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# Compressibilities of the Alkali Metals

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(Received April 13, 1938)

As a further test of the method of Wigner and Seitz (for the calculation of the energies of the monovalent metals), the pressure variation of the compressibilities of the alkali metals is determined and compared with recent experimental results of Bridgman which extend to pressures of the order of 45,000 kg/cm². Fröhlich's approximate analytic expression for the dependence of the energies of the alkali metals on volume suggests the following semi-empirical form:

$$W=a/v+b/v^{\frac{2}{3}}-c/v^{\frac{1}{3}}.$$

If the parameters are determined from (1) the lattice constant, (2) the energy, and (3) the compressibility (all at zero pressure), the expression gives values for the relative change in volume with pressure in close agreement with Bridgman's results. The constants so determined agree fairly well with Fröhlich's theoretical values. Compressibilities of Li and Na, as obtained from the more exact and fundamental calculations of the energies given in the preceding paper, are compared with the experimental values. Theoretical values for Na are in good agreement with experiment, but the corresponding values for Li are about fifteen percent too high. It is suggested that the polymorphic transition in Cs, which occurs at a pressure of about 22,000 kg/cm², is a transition from the normal body-centered to a face-centered form, resulting from the nonelectrostatic interaction energy of the ions, which favors close packing.

## I. INTRODUCTION

BRIDGMAN[1] has recently obtained rough experimental values of the compressibilities of a large number of the more compressible substances in the pressure range extending to about 45,000 kg/cm². Of particular theoretical interest are the results he obtained for the alkali metals. Thanks largely to the work of Wigner and Seitz,[2] it is possible to make fairly accurate calculations of a large number of properties of this particular group of metals. A calculation of the compressibility and its variation with pressure provides a very sensitive test of the general methods.

The instantaneous compressibility, $K$, of a metal at the absolute zero of temperature is determined from the energy, $W$, by means of the following equation:

$$1/K=-v(dp/dv)=v(d^2W/dv^2), \qquad (1)$$

where $v$ is the volume of the metal and $p$ is the pressure. Our problem is thus the calculation of the energy of a metal as a function of volume.

We have given, in the preceding paper,[3] a calculation of the energies of Li and Na. In Section III of the present paper, we discuss the compressibilities and their variation with pressure. Fröhlich[4] has given an approximate expression for the energy of an electron in its lowest state. Using the free electron value for the Fermi energy, he has determined the initial compressibilities of the alkali metals, and obtained rough agreement with experiment. A modification of Fröhlich's procedure is discussed in Section II. At the end of the paper, we give a brief discussion of the polymorphic transition in Cs, discovered by Bridgman.

## II. SEMI-EMPIRICAL CALCULATION OF THE VARIATION OF THE COMPRESSIBILITY WITH PRESSURE

In the present section we assume that the energy of the metal (per atom) is the sum of the energy of an electron in its lowest state, $E_0$, and the Fermi energy, $F$. We neglect the small correction term to the interaction energy of the valence electrons (given by Eq. (29), reference 3) and also the nonelectrostatic interaction energy of the ions.

According to Fröhlich,[4] for values of $r_s$ near the energy minimum (or, in the neighborhood of the normal lattice constant), the energy $E_0$ (in atomic units[5]) is given by the following

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[1] P. W. Bridgman, Proc. Am. Acad. **72**, 207 (1938).

[2] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934). E. Wigner, Phys. Rev. **46**, 1002 (1934); F. Seitz, Phys. Rev. **47**, 400 (1935).

[3] In the present issue. This paper will be referred to as (I).

[4] H. Fröhlich, Proc. Roy. Soc. **158A**, 97 (1937); *Electronentheorie der Metalle* (Berlin, 1936) p. 272.

[5] Unit of energy is the Rydburg (13.5 ev); unit of length is the Bohr radius ($0.528\times10^{-8}$ cm).



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approximate expression,

$$E_0 = a/r_s^3 - 3/r_s, \tag{2}$$

where $r_s$ is the radius of a sphere of atomic volume ($s$ sphere). The repulsive energy is inversely proportional to the atomic volume, and the attractive energy, resulting from the interaction of the valence electrons with the positive ions is inversely proportional to the lattice constant.

