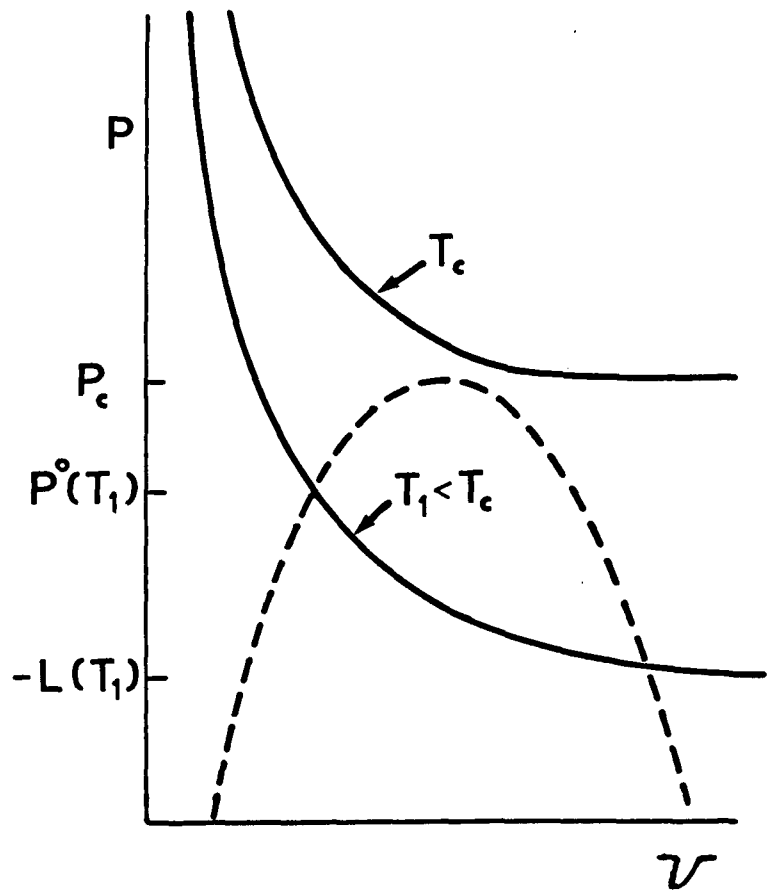


Figure 12. Behavior of the critical isotherm ($T = T_c$) predicted by the Tait-Tammann equation compared to the behavior of a subcritical isotherm at $T = T_1$.

