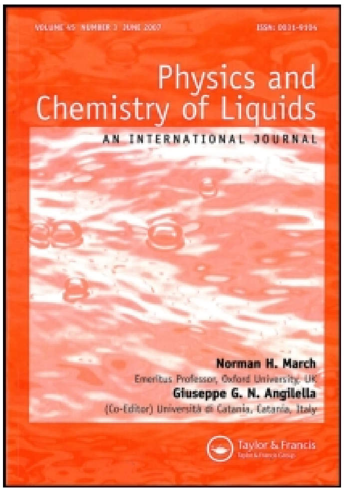

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An Interacting Hard Sphere Model for Liquid Sodium–Caesium Alloys

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By introducing a temperature dependent interchange parameter into a semi-empirical model for the Gibbs energy of mixing of liquid Na–Cs it is shown that the total entropy of mixing can be resolved into a hard sphere and an interaction energy contribution, both of which can be calculated from experimental data. By calculating the contribution to the entropy from the variation of molar volume with concentration it is therefore possible to obtain experimental values of $(\Delta S_\eta + S_\sigma)$, the contribution from the packing and misfit of the hard spheres. This sum can be fitted by caesium and sodium hard sphere diameters which change by less than 1.0% over the whole concentration range.

In sodium-rich alloys the long wavelength limit of the Faber–Ziman structure factors $a_{ij}(0)$ attain very large numerical values. There are contributions to these factors both from volume effects and from interaction forces. Analysis shows that the difference in molar volumes favours an arrangement of unlike near neighbours over the whole composition range; the ionic interactions have the opposite effect and completely dominate the behaviour in sodium-rich mixtures.

1 INTRODUCTION

A striking feature of the thermodynamic properties of liquid sodium–caesium is that whereas the entropy of mixing is no more than 3% greater than that of an ideal solution over the whole concentration range and is independent of temperature there is a marked departure from ideality in other properties, most notably revealed in the large rise above the ideal value in $S_{cc}(0)$ for sodium concentrations near to 0.8. (Full experimental data obtained by the authors and references to other data sources are given in Neale and Cusack,[1] herein referred to as I). Consequently attempts to model the system using the Flory–Huggins expression

$$(\Delta G \simeq)\Delta F = RT(c_1 \ln \phi_1 + c_2 \ln \phi_2) + \tfrac{1}{2}\chi(c_1\phi_2 + c_2\phi_1) \qquad (1)$$

fail by considerably overestimating the entropy of mixing; this is because the volume fractions ϕ_i of the components i differ widely from the atomic concentrations c_i for caesium-sodium alloys, the ratio of their atomic volumes being about 3.0. Although it is possible to choose a value of the interchange parameter χ in Eq. (1) for which the general features of the variations with concentration of activities and $S_{cc}(0)$ are fairly well described, the implicit assumption that the two terms on the right hand side of Eq. (1) can be identified respectively as contributions from the entropy and energy of mixing leads to a large overestimate of both quantities (Visser *et al.*[2]; see also Bhatia and March[3]). Although the Flory–Huggins expression for ΔS was originally derived for a lattice site model which did not take account of volume changes on mixing (up to 6% contraction for Na–Cs) it is surprising that it is no better an approximation than that for the mixing of two ideal gases. In this paper we show that a modest temperature dependence of χ, together with other refinements in the model, enables us to give an accurate description of all the thermodynamic properties of mixing over the whole range of concentration, temperature and pressure for which data are available.

In the next section the method of calculating the interchange parameter is explained, and model values of the various properties are compared with experiment in Section 3. The implications of these results for theories of the internal energy of the mixture and for the specification of hard sphere diameters are then discussed in Sections 4 and 5. Finally, the long wave length limit of the structure factors which are needed for these more fundamental approaches are given in Section 6, together with some concluding remarks.

2 THE GIBBS ENERGY OF MIXING

If physically realistic and accurate model expressions can be found for both the entropy and internal energy changes the equation for ΔG follows, for which a sensitive test is then to compare with experiment its predictions for the variation with composition of the concentration cell emf E, relative activities a_i and $S_{cc}(0)$. The expressions for these depend not only on ΔG but also on its first and second derivatives with respect to c. (In this paper we define $c \equiv c_2 = c_{\mathrm{Na}}$.)