The assumptions on which this formula is based are not very clear from Fröhlich's treatment. It is not difficult to show that (2) follows if

$$\gamma = (4\pi/3) r_s^3 [\psi_0(r_s)]^2 = 1, \tag{3}$$

or, in other words, if the value of the wave function at the boundary of the $s$ sphere is equal to its mean value. This relation must hold for all values of $r_s$ for which (2) is to be applied. One would expect that (3) will be approximately satisfied if the wave function of an electron in its lowest state is fairly flat throughout most of the volume. There is reason to suppose that this will be the case for values of $r_s$ near the actual atomic radius, since both $(d\psi_0/dr)_{r=r_s}$ and $(d^2\psi_0/dr^2)_{r=r}$ vanish when $E_0$ is a minimum.[6]

To derive (2) from (3), let us set $R = r\psi_0$, so that the Schrödinger equation for $R$ (in atomic units) is:

$$d^2R/dr^2 = (V(r) - E_0)R. \tag{4}$$

The potential $V(r)$ is that of a free (positive) ion. The boundary condition of Wigner and Seitz[2] is:

$$dR/dr = R/r \quad \text{at} \quad r = r_s. \tag{5}$$

Both $E_0$ and $R$ are functions of $r_s$, the point at which the boundary condition (5) is to be satisfied. Denoting derivatives with respect to $r_s$ by a prime, we have, differentiating (4),

$$d^2R'/dr^2 = (V(r) - E_0)R' - E_0'R, \tag{6}$$

so that, multiplying by $R$, integrating, and making use of (4) to eliminate $(V - E_0)RR'$, we obtain:

$$E_0' \int_0^{r_s} R^2 dr = \int_0^{r_s} [R'(d^2R/dr^2) - R(d^2R'/dr^2)] dr$$
$$= [R'(dR/dr) - R(dR'/dr)]_{r=r}. \tag{7}$$

[6] For a discussion of this point, see N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys*, (Oxford, 1936), p. 79. Values of $\gamma$ for Li and Na are tabulated in (I).

Differentiating the boundary condition (5) with respect to $r_s$, we have:

$$[(d^2R/dr^2) + (dR'/dr)]_{r=r_s} = [R'/r]_{r=r_s}. \tag{8}$$

Making use of this relation, we can eliminate $R'$ from (7) and obtain

$$E_0' \int_0^{r_s} R^2 dr = [R(d^2R/dr^2)]_{r=r_s}$$
$$= [V(r_s) - E_0(r_s)] R(r_s)^2. \tag{9}$$

We thus get the following differential equation for $E_0$, if condition (3) is satisfied:

$$dE_0/dr_s = (3/r_s)[V(r_s) - E_0(r_s)]. \tag{10}$$

Fröhlich's result (Eq. (2)) is obtained by integrating (10) with $V(r_s) = -e^2/r_s$. The latter will hold for values of $r_s$ larger than the radius of the ion core.[7]

It is, of course, impossible to tell *a priori* whether or not Fröhlich's formula will hold without making an explicit calculation of the wave functions using the actual potential of the ion, as Wigner and Seitz have done for Na and Li. Eq. (2) does give fairly good values for these metals. We will use, for comparison with the experimental data (of all the alkali metals) an expression of the form:

$$E_0 = a/r_s^3 - c/r_s, \tag{11}$$

treating $a$ and $c$ as empirical constants. The value of $c$ so obtained is then compared with the theoretical value (3) given by Eq. (2).

The Fermi energy $F$, expressed in atomic units, is

$$F = 2.21\alpha/r_s^2, \tag{12}$$

where $\alpha$ is the effective number of free electrons per atom. If the electrons are free, $\alpha$ is equal to unity. In general, $\alpha$ may be either greater or smaller than unity, and may be a function of $r_s$. It is known that the value of $\alpha$ for Li is much less than unity, and decreases as $r_s$ decreases, while for Na, $\alpha$ is slightly greater than unity and increases slowly as $r_s$ decreases.[8] As a first approximation, we may assume that $\alpha = 1$, so that the Fermi energy will be inversely proportional to the square of the lattice constant.

[7] The author is indebted to Professor E. Wigner for a discussion of Fröhlich's formula.

[8] Tables I and II, reference (I).

