

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY OF THE UNIVERSITY OF NEW ENGLAND, ARMIDALE, N.S.W., AUSTRALIA]

## Dimensions and Energies of Alkali Metal Crystals in Relation to Those of Their Gaseous Ions

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RECEIVED DECEMBER 14, 1963

The lattice energies of the alkali metals are found to be linearly related to the reciprocals of the van der Waals radii of the gaseous ions, and the lattice dimensions are directly proportional to the gaseous ion radii. These relationships are interpreted in terms of screening of the ions in the crystal by a uniform charge distribution, modified by an additional constant energy ascribed to "chemical" bonding. Application of the virial theorem leads to simple general expressions for the change of volume with pressure at 0°K. which adequately represent the data for the metals to 100,000 kg. cm.<sup>-2</sup>. The existence of a critical disruptive condition at negative pressures is also predicted.

### Introduction

The concept of the van der Waals radius of gaseous ions of the noble gas structure has proved useful in interpreting the energetics of aqueous ionic solutions<sup>1</sup> and ionic crystals.<sup>2</sup> Examination of a further condensed state of "ionic" matter, the alkali metal crystal, is a natural development of this line of thought.

**Relations between the van der Waals Radii and the Crystal Lattice Energies and Dimensions.**—For the alkali metals, the quantity corresponding to the lattice energy of an ionic crystal is the energy  $E_0$  required to convert the metal at 0°K. into free gaseous ions and electrons at rest at infinite separation. This energy is the sum of the latent heat of vaporization ( $L$ ) of the metal to monatomic vapor at 0°K. and the ionization potential  $I$  of the gaseous atom.

$$E_0 = L + I \quad (1)$$

In Fig. 1,  $E_0$  is plotted against the reciprocal of the van der Waals radius of the *gaseous* ion. There is an accurate linear relationship which may be represented by

$$E_0 = (A/r_v) + B \quad (2)$$

with  $A = 142 \text{ kcal. mole}^{-1} \text{ \AA}$  and  $B = 38 \text{ kcal. mole}^{-1}$ .

These metals all form body-centered cubic crystals under ordinary conditions; lithium has a hexagonal form at low temperatures, and cesium undergoes phase transitions above 23,000 atm. The "metallic radius"  $r_m$  can be defined as half the nearest neighbor distance. For several of the alkali metals the lattice parameters have been measured both at room temperature and at liquid air temperatures, so that a fairly accurate extrapolation to 0°K. can be made; for the others, the thermal expansion coefficients are known at room temperature and provide a reasonable guide to the extrapolation. The "metallic radii" at 0°K. so obtained are probably reliable to better than 1%. In Fig. 2 they are plotted against the van der Waals radii of the gaseous ions and are seen to be directly proportional to them within 1 or 2%. No such simple

$$r_m = 1.333r_v \text{ (0°K.)} \quad (3)$$

relations as (2) and (3) can be found if the crystal ionic radii of the metallic ions are used instead of  $r_v$ .

It seems likely that these results are not accidental, and it will now be shown that a very satisfactory treatment of the equilibrium properties of the metals

at 0°K. can be built up on the basis of these observations.

