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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, B . 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⁾

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

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

B = sum of the excluded volume per gram
= $\sum 6_x N_x$

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⁾

$$J = (v - B) / \phi \sum_x x 6_x N_x \quad (2)$$

$$L = (RTw) / M^0 \sum_x x 6_x N_x \quad (3)$$

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.

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