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Equations (11) and (12) suggest the following type of equation for the energy of an alkali metal:

$$W=A(v_0/v)+B(v_0/v)^{\frac{2}{3}}-C(v_0/v)^{\frac{1}{3}}, \qquad (13)$$

where $A$, $B$, and $C$ are independent of the volume, and $v_0$ is the atomic volume at zero pressure. The first and third terms come from the energy of an electron in its lowest state; the second from the Fermi energy. To determine the values of the three parameters, the following experimental data are used (all refer to 0°K and $p=0$):

(1) The lattice constant;

(2) The energy, given by the sum of the ionization potential and the atomic heat of sublimation, and

(3) The compressibility, $K_0$.

The values of the constants so obtained are checked in two ways. First, the empirical values of $B$ and $C$ are compared with the theoretical values given by Eqs. (12) and (2). The semi-empirical equation is then used to determine the change in compressibility with pressure (or, what amounts to the same thing, the relative change in volume with pressure) and the calculated values are compared with experiment.

Since the energy is a minimum when $v=v_0$ (or $p=0$) we have:

$$2C/3=2A+4B/3. \qquad (14)$$

The energy at zero pressure is given by:

$$-W=2A+B. \qquad (15)$$

Finally, the compressibility at zero pressure gives the relation:

$$3/K_0=2A+2B/3. \qquad (16)$$

To obtain (15) and (16) we have used the value of $C$ given by Eq. (14).

Table I gives the relevant data for the calculation of $A$, $B$, and $C$ for the alkali metals. Row (d) gives the energies, obtained from the sum of the ionization potential and the atomic heat of sublimation. The compressibilities, given in row (e) were obtained by extrapolating the experimental results, taken at room temperature, to $T=0$°K by means of the Debye equation of state, as discussed below. From the values given in these two rows, the constants $A$ and $B$ were determined by use of Eqs. (15) and (16); the results are given in rows (f) and (g). Row (i) gives the values of $\frac{2}{3}C$ obtained by substituting these values of $A$ and $B$ into Eq. (14). Row (h) gives the theoretical values of $B$ as obtained from Eq. (12) under the assumption that $\alpha=1$ (free electron value). Row (k) gives the theoretical values of $\frac{2}{3}C$ obtained from Eq. (2) of Fröhlich.

The empirical values of $B$, depending on the small difference between rows (d) and (e), are not at all accurate, but they are rather small for all metals except Li. The anomalous value for Li results from the fact that $\alpha$ is not constant, but decreases as the volume decreases. The Fermi energy cannot be expressed as a single term, but is given in fair approximation in the region of interest by the difference between a large positive term inversely proportional to the square of the lattice constant, and a negative term inversely proportional to the volume. The negative value of $B$ obtained for $K$ may perhaps be explained in a similar fashion. The differences between the theoretical and experimental values of $B$ for Na, Rb and Cs, are probably within the rather large experimental uncertainties.

A much more significant test of the theory is obtained from a comparison of the empirical and theoretical values of $C$ given in rows (i) and (h). The agreement is good for all metals except $K$, for which the empirical value is somewhat smaller than the theoretical.

As a second (experimental) test of the semi-empirical equation (13), we compare the relative

TABLE I. *Calculation of the parameters in the semi-empirical equation for the energies of the alkali metals:* $W=A(v_0/v)+B(v_0/v)^{2/3}-C(v_0/v)^{1/3}$. *The theoretical values of B are obtained from the free electron formula for the Fermi energy; theoretical values of C are obtained from Frohlich's formula for the energy of an electron in its lowest state. Units: row a,* $10^{-24}$ *cm³; rows b and c, ev/atom; rows d to j,* $10^{-12}$ *erg/atom.*

| | METAL | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|---|
| a | Atomic Volume ($v_0$) | 20.7 | 38.5 | 71 | 86 | 107 |
| b | Ionization Potential | 5.37 | 5.12 | 4.32 | 4.16 | 3.9 |
| c | Heat of Sublimation[1] | 1.70 | 1.13 | 0.86 | 0.82 | 0.82 |
| d | $-W_0$ | 11.2 | 9.8 | 8.2 | 7.9 | 7.5 |
| e | $3v_0/K$[2] | 8.4 | 9.4 | 8.9 | 8.1 | 7.5 |
| f | $A$(emp.) | 1.4 | 4.3 | 5.1 | 4.2 | 3.7 |
| g | $B$(emp.) | 8.4 | 1.2 | −2.1 | −0.6 | 0.0 |
| h | $B$(theor.) | 4.5 | 3.0 | 2.3 | 1.7 | 1.5 |
| i | $(2/3)C$(emp.) | 13.9 | 10.3 | 7.5 | 7.6 | 7.5 |
| j | $(2/3)C$(theor.) | 13.2 | 10.8 | 8.8 | 8.2 | 7.6 |

