

## Theory of Molten Alkali Alloys. I. Na-K System\*

J. R. CHRISTMAN

*Department of Physics, Rensselaer Polytechnic Institute, Troy, New York*

AND

H. B. HUNTINGTON

*Department of Physics, Rensselaer Polytechnic Institute, Troy, New York*

and

*Department of Metallurgy, Yale University, New Haven, Connecticut†*

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A theory of liquid alkali-metal alloys is proposed which takes advantage of the absence of structure factors in the diagonal elements of the augmented plane-wave Hamiltonian. The theory is used to calculate volume and compressibility deviations from ideal values for a 50-50 Na-K mixture, with the result that the calculated deviations are of the order of twice those found experimentally. The enthalpy of mixing also turns out too large. The sizes of the atomic cells for sodium and potassium tend to approach somewhat their average value on mixing. Also a small negative charge ( $\sim 0.04e$ ) is predicted to be transferred from the potassium to the sodium cell.

### I. INTRODUCTION

THE pure crystalline alkali metals have as a class been investigated probably more effectively and certainly more repeatedly than any other class of materials. To a large extent this popularity can be attributed to the close resemblance of these metals to the free-electron model as first demonstrated by the classic papers of Wigner and Seitz.<sup>1</sup> Offhand one might imagine that alloys of these metals would prove similarly tractable and exhibit similar free-electron-like propensities. Actually, alloying in the solid state is rare among binary systems of alkalis and in one or two cases there is even immiscibility in the liquid state. It is the difference in lattice parameter or, what is physically more significant, the variation in electron density from one metal to the next that is crucial in determining solubility. We have attempted a general approach to the problem of calculating the energy and related properties of alkali alloys. The initial application, to the 50-50 (atomic concentration) sodium-potassium mixture, serves as a trial run of the method and is described in detail in this report. The physical properties investigated are enthalpy of mixing, compressibility, individual cell sizes (or nearest-neighbor distances), and charge transfer.

In this research it was our aim to concentrate on that aspect of the mixing process which could be reduced to a problem of wave function matching between atomic cells of different electron density. We have chosen a model which we believe represents the liquid state in a simple and consistent manner and, since our interest lies in the mixing problem itself, we have, so far as possible, side-stepped the far more subtle problem of the solid-liquid phase transition. Qualitatively it is clear that in the cell with the smaller dimension and higher electron density one can expect the gradient of the wave

function to be negative at the cell boundary and conversely for the larger cell. It does not follow that the cells are necessarily neutral or even that one can predict the sign of the net cell charges without quantitative calculation.

To formulate our solution, we chose the augmented-plane-wave (APW) approach.<sup>2</sup> According to this method, one constructs a spherical cell around each atom and assumes a spherically symmetric potential within each cell and a constant potential outside all cells. Inside a cell one selects a linear combination of solutions to Schrödinger's equation such that the resulting function joins continuously to a plane wave at the cell boundary. For our problem we limited the number of these plane waves to one per wave function. The radial slope is then allowed to vary and substantial discontinuities can be expected, particularly between like neighbors. The great advantage which results from the use of single APW wave functions is that the calculation of the energy is then independent of the cell geometry, even to the extent that the number of nearest neighbors do not have to be specified. This "looseness" of the model appeared to be an agreeably simple way to simulate the nature of the liquid state.

To determine the wave functions and normal derivatives as functions of energy at the cell boundaries we used the quantum defect method.<sup>3</sup> Following the development of Slater and Saffren,<sup>4</sup> we chose the energy parameters within the cells to coincide with the expectation value of the energy for that electronic state, thus minimizing the expectation value with respect to those parameters. The electron energy is determined to terms in the square of the wave-propagation parameter, and the total energy is obtained by summing over the states below the Fermi energy. In this first effort we neglected the volume outside the atomic cells and dis-

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† Visiting Professor of Metallurgy and Solid State Physics during 1960-61, when this work was begun.

<sup>1</sup> E. P. Wigner and F. Seitz, *Phys. Rev.* **43**, 804 (1933); **46**, 509 (1934).

<sup>2</sup> J. C. Slater, *Phys. Rev.* **92**, 603 (1953).

<sup>3</sup> F. S. Ham, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 1, p. 127.

<sup>4</sup> M. M. Saffren and J. C. Slater, *Phys. Rev.* **92**, 1126 (1953).

regarded the distortions involved in making the cells space filling. It is known that for the pure solids these distortions cause only small corrections to the energy.

In order to compute the exchange-correlation energy we use a correlation-hole density which depends explicitly on the local electron density and on two other parameters, one of which is specified by normalization. The second is chosen so that the expression for the energy is identical to the Pines<sup>5</sup> result when the electron density is uniform throughout the liquid. Closed form solutions to the integrals involved in the exchange-correlation potential do not exist and rather than resort to numerical integration, the potential as a function of distance is fitted to a parabola.

In Sec. II we describe in detail the general approach and give explicit expressions for the energy and cell charge as functions of composition. We then particularize to single component and 50-50 binary systems. In Sec. III we give some of the details of the calculation as well as results for pure sodium, pure potassium and the 50-50 sodium-potassium mixtures. These results are presented and compared with experimental data. In a final Sec. IV we have analyzed the significance of our results and discussed plans for future work.

