On the Binding Forces in the Alkali and Alkaline Earth Metals According to the Free Electron Theory

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Although there have been a considerable number of attempts to work out in some detail the nature of the cohesive forces in the alkali metals, it has seemed worth while to see how far one could go with the simplest possible hypothesis, according to which the metal consists simply of singly charged positive ions in a sea of free electrons. Frenkel first showed that the fact that the electrons obey the Fermi statistics, results in an effective repulsive force which will be balanced by attractive electrical forces; but, as he pointed out, the finite size of the ions prevents this being more than a qualitative picture, and he suggested taking this into account by including repulsive forces between electrons and ions. In the present work an intrinsic ionic volume has been introduced into which the electrons are supposed to be unable to penetrate; this is simply subtracted from the atomic volume in the Fermi expression for the kinetic energy of the electrons. For the attractive potential an expression like those commonly employed to get the electrical potential of crystals is used; it involves a "Madelung constant" of a size about equal to those occurring in cases of uni-univalent crystals, and the same for all the alkali metals. For the alkaline earth metals appropriate modifications can be made. One can then calculate the energy of the metals from the experimental value of the atomic volume, getting excellent agreement with experiment in the case of the alkali metals, but not such good agreement in the case of the alkaline earth metals. The method appears not to be very successful in calculating the compressibilities, even in the case of the alkali metals (for which, alone, it was tried); but aside from the fact that the compressibilities at absolute zero may only be inferred from measurements around room temperature, it appears that a relatively small correction to the energy expression can give the correct compressibility without greatly upsetting the calculation of the energy. The latter then is to be considered as of significance, and gives some confidence in the essential correctness of the simple picture of the metal described above.

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§1. THE ENERGY OF AN ALKALI OR ALKALINE EARTH METAL

ACCORDING to the simplest possible picture of a metal, it should consist simply of a number of positive ions immersed in a Fermi electron gas. Such a picture is, indeed, capable of explaining and correlating many of the electric and magnetic properties of metals. If it comes anywhere near being a correct representation of the facts, it should also be capable of explaining the binding properties of at least the "most metallic" metals, such as the alkali and alkaline earth metals. A number of attempts have been made to study these binding properties on the basis of more elaborate theories.[1] All these investigations are valuable in throwing light on the nature of the forces operating in metals, but do not lessen the interest in seeing how far the most simple hypotheses will carry us.

The first consideration of the binding properties from this point of view is due to Frenkel.[2] He pointed out that the fact that the electrons obey the Fermi statistics results in what is effectively a repulsive force, which is balanced by the attractive force between the electrons and positive ions, much as the repulsive forces between ions of crystals are balanced by the electrical attraction between the positive and negative ions.

The mathematical formulation of these statements is as follows. In a univalent metal (at the absolute zero of temperature) the average kinetic energy per electron, due to the fact that in the Fermi statistics only two electrons can occupy

[1] See, e.g., Slater, Phys. Rev. **35**, 509 (1930); Taylor, Eyring and Sherman, J. Chem. Phys. **1**, 68 (1933); Wigner and Seitz, paper presented at the Washington meeting of the American Physical Society, April 28, 1933, Phys. Rev. **43**, 1048 (1933). (Just after this paper was submitted their article, Phys. Rev. **43**, 804 (1933) was received.)

[2] Frenkel, Zeits. f. Physik **49**, 31 (1928) especially p. 42; *Wave Mechanics, Elementary Theory*, Oxford University Press, 1932, p. 221 ff.

the same quantum state, is given by the expression

$$\epsilon = \tfrac{3}{5}(3/4\pi G V)^{\tfrac{2}{3}} h^2/2m = p/V^{\tfrac{2}{3}}, \qquad (1)$$

where $G = 2$ is the number of electrons which simultaneously may be in a given quantum state, V is the atomic volume, this being equal to the volume occupied by an electron in a univalent metal, h is Planck's constant, m the mass of an electron, and p is defined by the equation. The potential due to the electrical forces may be written in the form

$$U = -e^2 A V^{-\tfrac{1}{3}}, \qquad (2)$$

where e is the charge on the electron and A is a constant, which may be described as the Madelung constant for the metal.

