Table I: Association Equations for Continuous and Discontinuous Cases

| ———Continuous case——— | ———Discontinuous case——— |
Condition—all species present	Gap exists—some species absent
$C_1 = C_1$	$C_1 = C_1$
$C_x = C_x; \quad 2 \leq x \leq m$	$C_x = 0; \quad 2 \leq x < \alpha$
$\quad = 0; \quad m < x$	$\quad = C_x; \quad \alpha \leq x \leq m$
m is the size of the	$\quad = 0; \quad m < x$
largest species	m is the size of the largest species
$C_x = N_x/v$	Note: The gap need not start at
$N_x =$ no. of moles of	2 but could start at 3 or 4. This
particles of size x in mass w	entails only slight modification.
$v =$ volume	

Equilibrium constants (double index)

$$C_1 + C_x \rightleftarrows C_{x+1}$$
$$K_{1,x} = \frac{C_{x+1}}{C_1 C_x} \quad 1 \leq x$$

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Equilibrium constants (single index)

$$K_1 = 1$$
$$K_x = \frac{1}{2} \prod_{y=1}^{x-1} K_{1,y} = \frac{C_x}{C_1{}^x} \quad 2 \leq x \leq m$$
$$K_x = 0; \quad m < x$$

$$\sum_{z=1}^{m} C_x = \sum_{1}^{m} K_x C_1{}^x$$

Equilibrium constants (single index)

$$K_1 = 1$$
$$K_x = 0 \quad 2 \leq x < \alpha$$
$$K_\alpha = \frac{C_\alpha}{C_1{}^\alpha} \quad \alpha > 2$$
$$K_2 = \frac{C_2}{2C_1{}^2} = \frac{1}{2}K_{1,1} \quad \alpha = 1$$
$$K_x = K_\alpha \prod_{y=\alpha}^{x-1} K_{1,y} \quad \alpha < x \leq m$$
$$K_x = 0; \quad m < x$$
$$\sum_{z=1}^{m} C_x = C_1 + \sum_{y=\alpha}^{m} K_y C_1{}^y$$
Actually this definition is redundant, since considering the conditions on K_x and C_x the continuous definition can be used.

Hayward[14a] this is not the equation originally proposed by Tait but rather that called the Tait equation by Tamann. An interesting discussion of the various empirical two-constant compressibility equations is to be found in Hayward while a comparison of these equations is given by MacDonald.[14b] As discussed by Hayward, the fit of the various equations depends on the quality of the data. Up to rather high pressures most of the proposed equations fit about equally as well; therefore one has to employ other criteria in choosing which equation to use. For practicality in interpolation one would as a matter of course use the simplest equation compatible with the precision desired. For use in drawing theoretical deductions the equation to be used is the one with the soundest theoretical basis. On this ground we have chosen to use eq 5 which we shall name the general compressibility equation (GCE) or the Tamann–Tait equation. In this equation which from its derivation is applicable to gases, liquids, and solids, it is not predetermined whether J and L are constant with pressure, temperature or not. This depends entirely on the state and conditions. For gases, J and L are apparently variables. For liquids there are various

cases; for liquid Helium I and II both J and L are constant with pressure;[5] for Helium I, stable above the λ point, J is constant with temperature, L varies; for Helium II, stable below the λ point, L/J is constant with temperature with both J and L varying; according to other authors for a single class of substances J/v_0 is constant (v_0 is specific volume at a reference temperature) with temperature, both J and L being constant with pressure.[15,16] In the case of the solid alkali metals[6] both J and L are constant with pressure (Tamann–Tait law holds). Evidently a discussion of the compressibility equation of state will revolve around the constancy of J and L.

(14) (a) A. T. J. Hayward, N. E. L. Report 295, Natl. Eng. Lab., E. Kilbride, Glasgow, Scotland, 1967; *Brit. J. Appl. Phys.*, **18**, 965 (1967). (b) J. R. MacDonald, *Rev. Mod. Phys.*, **41**, 316 (1969).

(15) See for instance: A. Wohl, *Z. Phys. Chem.*, **99**, 234 (1921); A. Carl *ibid.*, **101**, 238 (1922); R. E. Gibson and O. H. Loeffler, *J. Phys. Chem.*, **43**, 207–217 (1939).

(16) R. Ginell and A. M. Ginell, "Humidity and Moisture," Vol. III, A. Wexler and W. A. Wildhack, Ed., Reinhold Publishing Co., New York, N. Y., 1965, pp 363–386.