## II. THEORETICAL ANALYSIS

### A. Wave Function and Energy in the Independent Particle Approximation

We assume a "muffin-tin" potential characterized by the spherically symmetric potential  $V_n$  inside the spherical cell with center at the  $n$ th atom and the constant potential  $V_0$  outside all cells. We take the function  $\psi_k = Ae^{i\mathbf{k}\cdot\mathbf{r}}$  for  $\mathbf{r}$  outside all spheres,

$$\psi_k = Ae^{i\mathbf{k}\cdot\mathbf{R}_n} \sum_l i^l (2l+1) j_l(kr_n) \times (R_{nl}(r, E)/R_{nl}(r_n, E)) P_l(\cos\theta) \quad (1)$$

for  $\mathbf{r}$  inside the  $n$ th sphere, to be the wave function of an electron in the molten metal. Here

$$\begin{aligned} \mathbf{R}_n &= \text{position of } n\text{th atom,} \\ r_n &= \text{radius of the } n\text{th cell,} \\ \theta &= \text{angle between } \mathbf{r} \text{ and } \mathbf{k}, \end{aligned}$$

and  $R_{nl}(r, E)$  satisfies the radial equation

$$-\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR_{nl}}{dr} \right) + \left[ V_n(r) + \frac{l(l+1)}{r^2} - E \right] R_{nl} = 0. \quad (2)$$

Bohr units (energy in Rydbergs, distance in Bohr radii) are used. These wave functions are everywhere continuous but have discontinuous normal derivatives at the cell boundaries.

<sup>5</sup> D. Pines, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 1, p. 367.

The energy parameter  $E$  is chosen, by a variational procedure,<sup>2,4</sup> to be the expectation value of the energy in the  $k$ th state. Thus  $E(\mathbf{k})$  satisfies

$$[E(\mathbf{k}) - k^2 - V_0] \omega = 4\pi \sum_n r_n^2 \times \sum_l (2l+1) j_l^2(kr_n) \phi_{nl}(r_n, E), \quad (3)$$

where

$$\omega = \text{volume not enclosed by spheres}$$

and

$$\phi_{nl} = \frac{1}{R_{nl}(r_n, E)} \left[ \frac{d}{dr} R_{nl}(r, E) \right]_{r=r_n}.$$

In spite of the fact that  $kr_n$  is greater than unity for many occupied states, theoretical investigations have shown that energies and wave functions may be represented, to a sufficiently good approximation, by expressions which are linear in  $k^2$ . The coefficients of higher order terms are small. We neglect these terms and write

$$E(k) = E_0 + k^2 E_2$$

and

$$\phi_{nl}(r_n, E) = \phi_{nl}(r_n, E_0) + k^2 E_2 [\partial \phi_{nl}(r_n, E) / \partial E]_{E=E_0}.$$

For convenience in writing this and later expressions, let

$$\begin{aligned} F_n(r_n, E_0) &= \phi_{n0}(r_n, E_0), \\ P_n(r_n, E_0) &= \phi_{n1}(r_n, E_0), \\ W_n(r_n, E_0) &= r_n^2 [\partial \phi_{n0}(r_n, E) / \partial E]_{E=E_0}. \end{aligned}$$

We also take  $\omega = 0$ . Then (3) becomes

$$\sum_n r_n^2 F_n(r_n, E_0) + \sum_n k^2 \left[ -\frac{1}{3} r_n^4 (F_n - P_n) + E_2 W_n \right] = 0$$

to order  $k^2$ . Thus  $E_0$  is the solution to

$$\sum_n r_n^2 F_n(r_n, E_0) = 0$$

and

$$E_2 = \frac{1}{3} \left( \sum_n r_n^4 (F_n - P_n) / \sum_n W_n \right).$$

The average electronic energy  $E_{av}$  is

$$E_{av} = E_0 + 0.6 k_F^2 = E_0 + \bar{E}_F,$$

where

$$k_F = (1/r_s)(9\pi/4)^{1/3}$$

and

$$r_s^3 = (1/N) \sum_n r_n^3.$$

For a binary system with concentrations  $x_1$  and  $x_2$  of components 1 and 2, respectively, the average energy is

$$E_{av} = E_0 + 0.6 k_F^2 E_2, \quad (4)$$

with

$$x_1 r_1^2 F_1 + x_2 r_2^2 F_2 = 0 \quad (5)$$

and

$$E_2 = \frac{1}{3} (x_1 r_1^4 (F_1 - P_1) + x_2 r_2^4 (F_2 - P_2)) / (x_1 W_1 + x_2 W_2). \quad (6)$$

Now

$$r_s^3 = x_1 r_1^3 + x_2 r_2^3. \quad (7)$$

In general, the potential  $V_n$  appearing in (2) is unknown although potentials which reproduce crystalline energy levels have been invented. We chose rather to employ the quantum defect method to obtain the derivatives  $\phi_{nl}(r_n, E_0)$ , (see Ham<sup>3</sup>). For the outer regions of the cell the functions  $R_{nl}(r, E)$  can be written as linear combinations of the two solutions to the hydrogen problem:

$$R_{nl}(r, E) = (1/r)[U_l^{(0)}(r, E) - \tan\pi\eta_{nl}U_l^{(1)}(r, E)]. \quad (8)$$

The particular choice of the functions  $U_l^{(0)}(r, E)$  and  $U_l^{(1)}(r, E)$ , and the determination of the “ $\eta$  defects” as a function of  $E$  are discussed in detail by Ham.<sup>3</sup> We have used the “unmodified defects” which do not include the effects of core polarization on the free-atom levels. In principle, one should correct for polarization in the free atom and then include a polarization term in the liquid energy. Some discussion of this approximation appears in the final section.