**A Modified Electrostatic Model for the Alkali Metals.**—The van der Waals radius of the gaseous ion,  $r_v$ , has been shown in previous papers to serve very well as the radius of a classical charged sphere having the same self energy as the actual ion *in vacuo*. When the gaseous ion enters a crystal or an aqueous solution it undergoes deformation and/or decrease of volume, as a *necessary* concomitant of the reduction (or in extreme cases total loss) of its self energy; for according to the virial theorem, the kinetic energy of the system must increase when the total energy decreases, and the energy loss is of such magnitude that only kinetic energy of electrons within the ions can provide the required increase. In the cases discussed previously it appears that the whole of the energy lost in the condensation of gaseous ions can be treated as loss of self energy and can be correctly calculated from a classical electrostatic model. Some new problems arise when we attempt to extend such models to the alkali metals, because the "anion" is now the valence electron. First, what is the "self energy" of an electron at rest *in vacuo*? Since it has zero momentum, the uncertainty principle indicates an infinite uncertainty in its position coordinates, so that it may be regarded as an infinitely dispersed finite charge, which of course has zero self energy. (We are not here concerned with its relativistic rest-mass energy, which we assume to be retained throughout.) From another point of view, we recall that in the wave-mechanical treatment of the hydrogen atom we do not have to allow for the self energy of the electron as a distributed charge about the nucleus; a single electron cannot "see" itself. When an electron is confined in a potential field it appears to gain not self energy but kinetic energy. This argument again suggests that the self energy of an electron at rest *in vacuo* should be taken as zero. In that case, we cannot give to the constant  $B$  in eq. 2 the facile explanation that it represents the self energy of the free electron, except in a purely formal way with the proviso that we do so in order to compensate for the inapplicability of a classical electrostatic model to the electron. Nevertheless it is curious that when the electron is solvated by liquid ammonia ( $\epsilon = 22$ ), as in solutions of alkali metals in ammonia, its solvation energy as judged from the photoelectric ionization threshold of the solution<sup>3</sup> is 34 kcal./mole, which corresponds with the expectation from the

(1) R. H. Stokes, *J. Am. Chem. Soc.*, **86**, 979 (1964).

(2) R. H. Stokes, *ibid.*, **86**, 982 (1964).

(3) Hasing, *Ann. Physik*, **37**, 509 (1940); quoted by M. C. R. Symons, *Quart. Rev.*, **13**, 99 (1959).

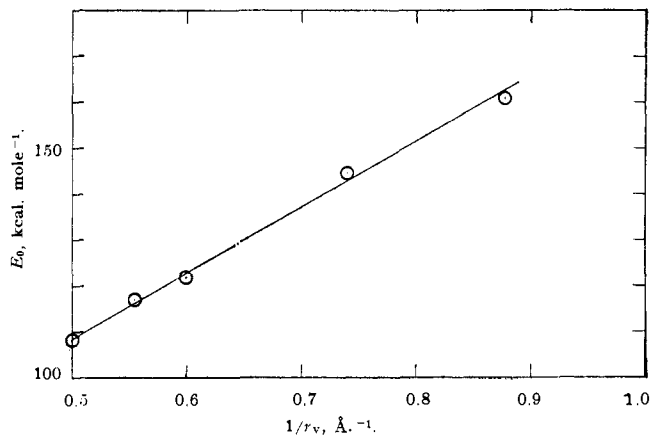


Fig. 1.—Lattice energies of the alkali metals at 0°K., as a function of reciprocals of van der Waals radii of the gaseous ions: points are, respectively, Cs, Rb, K, Na, and Li, ascending the line.

Born model for the solvation of a particle having a self energy *in vacuo* of 36.5 kcal. mole<sup>-1</sup>.

A more "chemical" interpretation of the quantity  $B$  of eq. 2 can be obtained by considering the energy of association of alkali metal atoms into dimers. At 0°K. these dimers are stable with respect to free atoms, their dissociation energies<sup>4</sup> falling from 26 kcal. mole<sup>-1</sup> for  $\text{Li}_2$  through 17 kcal. mole<sup>-1</sup> for  $\text{Na}_2$  to a nearly constant value of 10–11 kcal. mole<sup>-1</sup> for  $\text{K}_2$ ,  $\text{Rb}_2$ , and  $\text{Cs}_2$ . In the last three, the internuclear distances are comparable to those in alkali metal crystals. We might therefore expect in the metals, where there are eight nearest neighbors, a "chemical" binding energy of magnitude  $8 \times 10/2 \approx 40$  kcal./g.-atom; a small amount of repulsion from second-nearest neighbors could well reduce this slightly to the observed  $B$ -value of 38 kcal.

