Theory of Molten Alkali Alloys. III. K–Rb, K–Cs, and Rb–Cs†

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A theory previously formulated and applied to the mixing properties of binary alkali alloys involving sodium is used to investigate the more nearly ideal mixtures K–Rb, K–Cs, and Rb–Cs. Changes on mixing of various contributions to the total electronic energy, cell sizes, and cell charges are calculated and discussed. For the alloys studied charge transfer is small and less influential in determining relative cell sizes than for the sodium mixtures. Calculated heats of mixing are found to agree reasonably well with experiment. In particular, negative heats of mixing are found for Rb–Cs mixtures, while positive heats of mixing are obtained for the others.

I. INTRODUCTION

TWO previous papers[1,2] deal with a calculation of some of the mixing properties of those molten alkali alloys which contain sodium. Quantities of particular interest are changes on mixing of various contributions to the electronic energy, the atomic volume, and the cellular charges. Discussion of these quantities is based on the accommodation of conduction-electron wave functions in the region between atomic cells of different charge density. In the present paper the theory, as formulated in I and extended in II, is used to investigate the nearly ideal mixtures potassium-rubidium, potassium-cesium, and rubidium-cesium. Results for the less ideal mixtures sodium-potassium, sodium-rubidium, and sodium-cesium were presented in II.

The model and techniques of calculation are identical to those used to obtain the results of II and the reader is referred to that paper for details. In brief, each ion-core is imagined to be at the center of a spherical cell inside of which the potential is spherically symmetric. Conduction-electron wave functions are represented by single augmented plane waves[3] and the average energy E_T per conduction electron is written

$$E_T = E_0 + (3/5)E_2 k_F{}^2 + (3/7)E_4 k_F{}^4 + E_C + E_{ec} + E_{cc}, \quad (1)$$

where

$$k_F = (9\pi/4)^{1/3}/r_s, \quad (2)$$

$$r_s{}^3 = \sum_i x_i r_i{}^3. \quad (3)$$

r_i is the radius of the ith cell and x_i is the concentration of the ith constituent. The energy parameters E_0, E_2, and E_4 are related to the logarithmic derivatives ϕ_{il} of the radial parts of conduction-electron wave functions.

Here i labels the cell and l the angular momentum. The derivatives are evaluated at cell boundaries by means of the quantum-defect method.[4] In this work the second and third terms of (1) are abbreviated E_F and E_{F2}, respectively.

E_C and E_{ec} represent the average residual Coulomb and exchange-correlation energies, respectively. Screening of the ion-core potentials and variation of the electronic charge density from cell to cell are taken into account in the computation of these energies.

The number q_i of conduction electrons in the ith cell is also related to all the ϕ_{il} and is found, in general, to be different from unity. E_{cc} represents the interaction of the charged cells and is calculated on the basis of the nonrandom structure brought about by this interaction at finite temperatures.

The minimum of E_T as a function of the cell radii was found and values of the various parameters and energy components were calculated for the equilibrium radii. The computation was carried out for the mixtures and the single-constituent systems and appropriate differences were taken to find changes on mixing. Results for the single-constituent systems were presented in II and will not be repeated here. Results for binary systems which can be made from potassium, rubidium, and cesium are given and compared qualitatively with results for the sodium mixtures and quantitatively with experimentally measured values when possible.

II. RESULTS

Computed energies and parameters for the three binary systems considered here are shown in Tables I, II, and III. The first four rows of each table give r_s, the cell radius associated with each of the two constituent atoms, and the number q of electrons in the smaller cell. Here, as for the sodium mixtures, the larger cell decreases in size on mixing while the smaller increases and electrons are transferred from the larger to the smaller cell. Charge transfer is somewhat smaller than would be expected if the electronic charge density were uniform.

The following nine rows of each table show values of

[1] J. R. Christman and H. B. Huntington, Phys. Rev. **139**, A83 (1965). Hereafter this paper will be referred to as I.
[2] J. R. Christman, preceding paper, Phys. Rev. **153**, 217 (1967). Hereafter this paper will be referred to as II.
[3] J. C. Slater, Phys. Rev. **92**, 603 (1953); M. M. Saffren and J. C. Slater, *ibid.* **92**, 1126 (1953).
[4] F. S. Ham, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 1, p. 127.