The total energy of the metal per atom at absolute zero is then given by

$$E = \epsilon + U. \qquad (3)$$

At equilibrium at absolute zero

$$dE/dV = 0. \qquad (4)$$

This puts a condition on V_e, the equilibrium value of V, from which it may be calculated. As Frenkel noted this will give the same value of V_e for all the alkali metals. That this conclusion is not confirmed by the facts, is due, as he pointed out, to the finite size of the ions, and he attempted to correct for it by introducing non-electrostatic repulsive forces between the electrons and ions. On account of the difficulty of evaluating the constants involved, however, no numerical calculations were made.

If, however, in place of introducing these non-electrostatic forces in the form used by Frenkel, we simply correct[3] V in (1) by an amount V_i,

which we may call the intrinsic ionic volume, we get in place of (1)

$$\epsilon = p(V - V_i)^{-\tfrac{2}{3}} \qquad (5)$$

and (3) becomes

$$E = p(V - V_i)^{-\tfrac{2}{3}} - e^2 A V^{-\tfrac{1}{3}}. \qquad (6)$$

This assumes that the expression (2) is not altered by the fact that the ions occupy a finite volume. This cannot be strictly true, but is probably a reasonably good approximation as the forces between the ions and electrons depend largely on the average positions of the electrons; in any event (2) should not be as strongly affected by the finite volume of the ions as (1). Differentiation of (6) gives us

$$-\tfrac{2}{3}p(V_e - V_i)^{-5/3} + \tfrac{1}{3}e^2 A V_e^{-4/3} = 0, \qquad (7)$$

which provides a means of calculating V_i if V_e is known. If we solve for $V_e - V_i$ and put it in (6) we get for E_e, the equilibrium value of E,

$$E_e = p V_e^{-8/15}(e^2 A/2p)^{2/5} - e^2 A V_e^{-\tfrac{1}{3}}. \qquad (8)$$

It is seen that Eq. (8) provides us with a relation between the atomic volume, V_e, and the total energy of the metal, E_e. The latter quantity is the energy which is necessary to completely decom-

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similar nature (though differing somewhat in details) which remain as yet unpublished.

The question as to the exact physical cause of the existence of the intrinsic ionic volume is one about which it seems best not to make any definite statement at present. It has been suggested that it is due to the fact that the only way that a valence electron can get into the region near the nucleus of one of the positive ions is by being a penetrating electron, but such an electron (to speak in terms of the old quantum theory) can, on account of its high velocity while there, spend but a relatively short time in the neighborhood of the nucleus, and this region therefore acts to some extent like a region into which it cannot go. In addition to this, the electron may tend to get "promoted" out of such a penetrating orbit, and thus not go into the neighborhood of the positive nuclei at all, for such promotion, though requiring energy when the atoms are isolated, may actually result in a lowering of energy in the fairly closely packed metallic structure.

It may be well to mention at this point another repulsive potential which comes in, namely, the Heitler-London type repulsion of ions. On account of the large distances between the ions this contributes negligibly to the energy of the system, as is shown by a calculation very kindly sent to me by Dr. J. E. Mayer.

pose the crystal into gaseous ions and electrons at absolute zero. If we subtract from it the energy of ionization of the gaseous atom, we have a value of the energy of sublimation at absolute zero. Eq. (8) thus gives us the possibility of calculating the energy of sublimation from the experimental value of V_e; the result may then be compared with the experimental value of the energy of sublimation, and this comparison should give us some further information as to the validity of the simple electron-gas theory of metals.

In the case of a bivalent metal, if we continue to define V as the atomic volume, and V_i as the intrinsic volume of one ion, the volume $V - V_i$ is occupied by two electrons. This introduces the factor $2^{\frac{1}{3}}$ into the expression for ϵ, Eq. (5). Further, since there are two electrons per atom, if ϵ is to remain the energy per atom, we must introduce another factor of 2. Thus, if, for bivalent metals, we redefine p as $2^{5/3}$ times its former value, and introduce an appropriate new value for the Madelung constant A, we can repeat the argument which led to Eq. (8). Hence with the new values of p and A the latter equation may be taken as applying also to bivalent metals.