We now postulate that the alkali metals form geometrically similar systems, in which the scale at equilibrium at 0°K. is fixed by the van der Waals radii of the free ions; in particular, the nearest-neighbor distance is

$$d_0 = 2r_m = 2.666r_v \quad (4)$$

in accordance with Fig. 2. We may think of the electrons as being dispersed with nearly uniform density in the space between the ions; if we take a uniform shell extending from  $r_v$  to  $r_m = 1.333r_v$  containing on the average one electron, its screening effect on the ion is that of one electronic charge on the surface of a shell at a distance  $r'$  from the center of the ion, where

$$r' = r_v \frac{2}{3} \times \frac{(1.333)^3 - 1^3}{1.333^2 - 1^2} = 1.175r_v \quad (5)$$

The classical electrostatic energy of the "condenser" formed by the ion and spherical surface at  $r'$  is

$$E' = \frac{e^2}{2} \left( \frac{1}{r_v} - \frac{1}{r'} \right) \quad (6)$$

and on subtracting this from the self energy of the gaseous ion,  $e^2/2r_v$ , we obtain as the electrostatic contribution to the lattice energy

$$E'_0 = \frac{e^2}{2 \times 1.175r_v} = \frac{141.2}{r_v} \text{ kcal. mole}^{-1} \text{ \AA.} \quad (7)$$

(4) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500 (1952).

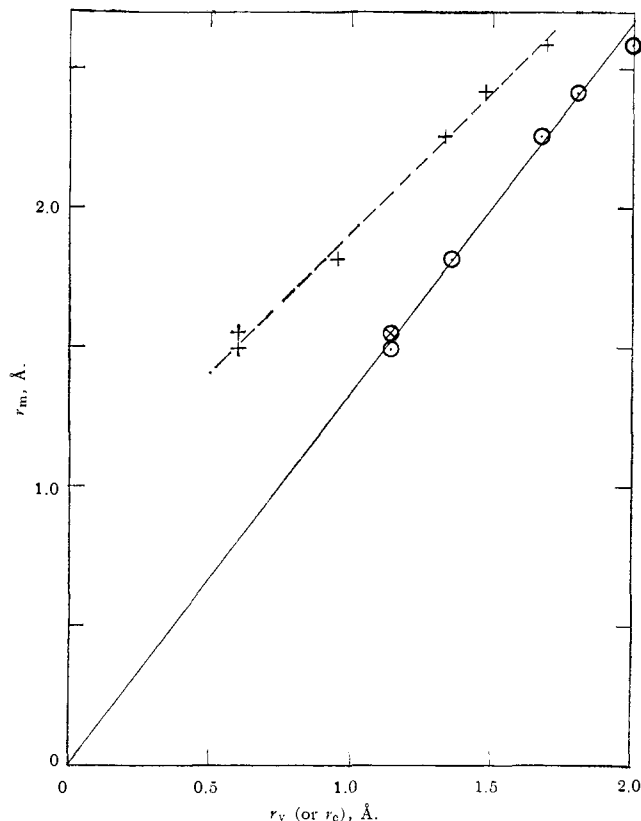


Fig. 2.—Metallic radii (= half nearest-neighbor internuclear distances at 0°K.) for the alkali metals as a function of the van der Waals radii of the gaseous ions (full line) and of Pauling's crystal radii (broken line). Points refer to Cs, Rb, K, Na, and Li, respectively, descending along the solid line. The upper of the two points shown for Li refers to the low-temperature hexagonal modification, and the lower to the normal body-centered cubic form.

in good agreement with the term  $A/r_v = 142$  kcal. mole<sup>-1</sup> Å. found from Fig. 1. In reality, of course, the electron is not confined exactly to the region ( $r_v - 1.333r_v$ ). It is generally considered, as in the Wigner-Seitz<sup>5</sup> model, to occupy a semiregular Archimedean polyhedron (the truncated octahedron) having a volume half that of the unit cell of the body-centered cubic lattice. In calculation this polyhedron is replaced by a sphere of radius  $r_s$  having the same volume, *i.e.*, the atomic volume of the metal; and in the first approximation the electron is treated as having uniform density within this sphere, with the ion as a point at its center.