TABLE I. Computed parameters and energies for potassium-rubidium mixtures (Bohr units). L_s is in Bohr radii; κ is in Ry Bohr radii².

x_K	0.125	0.250	0.375	0.500	0.625	0.750	0.875
r_s	4.39	4.89	4.86	4.82	4.78	4.75	4.71
r_K	4.80	4.78	4.76	4.74	4.73	4.71	4.69
r_{Rb}	4.94	4.93	4.91	4.89	4.87	4.85	4.83
q_K	1.019	1.016	1.014	1.011	1.009	1.006	1.003
E_0	−0.47951	−0.48237	−0.48528	−0.48826	−0.49130	−0.49436	−0.49753
E_2	1.1642	1.1550	1.1457	1.1363	1.1269	1.1174	1.1078
E_F	0.10602	0.10668	0.10738	0.10812	0.10890	0.10967	0.11054
E_4	−0.2570	−0.2538	−0.2504	−0.2470	−0.2435	−0.2400	−0.2366
E_{F2}	−0.00254	−0.00258	−0.00262	−0.00266	−0.00271	−0.00275	−0.00280
E_C	0.24369	0.24550	0.24734	0.24923	0.25116	0.25307	0.25510
E_{ee}	−0.23998	−0.24170	−0.24345	−0.24526	−0.24711	−0.24897	−0.25093
E_{cc}	0.00000	−0.00001	−0.00001	−0.00001	−0.00001	−0.00001	0.00000
E_T	−0.37231	−0.37446	−0.37664	−0.37884	−0.38107	−0.38334	−0.38563
L_s	31.7	23.5	20.6	19.4	19.5	21.3	27.6
ρ_K	0.979	0.985	0.990	0.993	0.996	0.998	0.999
$\kappa \times 10^{-3}$	4.18	4.18	4.11	4.04	3.97	3.91	3.83

TABLE II. Computed parameters and energies for potassium-cesium mixtures (Bohr units). L_s is in Bohr radii; κ is in Ry Bohr radii².

x_K	0.125	0.250	0.375	0.500	0.625	0.750	0.875
r_s	5.20	5.13	5.05	4.97	4.90	4.82	4.74
r_K	4.85	4.83	4.81	4.78	4.75	4.73	4.70
r_{Cs}	5.25	5.22	5.19	5.15	5.12	5.09	5.05
q_K	1.044	1.039	1.033	1.026	1.020	1.013	1.006
E_0	−0.44918	−0.45597	−0.46304	−0.47042	−0.47767	−0.48510	−0.49293
E_2	1.1924	1.1773	1.1630	1.1493	1.1357	1.1226	1.1102
E_F	0.09746	0.09901	0.10079	0.10283	0.10469	0.10670	0.10907
E_4	−0.4473	−0.4212	−0.3936	−0.3659	−0.3348	−0.3007	−0.2673
E_{F2}	−0.00356	−0.00355	−0.00352	−0.00349	−0.00339	−0.00323	−0.00307
E_C	0.23135	0.23508	0.23889	0.24279	0.24633	0.24986	0.25360
E_{ee}	−0.22787	−0.23135	−0.23495	−0.23869	−0.24214	−0.24562	−0.24935
E_{cc}	−0.00002	−0.00005	−0.00007	−0.00008	−0.00007	−0.00005	−0.00003
E_T	−0.35182	−0.35682	−0.36190	−0.36706	−0.37225	−0.37745	−0.38269
L_s	14.6	10.7	9.20	8.62	8.73	9.64	12.4
ρ_K	0.917	0.943	0.961	0.975	0.985	0.993	0.998
$\kappa \times 10^{-3}$	4.53	4.48	4.47	4.18	4.04	4.11	3.89

