

# DENSITIES AND HEATS OF MIXING OF LIQUID ALKALI ALLOYS

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Densities and heats of mixing at several concentrations of liquid alkali alloys are calculated using "mixed" model potentials for the ions with a jellium as a boundary condition. The results reproduce trends that are present in experimental data, though calculated and measured values are considerably different, especially when size-effects play an important role.

## Introduction

It is empirically well known that the alloying process in metallic systems is governed by differences in electronegativity and in atomic size.

A quantitative and more or less "*ab initio*" description of this process, however is rather complicated. It was shown by G. SOLT [1] that even the first structure-dependent approximation for the anisotropic atomic displacement field in dilute alloys of simple metals must include non-linear 3rd order response functions of the electron liquid.

The model and the method used in this paper can be considered as a „zeroth order” approximation to the problem of mixing liquid alkali metals. Ion cores described by model potentials are embedded into a positive jellium background and into an electron liquid and the energy of this system is then calculated by means of a simple version of the density functional formalism [2].

The density functional method [3] has proved to be a very useful tool for calculating various electronic properties of metals, e.g. formation energies of surfaces [3, 4] and vacancies, [5, 6]. In fact, our results reproduce the main features that are present in the experimental data [7] and in the numerical data obtained by CHRISTMAN [8—10].

## The Model and the Method of Calculation

When calculating the density and formation energy of a liquid metal consisting of atoms  $A$ , the following simple picture is accepted:

Let a spherical hole of radius  $r_s$  be formed in a homogeneous positive background, upon which the neutralizing electron liquid have a similar step-like density:

$$n_+(r) = n_0 \Theta(r - r_s), \quad n_0^{-1} = \frac{4\pi}{3} r_s^3. \quad (1)$$

Let the ion core of atom  $A$  at the centre of the hole be characterized by the model potential

$$V_A(r) = \begin{cases} -Z \frac{e^2}{r} & r > r_0 \\ -uZ \frac{e^2}{r_0} & r < r_0. \end{cases} \quad (2)$$

The parameters  $r_0$  and  $u$  were adjusted so as to lead to the correct density and elastic constants for the pure metals, in second order perturbation theory [11], and are listed in Table I [12].

Table I.

Parameters of the model potential [11, 12], and results of density, cell energy and cohesive energy for pure alkali metals

Metal	Potential parameters			Jellium density		Energy Ry/atom	Cohesive energy/Ry/atom/	
	$Z$	$r_0$	$u$	Calculation	Experiment		Calculation	Experiment [13]
Li	1	1.512	0.334	3.29	3.23	-0.54983	0.154	0.122
Na	1	2.074	0.3632	4.08	3.93	-0.46042	0.080	0.083
K	1	2.9725	0.5399	5.05	4.88	-0.38428	0.064	0.069
Rb	1	3.384	0.64	5.36	5.21	-0.36489	0.058	0.064
Cs	1	3.795	0.68	5.77	5.62	-0.34209	0.055	0.061

The bonding electrons of atom  $A$  are added to the neutralizing electron liquid which is then allowed to relax resulting an electron density  $n(\mathbf{r})$ . The "formation energy" is defined as the energy associated with  $n(\mathbf{r})$  with respect to that of the homogeneous electron liquid of density  $n_0$ .

A natural tool to calculate this "formation energy" is the density functional method [3], which is based on the fact, that the ground state energy of a system is the minimum of an energy functional with respect to the electron density. The energy, as a functional of the electronic density, can be written (in atomic units) as

$$E_0[n] = \int V_A(\mathbf{r})n(\mathbf{r}) dv + \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} dv dv' + G[n] \quad (3)$$

where for  $G[n]$  we have taken

$$G[n] = \frac{3}{10} (3\pi^2)^{2/3} \int n^{5/3} dv - \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int n^{4/3} dv + \frac{\lambda_w}{8} \int \frac{(\nabla n)^2}{n} dv - \int \left[ 0.0575 + 0.0155 \cdot \ln \left( \frac{4\pi}{3} n \right)^{1/3} \right] n dv \quad (4)$$

with the Nozières—Pines expression for the correlation energy. The constant  $\lambda_w$  in the gradient term was chosen to be 0.45 [6].

To find the actual electron density associated with the minimum of the functional

given in Eq. (3) a variational method was applied, assuming  $n(\mathbf{r})$  to be of the simple form

$$n(\mathbf{r}) = \begin{cases} n_0(1-\alpha) \exp[\beta(r-r_s)] & r < r_s \\ n_0(1-\alpha \exp[-|\beta|(r-r_s)]) & r > r_s. \end{cases} \quad (5)$$

Here the value of  $\alpha$  is determined by the neutrality condition, and  $\beta$ , together with  $r_s$  are the variational parameters.