2.1 Internal energy of mixing

In general this is related to other properties of mixing by

$$\Delta G = -T\Delta S + \Delta U + p\Delta V \tag{2a}$$

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_p \tag{2b}$$

$$\Delta V = \left(\frac{\partial \Delta G}{\partial p}\right)_T \tag{2c}$$

In Na–Cs the choice of possible models is simplified because both ΔS and ΔV are found to be independent of T and p. If this fact is used after Eq. (2a) has been inserted into Eqs. (2b) and (2c), we find that ΔU (which is positive) is independent of both T and p. It is highly unlikely, therefore, that molecular complexes or clusters of the type $Na_\mu Cs_\nu$ exist in the mixture.

The internal energy change can be expressed in terms of an interchange parameter ω by

$$\Delta U \equiv \omega\phi \tag{3}$$

where $\phi \equiv (c_1\phi_2 + c_2\phi_1)/2 = c_1c_2(V_1^0 + V_2^0)/2V$ and V_i^0, V are pure component and alloy molar volumes. Since ΔU is independent of T and p and the dependence of ϕ on T and p is negligible the parameter ω depends only on c. In fact ω varies by less than 5% over the concentration range 0.05 to 0.85 (Figure 1), but it is clearly increasing appreciably outside this range, a point we return to later.

2.2 Entropy of mixing

In the original Flory–Huggins expression for the change in Helmholtz energy the entropy change is given as

$$\Delta S_{FH} = -R\{c_1 \ln\phi_1 + c_2 \ln\phi_2\} = -R\{c_1 \ln(c_1V_1^0/V^{id}) + c_2 \ln(c_2V_2^0/V^{id})\}$$

and the alloy molar volume is assumed to be $V^{id} = c_1V_1^0 + c_2V_2^0$. This is in poor agreement with experimental entropy changes and its use in Eq. 1 with a value of χ chosen to fit the peak value of $S_{cc}(0)$ was found in I to produce the general shape of the observed $S_{cc}(0)$ but shifted along the concentration scale by about 0.07 towards the sodium end. Better results for all of the properties of mixing were obtained when the ideal volume is replaced by the actual molar volume V, the entropy of mixing being given by

$$\Delta S = -R\{c_1 \ln(c_1V_1^0/V) + c_2 \ln(c_2V_2^0/V)\} \tag{4}$$

This is easily shown to equal $\Delta S_{\mathrm{gas}} + S_c$, the sum of the first two terms in the mixing entropy of the hard sphere model, viz.

$$\Delta S_{hs} = \Delta S_{\mathrm{gas}} + S_c + \Delta S_\eta + S_\sigma \tag{5}$$

where

$$\Delta S_{\mathrm{gas}} = R(\ln\Omega - c_1\ln\Omega_1 - c_2\ln\Omega_2)$$

$$S_c = -R(c_1\ln c_1 + c_2\ln c_2)$$

and Ω_i, Ω are the volumes per particle in the pure components and in the alloy. ΔS_η and S_σ are respectively the packing and misfit contributions to the entropy of mixing of hard spheres for which explicit formulae are given later. (Visser *et al.*[2] considered a similar model for Na–Cs and noted that ΔS_{hs} contains ΔS_{FH} as a first approximation.)

Equation (4), which may be thought to be an improvement on ΔS_{FH}, still overestimates the entropy change by about 10%; and if this expression is used together with a value for χ which fits the peak value of $S_{cc}(0)$, the resulting model values of the enthalpy of mixing turn out to be 17% higher than the experimental values.

2.3 Interacting hard sphere model

A further difficulty is that there is a large decrease in the peak value of $S_{cc}(0)$ when T is increased from 110°C to 200°C, and χ has to be increased by $\sim 6\%$ in order to obtain a reasonable fit to $S_{cc}(0)$. Thus the temperature variation of χ cannot be ignored when calculating ΔS and ΔH from the model ΔG, for which we now write

$$\Delta G = -T\Delta S_{hs} + \chi\phi + p\Delta V \tag{6}$$

Here ΔS_{hs} rather than expression (4) is identified as the kinetic energy contribution to the entropy change and there is now also a potential energy contribution from the temperature variation of $\chi\phi$. Equation (6) could also be written in terms of the interchange parameter ω already introduced, viz.

$$\Delta G = -T(\Delta S_{hs} + \Delta S') + \omega\phi + p\Delta V$$

the additional entropy contribution being given by $-T\Delta S' = (\chi - \omega)\phi$.