In order to apply Eq. (8) to calculate the energy of the metal, it is necessary, as we have mentioned, to use an experimental value of V_e. For the alkali metals, I have used the estimates made by Simon and Vohsen[4] of the atomic volumes at the absolute zero of temperature. For the alkaline earth metals I have simply used the densities calculated from the crystal structure data given by Wyckoff.[5] These data are presumably for room temperature, but since these elements are rather high melting the values should deviate but a very few percent from the values at absolute zero; furthermore, the error thus made should be about the same for all the alkaline earths.

It is also necessary to make some estimate of the value of A. Sherman,[6] in a recent review, has tabulated the values of the Madelung constant

for a number of different crystal structures. For various uni-univalent crystals, which resemble univalent metals, it ranges from about 2.0 to 2.4, while for uni-bivalent crystals which are like bivalent metals it ranges from about 6.5 to 8.0. We have chosen the value 2.08 for the alkali metals, and the value 6.6 for the alkaline earths.

In Table I we have given the results of the application of Eq. (8). The second column gives

TABLE I. *Calculation of the energy of sublimation.*
(All energies in volt-electrons)

Metal	$V_e(A^3)$	ϵ_e	$-U_e$	$-E_e$	I	H_s (calc.)	H_s (expt.)*
Li	20.71	3.704	10.831	7.127	5.368	1.76	1.66
Na	37.60	2.695	8.878	6.183	5.116	1.07	1.13
K	71.6	1.912	7.164	5.252	4.321	0.93	0.94
Rb	87.6	1.717	6.698	4.981	4.159	0.82	0.865
Cs	108.7	1.530	6.232	4.702	3.877	0.825	0.83
Mg	23.5	11.00	32.96	21.96	22.58	−0.62	1.58
Ca	43.0	7.97	26.95	18.98	17.91	1.07	2.06
Sr	55.4	6.96	24.76	17.80	16.65	1.15	1.72
Ba	62.9	6.50	23.73	17.23	15.14	2.09	2.13

* These values are for room temperature, but differ very little from the values for absolute zero.

the value of V_e, and in succeeding columns we have given[7] ϵ_e, U_e and E_e. Finally we have tabulated the ionization potential[8a] (I) and obtained the heat of sublimation (H_s) and compared the latter with the experimental values,[8b] which are tabulated in the last column. It will be seen that the agreement between the calculated and experimental values is very good in the case of the alkali metals, and this is especially notable when we consider that the calculated value of H_s is a rather small difference between two large quantities.[9]

It may be argued that the good agreement is conditional upon the choice of A, in which we are allowed some latitude. This is of course true, but aside from the intrinsic reasonableness of the values of A chosen, we may note that we

[4] Simon and Vohsen, Zeits. f. physik. Chemie **133**, 165 (1928).

[5] Wyckoff, *The Structure of Crystals*, 2nd edition, Chemical Catalog Co., 1931, p. 204.

[6] Sherman, Chem. Rev. **11**, 95 (1932). Table on p. 107. Our A corresponds to Sherman's A_{δ_0}.

[7] Frenkel, Zeits. f. Physik **50**, 234 (1928), has shown that for a system in which all the forces are electrical the kinetic energy will be minus twice the potential energy. In this case, this amounts practically to $|\epsilon| = \frac{1}{2}|U|$. It will be observed that this is not the case in Table I. This is presumably because the introduction of an intrinsic ionic volume implies forces which for our purposes are not electrical forces.

[8] (a) Sherman, reference 6, p. 138; (b) ibid., p. 136.

[9] The following values of V_i/V_e, obtained in the calculation, may be of interest: Li, 0.315; Na, 0.419; K, 0.465; Rb, 0.487; Cs, 0.509.

have used the same value for all the alkali metals, which lends added significance to our calculations, as we see that we reproduce very well the trends in the value of H_s.

In the case of the alkaline earth metals the agreement is by no means so satisfactory, though even here the percentage error in E_e is not large. We have chosen the rather low value of 6.6 for A in order to get good agreement with barium. Of all the alkaline earth metals, barium is the one to which a simple free electron theory would be expected to be the most applicable. With this value of A it is seen that the experimental values show a marked trend away from the theoretical in the case of the alkaline earths, and in every case the experimental value of the heat of sublimation is larger. This is perhaps to be expected, since it implies a lower energy for the metal than we have calculated; if the values of the constants we have used are correct and the theory right as far as it goes, but our results are incorrect through neglect of some factor which ought to be taken into account, we should expect the deviation to be in this direction, since the actual metal will tend to seek the lowest possible energy level. On the other hand, there remains the possibility that the Madelung constant will vary more from metal to metal in the case of the alkaline earths than in the case of the alkalis because of the effect of the more complicated repulsions and attractions on the distribution of the electrons of the former.

