COMPRESSIBILITY OF SOLIDS AND TAIT'S LAW—II. ATOMIC RADII OF THE ALKALI METALS

R. GINELL and T. J. QUIGLEY*

Department of Chemistry, Brooklyn College of The City University of New York

(*Received* 12 *July* 1965)

Abstract—The previously undetermined constant A is evaluated unambiguously and a general method of performing such evaluations is given. The atomic radii of the alkali metals in the solid state are calculated from the compressibility parameters of the metals through an evaluation of the excluded volume, beth, Б. The values obtained are in excellent agreement with both the Slater and Bragg values. It is shown that on compression, the volume decrease is due to the disappearance of the defect volume and the internal volume in the aggregates and that up to about 100,000 kg/cm² for lithium, sodium, potassium and rubidium and to about 23,000 kg/cm² for cesium the radii of the alkali metals probably do not decrease.

INTRODUCTION

IN A previous publication[1] (herein called I) it has been shown that the alkali metals obey Tait's law quite exactly and that from the Tait coefficients, J and L, the volume at constant temperature can be determined precisely from the pressure, in the whole range investigated, that is, up to 100,000 kg/cm². While this information is important, the utility of the determination of the Tait coefficients can be extended much further to give us a deeper insight into the nature of the solid state. This information is the outcome of the fact that the Tait equation, which was first proposed as an empirical law[2] has been theoretically derived[3,4] from the general association equation of state[5]

$$\frac{Pv}{RT} = \frac{\sum_x N_x}{1-(Б/v)} \quad (1)$$

where N_x is the number of particles in moles of
size x per gram and
$\sum N_x$ is the total number of particles per gram
$Б$ = sum of the excluded volume per gram
$= \Sigma \delta_x N_x$
v = specific volume
P,R,T have their usual meaning

In the Association theory (see Ref. 7) solids are considered to consist of an agglomerate of small aggregates of atoms (mosaic crystal). Each of these aggregates has perfect order and consists of a number of unimers (atoms here). The aggregates are of different sizes and are connected by defect spaces. The number of unimers in a given weight is the stoichiometric number of formula moles called here formoles. The number of aggregates or particles or j-mers is a significant quantity called the avmolity (Avogadro moles) in the theory.

This paper is devoted to an exposition of such insights and to computations derived from them.

EQUATIONS AND COMPUTATIONS

From the derivation of Tait's Law the following relationships emerge[4]

$$J = (v-Б)/\phi \sum_x x\delta_x N_x \quad (2)$$

and

$$L = (RTw)/M^0 \sum_x x\delta_x N_x \quad (3)$$

where J and L are the Tait's coefficients
w = weight of the sample = 1 g here
M^0 = Molecular weight of the 1-mer, here the at. wt.
$\phi = Av(L/J)e^{v/J}$ where A is an undetermined integration constant.

* Present address: St. Francis College, Brooklyn, N.Y.

These equations and the general equation of state enable us to derive equations for some of the internal variables[4] of solids: namely

$$(v - \text{Б}) = \frac{wRTJ\phi}{LM^0} = \frac{ARTwve^{v/J}}{M^0} \qquad (4)$$

$$\sum_x N_x = \frac{wJP\phi}{M^0 L} = \frac{AwPve^{v/J}}{M^0} \qquad (5)$$

$$Zn = \frac{\Sigma x N_x}{\Sigma N_x} = \frac{w/M^0}{\Sigma N_x}$$

$$= \frac{L}{JP\phi} = \frac{e^{-v/J}}{APv} \qquad (6)$$

where $(v - \text{Б})$ is the defect volume and Zn is the number average degree of association.

Since as originally derived A is an undetermined integration constant, the first computations were of the values of $(v - \text{Б})/A$, (ZnA) and ϕ/A as a function of pressure. The calculations were carried out on an IBM 1620 computor and the input consisted of J, L, R, T, w, M^0, H and the pressure range. H is the integration constant in the integrated form of Tait's equation as evaluated in I. Table 1 summarizes the values of the input variables. Except in the case of potassium where the Br II values (see I) were used, the combined Br II and Br III values for J and L as derived from Bridgman's data were chosen. The data from

the two sets were combined in the following manner. For each set separately (Br II and Br III) a set of equally spaced values of P vs. dP/dv was calculated from the experimental data over the range covered. These calculated values from the separate sets were then combined to find the best values of J and L for the combined set. The raw data could not be combined since they covered different ranges and were given at different intervals. In this way all the data were used and the best values derived therefrom.