At this point a possible next step would be to regard ΔS_{hs} as calculable using the experimentally determined volumes together with hard sphere diameters obtained from independent calculations of the properties of pure Na and pure Cs (Table I of Visser *et al.*[2]). We prefer, however, to allow for the possibility that the effective diameters may be composition dependent, and therefore regard ΔS_{hs} (as well as χ) as a parameter to be calculated by fitting to the experimental data. From Eq. (6) we now have

$$\begin{aligned}\Delta S &= -(\partial\Delta G/\partial T)_p \\ &= \Delta S_{hs} + T\left(\frac{\partial \Delta S_{hs}}{\partial T}\right)_p - \phi\left(\frac{\partial\chi}{\partial T}\right)_p - \chi\left(\frac{\partial\phi}{\partial T}\right)_p - p\left(\frac{\partial\Delta V}{\partial T}\right)_p\end{aligned} \tag{7}$$

in which for Na–Cs the last term on the right hand side is zero. Equations (6) and (7) contain four unknown quantities: ΔS_{hs}, χ and their temperature derivatives. It seems reasonable to assume that the latter are constant over the limited range of available data. It would then appear that by writing Eq. (6) and (7) for two different temperatures an exact solution is possible. Unfortunately Eq. (7) at two different temperatures are very nearly the same (they would in fact be identical if ϕ and ΔS_{hs} were independent of T) so this method is unreliable. Since, however, the values of the hard sphere diameters of pure Na and Cs (taken from the references quoted) give packing and

TABLE I

Contributions to the entropy of mixing, in $\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}$, at $T = 383\mathrm{K}$, $p = 1$ bar

c	ΔS(id.)	ΔS(vol.)	$\Delta S_\eta + S_\sigma$	$\Delta S'$	Total	Excess
0.1	2.703	0.213	0.035	−0.227	2.724	0.021
0.2	4.161	0.391	0.067	−0.398	4.221	0.060
0.3	5.079	0.533	0.096	−0.528	5.179	0.100
0.4	5.596	0.635	0.119	−0.622	5.728	0.132
0.5	5.763	0.693	0.134	−0.676	5.915	0.152
0.6	5.596	0.703	0.140	−0.695	5.744	0.148
0.7	5.079	0.656	0.133	−0.668	5.199	0.120
0.8	4.161	0.537	0.110	−0.561	4.247	0.086
0.9	2.703	0.329	0.067	−0.301	2.797	0.094

misfit entropies of mixing which are nearly equal and of opposite sign the sum $(\Delta S_{\mathrm{gas}} + S_c)$ alone is a good first approximation to the hard sphere entropy of mixing. Eq. (6) then yields $\chi \simeq \{\Delta G - p\Delta V + T(\Delta S_{\mathrm{gas}} + S_c)\}/\phi$ at two temperatures, from which a first approximation value of $\partial\chi/\partial T$ is found. This is now used in Eq. (7) to obtain $\Delta S_{hs} + T(\partial \Delta S_{hs}/\partial T)$ at the same two temperatures. The assumed linear variation of ΔS_{hs} with T turns out to be very small and the resulting improved values of ΔS_{hs} are now inserted into Eq. (6) and the cycle of operations repeated. After several iterations virtually exact fits were obtained, the final values of ΔS_{hs}, χ and their temperature derivatives being consistent with Eqs. (6) and (7) in which all other quantities are experimental.