§2. THE COMPRESSIBILITY

It should be possible, from the second derivative of E, to get the value of the compressibility at the absolute zero of temperature. We have the general thermodynamic equation

$$P = T(\partial P/\partial T)_V - (\partial E/\partial V)_T, \qquad (9)$$

where P is the external pressure and T is the temperature. From this we see

$$(\partial P/\partial V)_T = T(\partial^2 P/\partial V \partial T) - (\partial^2 E/\partial V^2)_T. \qquad (10)$$

At $T = 0$ the first term on the right drops out, and we may write for the compressibility at equilibrium $(P = 0)$, which is defined as $\kappa_e = - V_e^{-1}(\partial V /\partial P_e)_T$ the well-known relationship

$$\kappa_e = V_e^{-1}[(\partial^2 E/\partial V_e^2)_T]^{-1}. \qquad (11)$$

Differentiating (6) twice and using the relation (7) we find

$$\left(\frac{\partial^2 E}{\partial V_e^2}\right)_T = \frac{10}{9} p\left(\frac{e^2 A}{2p}\right)^{8/5} V_e^{-32/15} - \frac{4}{9} e^2 A V_e^{-7/3}, (12)$$

which may be used in (11) to give the compressibility. It is, however, more satisfactory to compare the theoretical and experimental values of $(\partial^2 E/\partial V_e^2)_T$ and this has been done in Table II.

TABLE II. *Calculation of* $\partial^2 E/\partial V_e^2$.

(All energies in ergs and volumes in cm³—all quantities to be multiplied by 10^{33})

Metal	$\partial^2 \epsilon/\partial V_e^2$	$-\partial^2 U/\partial V_e^2$	$\partial^2 E/\partial V_e^2$ (calc.)	$\partial^2 E/\partial V_e^2$ (expt.)
Li	32.6	17.8	14.8	5.8
Na	9.14	4.44	4.70	1.9
K	2.32	0.99	1.33	0.53
Rb	1.51	0.62	0.89	0.17
Cs	0.95	0.37	0.58	0.065

The experimental values of $(\partial^2 E/\partial V_e^2)_T$ have been computed from the data of Bridgman[10] by the use of Eq. (10). A word as to how this was done will perhaps not be out of place. The method Bridgman uses to present his data is to give $\Delta V/V_0$ as a function of P, the applied pressure. Here ΔV is the change of volume when the substance is compressed from zero pressure to pressure P, and V_0 is some standard volume, usually the volume of the substance at zero pressure and room temperature. ΔV, however, is not the difference between the actual volume of the metal, at pressure P and temperature T, and V_0, but it is the difference between the volume at pressure P and the volume at zero pressure and the same temperature. Bridgman's method of presenting the data is not, however, the most convenient for our purposes, and in Figs. 1 and 2, I have plotted $V_0(\partial P/\partial V)_T$ as a function of $\Delta'V/V_0$. My $\Delta'V$ differs from Bridgman's ΔV in that I have corrected for the thermal expansion where data for more than one temperature is given. Thus, in all cases $\Delta'V$ is the same as ΔV for the lower temperature. For the higher temperature, however, $\Delta'V$ is the difference between the actual volume at the given pressure and temperature and the volume at zero pressure and the lower temperature. (The latter volume may for our purposes be taken as equal to V_0). In this way, the differences in the ordinates of the curves give one directly $V_0(\partial^2 P/\partial V \partial T)$, whence we may get $V_0(\partial^2 E/\partial V^2)_T$ from (10).

In the case of lithium Bridgman gives $\Delta V/V_0$ as a function of P for 30 and 75°C by means of formulas. From these formulas and their derivatives all necessary information is readily obtained. In the case of sodium

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[10] Bridgman, Proc. Am. Acad. **58**, 202 (1923); **60**, 399, 409 (1925).