In calculating the values of J and L we noted Bridgman's assertion that these were room temperature values. However he does not identify this temperature further. In I, since the temperature does not appear explicitly, this posed no problem, although minor variations in the room temperature in Bridgman's work would have the effect of introducing small irregularities into the curves. Perhaps some of the apparently systematic variations in some of the curves in I, notably in the case of potassium, can be traced to systematic variation of this sort during the various experimental runs. In the calculations in this paper we must use the temperature explicitly and have chosen room temperature as 300°K. This choice is undoubtedly wrong but a reasonable choice must be made.

In this paper we will confine ourselves to a consideration of pressure effects at constant temperature and an examination of the Bridgman data previously analyzed in I. The interesting results of

Table 1. Values † of the input parameters for the determination of $(v - \text{Б})/A$, ZnA, and ϕ/A. Pressure range 0–100,000 kg/cm² (except as noted). Temperature 300°K (room temperature). R (gas constant) $= 84\cdot783$ (kg/cm²)cm³ mole°C

Metal	M^0 (at. wt.)	J(cm³)	L(kg/cm²)	$H \times 10^{-6}$ (kg/cm²)	Source†
Lithium	6·939	0·372105*	24211·7*	3·62242*	Br II–Br III
Sodium	22·9898	0·185566	14416·8	3·25935	Br II–Br III
Potassium	39·102	0·184129	3453·65	2·12937	Br II
Rubidium	85·47	0·104465	3660·75	1·97998	Br II–Br III
Cesium low pressure 0–23,000	132·91	0·112291	5453·45	0·58229	

* The numbers in these columns are truncated. Computations were made using a minimum of 8 digits. In certain cases 15 or 20 digits were used.

† The determination of these values is described in Ref. 1. The weight of all sample w^- was taken as 1 g so that the volumes calculated were the specific volumes.
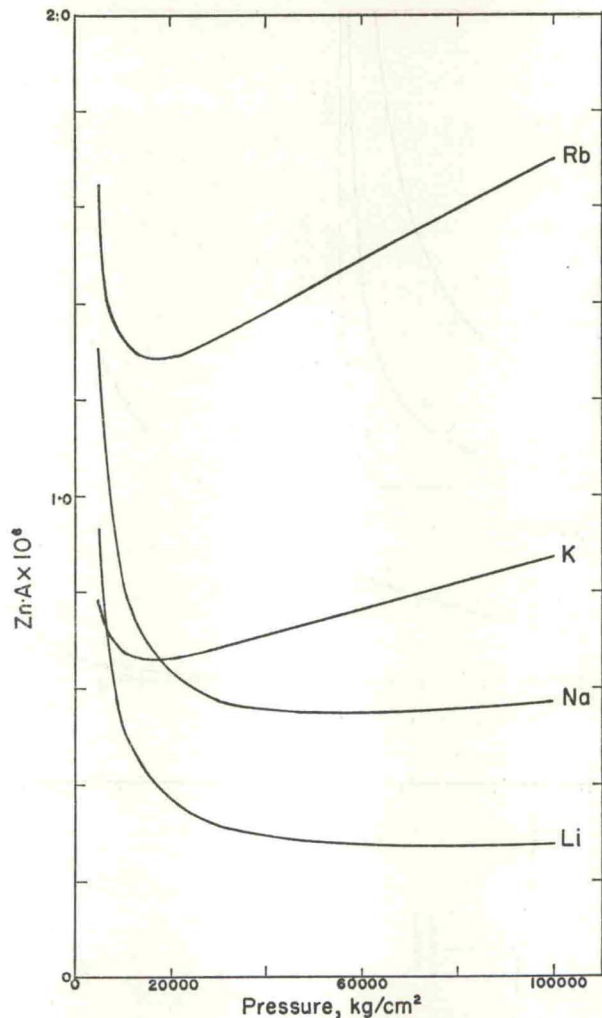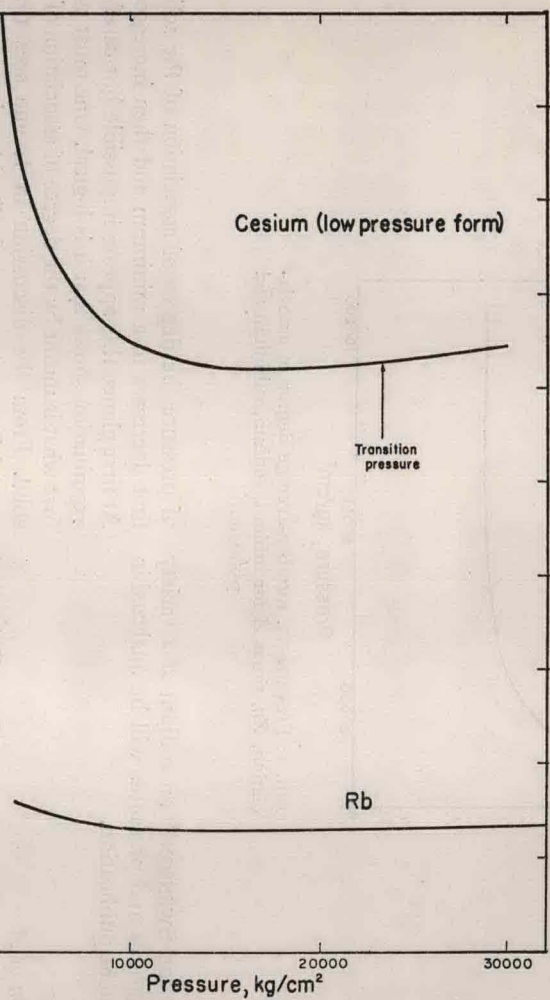
Fig. 1. Pressure vs. number-average degree of associa-ciation, Zn, times A for lithium, sodium, rubidium and potassium.