### B. Electron-Electron Interaction

When the space occupied by the liquid can be divided into  $N$  cells such that each surrounds one ion and the cells are space filling, then the Coulomb and exchange-correlation energies per electron can be written

$$E_c = \frac{1}{N} \sum_n \int \int_{\text{volume of } n\text{th cell}} \frac{\rho_n(\mathbf{r}_1)\rho_n(\mathbf{r}_2)}{r_{12}} d\tau_1 d\tau_2$$

and

$$E_{ec} = \frac{1}{N} \sum_n \int_{\text{all space}} d\tau_2 \int_{\text{volume of } n\text{th cell}} \frac{\rho_n(\mathbf{r}_1, \mathbf{r}_2)\chi(r_1, r_2)}{r_{12}} d\tau_1.$$

$$E_{ec} = -\frac{1}{N} \sum_n \frac{0.6}{\sqrt{(2\pi)}} K q_n \left\{ 1 + \frac{r_s}{r_n} q_n^{1/3} + \left(\frac{\pi}{8}\right)^{1/2} \frac{1}{K r_n} [H(\sqrt{2}K r_n) - H(\sqrt{2}K r_n q_n^{1/3})] \right\} \\ - \frac{1}{N} \sum_n \frac{0.8}{\sqrt{(2\pi)}} K q_n \left\{ \frac{r_s}{r_n} q_n^{1/3} [1 - \exp(-\frac{1}{2}K^2 r_s^2 q_n^{2/3})] + \exp(-\frac{1}{2}K^2 r_n^2) \right\}, \quad (9)$$

where

$$H(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-\alpha^2} d\alpha$$

is the error integral.

The Coulomb energy  $E_c$  can be written

$$E_c = (1/N) \sum_n 1.2(q_n^2/r_n)$$

and the total electron-electron interaction energy for a binary system

$$E_{\text{int}} = E_c + E_{ec}. \quad (10)$$

Originally an approximate electron-electron potential

Here

$$r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|,$$

$$\rho_n = \text{electronic number density in the } n\text{th cell,}$$

and

$$\chi(\mathbf{r}_1, \mathbf{r}_2) = \text{exchange-correlation density.}$$

We assume that  $\rho_n$  is the constant  $3q_n/4\pi r_n^3$ , where  $q_n$  is the number of conduction electrons in the  $n$ th cell and that  $\chi$  has the form

$$\chi(\mathbf{r}_1, \mathbf{r}_2) = A(\rho_n/\rho_0) \exp[-\frac{1}{2}r_{12}^2 K^2 (\rho_n/\rho_0)^{2/3}],$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are both in the  $n$ th cell. When  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are in different cells, we assume that on the average the density outside the cell of interest is the uniform background density  $\rho_0$  and obtain  $\chi(\mathbf{r}_1, \mathbf{r}_2) = A \exp[-\frac{1}{2}r_{12}^2 K^2]$ , ( $\mathbf{r}_1$  and  $\mathbf{r}_2$  in different cells). The average density  $\rho_0$  is given by

$$\rho_0 = (3/4\pi r_s^3)$$

and the constants  $K$  and  $A$  are chosen so that when  $\rho_n = \rho_0$  for all  $n$  then the correlation-exchange charge is unity and the expression for the energy is that given by Pines.<sup>5</sup> The first condition leads to

$$A = -(K/\sqrt{(2\pi)})^3$$

and the second to

$$K = (\frac{1}{2}\pi)^{1/2} \left[ \frac{0.916}{r_s} + 0.140 - 0.0626 \ln r_s + 0.0028 r_s \right].$$

Evaluation of the energy was carried out by fitting the exchange-correlation potential to a parabola through the values at the center and boundary of the spherical cell. The explicit equation obtained for  $E_c$  is

was included in the Schrödinger equation itself. The results of the above perturbation technique, however, did not differ from those obtained by the earlier method by more than  $10^{-5}$  Ry.

### C. Normalization and Charge Transfer

The number of electrons  $q_n$  in the  $n$ th cell is related to all of the  $r_n$  and to  $E_0$  through the equation

$$q_n = \frac{V}{\pi^2} \int_0^{k_F} k^2 dk \int_{\text{volume of } n\text{th cell}} \psi_k^* \psi_k d\tau_n \quad (11)$$

TABLE I. Computed parameters and energies for potassium (Bohr units).