[1] Bichowsky and Rossini, *Thermochemistry of Chemical Substances*, (Reinhold, 1936).
[2] From Bridgman's data, extrapolated to $T=0$°K.

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change in volume with pressure given by the theory, with the experimental values of Bridgman.[1] It is first necessary to extrapolate the observed values to $T=0°K$. To do this, we use the Debye equation of state,[9] although it probably does not apply accurately to the alkali metals. The Debye equation is:

$$p=-(dW/dv)-3kT(d\theta/\theta dv)D(\theta/T). \quad (17)$$

Here $W$ and $v$ are the energy per atom and the atomic volume, respectively, and $\theta$ is the characteristic temperature. The function $D(x)$ is defined by:

$$D(x)=\frac{3}{x^3}\int_0^x \frac{\xi^3 d\xi}{e^\xi-1}. \quad (18)$$

For small $x$ ($T$ large), $D(x)\simeq 1$. The value of $d\theta/dv$ is obtained from Grüneisen's law:

$$3\alpha/K=-(d\theta/dv)(c_v/\theta), \quad (19)$$

in which $\alpha$ is the linear coefficient of thermal expansion,* $K$ is the compressibility, and $c_v$ is the atomic heat capacity:

$$c_v=3k[D(\theta/T)-(\theta/T)D'(\theta/T)]. \quad (20)$$

Using (19) and (20), we have, for small values of $\theta/T$,

$$p=-(dW/dv)+\Delta p, \quad (21)$$

where

$$\Delta p=(3\alpha T/K)[1-(3\theta/8T)+(1/10)(\theta/T)^2-\cdots]. \quad (22)$$

The second term of Eq. (21), $\Delta p$, represents the pressure due to the thermal motion of the ions, which must be subtracted from the observed pressures (at room temperature) to obtain the pressure at $T=0°K$. Although this term depends on the volume, the change is probably not very great except at very high pressures. In this region, the correction term is but a small fraction of the total pressure. We have therefore assumed that $\Delta p$ is independent of volume, and to determine its value we have used the values of $\alpha$, $K$, and $\theta$ for zero pressure and room temperature. Table II gives the values of $\Delta p$ for the alkalis, together with the relevant data used in the calculation. The total relative change in volume due to thermal expansion from room temperature down to $T=0°K$ is also given.

A plot of the relative change in volume of the different alkalis as a function of pressure is given in Fig. 1. The heavier lines represent the experimental values extrapolated to the absolute zero of temperature; the lighter lines are the theoretical values obtained from the semi-empirical formula (13). From this equation we find

$$pv_0=y^4(y-1)[2A+\tfrac{2}{3}B+A(y-1)], \quad (21)$$

with $$y=(v_0/v)^{\frac{1}{3}}.$$

The values of $A$ and $B$ which were used are given in rows (f) and (g) of Table I.

The agreement is good for all metals except Rb. Professor Bridgman informs me that the initial compressibility for this metal is less certain than for the other alkalis. The initial compressibilities were used in the determination of the parameters, so that the slopes of the theoretical curves agree with the slopes of the experimental curves at the origin. It is the shape of the curve which is important for a test of the validity of the theory. The shape is determined mainly by the factor $y^4(y-1)$ in Eq. (21). (The term $A(y-1)$ in the brackets is small.)

There is a tendency for the theoretical curves to be slightly above the observed at the highest pressures. The nonelectrostatic interaction energy of the ions, which we have neglected, is not large enough to account for this discrepancy. The general agreement would have been better if the parameters had been adjusted to make the experimental and theoretical curves match at some high pressure, rather than to fit the initial compressibilities.