A more realistic model would be to consider the ion as contracting to some extent on entering the metal, and the electron density as being somewhat greater near the ion than at the surface of the cell polyhedron, as would be consistent with the stronger field near the ion. However the much simpler course of treating the electron as uniformly spread through the region ( $r_v - r_m$ ) is adequate for the electrostatic model, and it should be noted that any reasonable modification of the electron density in this region makes remarkably little difference to the calculated electrostatic energy.

So far, we have offered what is a simple explanation of the observed relations 1 and 2, rather than a theory. To justify calling it a theory, it must predict something other than its starting points. The photoelectric

(5) See F. Seitz, "Modern Theory of Solids," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

work function and the compressibility provide suitable tests.

**The Photoelectric Work Function.**—Since eq. 1 gives the total energy of the metal relative to the ion and electron at infinity, and since we are assuming Coulombic interactions, the mean kinetic energy at 0°K. must according to the virial theorem be  $+E_0$ , while the mean potential energy is  $-2E_0$ . Now except for a negligibly small zero-point energy of lattice vibration, the kinetic energy must be that of electrons. If the ion were structureless and incompressible, the only electronic kinetic energy would be that of the free valence electrons, and for these the kinetic energy at the top of the filled band would, according to a well known result,<sup>6</sup> be  $5/3$  of the mean K.E., *i.e.*,  $5/3 E_0$ . In the potential well  $-2E_0$ , the total energy of an electron at the top of the filled band relative to a free electron at rest *in vacuo* would therefore be  $-E_0/3$ ; the provision of this energy by absorption of a sufficiently energetic photon should lift it out of the metal. The photoelectric work function  $\phi$  should therefore be simply  $E_0/3$ . Within the rather large uncertainty of the experimental values, this is true for lithium and sodium; for the higher alkali metals  $\phi$  is increasingly

TABLE I  
CALCULATED AND OBSERVED PROPERTIES OF THE ALKALI METALS

Property	Li	Na	K	Rb	Cs
$r_v^a$	1.139	1.352	1.670	1.802	1.997
$r_m$ (calcd.) <sup>b</sup>	1.518	1.802	2.226	2.402	2.662
$r_m$ (obsd.) <sup>c</sup>	1.495	1.818	2.257	2.411	2.584
$E_0$ (calcd.) <sup>d</sup>	162.5	142.4	122.5	116.4	108.7
$E_0$ (obsd.) <sup>e</sup>	160.8	144.5	121.8	116.8	110.1
$L$ (calcd.) <sup>f</sup>	38.2	23.9	22.4	20.1	17.4
$L$ (obsd.) <sup>g</sup>	36.5	26.0	21.7	20.5	18.8
$\phi$ (calcd.) <sup>h</sup>	2.35	2.06	1.77	1.68	1.57
$\phi$ (obsd.) <sup>i</sup>	2.28-	2.06-	2.0-	2.09-	1.9-
	2.42	2.47	2.26	2.16	1.96
$10^{12}\beta_0$ (calcd.) <sup>j</sup>	8.6	16.4	35.9	47.5	69.3
$10^{12}\beta$ (obsd.) <sup>k</sup>	8.8	15.8	36.2	52.8	71.0
$V_0$ (calcd.) <sup>l</sup>	13.0	21.7	40.9	51.4	70.0
$V_0$ (obsd.) <sup>m</sup>	12.4	22.3	42.7	52.0	64.0
$r_c^n$	0.60	0.95	1.33	1.48	1.69
$b^o$	0.54	2.16	5.93	8.18	12.18