$\Delta V/V_0$ was given as a function of P for 30 and 75° by means of tables. Approximate values of $V_0(\partial P/\partial V)_T$ were obtained simply by taking differences of $\Delta V/V_0$ over a pressure interval, and dividing into the difference in pressure. These were used as the ordinates for the figure and the mean values of $\Delta V/V_0$ over the intervals were used as the corresponding abscissas. This will give a curve which is very approximately correct. In the case of potassium, data were given in the form of a table, but for 45° only. However the thermal expansion was given as a function of the pressure, and, similarly, in the cases of rubidium and caesium data for only one temperature, 50°C, were given, but it was stated that the thermal expansion was independent of pressure up to 8000 or 9000 kilograms per cm. This enables one to get $\partial^2 P/\partial T\partial V$ in the following way:

$$(\partial P/\partial T)_V = -(\partial P/\partial V)_T(\partial V/\partial T)_P.$$

Hence

$$\partial^2 P/\partial T\partial V = -(\partial^2 P/\partial V^2)_T(\partial V/\partial T)_P$$
$$-(\partial P/\partial V)_T[\partial(\partial V/\partial T)_P/\partial V].$$

The second term on the right-hand side of the last expression drops out for rubidium and caesium, since the thermal expansion is independent of pressure (hence of volume) in the low part of the pressure range, and can be evaluated from the data given for potassium. The first term can also be evaluated in terms of the data given and the thermal expansion. In this way I have obtained sufficient material to calculate $(\partial^2 E/\partial V^2)_T$ for potassium, rubidium, and caesium, and I have given in Table II the value obtained for 45° or 50°C and that particular pressure at which, as nearly as may be judged from the density data,[11] the substances have the same atomic volume as at absolute zero and zero pressure. In all cases I have plotted the values of $V_0(\partial^2 E/\partial V^2)_T$ as a function of $\Delta'V/V_0$ in Figs. 1 and 2 (dotted curves). In each case the value given in Table II is the value for the mean of the temperatures for which curves are drawn and at such a pressure that the substance has an atomic volume equal to that at absolute zero and zero pressure.

It is seen from Table II that there is a considerable discrepancy[12] between the calculated

[11] Landolt-Börnstein Tabellen. The "mean values" of the densities, listed at the side of the tables, were those used.

[12] Professor Slater has pointed out to me that this discrepancy is in the direction to be expected. For if we gradually separate the atoms of a metal and let the electrons go where they will, they will not be uniformly distributed through the space allotted to them, but each one will tend to attach itself to an atom. We thus do not finally arrive at a state of ions and free electrons, but we have instead simply separated atoms. The energy involved in this process is just the energy of sublimation, which is a much smaller quantity than E. If this process is already starting in the actual metal we should expect the minimum of the potential curve to be flattened out, and hence

and experimental values of $(\partial^2 E/\partial V_e^2)_T$. One is tempted to ask whether this discrepancy would still exist, if one could evaluate $(\partial^2 E/\partial V_e^2)_T$ at the absolute zero. It is impossible to answer this question at present, but we may make the following observations. From the calculated values of $(\partial^2 E/\partial V_e^2)_T$ (neglecting the effect of the higher derivatives) it appears that the energy necessary to compress the metal (if it behaved as it should according to the calculation) to 95 percent of V_e would in all cases be around 0.005 volt; to compress it to 90 percent of V_e would require around 0.02 volt. This will give some idea of the amount of energy due to thermal agitation which would have to be "squeezed out" on compression at room temperatures, if that is the cause of the deviation of the experimental value of $(\partial^2 E/\partial V_e^2)_T$ from that calculated for absolute zero. As the value of kT for $T = 300°$ abs. is around 0.026 volt these amounts of energy seem a little large, but not, perhaps, entirely beyond reason. In any event, it is obvious, simply by looking at the curves in Figs. 1 and 2, that
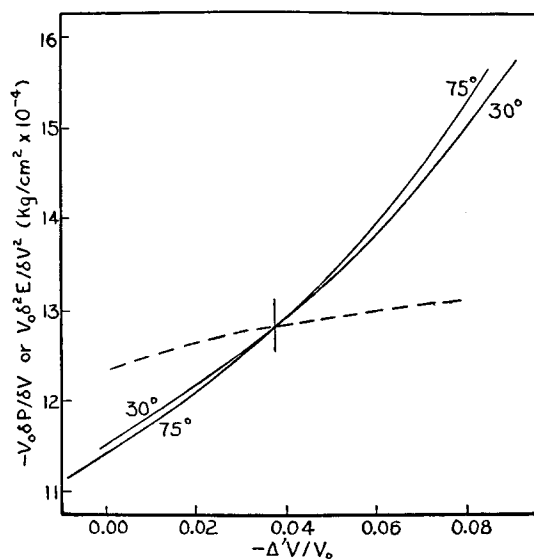