## III. Compressibilities of Li and Na

It is much more desirable to have a calculation which is based on fundamental principles, so that there are no parameters to be determined from experiment. In order to determine the compressibility and its variation with pressure, it is necessary to have an accurate calculation of the energy as a function of volume. Such a calculation for Li and Na is given in the preceding paper.[3] In Fig. 2, we show the theoretical curves

[9] See, for example, J. K. Roberts, *Heat and Thermodynamics* (Blackie, 1933).

* Not to be confused with the effective number of free electrons per atom, for which the same symbol has been used.

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of the compressibilities as a function of volume, as determined from these energy values. For comparison, experimental curves derived from Bridgman's data,[1] extrapolated to $T=0°K$, as indicated above, are also given. The abscissa gives the relative change in volume from the observed volume at zero pressure. The smallest volumes correspond to a pressure of about 40,000 kg/cm². The curves for Na are in very good agreement, but the theoretical values for Li are about 15 percent too high. The difference in the latter case is perhaps due to our neglect of terms of higher order than those in $k^2$ in the calculation of the Fermi energy.

The reciprocal of the compressibility is given essentially by the second derivative of the energy with respect to volume. It is interesting to note that the second derivative of the Fermi energy of Li is negative, and that the main contribution to $1/K$ comes from the energy of an electron in its lowest state, $E_0$. On the other hand, the second derivative of $E_0$ is small for Na, and the main contribution comes from the rapid increase of the Fermi energy with decreasing volume.

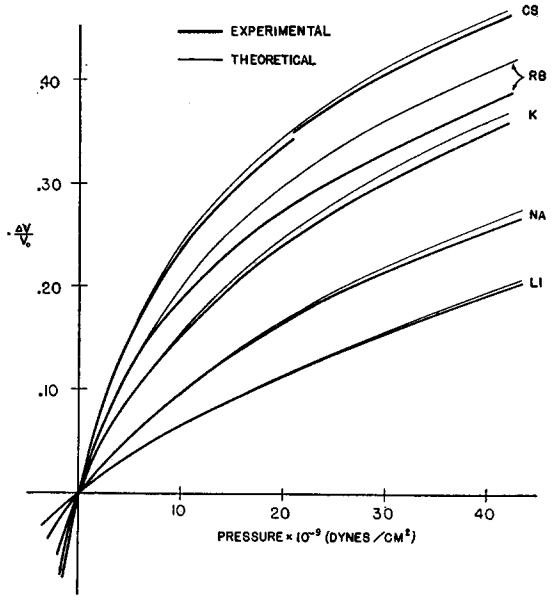


FIG. 1. Relative change in volume of alkali metals with pressure. Light lines are theoretical values obtained from the semi-empirical equation (13). Bridgman's experimental data, extrapolated to $T=0°K$, are represented by the heavy lines. The initial compressibilities have been used to fix the values of the parameters in the semiempirical equation, so that the slopes of the experimental and theoretical curves are in agreement at the origin. The break in the curve for Cs is due to a polymorphic transition.

## IV. Polymorphic Transition in Cs

At ordinary pressures, the alkali metals are body centered. It is not yet known why this structure is preferred over, for example, the close packed cubic structure (face centered). Fuchs[10] has shown that, for equal atomic volume, the energies of the valence electrons in the two structures differ by only about $10^{-3}$ ev per electron. He attributes the face-centered structure of the noble metals (Cu, Ag and Au) to the repulsion between the closed $d$ shells of the ions, which naturally favors the close packing. The nonelectrostatic energy of the ions in the alkali metals (resulting both from the exchange repulsion and the van der Waals energy) will also be lower in a face-centered lattice than in a body-centered lattice, but this energy is so small at ordinary pressures that it has little influence on the structure. As the volume is decreased, the energy of the ions will increase relatively to the energy of the valence electrons, so that one would expect that at very high pressures the alkali metals would take up a close packed structure. The rare gas solids are, of course, face centered, and it is likely that the alkali metals are also face centered at very high pressures.