BEECROFT and SWENSON[6] on sodium at a variety of temperatures and pressures will be analyzed in a subsequent publication.

Evaluation of A

The first calculations were of $(v-Б)/A$ and ZnA as given by equations (4) and (6). The results of these calculations are shown on Figs. 1, 2 and 3. As can be seen the curve of ZnA shows a minimum. This implies that on the application

of pressure the degree of association of the solid first decreases to a minimum and then increases. At first glance this appears impossible but careful examination shows that it is logical. One must ask first what is meant by the degree of association of a solid. From the discussion in I, one sees that essentially the structure of a liquid and a solid are alike: both consist of small particles separated by defect space. The essential difference is that the liquid particles exhibit approximate 5-symmetry while the solid particles have 3, 4 or 6 symmetry.

Cesium (low pressure form)

Transition
pressure

Rb

Pressure, kg/cm²

Pressure vs. number-average degree of association, Zn,
for cesium. The ZnA scale is compressed here com-
Fig. 1 and the pressure scale is expanded. The curve
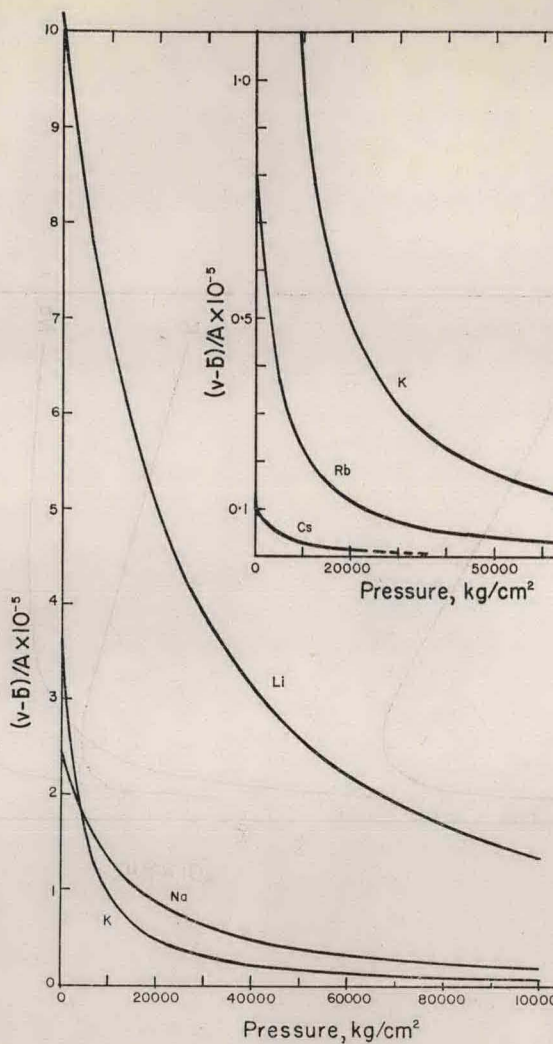for rubidium is repeated for comparison.