In this way the energy functional has to be replaced by an energy function depending on variables  $\beta$  and  $r_s$ . Minimization of the "formation energy" with respect to these parameters leads to the calculated density parameter  $r_{sA}$  and to the cell energy  $E_A$ , which apart from the ionization potential of atom  $A$ , is the cohesive energy. As to a mixture of atoms  $A$  and  $B$  with concentrations  $c_A=c$  and  $c_B=1-c$ , respectively, a mixed model potential

$$V_M = cV_A + (1-c)V_B \quad (6)$$

is introduced into the hole of radius  $r_s$ , as usual in a virtual crystal model. Following the procedure described above for the pure "metal", the density parameter  $r_{sM}$  and the cell energy  $E_M$  of the mixture can be calculated. The heat of mixing is given by

$$E = E_M - cE_A - (1-c)E_B. \quad (7)$$

### Results and discussion

To show the quality of the described model and method, we listed results for the pure alkali metals in Table I. It can be seen that, except for Li, there is a good agreement between the calculated and measured values of the densities and that of the cohesive energies.

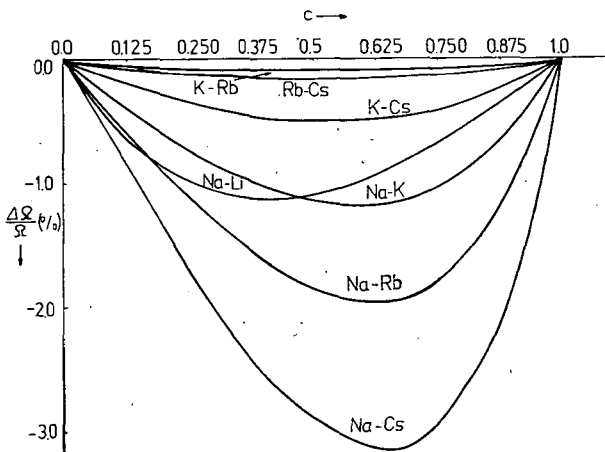


Fig. 1. Percent change on mixing of atomic volume as a function of concentration. The concentration refers to the first component of the mixture

Table II.

The calculated density parameters ( $r_s$  in atomic units), cell energies ( $E_M$  in Rydbergs) and heats of mixing ( $\Delta E$  in  $10^{-3}$  Rydbergs),  $c$  is the fraction of the first component

$c$	0.125	0.250	0.375	0.500	0.625	0.750	0.875	
Na—Li	$r_s$	3.405	3.512	3.616	3.715	3.812	3.905	3.995
	$E_M$	-0.53501	-0.52157	-0.50929	-0.49800	-0.48756	-0.47788	-0.46886
	$\Delta E$	3.64	5.91	7.01	7.12	6.39	4.01	2.73
Na—K	$r_s$	4.941	4.830	4.716	4.598	4.476	4.350	4.219
	$E_M$	-0.39149	-0.39920	-0.40746	-0.41636	-0.42598	-0.43643	-0.44785
	$\Delta E$	2.31	4.11	5.37	5.99	5.89	4.96	3.05
Na—Rb	$r_s$	5.221	5.078	4.929	4.775	4.614	4.446	4.270
	$E_M$	-0.37327	-0.38235	-0.39225	-0.40210	-0.41508	-0.42841	-0.44339
	$\Delta E$	3.56	6.42	8.46	9.56	9.52	8.13	5.09
Na—Cs	$r_s$	5.593	5.409	5.218	5.016	4.805	4.580	4.341
	$E_M$	-0.35153	-0.36193	-0.37346	-0.38638	-0.40099	-0.41774	-0.43724
	$\Delta E$	5.35	9.75	13.0	14.87	15.06	13.1	8.39
K—Rb	$r_s$	5.321	5.283	5.245	5.206	5.167	5.128	5.088
	$E_M$	-0.36713	-0.36942	-0.37176	-0.37415	-0.37660	-0.37910	-0.38166
	$\Delta E$	0.18	0.32	0.40	0.44	0.41	0.33	0.20
K—Cs	$r_s$	5.685	5.600	5.213	5.424	5.333	5.240	5.145
	$E_M$	-0.34652	-0.35115	-0.35600	-0.36109	-0.36643	-0.37206	-0.37800
	$\Delta E$	0.83	1.49	1.91	2.10	2.03	1.67	1.01
Rb—Cs	$r_s$	5.720	5.670	5.620	5.569	5.517	5.465	5.412
	$E_M$	-0.34468	-0.34734	-0.35006	-0.35286	-0.35574	-0.35870	-0.36175
	$\Delta E$	0.26	0.45	0.58	0.63	0.60	0.49	0.29

Calculated values of the density parameters, the cell energies and the heats of mixing for binary systems appear in the Table II. Values of these quantities are given for seven concentrations  $c$  of the first component.