TABLE II. *Data used in the extrapolation of Bridgman's results to $T=0°K$.*

| Metal | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| $\alpha\times10^5$ | 5.6 | 7.1 | 8.3 | 9.0 | 9.7 |
| $(1/K)\times10^{-9}$ (dynes/cm²) | 120 | 58 | 32 | 23 | 19 |
| $\theta/\tau$ | 1.5 | 0.6 | 0.40 | 0.29 | 0.20 |
| $\rho\times10^{-9}$ (dynes/cm²) | 3.5 | 2.8 | 2.0 | 1.6 | 1.5 |
| $\frac{v_T-v_0}{v_0}$ (calc.) | 0.031 | 0.043 | 0.060 | 0.080 | 0.084 |

[10] K. Fuchs, Proc. Roy. Soc. **A151**, 585 (1935).

The metal for which the transition should take place at lowest pressure is Cs, since it not only has the largest ion of the alkali metals, but also has the highest compressibility. Bridgman has found a polymorphic transition in Cs at a pressure of about 22,000 kg/cm². The change in volume at the transition point is 0.00336 cm³/g, and the latent heat, determined from the change in transition pressure with temperature is 8.49

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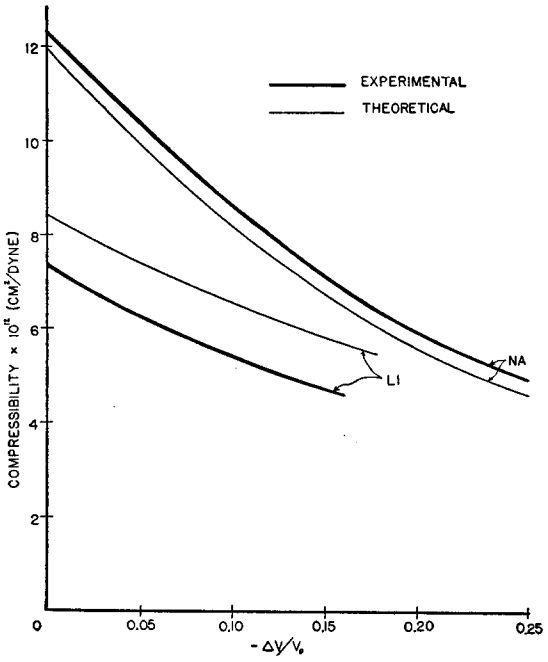


FIG. 2. Compressibilities of Li and Na as a function of pressure. Theoretical values are obtained from direct calculations of the energies (given in the preceding paper); experimental from Bridgman's data, extrapolated to $T=0°K$.

kg cm/g (0.2 cal./g). The small latent heat shows that the difference in entropy between the two phases is small.

A rough test of the theory that the transition is due to the nonelectrostatic energy of the ions may be obtained from the change in volume at the transition point. Let the free energy of the low pressure phase be $F_1(v)$ that of the high pressure phase be $F_2(v)$, and the corresponding volumes at the transition point be $v_1$ and $v_2$. Expressing the condition that the pressures of the two phases are equal at the transition point, we have, for $v_1-v_2$ small,

$$\left[\frac{d(F_1-F_2)}{dv}\right]_{v=v_1}=\frac{v_1-v_2}{v_1}\left(\frac{1}{K_1}\right)_{v=v_1}, \qquad (22)$$

where $K_1$ is the compressibility of the low pressure phase. The right-hand side may be evaluated from experimental data. The result is $0.83\times10^9$ dynes/cm$^2$.[11] In order to obtain a rough theoretical value for the left hand side of the equation, we will assume that the main contribution comes from the difference in the repulsive energy of the ions in the two phases. The difference in energy of the valence electrons, which presumably favors the body-centered lattice, will not change rapidly with volume, so that the derivative will be small. If we assume that the van der Waals energy of the ions varies as $1/r^6$, the difference between its values for the body-centered and face-centered structures is very small.

The exchange repulsion between the alkali ions has been estimated by Mayer and collaborators[12] from an analysis of the alkali-halide crystals. They find, for the mutual repulsive energy of two ions a distance $r$ apart,

$$W=A_i \exp\left[(2r_i-r)/\rho\right], \qquad (23)$$

where, if $A_i$ is taken to be $1.25\times10^{-12}$ ergs, the ionic radius $r_i=1.455$A for the Cs ion, and $\rho=0.345$A for all the alkali and halide ions. Using these values, we have estimated the contribution of the repulsion of the ion cores to (22) and find a value which is only about one-fifth of that observed. However, direct calculations[13] of the repulsion between the rare gas atoms He and Ne show that the energy can be given approximately by the form (23), with $\rho=0.21$A, a value much smaller than that of the above authors. The larger value probably results from the fact that it is a kind of a mean between the values for the alkali ions and the halide ions, and the latter are probably much larger than the former. If we take $\rho=0.21$A for the Cs ion, and take the same value for $A_i(1.25\times10^{-12}$ ergs) we estimate, from the lattice constant of the corresponding rare gas solid, that $r_i\sim1.75-1.80$A. With these values, one obtains results of about the right order of magnitude for (22).