Fig. 3. Pressure vs. defect volume, $(v-Б)$, for th

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

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

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

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

Metal	P_{min} (kg/cm²)	v_{min} (cm³)	$A \times 10^6$	ϕ_{min}	Zw_{min}
					exact to 10 digits
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 beth, Б, for the alkali metals many other quantities become accessible to calculation. One of these is the atomic radius. Beth 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, $(v-Б)$, which is the volume between particles, the excluded volume, Б; and finally the internal volume which is the space in Б 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

$$(4r)^2 = 3l^2$$

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 Б is the excluded volume per gram, $БM^0$ is the excluded volume per formole where M^0 is the molecular weight (here at. wt.). Hence

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

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

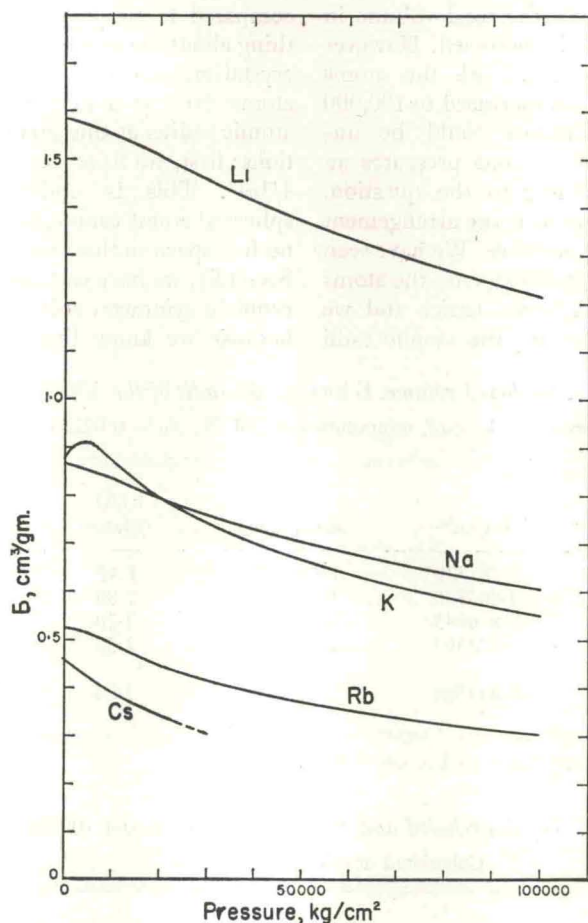$$r = \left(\frac{3\sqrt{3}}{32N_0}БM^0\right)^{1/3} \tag{16}$$

FIG. 4. Pressure vs. excluded volume, Б, for the alkali
metals. See text for discussion of potassium curve.

The corresponding formula for a f.c.c. configuration is

$$r = \left(\frac{БM^0}{4\sqrt{(2N_0)}}\right)^{1/3} \tag{17}$$

while for a simple cubic array it is

$$r = \left(\frac{БM^0}{8N_0}\right)^{1/3} \tag{18}$$

We now assume that the associated particles in the solid are large enough so that the end effects are negligible. Using our value of A calculated at the minimum point, we calculate Б at 1 atm. using equation (4). Thus we arrive at the values given in Table 3. As can readily be seen these values are as good as the SLATER[8] or the BRAGG[9] values which are derived from X-ray measurements.

In Fig. 4 is shown a graph of the excluded volume, Б, as a function of the pressure. Whether the maximum in the potassium curve is real, is questionable. However we have already discussed the fact that the potassium values are not good. The excluded volume decreases because as the particles decrease in size the internal volume is released and becomes part of the defect volume. As the pressure increases the defect volume also decreases. This means that the decrease in volume with increase in pressure is generally due to a squeezing out of defect volume. In Table 4 it can be seen that the

excluded volume approaches the total volume in magnitude as the pressure is increased. However the question still remaining is: are the atoms compressed as the pressure is increased to 100,000 kg/cm²? If the atomic radius could be unbiguously calculated at the various pressures an answer might be forthcoming to the question. However the problem is; what is the arrangement of the atoms at increasing pressure? We have seen that we could assume that at one kg/cm², the atoms are arranged in a body-centered lattice and we could get very good values for the atomic radii

compared to the X-ray values. We know something about the atoms at one other point. Here the crystal–array symmetry has been disrupted and the atoms exist as 1-mers. We have calculated the atomic radius at this point under several assumptions: first, we have assumed that their volume is $4/3\pi r^3$. This is undoubtedly wrong because spherical atoms cannot be packed in a volume with no free space so that this value should be too high. Secondly, we have calculated the radius as if body-centered symmetry still existed. This also is wrong because we know that this symmetry does not