3 RESULTS

From the parameters thus fitted, the various contributions to the properties of mixing are now calculated. The entropy of mixing is the sum of the hard sphere contributions

$$\Delta S(\text{ideal}) = -R\{(1-c)\ln(1-c) + c\ln c\}$$

$$\Delta S(\text{volume}) = R\{\ln V - (1-c)\ln V_1 - c\ln V_2\}$$

and

$$(\Delta S_\eta + S_\sigma) = \text{fitted } \Delta S_{hs} - \Delta S(\text{ideal}) - \Delta S(\text{volume})$$

together with the contribution $\Delta S'$ from the temperature derivatives in Eq. (7). These are all given in Table I. The reason for the small positive excess entropy, defined as ΔS(expt) − ΔS(ideal), is now seen to lie in the near cancellation of the contributions in columns 3 and 5 arising from (a) the differing molar volumes of Na, Cs and alloy, and (b) the change in potential energy on mixing.

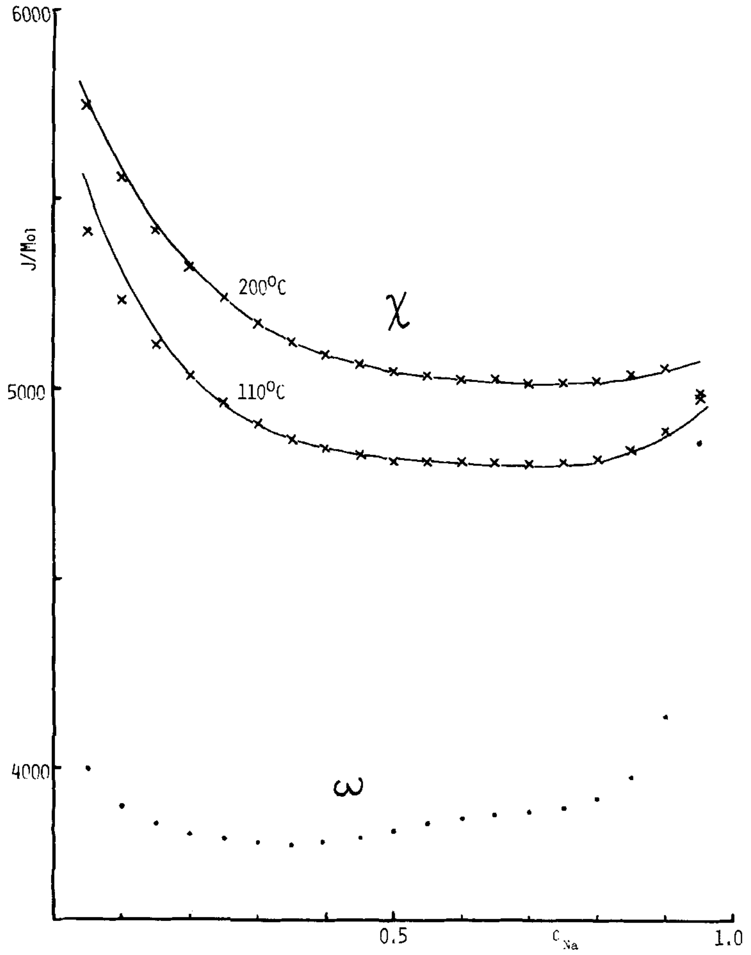

FIGURE 1 Variation of interchange parameters with Cs–Na composition. • × parameters fitted (exactly) to data, ——— approximate polynomial representation for model calculations.

Model cell emf, relative activities and $S_{cc}(0)$ are related to the model ΔG by

$$E = -\{\Delta G + (1 - c)(\partial \Delta G/\partial c)\}/F$$

$$a_{\mathrm{Na}} = \exp(\Delta \bar{G}_{\mathrm{Na}}/RT) = \exp(-FE/RT)$$

$$a_{\mathrm{Cs}} = \exp(\Delta \bar{G}_{\mathrm{Cs}}/RT) = \exp\{(\Delta G + cFE)/RT(1 - c)\}$$

$$S_{cc}(0) = RT/(\partial^2 \Delta G/\partial c^2)$$

in which quantities on the right hand side are model values. (F is the Faraday constant.) For analytical convenience ΔG and its derivatives are obtained by approximating the concentration variation of the fitted parameter χ by a 4th order polynomial in c as shown in Figure 1. For a given temperature χ is seen to be almost independent of composition over most of the middle part of the