<sup>a</sup> van der Waals radius (in Å.) of gaseous cation, as calculated in preceding papers.<sup>1,2</sup> The value for  $\text{Li}^+$ , 1.139 Å., is that adopted in ref. 2; the remainder are from ref. 1. <sup>b</sup> Calculated "metallic radius"  $r_m = 1.333r_v$ . <sup>c</sup> Observed "metallic radius" = 0.5 internuclear distance of nearest neighbors (in Å.) in metal, extrapolated to 0°K. (data from "Interatomic Distances," The Chemical Society, London, 1958). <sup>d</sup>  $E_0$  (calcd.) = lattice energy in kcal. mole<sup>-1</sup> relative to ions and electrons at rest *in vacuo*, from eq. 2. <sup>e</sup>  $E_0$  (obsd.) from National Bureau of Standards Circular 500, at 0°K. for Li, Na, K and at 298°K. for Rb and Cs. <sup>f</sup>  $L$  (calcd.) = heat of sublimation to free atoms at 0°K. =  $E_0$  (calcd.) -  $I$  where  $I$  is the experimental ionization potential; units kcal. mole<sup>-1</sup>. <sup>g</sup>  $L$  (obsd.) = heat of sublimation, at 0°K. for Li, Na, K, and at 298°K. for Rb, Cs; from N.B.S. Circular 500; units kcal. mole<sup>-1</sup>. <sup>h</sup>  $\phi$  (calcd.) = photoelectric electronic work function in e.v., from  $\phi = E_0/3$ . <sup>i</sup>  $\phi$  (obsd.), range of experimental values recorded in "Handbook of Chemistry and Physics," 44th Ed., 1962-1963, Chemical Rubber Publishing Co., Cleveland, Ohio. <sup>j</sup>  $\beta_0$  (calcd.) = compressibility at low pressures and 0°K. from eq. 11; *i.e.*, without covolume term; units cm.<sup>2</sup> dyne<sup>-1</sup>. <sup>k</sup>  $\beta$  (obsd.) = observed room temperature isothermal compressibility; from C. Kettel "Introduction to Solid State Physics," John Wiley and Sons, Inc., New York, N. Y., 1953 (converted to cm.<sup>2</sup> dyne<sup>-1</sup>). <sup>l</sup>  $V_0$  (calcd.) = molar volume (cm.<sup>3</sup> mole<sup>-1</sup>) at 0°K. and zero pressure for body-centered cubic structure with  $r_m = 1.333r_v$ . <sup>m</sup>  $V_0$  (obsd.) = experimental molar volume extrapolated to 0°K. <sup>n</sup>  $r_c$  = Pauling's crystal radius of cation (derived from internuclear distances in alkali halide crystals). <sup>o</sup>  $b$  = "covolume" inaccessible to valence electrons  $v = 4\pi Nr_c^3/3$  (cm.<sup>3</sup> mole<sup>-1</sup>).

(6) Reference 5, Chapter IV.

greater than  $E_0/3$ , as shown in Table I. Now this is just what is to be expected; the  $\text{Cs}^+$  ion, for instance, is much more compressible than  $\text{Li}^+$ ; therefore some of the mean kinetic energy  $E_0$  resides in the increased K.E. of its internal electrons, leaving a lower mean K.E. per valence electron, so that an energy jump greater than  $E_0/3$  is needed for a valence electron to escape.

**Pressure-Volume Relationships at 0°K.**—Consider first a crystal in which the ions are incompressible and very small, the volume being almost entirely that of the valence electrons. The effect of isotropic pressure on such a crystal will be simply to scale down all distances except the dimensions of the ions. The potential energy, being Coulombic, will therefore vary as  $V^{-1/2}$ . The kinetic energy of free electrons will vary as  $V^{-2/3}$ . Now in the absence of external pressure the equilibrium volume is  $V_0$ , and the K.E. and P.E. are, respectively,  $E_0$  and  $-2E_0$ . The total energy at volume  $V$  is therefore

$$E = -E_0[2(V_0/V)^{1/2} - (V_0/V)^{2/3}] \quad (8)$$

Since at 0°K.,  $P = -\partial E/\partial V$ , we obtain on differentiating (8) with respect to  $V$

$$P = \frac{2}{3} \frac{E_0}{V_0} \left[ \left( \frac{V_0}{V} \right)^{3/2} - \left( \frac{V_0}{V} \right)^{4/3} \right] \quad (9)$$

The compressibility  $\beta$  at 0°K. is both the adiabatic and the isothermal compressibility and is given by a further differentiation as

$$\frac{1}{\beta} = V \frac{\partial^2 E}{\partial V^2} = \frac{2}{9} \frac{E_0}{V_0} \left[ 5 \left( \frac{V_0}{V} \right)^{5/2} - 4 \left( \frac{V_0}{V} \right)^{4/3} \right] \quad (10)$$