$r_K$	4.6	4.7	4.8	4.9	5.0
$k_F$	0.417208	0.408331	0.399824	0.391664	0.383831
$E_0$	-0.503850	-0.498786	-0.493665	-0.488476	-0.483295
$E_2$	1.10522	1.09996	1.09522	1.09094	1.08608
$\bar{E}_F$	0.115427	0.110040	0.105048	0.100411	0.096006
$E_c$	0.260869	0.255319	0.250000	0.244897	0.240000
$E_{sc}$	-0.256479	-0.251176	-0.246077	-0.241172	-0.236449
$E_{av}$	-0.384033	-0.384603	-0.384694	-0.384340	-0.383738

subject to the normalization condition

$$\sum_n \int_{\text{volume of } n\text{th cell}} \psi_k^* \psi_k d\tau_n = 1. \quad (12)$$

It can be shown that

$$\int_{\text{volume of } n\text{th cell}} \psi_k^* \psi_k d\tau_n = -\sum_l 4\pi r_n^2 (2l+1) \times j_l^2(kr_n) (\partial \phi_{nl} / \partial E) |A|^2 \approx -4\pi |A|^2 [W_n + k^2 U_n],$$

where the last expression is valid to order  $k^2$  and

$$U_n = r_n^2 [E_2 \partial^2 \phi_{n0}^* / \partial E^2 |_{E=E_0} + \frac{1}{3} r_n^2 \partial \phi_{n1} / \partial E |_{E=E_0} - \frac{1}{3} r_n^2 \partial \phi_{n0} / \partial E |_{E=E_0}].$$

The normalization condition (12) yields

$$|A|^2 = -\frac{1}{4\pi} \left[ \frac{1}{\sum_n W_n} - \frac{\sum_n U_n}{(\sum_n W_n)^2} k^2 \right]$$

and this value substituted into (11) gives

$$q_n = N \left[ \frac{W_n}{\sum_j W_j} + 0.6 k_F^2 \frac{U_n \sum_j W_j - W_n \sum_j U_j}{(\sum_j W_j)^2} \right].$$

For the binary system

$$q_1 = \frac{W_1}{x_1 W_1 + x_2 W_2} + 0.6 k_F^2 \frac{x_2 (U_1 W_2 - U_2 W_1)}{(x_1 W_1 + x_2 W_2)^2}$$

and

$$q_2 = \frac{W_2}{x_1 W_1 + x_2 W_2} + 0.6 k_F^2 \frac{x_1 (U_2 W_1 - U_1 W_2)}{(x_1 W_1 + x_2 W_2)^2}.$$

For the binary system it is sometimes convenient to use the charge transfer  $y_n$  defined by

$$q_n = 1 + y_n.$$

Equations valid for a one-component system are derived from those for the binary system by setting  $x_1=1$  and  $x_2=0$ . Thus

$$E_{av} = E_0 + 0.6 k_F^2 E_2 + E_{int},$$

where  $E_0$  is the solution to

$$F(r_s, E_0) = 0, \\ E_2 = -\frac{1}{3} (r_s^4 P/W),$$

and

$$E_{int} = (1.2/r_s) - (0.916/r_s) - 0.140 + 0.0626 \ln r_s - 0.0028 r_s.$$

The equation for the charge  $q$  gives  $q=1$  identically.

### III. METHOD OF CALCULATION AND RESULTS

#### A. Method of Calculation

The functions

$$U_l^{(0)}(r, E), \\ U_l^{(1)}(r, E), \\ D_l^{(0)}(r, E) = r(\partial/\partial r) U_l^{(0)},$$

and

$$D_l^{(1)}(r, E) = r(\partial/\partial r) U_l^{(1)}$$

are tabulated by Blume, Briggs, and Brooks<sup>6</sup> for values of  $r$  from 2.0 to 8.3 in intervals of 0.1, values of  $E$  from -0.07 to -1.20 in intervals of 0.01, and for  $l=0, 1$ , and 2. Thus

$$F_n = -\frac{1}{r_n} \left[ \frac{D_0^{(0)}(r_n, E_0) - \tan \pi \eta_{n0} D_0^{(1)}(r_n, E_0)}{U_0^{(0)}(r_n, E_0) - \tan \pi \eta_{n0} U_0^{(1)}(r_n, E_0)} - 1 \right]$$

and

$$P_n = -\frac{1}{r_n} \left[ \frac{D_1^{(0)}(r_n, E_0) - \tan \pi \eta_{n1} D_1^{(1)}(r_n, E_0)}{U_1^{(0)}(r_n, E_0) - \tan \pi \eta_{n1} U_1^{(1)}(r_n, E_0)} - 1 \right]$$

can easily be computed for those values of the arguments which are tabulated. Values of  $F_{Na}$ ,  $P_{Na}$ ,  $F_K$ ,  $P_K$  were calculated for the ranges of  $r_{Na}$  or  $r_K$  and  $E_0$  of interest, namely from about the pure crystal values to slightly beyond the average values. The intervals here were also 0.1 for  $r$  and 0.01 for  $E_0$ . Derivatives with respect to energy were obtained by taking first and second differences. All computations were made by means of a desk calculator.

For the mixture, relevant quantities were computed in terms of  $\Delta\Gamma = \Gamma - \Gamma_0$  and  $r_{Na}$ . Here  $\Gamma = 2r_s^3$  and

TABLE II. Computed parameters and energies for sodium (Bohr units).

$r_{Na}$	3.7	3.8	3.9	4.0	4.1
$k_F$	0.518691	0.505041	0.492091	0.479789	0.468087
$E_0$	-0.629227	-0.621474	-0.613561	-0.605562	-0.597540
$E_2$	1.01699	1.01534	1.01579	1.01532	1.01481
$\bar{E}_F$	0.164166	0.155387	0.147586	0.140234	0.133410
$E_c$	0.324324	0.315789	0.307692	0.300000	0.292682
$E_{sc}$	-0.316026	-0.308121	-0.300594	-0.293418	-0.286566
$E_{av}$	-0.456763	-0.458419	-0.458877	-0.458746	-0.458014

<sup>6</sup> M. Blume, N. Briggs, and H. Brooks, Technical Report No. 260 Croft Laboratory, Harvard University, 1959 (unpublished).