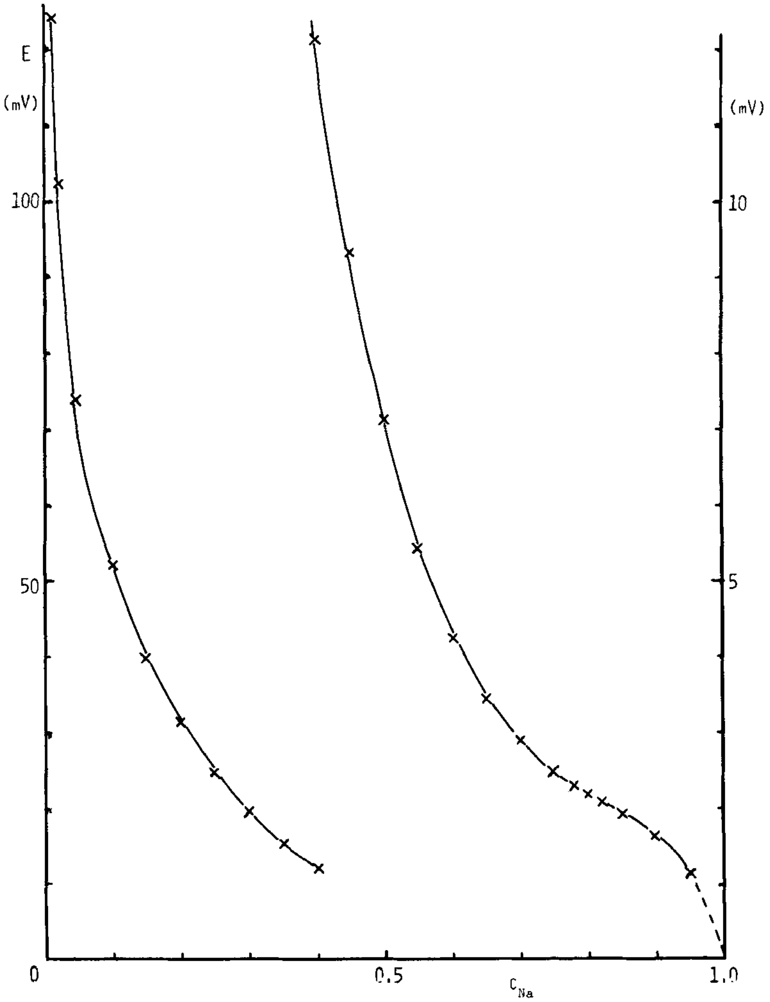

FIGURE 2 Cell emf at 110°C, 1 bar. × observed ——— model (note change of scale at $c_{Na} = 0.4$).

concentration range, but rises noticeably for Na mole fractions above 0.8 and appreciably (as much as 16%) for Cs mole fractions above 0.7.

It was also necessary to express in simple analytical form that part of the entropy arising from packing and misfit in the hard sphere mixture, the sum $(\Delta S_\eta + S_\sigma)$ being well represented by a 4th order polynomial in c. The model polynomials for χ, $(\Delta S_\eta + S_\sigma)$ and also for ΔV are given in the Appendix. Results of the model calculations are shown in Figures 2, 3 and 4 where the exactness of fit follows from that of Eq. 6. The errors in the experimental points are discussed in I.