TABLE III. Computed parameters and energies for rubidium-cesium mixtures (Bohr units). L_s is in Bohr radii; κ is in Ry Bohr radii².

x_{Rb}	0.125	0.250	0.375	0.500	0.625	0.750	0.875
r_s	5.24	5.19	5.15	5.11	5.07	5.03	5.00
r_{Rb}	5.03	5.01	5.00	4.99	4.99	4.98	4.97
r_{Cs}	5.26	5.25	5.24	5.23	5.21	5.20	5.19
q_{Rb}	1.027	1.023	1.019	1.015	1.011	1.008	1.004
E_0	−0.44658	−0.45083	−0.45510	−0.45944	−0.46373	−0.46810	−0.47241
E_2	1.2024	1.1974	1.1927	1.1884	1.1842	1.1805	1.1768
E_F	0.09694	0.09809	0.09925	0.10048	0.10167	0.10295	0.10417
E_4	−0.4451	−0.4211	−0.3960	−0.3705	−0.3437	−0.3163	−0.2884
E_{F2}	−0.00344	−0.00336	−0.00326	−0.00315	−0.00302	−0.00286	−0.00269
E_C	0.22941	0.23138	0.23329	0.23518	0.23695	0.23873	0.24036
E_{ee}	−0.22612	−0.22798	−0.22981	−0.23163	−0.23336	−0.23511	−0.23673
E_{cc}	−0.00001	−0.00001	−0.00002	−0.00002	−0.00002	−0.00001	−0.00001
E_T	−0.34980	−0.35273	−0.35565	−0.35858	−0.36150	−0.36441	−0.36731
L_s	24.5	18.4	16.2	15.4	15.9	17.6	22.6
ρ_{Rb}	0.963	0.975	0.983	0.989	0.994	0.997	0.999
$\kappa \times 10^{-3}$	4.88	4.79	4.72	4.60	4.61	4.56	4.42

the various energies and energy parameters. Except for the remark that mixture energies and parameters are nearly equal to averages of corresponding single constituent values, discussion of these quantities is postponed until changes on mixing are presented.

Although the model is, for the most part, independent of structure, the interaction energy of the charged cells is sensitive to structure and tends to bring about some local ordering: at finite temperatures there are more unlike than like atoms in the neighborhood of a given atom. In order to estimate E_{cc} a structure which is dependent only on the screened Coulomb interaction of the cells is introduced. The quantity ρ, given in the next to last row of each table, is a measure of local deviations from randomness. If A denotes the smaller of the two atoms, then ρ_A is the ratio of the density of A atoms at the distance $2r_s$ from an A atom to the density at infinite distance.

TABLE IV. Derivatives of energy terms with respect to
radius r_B of larger cell (Bohr units).

Mixture	K-Rb	K-Cs	Rb-Cs
$\partial E_0/\partial r_B$	+0.029	+0.030	+0.026
$\partial E_F/\partial r_B$	−0.027	−0.025	−0.024
$\partial E_C/\partial r_B$	−0.028	−0.031	−0.029
$\partial E_{ec}/\partial r_B$	+0.026	+0.026	+0.024

L_s is the Debye-Hückel screening length for the cell-cell interaction. For the three mixtures considered here the cellular charges are small, the structures are nearly random locally, and E_{cc} is small. Results shown were calculated for a temperature of 400°K.

Compressibilities κ of the binary mixtures were also calculated and are listed in the last row of each table.

It is of interest to note the influence of charge transfer on the relative cell sizes. As explained in II, the search for the minimum of E_T consists of two steps. First, for each of several values of the radius r_A of the smaller cell, the minimum of E_T with respect to the radius r_B of the larger cell is found. In the second step, the minimum of the resulting function of r_A is found. It is chiefly during the first of these two minimum-finding steps that the relative cell sizes are determined and charge transfer is influential.