TABLE III. Energy parameters and charge transfer for Na-K (Bohr units).

$r_{\text{Na}}$	3.9	4.0	4.1	4.2	4.3	4.4
	$\Delta\Gamma = +10$					
$E_0$			-0.537900	-0.539818	-0.541241	-0.542083
$\bar{E}_F$			+0.115598	+0.115538	+0.115467	+0.115426
$E_c$			+0.269577	+0.269847	+0.271418	+0.274312
$E_{cc}$			-0.264420	-0.264621	-0.264801	-0.264962
$E_{\text{av}}$			-0.417145	-0.419054	-0.419157	-0.417307
$y$			-0.061023	+0.004245	+0.070210	+0.136983
	$A = -0.419157, B = +0.00849, C = +0.09765, D = 0.0245$					
	$\Delta\Gamma = 0$					
$E_0$		-0.542601	-0.544764	-0.546377	-0.547376	
$\bar{E}_F$		+0.120415	+0.120331	+0.120266	+0.120217	
$E_c$		+0.274877	+0.274777	+0.276092	+0.278908	
$E_{cc}$		-0.269223	-0.269444	-0.269644	-0.269844	
$E_{\text{av}}$		-0.416532	-0.419100	-0.419663	-0.418095	
$y$		-0.079832	-0.021864	+0.054943	+0.124452	
	$A = -0.419663, B = +0.004815, C = +0.10655, D = +0.021$					
	$\Delta\Gamma = -10$					
$E_0$	-0.547486	-0.549864	-0.551690	-0.552841		
$\bar{E}_F$	+0.125749	+0.125655	+0.125578	+0.125537		
$E_c$	+0.280700	+0.280236	+0.281323	+0.283973		
$E_{cc}$	-0.274420	-0.274655	-0.274888	-0.275094		
$E_{\text{av}}$	-0.415457	-0.418628	-0.419677	-0.418425		
$y$	-0.096675	-0.028116	+0.042064	+0.112842		
	$A = -0.419677, B = +0.00072, C = +0.11505, D = +0.030$					

$\Gamma_0 = (3.9)^3 + (4.8)^3 = 169.911 a_h^3$ , a close approximation to the sum of the cubes of the pure component values. Because the several contributions to the average energy are strongly dependent, the order of computation is fairly rigidly set. For selected values of  $r_s$  and  $r_{\text{Na}}$ ,  $E_0$  was computed by linear extrapolation between the two tabulated energies which produced the smallest magnitudes of  $x_{\text{Na}}r_{\text{Na}}^2F_{\text{Na}} + x_{\text{K}}r_{\text{K}}^2F_{\text{K}}$ . Functions appearing in the expressions for  $E_2$  and the charge were also computed by means of linear extrapolation in  $r_k$  and  $E_0$ .

For a given  $\Delta\Gamma$ ,  $E_{\text{av}}$  was fitted to a cubic through the four values of  $r_{\text{Na}}$  closest to its minimum and the resulting expression minimized with respect to  $r_{\text{Na}}$ . The quantity  $y = q_{\text{Na}} - 1$  was also fitted to a cubic and the resulting expression used to find  $y$  at the equilibrium  $r_{\text{Na}}$ . The procedure described above was carried out for  $\Delta\Gamma = -10 a_h^3$ , 0, and  $+10 a_h^3$  and, with  $E_{\text{av}}$  fitted to a quadratic in  $\Delta\Gamma$ , the equilibrium volume, equilibrium energy, and compressibility were computed.

The relevant equations simplify considerably for a one-component liquid, as was noted in the previous section. With the equation given there we computed  $E_{\text{av}}$  as a function of  $r_{\text{Na}}$  for pure sodium and for pure potassium and, with the results of the three calculations, we computed the enthalpy of mixing and the deviation of volume and compressibility from ideal mixture values.

## B. Results

The various contributions to the energy are given in Tables I through IV. We give here cubic expressions which fit  $E_{\text{av}}$  at the four points closest to its minimum,

a listing of equilibrium values, and some discussion of the results. Experimentally determined compressibilities when quoted are from Abowitz and Gordon<sup>7</sup> whose measurements were at  $T = 100^\circ\text{C}$ . Experimental cell radii were computed from density measurements reported in the Sodium-Potassium Supplement of the Liquid Metals Handbook,<sup>8</sup> and are also at  $T = 100^\circ\text{C}$ . Graphical interpolation of experimental data was used when necessary.

1. *Pure potassium* (see Table I).  $E_{\text{av}}$  was fitted to a cubic at  $r_{\text{K}} = 4.6, 4.7, 4.8,$  and  $4.9$  with the result

$$E_{\text{av}} = -0.384694 + 0.001372(r_{\text{K}} - 4.8) + 0.02225(r_{\text{K}} - 4.8)^2 - 0.005667(r_{\text{K}} - 4.8)^3.$$

TABLE IV. Na-K parameters as functions of volume (Bohr units).

