From the fact that particles with approximate 5-symmetry cannot totally fill space but form a more or less irregular body with many internal voids, arise the special properties of liquids, while the fact that particles with a regular 3, 4 or 6 symmetry can fill space and occupy fixed positions give rise to the properties of solids. Solids (with certain exceptions) generally consist of a mosaic of crystallites. As pressure is applied, these crystallites are distorted, that is they lose symmetry. The loss in symmetry is not micro-uniform throughout all the mass of the solid but micro-heterogeneous. In essence what we are saying is that the average size of these particles, each of perfect symmetry, is broken down to smaller particles also each of perfect symmetry. This entails a decrease in the average degree of association. Another way of looking at this process is from energy considerations. An increase in pressure results in an increase in potential energy in the solid. This energy is stored as broken bonds. If bonds break this entails a breakup of the crystallite particles.

Understanding now what is happening under the application of pressure, the question is, what is the meaning of the minimum? To answer this question we proceed as follows: at the minimum the value of $(\partial Zn/\partial P)_T$ is zero; hence taking the derivative of equation (6) we have

$$\left(\frac{\partial ZnA}{\partial P}\right)_T = \frac{\partial}{\partial P}[1/Pv \exp(v/J)] = 0 \qquad (7)$$

carrying out the operation and simplifying we have

$$\frac{1}{P} = \left(\frac{1}{v} + \frac{1}{J}\right)\frac{\partial v}{\partial P}$$

Inserting Tait's equation

$$-\left(\frac{\partial v}{\partial P}\right)_T = \frac{J}{L+P}$$

and simplifying we have as conditions at the minimum that

$$\frac{v_{\min}}{P_{\min}} = \frac{J}{L} \qquad (8)$$

Let us now proceed further.

It has been shown[7] that

$$Zw = \frac{1}{v\phi} \qquad (9)$$

where Zw is the weight average degree of association. From equation (6)

$$Zn = \frac{L}{JP\phi}$$

when $Zw = Zn$ then

$$\frac{v}{P} = \frac{J}{L} \qquad (10)$$

From the identity of equation (10) with equation (8) we see that at the minimum in the Zn curve, $Zn = Zw$, i.e. the weight-average degree of association is equal to the number-average degree of association. The question then is under what condition are the weight and number averages equal? It is well known that this occurs only when the substance under investigation is homogeneous in molecular weight. Considering the fact that the solid under pressure is decreasing in molecular weight, the simplest and most logical assumption to make is that at the minimum

$$Zn = Zw = 1 \qquad (11)$$

If this is the case then the integration constant A can be evaluated. ZnA is known and hence

$$(ZnA)_{\min} = A \qquad (12)$$

This gives us an unambiguous general method of deriving the value of A.

Computation of A

There are several methods of varying precision of evaluating A from the experimental data.

(1) One can use equation (8) together with the integrated Tait equation

$$(P+L)\exp(v/J) = H \qquad (13)$$

to get

$$P = L \log H - L \log(P+L) \qquad (14)$$

or

$$v = J \log H - J \log[(Lv/J)+L] \qquad (15)$$

These equations can be solved for P or v by iteration.

(2) Graphically one can plot P/v vs. P and determine the value of

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