In our model  $r_s$  equals to the radius of a cell, so we can calculate the average atomic volume  $\Omega$ . If the two components were alloyed according to the laws of ideal mixing, the atomic volume  $\Omega_{IM}$  for the mixture would be given by Vegard's law;

$$\Omega_{IM} = c\Omega_A + (1-c)\Omega_B \quad (8)$$

where  $\Omega_A$  and  $\Omega_B$  are the cell volumes for the pure metals. Calculated values of the average cell volume  $\Omega_M$  differs from the ideal value  $\Omega_{IM}$  as shown in Fig. 1. All deviations are negative and the magnitudes are in correlation with the density difference of the pure components. Experimental data are available only for the 50—50% Na—K mixture at 100 °C [8]. This value, marked with a circle in Fig. 1. agrees well both in sign and in magnitude with the calculated one. Our results are similar in tendency to those of Christman [9, 10], with the exception of the K—Rb mixture for

which Christman obtained small positive deviations. As to the magnitude our results are about the half of those of Christman in all cases.

Another feature of the results shown in Table II is the similarity between the mixture energy  $E_M$  and the average of the pure component energies. For our model this similarity reflects the reality of using the "mixed" potentials. Small differences result in nonzero heats of mixing given by Eq. (7).

Calculated values of  $\Delta E$  as a function of concentration are shown in Figs. 2—7 together with the heats of mixing measured by YOKOKAWA AND KLEPPA [7]. Agreement in sign is clearly shown except for the Rb—Cs mixture, where calculated values are positive and the experimental ones are negative. In addition, the shape of theoretical and experimental curves are very similar, but at the same time magnitudes of calculated heats of mixing are much higher than the experimental ones. It can be seen

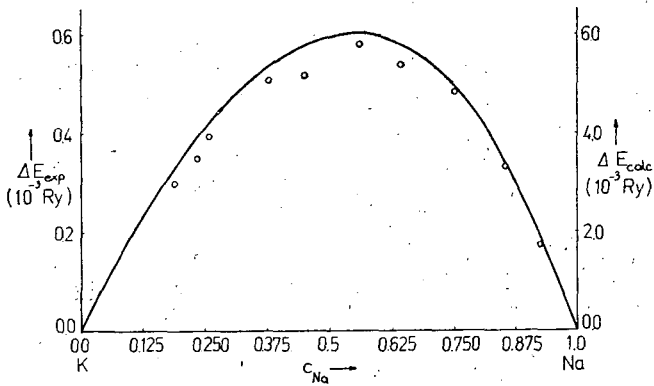


Fig. 2. Sodium—Potassium heat of mixing as a function of sodium concentration  
 $c_{Na}$  (—calculated,  $\circ$  experimental [7])

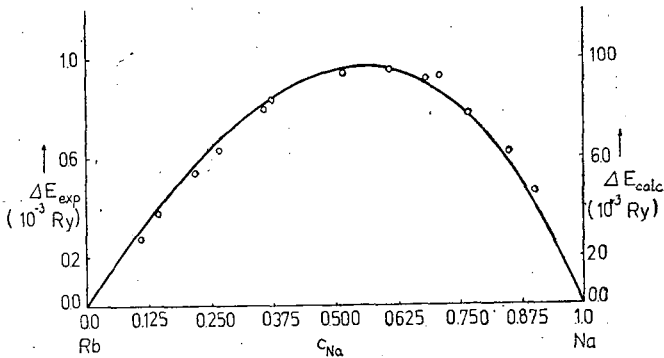


Fig. 3. Sodium—Rubidium heat of mixing as a function of sodium concentration  
 $c_{Na}$  (—calculated  $\circ$  experimental [7])

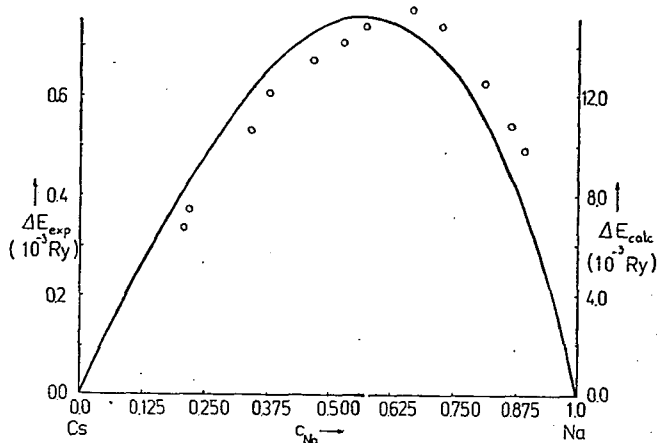


Fig. 4. Sodium—Cesium heat of mixing as a function of sodium concentration  $c_{Na}$  (—calculated,  $\odot$  experimental [7])