$\Delta\Gamma$	-10	0	+10
$r_s$	4.3081	4.3961	4.4807
$r_{\text{Na}}$	4.0969	4.1773	4.2558
$r_{\text{K}}$	4.5004	4.5950	4.6850
$E_0$	-0.551643	-0.546062	-0.540678
$\bar{E}_F$	+0.125580	+0.120279	+0.115497
$E_c$	+0.281266	+0.275665	+0.270562
$E_{cc}$	-0.274881	-0.269599	-0.264724
$E_{\text{av}}$	-0.419678	-0.419717	-0.419343
$y$	+0.039861	+0.039425	+0.040955

<sup>7</sup> G. Abowitz and R. B. Gordon, J. Chem. Phys. **37**, 125 (1962).

<sup>8</sup> *Liquid Metals Handbook, Sodium-NAK Supplement*, edited by C. B. Jackson *et al.* (U. S. Government Printing Office, Washington, D. C., 1965).

At the minimum of  $E_{av}$ ,

$$r_K = 4.7695a_h,$$

$$E_{av} = -0.384715 \text{ Ry},$$

and

$$d^2E_{av}/dr_K^2 = 0.044693 \text{ Bohr units.}$$

Thus the calculated compressibility  $\beta_K$  is

$$\beta_K = 12r_K/(d^2E_{av}/dr_K^2) = 4.023 \times 10^3 \text{ Bohr units}$$

$$= 27.36 \times 10^{-12} \text{ cm}^2/\text{dyn.}$$

This value is to be compared with the experimental value of  $34.9 \pm 0.2 \times 10^{-12} \text{ cm}^2/\text{dyn.}$  Experimentally  $r_K = 5.030a_n$ .

It is of interest to note the various contributions to the first and second derivatives of  $E_{av}$  with respect to  $r_K$  and they are listed in the following table:

$$dE_0/dr_K = +0.0513, \quad d^2E_0/dr_K^2 = +0.006,$$

$$d\bar{E}_F/dr_K = -0.0492, \quad d^2\bar{E}_F/dr_K^2 = +0.037,$$

$$dE_c/dr_K = -0.0527, \quad d^2E_c/dr_K^2 = +0.022,$$

$$dE_{ec}/dr_K = +0.0506, \quad d^2E_{ec}/dr_K^2 = -0.020.$$

2. *Pure sodium* (see Table II). Here

$$E_{av} = -0.458877 - 0.001655(r_{Na} - 3.9)$$

$$+ 0.02945(r_{Na} - 3.9)^2.$$

This expression is the first three terms of a cubic expansion fit at  $r_{Na} = 3.8, 3.9, 4.0,$  and  $4.1$ . Our calculation lacked the accuracy necessary to obtain the fourth term. At the minimum of  $E_{av}$ ,

$$r_{Na} = 3.9280a_h,$$

$$E_{av} = -0.458900 \text{ Ry},$$

and

$$d^2E_{av}/dr_{Na}^2 = 0.059236 \text{ Bohr units.}$$

These values lead to a compressibility  $\beta_{Na}$  of

$$\beta_{Na} = 2.50 \times 10^3 \text{ Bohr units} = 17.0 \times 10^{-12} \text{ cm}^2/\text{dyn}$$

as compared to the experimental value of

$$16.91 \pm 0.07 \times 10^{-12} \text{ cm}^2/\text{dyn.}$$

Experimentally  $r_{Na} = 4.049 a_h$ .

For sodium the contributions to the first and second derivatives of  $E_{av}$  are

$$dE_0/dr_{Na} = +0.0799, \quad d^2E_0/dr_{Na}^2 = +0.010,$$

$$d\bar{E}_F/dr_{Na} = -0.0746, \quad d^2\bar{E}_F/dr_{Na}^2 = +0.047,$$

$$dE_c/dr_{Na} = -0.0778, \quad d^2E_c/dr_{Na}^2 = +0.039,$$

$$dE_{ec}/dr_{Na} = +0.0725, \quad d^2E_{ec}/dr_{Na}^2 = -0.035.$$

3. *50-50 sodium-potassium mixture* (see Tables III and IV). For this case minimization of  $E_{av}$  with respect to  $r_{Na}$  was accomplished at each volume by means

of a cubic expression fit to the four points closest to the minimum. Table III gives the various contributions to the energy as well as the coefficients in the expressions

$$E_{av} = A + B(\Delta r_{Na}) + C(\Delta r_{Na})^2 + D(\Delta r_{Na})^3.$$

In each case  $\Delta r_{Na} = r_{Na} - r_{Na0}$  with  $r_{Na0}$  equal to the tabulated value for which  $E_{av}$  is closest to its minimum. The charge transfer  $y$ , defined so that there are  $1+y$  electrons in a sodium cell and  $1-y$  electrons in a potassium cell, is also given. Note that at a given volume the greatest variation occurs in  $E_0$  and  $E_c$  and it is chiefly the balancing of these two energies which determines the relative cell sizes.

$$\partial E_0/\partial r_{Na} = -0.0145,$$

$$\partial \bar{E}_F/\partial r_{Na} = -0.0006,$$

$$\partial E_c/\partial r_{Na} = +0.0171,$$

$$\partial E_{ec}/\partial r_{Na} = -0.0020.$$

Table IV gives the equilibrium values of the various quantities as functions of  $\Delta\Gamma$ .  $E_{av}$  was fitted to the quadratic expression

$$E_{av} = -0.419717 + 0.001675(\Delta\Gamma/100)$$

$$+ 0.02065(\Delta\Gamma/100)^2$$

and the following values were obtained at equilibrium:

$$\Delta\Gamma = -4.0556,$$

$$\Gamma = 165.855,$$

$$r_{Na} = 4.1449,$$

$$r_K = 4.5572,$$

$$E_{av} = -0.419751.$$

All four terms contribute about equally to the derivatives of  $E_{av}$  with respect to volume.