FIG. 1. $V_0\partial P/\partial V$ (solid lines) and $V_0\partial^2 E/\partial V^2$ (broken line) for Li. Vertical line indicates volume at 0°K.

$(\partial^2 E/\partial V_e^2)_T$ will be smaller than calculated. There is nothing in the correction made below which is inconsistent with this view of the behavior of the metal. The Heitler-London type repulsion mentioned[3] will, if taken into account, tend to increase the discrepancy in the compressibilities, but this is presumably not as important as the effect just considered.
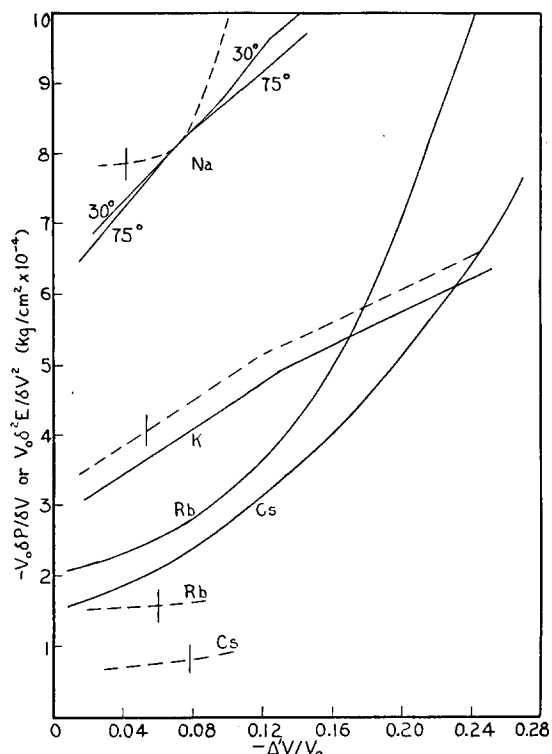
Fig. 2. $V_0\partial P/\partial V$ (solid lines) and $V_0\partial^2 E/\partial V^2$ (broken lines) for the alkali metals except Li. Vertical lines indicate volumes at 0°K.

some theory which neglects fewer things than the present one will be necessary to account for their behavior at a single temperature, and one is tempted to think that this peculiar behavior may have something to do with the thermal motion. This feeling is strengthened by the following considerations. It is possible, from the data given by Bridgman, to calculate $(\partial P/\partial T)_V$ from the relation $(\partial P/\partial T)_V = -(\partial P/\partial V)_T(\partial V/\partial T)_P$. Thus we can evaluate $(\partial E/\partial V)_T$ from (9) and find the value of $\Delta V/V_0$ at which it is zero. This can be compared with the value of $\Delta V/V_0$ which gives a volume, at the temperature considered, equal to the equilibrium volume at absolute zero. This is done in Table III, and it is seen that in general the two values of $\Delta V/V_0$ are not equal. The

Table III. Comparison of volume for which $\partial E/\partial V = 0$ and volume at absolute zero.

	Li (30°C)	Na (30°C)	K (45°C)	Rb (50°C)	Cs (50°C)
$-\Delta V/V_0$ for $\partial E/\partial V = 0$	0.049	0.062	0.053	0.12	0.145
$-\Delta V/V_0$, absolute zero	0.038	0.042	0.053	0.06	0.08

difference may be due to experimental error in the densities and in the compressibility measurements, in the cases of lithium and sodium, but it hardly seems possible that this can account for the very large differences in the cases of rubidium and caesium. These considerations lead us to believe that the deviation between the experimental and theoretical values of $(\partial^2 E/\partial V_e^2)_T$ might well be reduced if we had the correct experimental value for absolute zero, but we cannot draw any definite conclusion.