Some general relationships can be derived. One can rewrite eq 3 as

$$\frac{d \ln u}{dv} = \frac{1}{J} \tag{6}$$

from whence on integrating

$$u = E e^{\int dv/J} \tag{7}$$

E = constant of integration. From eq 7 and eq 1 we get that

$$C = \frac{PE e^{\int dv/J}}{RT} \tag{8}$$

J and L Constant with Pressure. An important case of the compressibility equation is that when J and L are constant with pressure. Here eq 7 becomes

$$\left(1 - \frac{Б}{v}\right) = E e^{v/J} \tag{9}$$

$$C = \frac{PE}{RT} e^{v/J} \tag{10}$$

and

$$Zn = \frac{\sum i C_i}{\sum C_i} = \frac{wRT}{M^0 v P E e^{v/J}} \tag{11}$$

where Zn is the number average degree of association. Zn exhibits a minimum with an increase in pressure. Differentiating eq 11 with respect to volume, and using eq 5 with J and L constant, we have

$$\frac{dZn}{dv} = Zn\left[\frac{1}{v} - \frac{L}{PJ}\right]$$

Since at the minimum $dZn/dv = 0$, hence at this point

$$\frac{v}{P} = \frac{J}{L} \tag{12}$$

All these equations are the same for both the continuous and the discontinuous cases, and the quantities $(1 - Б/v)$, C and Zn are all calculatable in terms of constant of integration, E. In previous publications[7] on the continuous case, the equations are slightly different from those given above, being given in terms of another integration constant, A. They can be reconciled by setting

$$E = ARTw/M^0 \tag{13}$$

where A is the constant of integration evaluated in ref 7. In that work A was evaluated by making the assumption that $Zn = Zw = 1$ when $P/v = L/J$. This is true at the point where Zn is a minimum.[1,7] Since Zw and Zn, the weight and number average degrees of association, are comparable quantities their behavior is similar and Zw should show a minimum around the same point where Zn does. However, since from ref 4b

$$\varphi = -d \ln C_1/dv = A(L/J)v e^{v/J} \tag{14}$$

and from ref 1, $Zw = 1/v\varphi$, then

$$Zw = \frac{1}{A(L/J)v^2 e^{v/J}} \tag{15}$$

But the right-hand side of eq 15 exhibits no minimum, hence at pressures less than the pressure at the minimum, Zw becomes less than Zn. This is manifestly impossible, since from the definitions of Zw and Zn, their behavior must be parallel. Zw must always be greater than, or equal to Zn.

Examining the derivation of Zw in ref 1, we see that eq 16 is derived under the assumption that $dK_x/dv = 0$. If all the j-mers are present, as they are in the continuous case, this is probably justified, but if the j-mers between $j = 2$ and $j = \alpha$ are absent, α being a new variable, the size of the smallest of the multiply packed j-mers, then it is not justified. Since $K_x = 0$ for $x < \alpha$ and $K_x \neq 0$ for $x \geq \alpha$, then as the pressure changes and species appear and disappear, α changes in value. Under these conditions the assumption that $dK_x/dv = 0$ is invalid.

If we redefine φ to be

$$\varphi = -(\partial \ln C_1/\partial v)_\alpha \tag{16}$$

then $(\partial K_x/\partial v)_\alpha = 0$ and $Zw = 1/v\varphi$ in terms of the new definition of φ. This can readily be seen by rederiving the relationship of φ and Zw in the same way as in ref 4b.

Now from eq 1 we have

$$-\left(\frac{\partial v}{\partial P}\right)_\alpha = \frac{u/(\partial u/\partial v)_\alpha}{\dfrac{-RT(\partial C/\partial v)_\alpha}{(\partial u/\partial v)_\alpha} + P} \tag{17}$$

$$= \frac{J_v}{L_v + P}$$

where

$$J_v = u/(\partial u/\partial v)_\alpha \tag{18}$$

and

$$L_v = \frac{-RT(\partial C/\partial v)_\alpha}{(\partial u/\partial v)_\alpha} \tag{19}$$

These definitions of J_v and L_v are analogous to the definitions of J and L which one defined in terms of the total derivatives; but while J and L are constant with pressure changes, J_v and L_v are not constants.

Now since $C = \sum K_x C_1^x$

$$(\partial C/\partial v)_\alpha = \sum x K_x C_1^x (\partial \ln C_1/\partial v)_\alpha$$

$$= -\varphi \sum x C_x \tag{20}$$

Whence using eq 19

$$\lambda = \frac{L_v}{J_v} = RT \varphi \sum x C_x/u \tag{21}$$