The compressibility  $\beta$  was found to be

$$\beta = (2\pi/3)(\Gamma \partial^2 E/\partial \Gamma^2)^{-1} = 3.057 \times 10^{-3} \text{ Bohr units}$$

$$= 20.79 \times 10^{-12} \text{ cm}^2/\text{dyn.}$$

#### IV. DISCUSSION OF RESULTS AND FUTURE PLANS

The calculation presented here is intended to give changes of the various physical quantities on alloying and as such does not include some contributions which would be required for accurate computations of the quantities themselves. In the first part of this section we shall discuss the corrections as they affect the results given in Sec. III, while in a second part we shall test the assumption that their change on alloying is negligible by comparing our values with experimental results. The final paragraph of this section gives an outline of future plans.

*Discussion and Assumptions.* For our calculation the basic equation, which incorporates only diagonal ele-

ments of the Hamiltonian, is

$$4\pi \sum_n r_n^2 \sum_l (2l+1) j_l^2(kr_n) \phi_{nl}(r_n, E) = 0.$$

It does not depend on the structure of the material and yet takes into account the average of the wave-function distortion which arises from the accommodation of neighboring cells. Off-diagonal elements, which involve the correlation in atomic positions, have been largely ignored up to this point.

The radii which appear in the basic equation are equivalent sphere radii and the potentials due to the single ion core are artificially extended throughout the equivalent spheres. In reality there are regions in both solid and liquid where the potential can be better approximated by a constant. Addition of the term

$$[E - k^2 - V_0]\omega$$

to the left side of the basic equation partially corrects for the "free volume" in such a way that structure is not introduced. Now the radii are no longer equivalent sphere radii. In the solid they are usually taken to be inscribed sphere radii although, with the proper choice of  $V_0$ , the results should not be sensitive to small changes in their values.

A second correction, which takes into account atomic correlations and which requires the use of off-diagonal elements for its description, is needed. For the solid, correlations are specified when the lattice or reciprocal lattice is given. Hence, the atomic correlation correction reduces to a boundary-condition whereby functions with propagation vectors differing from  $\mathbf{k}$  by a reciprocal lattice vector are added to the original wave with proper amplitude to satisfy the Bloch boundary conditions on the polyhedral cell. For the liquid, no such symmetry exists and the augmented-plane-wave states are mixed to a larger extent. One would expect the influence of configuration interaction to be strongest near the zone boundaries but the alkalis, because their Fermi surfaces are nearly spherical, have few electrons in these states. For the pure molten metals this may be less true as the melting process tends to disperse the critical interaction regions more broadly in  $k$  space. With alloying, the regions may be still further widened because of the disparity in cell size. Conceivably, these considerations may have bearing on the energetics of alloying.

As a check for our procedure we compared our results for the pure metals against calculations by Ham<sup>9</sup> and Brooks<sup>10</sup> designed for the crystalline state. On the whole agreement was satisfactory. Discrepancies between our results and those of Brooks, who used essentially the same boundary conditions, are explained by consideration of the free-atom polarization correction and our omission of the term in  $K_F^4$ . We carried out a potassium calculation which included the polarization correction and used a cutoff radius equal to the equivalent

sphere radius. Results are given below (in Bohr units):

$r_s$	4.7	4.8	4.9
$E_0$	-0.4950	-0.4906	-0.4860
$E_2$	1.164	1.153	1.142

These values, when interpolated to the  $r_s$  value used by Brooks, check quite well with those obtained by him.

In his use of Green's-function technique, Ham took explicit account of structure considerations. His results do not appear to be significantly different from ours.

Correction for free atom polarization leads to a much larger equivalent sphere radius, a smaller compressibility, and a larger average energy as shown below for potassium (in Bohr units):

	no polarization	polarization	experimental
$r_s$	4.77	4.98	4.86
$E_{av}$	-0.385	-0.378	-0.389
$\beta$	$4.02 \times 10^3$	$3.90 \times 10^3$	$3.68 \times 10^3$ (solid) $5.13 \times 10^3$ (liquid)

Except for the liquid compressibility value which was measured at  $T=373^\circ\text{K}$ , the "experimental" values are obtained by extrapolation to  $0^\circ\text{K}$ . The experimental value of  $E_{av}$  is the heat of sublimation plus the ionization energy.

Omission of free atom polarization corrections leads to values of  $E_{av}$  close to the measured value, and so seems justified for a preliminary calculation (for this reason they were ignored for the first run through). The calculated equilibrium  $r_s$  and compressibility, however, are too small.