If we suppose that a considerable discrepancy will still persist at absolute zero, we may then ask whether the calculation of the energy of sublimation retains any significance, considering that its logical extension leads to results not in accord with the facts. Undoubtedly such lack of agreement, assuming, as really seems probable, that some of it at least still persists at absolute zero, is due to the crudity of the picture of the metal we have employed. Nevertheless, it seems entirely possible that such a picture will be of value in determining the energy of the metal, and yet will not be sufficiently exact when we attempt to determine the compressibility, since these two properties will not necessarily be equally sensitive to the errors which may be involved in our approximations.

It will therefore be of interest to see if a modification can be introduced into our expressions which will correct the discrepancy between the observed and calculated values of $(\partial^2 E/\partial V_e^2)_T$ without upsetting the calculation of E_e. To this end we shall make a purely formal modification in U, without attempting to attach any physical significance to it. We write for U, instead of the expression (2), the expression

$$U = -e^2 A V^{-\frac{1}{3}}[1 + \alpha V_e^{-1}(V - V_e)], \quad (13)$$

α being the constant coefficient of what may be called a first order correction term. When $V = V_e$, it will be seen that U has its original form (though we may wish to change the value of A slightly) but the equilibrium condition $(\partial E/\partial V_e)_T = 0$ now yields a slightly different value of $V_e - V_i$. We now have, instead of (7)

$$-\tfrac{2}{3}p(V_e - V_i)^{-5/3} + \tfrac{1}{3}e^2 A V_e^{-4/3}(1 - 3\alpha) = 0, \quad (14)$$

which gives us in place of (8)

$$E_e = p V_e^{-8/15} (e^2 A /2p)^{2/5} (1 - 3\alpha)^{2/5} - e^2 A V_e^{-1/3} \quad (15)$$

and in place of (12)

$$\left(\frac{\partial^2 E}{\partial V_e^2}\right)_T = \frac{10}{9} p \left(\frac{e^2 A}{2p}\right)^{8/5} V^{-32/15} (1 - 3\alpha)^{8/5}$$

$$- (4/9) e^2 A V_e^{-7/3} (1 - (3/2)\alpha). \quad (16)$$

Now if we give α the reasonably small value, 1/6 to 1/14 depending on the metal, we will cure the discrepancies in $(\partial^2 E/\partial V_e^2)_T$, even the very large ones in rubidium and caesium. But such a value of α will increase the value of E_e by amounts varying from 0.2 to 0.35 volt. This change can be met by lowering the value of A .by about 4 percent. While this brings A down to about the lower limit for uni-univalent salts, the value is still quite reasonable, and still with the same value of A for all the alkalis and a suitable value of α we can fit both the energies of sublimation (within about ± 0.12 volt) and the compressibilities. While, as stated above, no special significance is to be attached to the particular form of correction used, it gives us some confidence in the essential correctness of the picture of the metal as composed of a series of singly-charged positive ions in a sea of free electrons, and seems to justify to a considerable extent the idealizations we have made in calculating the heat of sublimation. It must be admitted that corrections can be introduced in a form which is not as favorable to this thesis as the particular one we have used. I believe, however, that the essential point is that U is given pretty well by the expression (2) and that the approximate forms of U and ϵ then suffice to use in the equilibrium condition (4) to obtain a value of $V_e - V_i$ which can be substituted back into the term ϵ, which is relatively unimportant in E; while, on the other hand, $\partial^2 \epsilon/\partial V^2$ is the most important term in $(\partial^2 E/\partial V^2)_T$ and the value of $V_e - V_i$ obtained from the equilibrium condition then becomes of more importance. It might perhaps be more logical, since we admit that some modification of the expression (2) is needed, to also admit that A may vary slightly from one metal to another and compare the experimental and calculated values of E rather than those of H_s. Perhaps we may best state, as our conclusion, simply that the experimental and calculated values of E agree well within the differences which might be expected to occur due to differences in the value of A. This conclusion is still a significant one, for the actual variation in E from one metal to another is much greater than could be expected simply from differences in A.