Table IV shows the first derivatives of the energy components with respect to the radius r_B of the larger atom. The radius r_A is held constant and the derivatives are evaluated near the equilibrium values of the two radii. All reported values of derivatives are for 50-50 mixtures. The table shows that, while relative cell sizes are determined chiefly by E_0 and E_F, there are some contributions from E_C and E_{ec}. The combined contribution of the Coulomb and exchange-correlation terms opposes the tendency toward similar cell sizes. The derivative of E_{F2} is at least an order of magnitude smaller than those given and is not included in the table.

Changes on mixing of the various energy components are shown in Figs. 1 and 2 as functions of the concen-
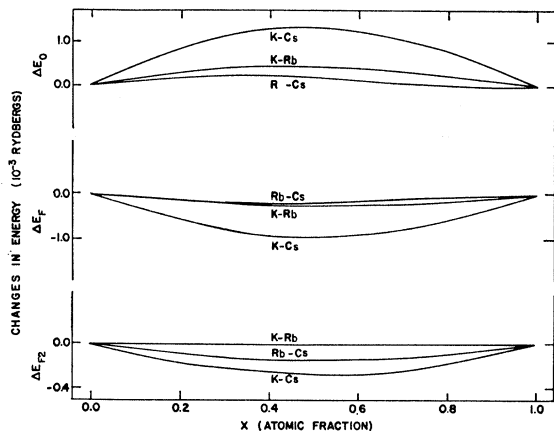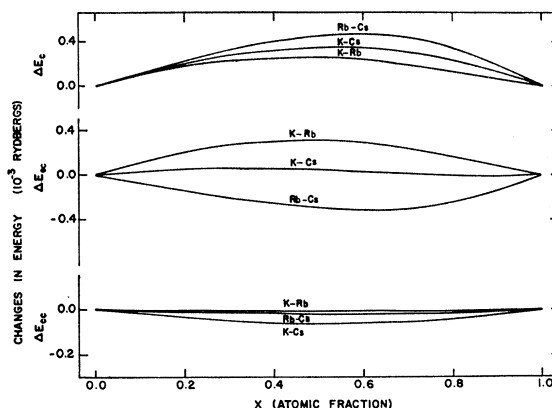
FIG. 2. Changes on mixing ΔE_C, ΔE_{ec}, and ΔE_{cc} as functions of the concentration x of the smaller atom.

tration x of the smaller atom. The change ΔE in the energy component E is given by

$$\Delta E = E - \sum_i x_i E_i, \qquad (4)$$

where E is the value for the mixture and E_i the value for the ith constituent in the unmixed state.

The smallness of the changes on mixing (they are on the order of 10^{-3} of the energies themselves) results, of course, from the near equality of the mixture energies and the appropriate average of the single-constituent energies. Small deviations from $\Delta E = 0$ reflect differences in cell sizes and in logarithmic derivatives of wave functions at cell boundaries. As pointed out in II, the qualitative behavior of the mixture parameters E_0, E_F, and E_{F2} may be deduced from the average of the single constituent parameters weighted by $r_i^2 \partial \phi_{i0}/\partial E_0$ [see Eq. (26) in II]. In the lowest order approximation these factors are evaluated at the cell radius and energy of the appropriate unmixed alkali. For the alkalis the factor $\partial \phi_{i0}/\partial E_0$ tends to smaller values as the atomic number and cell radius increase, but, because of the area factor, the parameter associated with the larger atom is slightly favored in the weighted average. The results shown in Fig. 1 are consistent with this qualitative behavior. In this connection it should be noted that since E_{F2}, as reported in II, is less negative for rubidium than for potassium, the slightly positive ΔE_{F2} obtained for potassium-rubidium mixtures is not surprising.

Changes ΔE_T on mixing of the total energies are shown in Fig. 3 along with heats of mixing measured by Yokokawa and Kleppa.[5] The calculated curves agree in sign and order of magnitude with the experimentally determined curves but, for all mixtures, the former are slightly more positive than the latter.

For each of the three mixtures studied, the sum of the changes in the electrostatic energies E_C, E_{ec}, and E_{cc} is always positive. This result is consistent with a

FIG. 1. Changes on mixing ΔE_0, ΔE_F, and ΔE_{F2} as functions of the concentration x of the smaller atom.

