

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  $(\partial Z_n/\partial P)_T$  is zero; hence taking the derivative of equation (6) we have

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

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

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

Let us now proceed further.

It has been shown<sup>(7)</sup> that

$$Z_w = \frac{1}{v\phi} \quad (9)$$

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

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

when  $Z_w = Z_n$  then

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

From the identity of equation (10) with equation (8) we see that at the minimum in the  $Z_n$  curve,  $Z_n = Z_w$ , 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

$$Z_n = Z_w = 1 \quad (11)$$

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

$$(Z_n A)_{\min} = A \quad (12)$$

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

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

to get

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

$$\text{or } v = J \log H - J \log[(Lv/J) + L] \quad (15)$$

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

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

Table 2. Evaluation of  $A$  and the parameters at the minimum in the Zn curve

Metal	$P_{\min}$ (kg/cm <sup>2</sup> )	$v_{\min}$ (cm <sup>3</sup> )	$A \times 10^6$	$\phi_{\min}$	$Zw_{\min}$
					<i>exact to 10 digits</i>
Lithium	84,819.8*	1.303580*	0.272219*	0.767118*	1
Sodium	55,284.8	0.711600	0.549218	1.405284	1
Potassium	16,239.1	0.865777	0.645614	1.155032	1
Rubidium	16,807.0	0.479612	1.258094	2.085020	1
Cesium low pressure	17,608.1	0.362564	6.203762	2.758131	1

\* These values are truncated values from the computation in which 20 digits were used.

(3) One can interpolate in a table of  $P/v$  vs.  $P$  the value of  $L/J$  using Lagrangian interpolation.

All these computational methods have been tried. The test of the precision of the answer is to calculate  $Zw$  which should be equal to 1. The methods in 1 are computationally difficult since obtaining the logarithm to a sufficient number of digits is difficult. Method 2 is inherently imprecise, although by this method very good preliminary results were obtained, the calculation of  $Zw$  showed that they were imprecise. We used method 3 which is very precise. The results are reported in Table 2.

#### ATOMIC RADII

Since we now know  $B$ , for the alkali metals many other quantities become accessible to calculation. One of these is the atomic radius.  $B$  is the excluded volume of the metal, i.e. it is the volume of the associated particles in the metal. These particles may be considered to be composed of spherical atoms packed in a particular array. In the alkali metals this array is b.c.c. This configuration in addition to the atoms also has internal free space; we will call this space the internal volume of the particles. We now differentiate between the total volume,  $v$ ; the defect volume,  $(v - B)$ , which is the volume between particles, the excluded volume,  $B$ ; and finally the internal volume which is the space in  $B$  not occupied by the spherical atoms. To obtain the atomic radii we must first evaluate how much of the excluded volume is the internal volume.

In a body-centered array, the atoms conceived as spherical balls are touching along the diagonal

of the unit cell. Hence in terms of the radius,  $r$ , of the atom the length,  $l$ , of the unit cell is

$$(4r)^2 = l^2$$

or

$$l = \frac{4}{\sqrt{3}}r$$

since four atomic radii lie along the unit cell diagonal. The volume of the unit cell is then

$$l^3 = \frac{64}{3\sqrt{3}}r^3$$

Since for body-centered packing each unit cell has two atoms the volume per atom is

$$\text{volume per atom} = \frac{32}{3\sqrt{3}}r^3$$

The volume per Avogadro number of atoms (formole) is

$$\text{vol/formole} = \frac{32}{3\sqrt{3}}r^3 N_0$$

Also since  $B$  is the excluded volume per gram,  $BM^0$  is the excluded volume per formole where  $M^0$  is the molecular weight (here at. wt.). Hence

$$BM^0 = \frac{32}{3\sqrt{3}}r^3 N_0$$

solving for  $r$  we have for a b.c.c. array

$$r = \left( \frac{3\sqrt{3}}{32N_0} BM^0 \right)^{1/3} \quad (16)$$