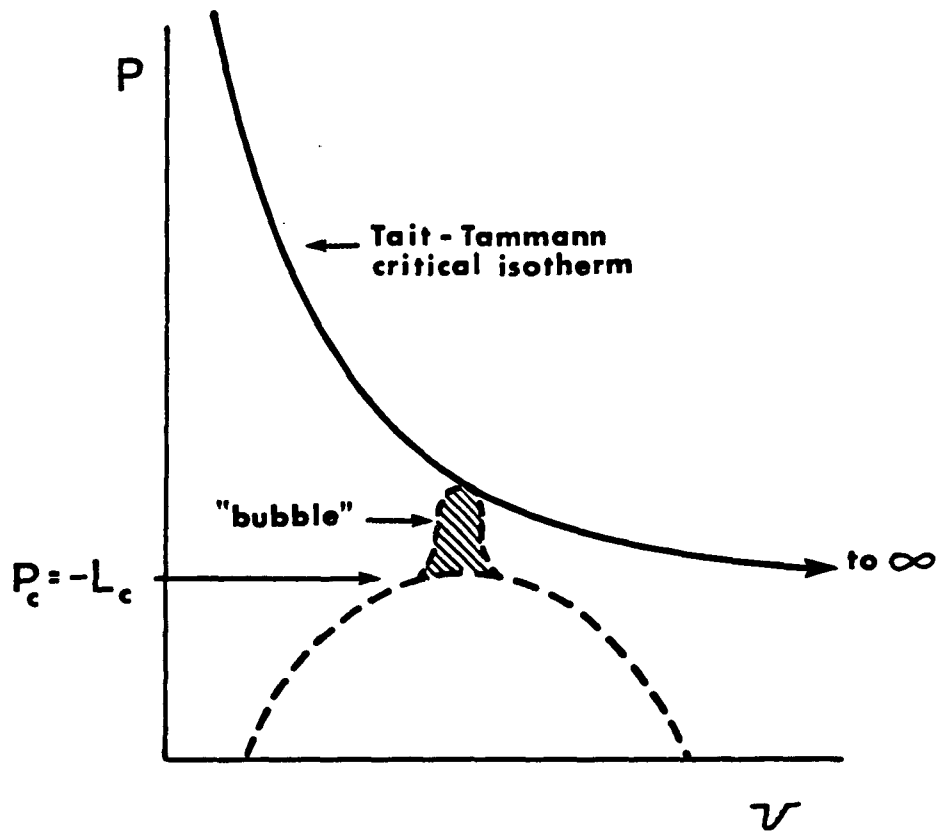


Figure 13. Mayer and Mayer's Figure 14.3 (69) redrawn to include the Tait-Tammann critical isotherm. P_c has here been placed at the bottom of the bubble, instead of at the top, since this P_c is the one predicted by Equation 185.

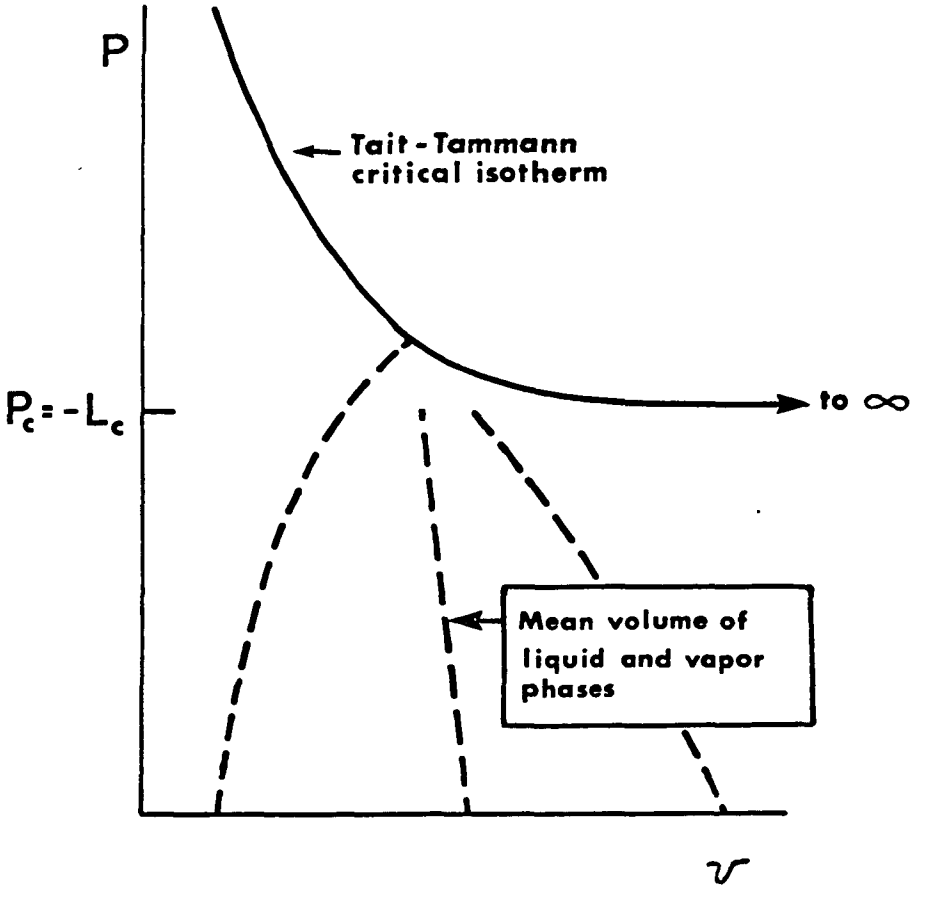


Figure 14. Discontinuity in density at the critical point, as suggested by Ginell.

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AUTOBIOGRAPHICAL STATEMENT

Born July 3, 1940, and educated in the public school system of New York City, I received the Bachelor of Arts degree in chemistry from Columbia University in 1961. My first two years of graduate school were spent at Rice University studying organic chemistry. Upon transferring to CUNY, I switched my major to theoretical physical chemistry, completing the doctorate in 1971 under the tutelage of Professor Robert Ginell. While at CUNY, I taught general chemistry and integrated physical science, serving on the curriculum committee of the latter course. It is in this area that I hope to pursue my career.