Table 3. *Excluded volume,* Б *and atomic radii of the alkali metals.*

Pressure = 1 kg/cm², temperature = 300°K, $N_0 = 6 \cdot 02283 \times 10^{23}$

Metal	Б (cm³)	r (Å) (this paper)	r (Å) (Slater)	r (Å) (Bragg)
Lithium	1·585320*	1·43675*	1·45	1·50
Sodium	0·867506	1·75192	1·80	1·77
Potassium	0·876645	2·09854	2·20	2·07
Rubidium	0·524303	2·29461	2·35	2·25
Cesium low pressure form	0·457988	2·54125	2·60	2·37

* Truncated from 20 digits used in calculation.

Table 4. *Total, excluded and defect volumes at* 1 *and* 100,000 *kg/cm².*

Calculated densities at 1 kg/cm²

Metal	Pressure (kg/cm²)	Total volume (v/g)	Excluded volume (Б/gm)	Defect volume (v−Б/g)	Density calculated = 1/v at 1 kg/cm²	Density rubber handbook*
Lithium	1	1·86351†	1·58532†	0·27819†	0·537†	0·534 (20°C)
	100,000	1·25508	1·21855	0·03652		
Sodium	1	1·00401	0·86751	0·13650	0·996	0·971 (20°C)
	100,000	0·61963	0·60901	0·01062		
Potassium	1	1·18282	0·87664	0·30617	0·845	0·862 (20°C)
	100,000	0·55689	0·55208	0·00481		
Rubidium	1	0·65739	0·52430	0·13308	1·521	1·532 (20°C)
	100,000	0·30814	0·30594	0·00220		
Cesium	1	0·52446	0·45800	0·06647	1·907	1·8785 (15°C)
	23,000	0·33897	0·33074	0·00824		1·873 (20°C)

* *Handbook of Chemistry and Physics*, 45th ed. (1964–65). The Chemical Rubber Co., Cleveland, Ohio.
† Rounded off from 20 digits.

Table 5. Approximate values of radii at the minimum point

	Pressure at minimum (kg/cm^2)	Radius in Å calculated from $(4/3)\pi r^3$	Radius in Å calculated as if in b.c.c. symmetry	Average radius at minimum	Radius in Å this paper at 1 kg/cm^2	$v/\text{Б}$ at minimum
Lithium	84,819·81	1·513	1·331	1·422	1·437	1·0343
Sodium	55,284·75	1·847	1·624	1·786	1·752	1·0289
Potassium	16,239·13	2·339	2·057	2·198	2·099	1·0485
Rubidium	16,807·03	2·501	2·200	2·351	2·295	1·0383
Cesium	17,608·07	2·646	2·327	2·487	2·541	1·0309

exist. Thirdly, we have taken an average of these two results. This is also wrong since averaging cannot remove the errors. Nonetheless the values (Table 5) obtained are comparable with those in Table 3 and show that the atoms are not likely to be squeezed at these pressures. At high pressures they undoubtedly are, however, squeezed since the ratio of the total volume to the excluded volume is approaching 1. It is noteworthy that at the minimum point the ratio $v/\text{Б}$ is approximately constant.

In Table 4 is also shown a calculation of the density compared to the published values. The densities are calculated from the volumes computed by Tait's Law. The comparison is good considering that they are based on the whole compressibility curve.

Further work is in progress.

REFERENCES

1. GINELL R. and QUIGLEY T. J. *J. Phys. Chem. Solids* **7**, 1157 (1965).
2. TAIT P. G., *Scientific Papers*, Vol. 2. Cambridge University Press, London (1898).
3. GINELL R., *J. Chem. Phys.* **34**, 1249 (1961).
4. GINELL R., *J. Chem. Phys.* **34**, 2174 (1961); 35, 1135 (1961).
5. GINELL R., *J. Chem. Phys.* **23**, 2395 (1955).
6. BEECROFT R. I. and SWENSON C. A., *J. Phys. Chem. Solids* **18**, 329 (1961).
7. GINELL R., *Advances in Thermophysical Properties at Extreme Temperatures and Pressures*, pp. 41–48. Am. Soc. Mech. Engs., New York, N.Y. (1965).
8. SLATER J. C., *J. Chem. Phys.* **41**, 3199 (1964).
9. BRAGG W. L., *Phil. Mag.* **40**, 169 (1920).