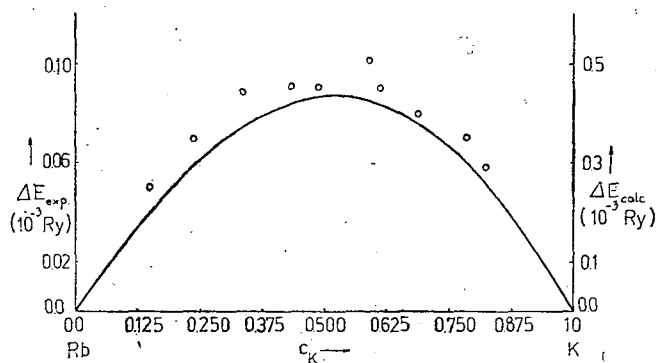


Fig. 5. Potassium—Rubidium heat of mixing as a function of potassium concentration  $c_K$  (—calculated,  $\odot$  experimental [7])

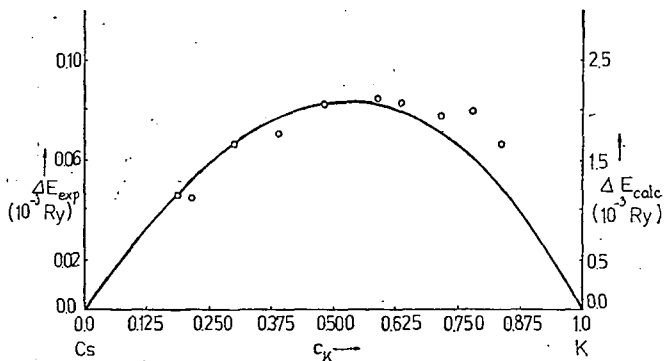


Fig. 6. Potassium—Cesium heat of mixing as a function of potassium concentration  $c_K$  (—calculated,  $\odot$  experimental [7])

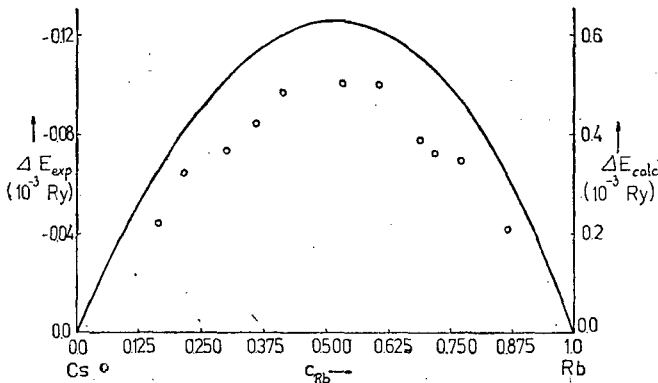


Fig. 7. Rubidium—Cesium heat of mixing as a function of rubidium concentration  $c_{Rb}$  (—calculated,  $\circ$  experimental [7])

that the great numerical differences between the theory and experiment occur in cases of large difference in densities of the two components, *i.e.* when size effects play an essential role.

These differences are not surprising according to our approximations, namely to the inflexibility of the density profile given by Eq. (5), which has lead in all cases to a nearly flat electron distribution.

Furthermore, the mixed potential given by Eq. (6) with a jellium as a boundary condition, can not describe properly the screening effects [14].

### Conclusions

In the present paper we studied the mixing process of binary alkali systems. Despite the simplifications of the model *i.e.* the statistical treatment of the density functional formalism and the use of the jellium picture, as well as the low flexibility of the trial density function, the calculated density parameters and average atomic volumes are realistic. As regard the heats of mixing this model can reproduce the diverse features of experimental data.

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## ПЛОТНОСТИ И ТЕПЛОТЫ СМЕШЕНИЯ СПЛАВОВ ЖИДКИХ ЩЕЛОЧНЫХ МЕТАЛЛОВ

*И. Ваши и И. Дьемант*

Расчитаны плотности и теплоты смешения сплавов жидких щелочных металлов при различных концентрациях воспользуясь смешанными модельными потенциалами для ионов и гелей для граничных условий. Результаты показывают тенденции проявляющиеся в экспериментальных данных, но значения измерений значительно различаются, особенно тогда, когда размерные эффекты играют важную роль.