*Discussion of alloying.* Having compared our calculations for the pure substances with solid-state calculations, we now compare the changes on alloying of the various quantities with experimental results. If sodium and potassium alloyed according to the laws of ideal mixing, then the atomic volume  $V_{IM}$  for the mixture would be given by Vegard's law:

$$V_{IM} = x_{Na} V_{Na} + x_K V_K,$$

where  $V_{Na}$  and  $V_K$  are the atomic volumes for the pure substances and  $x_{Na}$  and  $x_K$  are the atomic concentrations. The compressibility  $\beta_{IM}$  of the ideal mixture would be

$$\beta_{IM} = (1/V_{IM}) [x_{Na} V_{Na} \beta_{Na} + x_K V_K \beta_K],$$

where  $\beta_{Na}$  and  $\beta_K$  are the compressibilities of the pure materials. In Table V the ideal mixture values are given and compared with results for the actual mixture. Experimental data for atomic volume were derived from data given in the Sodium-Potassium Supplement of the Liquid Metals Handbook<sup>8</sup> and for compressibility from Abowitz and Gordon.<sup>7</sup> In all cases interpolation of experimental data was necessary. Calculated deviations from ideal mixing values of both volume and compressibility compare favorably as to sign and order of magnitude with experimental values.

<sup>9</sup> F. S. Ham, Phys. Rev. **128**, 82 (1962).

<sup>10</sup> H. Brooks, Nuovo Cimento Suppl. **7**, 165 (1958).

TABLE V. Deviations from ideal mixture values.

	Sodium	Potassium	Ideal mixture (50-50)	Mixture (50-50)	Percent deviation (%)
Atomic volume (Bohr units) calculated	253.87	454.47	354.17	347.37	-1.9
Atomic volume (Bohr units) experimental 100°C	277.97	533.05	405.51	400.79	-1.2
Compressibility (Bohr units) calculated	$2.50 \times 10^8$	$4.02 \times 10^8$	$3.48 \times 10^8$	$3.06 \times 10^8$	-12.1
Compressibility (Bohr units) experimental 100°C	$2.49 \times 10^8$	$5.14 \times 10^8$	$4.23 \times 10^8$	$3.96 \times 10^8$	-6.4

The first three columns of Table VI summarize calculated quantities previously given; the fourth gives the average of sodium and potassium values and the fifth the change on mixing.  $E_{av}$  increases by 0.0021 Ry per atom or 655 cal per mole. This is to be compared with the experimental value<sup>11</sup> of 175 cal per mole at 111°C. We have neglected a small correction to  $E_{av}$  of the mixture due to cell-cell interaction. At finite temperatures, the distribution of spheres about a given sphere will not be 50-50 but, because of the charge transfer, unlike spheres will tend to attract each other. Boltzmann statistics were used to find the probable number of nearest neighbors of each kind and the electrostatic energy was calculated. Using the cell sizes and charges given in Sec. III, we find the energy of mixing at 100°C is reduced by about 0.00029 Ry per atom or 90 cal per mole to 565 cal per mole.

TABLE VI. Mixing energies for Na-K.

	Sodium	Potassium	Na-K (50-50)	Average of Na and K	NaK-Av
$E_0$	-0.611326	-0.495232	-0.548302	-0.553219	+0.004977
$E_F$	+0.145477	+0.106529	+0.122366	+0.126003	-0.003637
$E_c$	+0.305498	+0.251597	+0.277877	+0.278547	-0.000670
$E_{cc}$	-0.298549	-0.247609	-0.271692	-0.273079	+0.001387
$E_{av}$	-0.458900	-0.384715	-0.419751	-0.421808	+0.002057

<sup>11</sup> T. Yokokawa and O. J. Kleppa, J. Chem. Phys. (to be published).

The error in the enthalpy change is, of course, reflected in the free energy change and is such that immiscibility is predicted. The ideal mixing part of the entropy change,  $k \ln 2$ , contributes  $-T\Delta S = -514$  cal per mole at 100°C to  $\Delta F$ . Using the values of  $\Delta S$  quoted by Hultgren *et al.*,<sup>12</sup> we find a deviation from ideal mixing of about 36 cal per mole so that  $-T\Delta S = -478$  cal per mole at 100°C and  $\Delta F = +87$  cal per mole. Thus, our calculated free energy is just slightly too large to produce binding but is much larger than the measured result,  $-260$  cal per mole, given by Hultgren *et al.*<sup>12</sup> Possibly this shortcoming of the theory could be corrected by consideration of configuration interactions.

*Future Plans.* We expect to investigate in a more systematic way some of the corrections discussed in the first part of this section. In particular the role played by  $\omega$  (the volume outside the spherical cells) will be studied in greater detail and an attempt will be made to take into account the temperature variation of the thermodynamic quantities. In addition we wish to apply the analysis developed to the alloying of other alkalis with the hope of understanding miscibility of these elements. Some consideration will be given to possible short-range order.

*Note added in proof.* More recent work incorporating the quantum defects given by Brooks and Ham [Phys. Rev. **112**, 344 (1958)] and an expansion to terms in  $k^4$  has yielded an appreciably improved result for the heat of mixing. Detailed discussion will be given in a later paper.

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<sup>12</sup> R. Hultgren, R. Orr, P. Anderson, and K. Kelly, *Selected Values of Thermodynamic Properties of Metals and Alloys* (John Wiley & Sons, Inc., New York, 1963).