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[5] T. Yokokawa and O. J. Kleppa, J. Chem. Phys. **40**, 46 (1964).

FIG. 3. Heats of mixing ΔE_T as functions of the concentration x of the smaller atom.

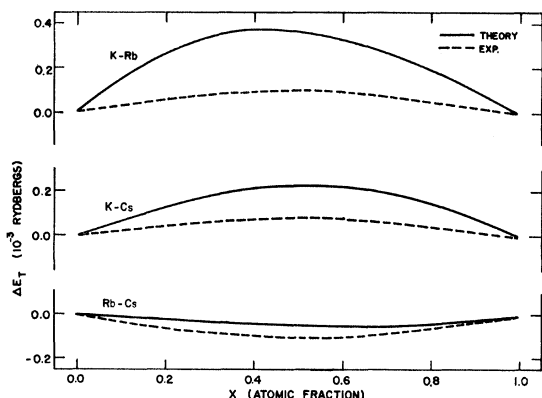FIG. 4. Percent change on mixing of atomic volume as a function of the concentration of the smaller atom.

transfer of electrons from the larger to the smaller atom. Although ΔE_0 is always positive and ΔE_F is always negative, their relative magnitudes vary slightly from mixture to mixture and sum to a negative quantity for rubidium-cesium mixtures. On the other hand, both the sum $\Delta E_0 + \Delta E_F$ and the heat of mixing ΔE_T are positive for potassium-rubidium and potassium-cesium mixtures.

Note that ΔE_T is calculated as the small algebraic sum of numbers which are relatively large in magnitude and that, while each component follows the "area rule" discussed above, the rule is not sufficiently accurate to hold for the sum. In fact, the rule gives a positive ΔE_T for rubidium-cesium mixtures; the detailed calculation must be carried out in order to achieve agreement in sign with the measured results.

Figure 4 shows calculated changes on mixing of the average atomic volume as a function of the concentration x of the smaller atom. The curve for potassium-rubidium mixtures is slightly positive while the curves for the others are negative.

III. COMPARISON WITH SODIUM MIXTURES AND CONCLUSIONS

In this paper as well as in I and II, study of the metallic mixing process has been based on changes in the conduction electron wave functions near boundaries of atomic cells. Gross features of the mixing process are much the same for the six alkali mixtures described in
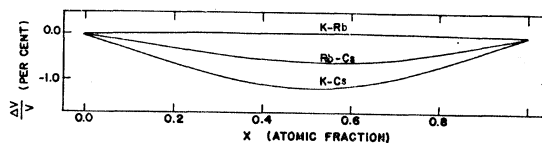
this paper and in II. For all six mixtures the electronic charge density varies from cell to cell and, upon mixing, there are changes in cell sizes which reduce this variation and the "mismatch energy" $\Delta E_0 + \Delta E_F + \Delta E_{F2}$. Accompanying the change in cell size is a transfer of electrons, always from the larger to the smaller cell. The importance of changes in cell sizes and charges for the binding of molten alkali alloys has been emphasized in this work.

For the six alloys studied, mixture values of E_0, E_F, and E_{F2} are close to the appropriate averages of the single constituent values but deviate from them in the direction of the value associated with the larger atom in the unmixed state. Except for rubidium-cesium mixtures, for which $|\Delta E_F| > |\Delta E_0|$, this statement is also true for the sum of these three energies.

Changes on mixing of the s-wave functions are greater for the sodium mixtures than for the others and, as a result, changes in cell sizes and charges are also greater for the former than for the latter. The somewhat smaller charge transfer which occurs in the formation of the three nearly ideal mixtures results in several important differences between the two sets of mixtures studied. The electrostatic energies E_C and E_{ec} are not as important in determining relative cell sizes for the nearly ideal mixtures as they are for the sodium mixtures and the equilibrium cell volumes for the former are proportionately closer to the average atomic volume. The relatively large charge transfer for the sodium mixtures also gives rise to a comparatively large cell-cell interaction energy and an atomic distribution which is less random.