In particular the initial compressibility at low pressures,  $\beta_0$ , is given by (10) with  $(V_0/V) = 1$ , *i.e.*

$$\beta_0 \equiv \left( -\frac{1}{V} \frac{\partial V}{\partial P} \right)_{P=0} = \frac{9V_0}{2E_0} \quad (11)$$

a result of such simplicity that its correctness, as shown in Table I, is hard to credit. The experimental data for  $\beta_0$  quoted are, however, isothermal compressibilities at room temperature, so perhaps there are compensating errors.

Even more striking is the fact that eq. 9 reproduces the experimental values of Bridgman<sup>7</sup> for lithium up to 100,000 atm. with an error of only a few per cent in the volume. For the other alkali metals the agreement is poorer, but again this is consistent with expectation since in these cases the compression of the ions themselves cannot be neglected. An obvious refinement is to treat the ions as having a fixed volume  $b$  not accessible to the valency electrons, so that the mean kinetic energy at volume  $V$  becomes

$$\text{K.E.} = E_0 \left( \frac{V_0 - b}{V - b} \right)^{2/3} \quad (12)$$

The corresponding potential energy is now severely restricted in form. To retain the necessary minimum in the total energy at  $V = V_0$ , and at the same time to satisfy the virial theorem at  $V = V_0$  and to reduce to (8) when  $b = 0$ , we can do little else but write

(7) P. W. Bridgman, "The Physics of High Pressure," G. Bell & Sons, London, 1958.

$$E = -E_0(2x - x^2); \quad x = [(V_0 - b)/(V - b)]^{1/3} \quad (13)$$

which leads to

$$P = \frac{2}{3} \frac{E_0}{V_0 - b} (x^5 - x^4) \quad (14)$$

$$\beta_0 = 9(V_0 - b)^2/2E_0V_0 \quad (15)$$

and

$$\frac{1}{\beta} = \frac{2E_0V}{9(V_0 - b)^2} [5x^8 - 4x^7] \quad (16)$$

In these equations it would be reasonable to put  $b$  equal to the molar volume of the cation in ionic crystals,  $4\pi Nr_c^3/3$ , since we expect the outermost parts of the electron distribution of the ion's own electrons in the metal to be merged with the valence electron cloud, while the "hard core" of the ion is about the same size as in the alkali halide crystal. Using Pauling's crystal radii to calculate  $b$  we obtain from (4) good agreement with the experimental values<sup>7</sup> for  $V$  as a function of  $P$  up to 100,000 atm. for all the alkali metals except cesium as shown in Fig. 3. (In the case

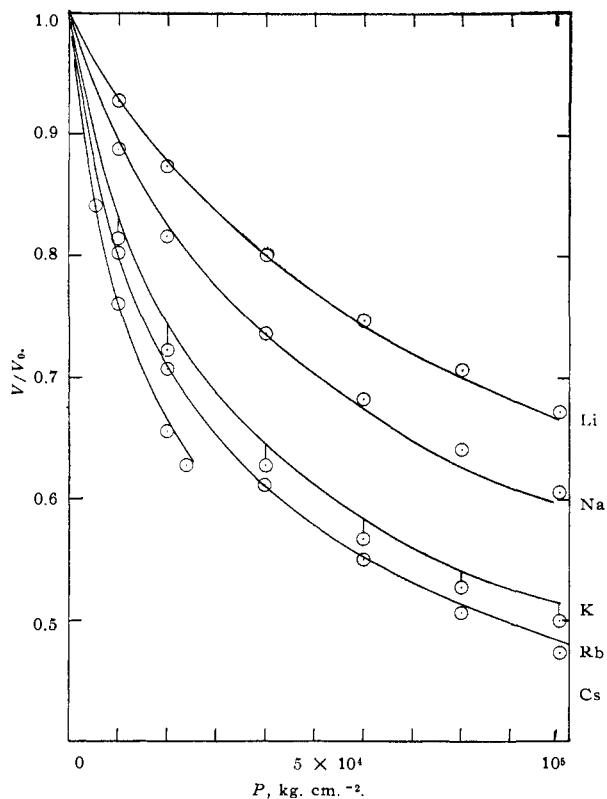


Fig. 3.— $P$ - $V$  relationships for the alkali metals to  $10^5$  atm.; circles from Bridgman's experimental data, full lines from eq. 14.