Due to the difficulties in estimating the difference between the energies of the valence electrons in the two different structures, and also to the difficulty in estimating the interaction energy of

[11] This value is for room temperature. In order to compare with theory, we should take the value at absolute zero. Without a knowledge of the thermal expansion in the two phases, the change with temperature cannot be determined, but it is probably not very great. As we are interested only in the order of magnitude, we use the room-temperature value.

[12] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932); M. Huggins and J. E. Mayer, J. Chem. Phys. **1**, 643 (1933).

[13] J. C. Slater, Phys. Rev. **32**, 349 (1928) (He); W. E. Bleik and J. E. Mayer, J. Chem. Phys. **2**, 252 (1934) (Ne).

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the ions, one cannot be certain, but it does seem probable that the transition in Cs is from a body centered to a more close packed structure, which is probably face centered.

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# Electronic Structure of the First Row Hydrides

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Stehn's formulae for the energies of the first row hydrides, BH to FH, in terms of Heitler-London exchange integrals have been applied to more recent data. The empirically derived values for the integrals are now smooth functions of the atomic number, $Z$. They are also considered as functions of the internuclear distance, $r_e$, and taken in conjunction with data on BeH, and with the facts that $r_e$ and the force-constant, $k$, are smooth functions of $Z$, but invariant to electronic excitation, the results show that it is $2s^2-1s$ exchange that predominates in fixing the internuclear distance and force-constant. On the contrary, the dissociation energies cannot be expected to be smoothly dependent on $Z$, $r_e$ or $k$. The heat of dissociation of NH is calculated by Stehn's formulae, after interpolating one exchange integral.

## INTRODUCTION

PRESENT theories of heats of dissociation of molecules with more than four electrons are quite crude, and any correlation between theory and experiment, even for the simplest molecules would have value in giving theoretical thermochemistry a better quantitative basis. Stehn [1] made a considerable contribution in deriving formulae for the energies of the first row hydrides, BH, CH, NH, OH, FH, in terms of exchange and Coulomb integrals which can be determined empirically and tested for self-consistency. Since his publication new data have appeared, and in this paper the integrals are recalculated. The three classes of integrals are now smooth functions of the atomic number, and combined with facts known about the internuclear distances and force-constants give a more detailed picture of the orbitals in these molecules.

## REDETERMINATION OF THE INTEGRALS

Stehn applied the usual Heitler-London theory, building the molecules from a hydrogen $1s$ electron and various configurations of the heavy atom, to obtain expressions for the electronic energy

$$W=A+a_1B+a_2K+a_3J_\pi+a_4J_\sigma, \qquad (1)$$

where $A$ is the atomic level of the heavy atom into which the molecule adiabatically decomposes, $B$ is an atomic exchange integral, $K$ the exchange of the hydrogen $1s$ electron with $s$ electrons plus Coulomb terms, $J_\pi$ and $J_\sigma$ the exchange with $\pi$ or $\sigma p$ electrons. The $a$'s are numerical coefficients of the matrix elements. Stehn noticed that the internuclear distance remains practically the same in all excited states of any one molecule, so that the $J$'s and $K$ remain the same, permitting simultaneous equations in them to be set up and solved. In this application then the principal defect of the Heitler-London method, that of nonorthogonality, cancels out; but other corrections, such as higher order terms destroy the linearity of Eq. (1).

## DISCUSSION OF THE DATA

The excitation energies $\nu_{\text{mol}}$ and $\nu_{\text{atom}}$ are usually known quite accurately, and sometimes the $J$ integrals can be calculated from them alone. But a complete solution also depends on one dissociation energy, which is invariably the weakest datum. However, for any one molecule only one

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[1] J. R. Stehn, J. Chem. Phys. 5, 186 (1937).

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