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

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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]

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

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
= $\sum б_x N_x$
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]

$$J = (v-Б)/\phi \sum_x x б_x N_x \tag{2}$$

and

$$L = (RTw)/M^0 \sum_x x б_x N_x \tag{3}$$

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.

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

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

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

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

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

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)* $= 84.783$ $(kg/cm^2)cm^3 \, mole°C$

Metal	M^0 (at. wt.)	$J(cm^3)$	$L(kg/cm^2)$	$H \times 10^{-6}$ (kg/cm^2)	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.