of cesium eq. 14 fails at the first phase change at 23,000 atm.; thereafter different values of  $E_0$  and  $V_0$  from those for the normal metal are obviously required.) When it is noted that the  $b$ -values are *not* chosen for best fit to the experimental  $P$ - $V$  curves, but are taken from an independent source, eq. 14 is obeyed with pleasing accuracy. The neglect of thermal energy terms implicit in the use of room temperature compression data is probably unimportant at the extreme pressures considered here.

An interesting feature of eq. 9-16 is that they predict a catastrophic process at  $x = 0.8$ , which corresponds

to an expanded state where  $(V - b)/(V_0 - b) = 1.95$ . Here the pressure is negative, corresponding to a uniform isotropic tension (about  $-30,000$  atm. for Li). At this point the compressibility becomes infinite and changes sign, the  $P$  vs.  $V$  curve having a minimum; the metal expanded beyond this point would be unstable and a phase change, presumably to individual atoms, would occur. Unfortunately such an "isotropic tensile strength" has not been determined to my knowledge (especially at  $0^\circ\text{K}$ .), but it is worth noting that the ordinary tensile strength of aluminum is of the order of  $-2000$  atm. This figure applies to a fairly soft metal with all the usual imperfections, at room temperature, in unidirectional tension, so perhaps the figure of  $-30,000$  atm. for a perfect lithium crystal in uniform isotropic tension at  $0^\circ\text{K}$ . is not unreasonable.

### Conclusions

The very simple electrostatic model outlined for the alkali metals can be summed up by the propositions that:

(a) The "metallic radius" (*i.e.*, half the nearest-neighbor distance in the metal) is given by  $r_m = 1.333r_v$ .

(b) At equilibrium the binding energy, relative to the ions and electrons at infinite separation, is that of the interaction of an ion of radius  $r_v$  with a uniform electron cloud between  $r_v$  and  $r_m$ , plus a further 38 kcal. mole<sup>-1</sup> associated in some way with electronic interactions.

(c) The kinetic energy of the valence electrons varies with volume in the same way as for an electron gas and is related to the binding energy and the potential energy through the virial theorem in the form appropriate to Coulomb interaction.

(d) The ions in the metal crystal have a covolume  $b$  which is here identified with the volume of spheres having the radii found from studies of alkali halide crystals and which is effectively inaccessible to the valency electrons.

These assumptions lead to the equations

$$E_0 = (141.2/r_v) + 38 \text{ (kcal. mole}^{-1} \text{ and } \text{Å.)}$$

$$V_0 = 8.788r_v^3 \text{ (} V_0 \text{ in cm.}^3 \text{, } r_v \text{ in } \text{Å.)}$$

to eq. 14-16 for the pressure and compressibility, and to the result

$$\phi = E_0/3$$

for the photoelectric work function when  $b = 0$ . In Table I and Fig. 3 comparisons are made entirely with calculated values starting from the van der Waals radii  $r_v$ , which are themselves derived from data on the noble gases. The pressure-volume calculations also require the  $b$ -values, obtained from Pauling's crystal radii for the cations.

Though this treatment has two arbitrary features (the scale factor 1.333 and the inadequately understood 38 kcal.), its success in accounting for the equilibrium properties is at least equal to that of more sophisticated theories. It makes no attempt to deal with transport properties and is here confined to properties at  $0^\circ\text{K}$ .

**Acknowledgment.**—The author is indebted to numerous colleagues for critical discussion, in particular Drs. J. E. Banfield, L. G. Hepler, and N. V. Riggs.