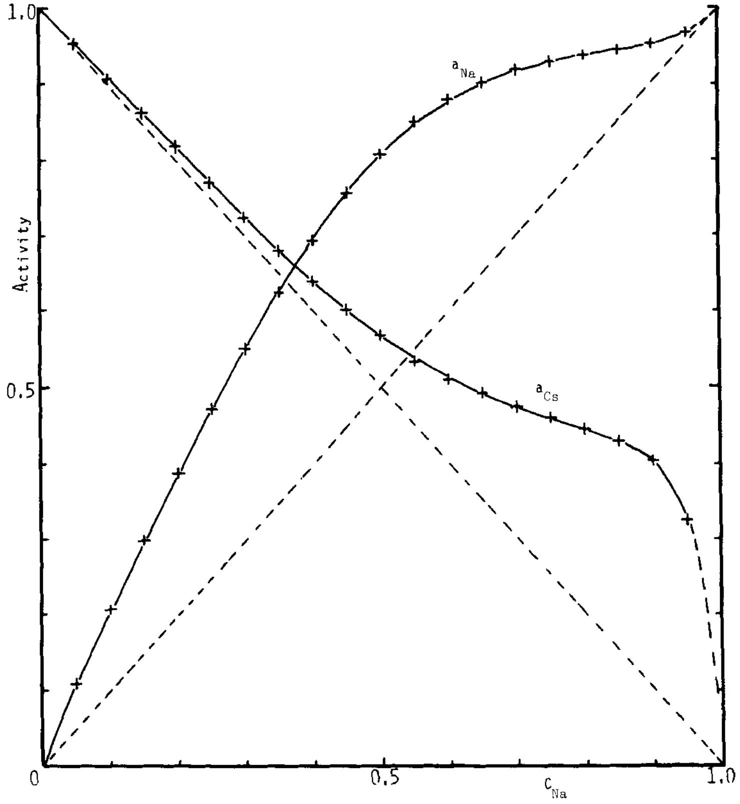

FIGURE 3 Relative activities in Cs–Na at 110°C, 1 bar × observed ——— model.

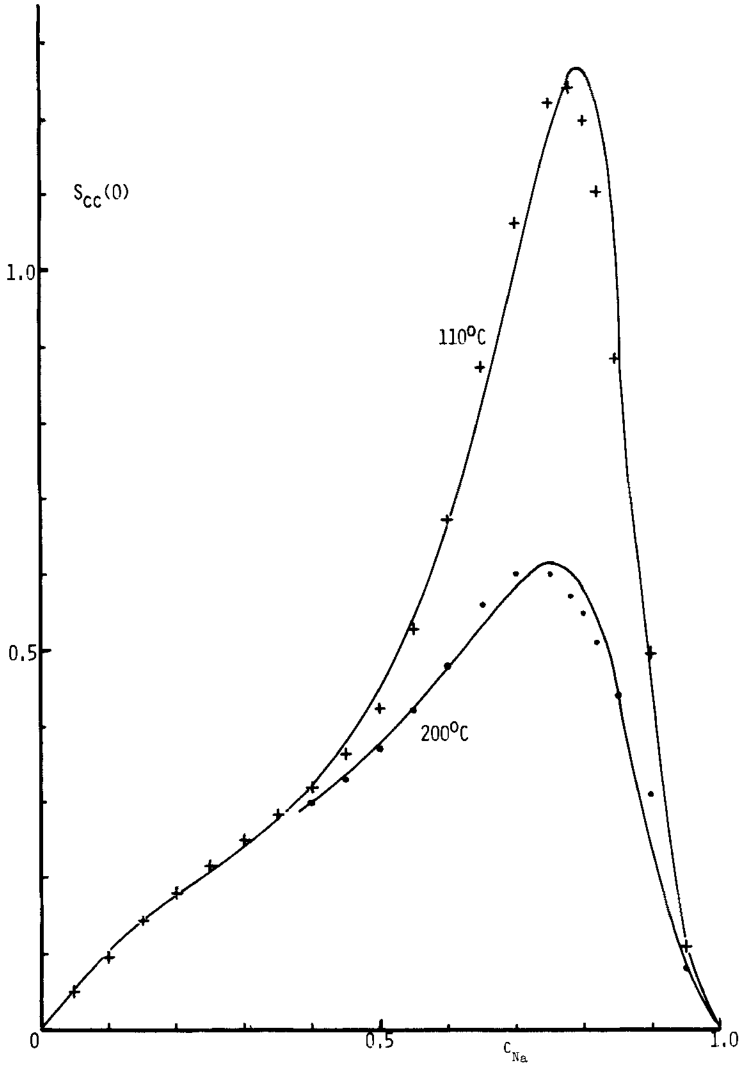

FIGURE 4 $S_{cc}(0)$ at 110°C and 200°C ($p = 1$ bar) + • observed ——— model.

4 THE ENERGY INTERCHANGE PARAMETERS

In the fitting process χ was taken to be linear in T, an assumption that can be further justified as follows. Referring to Eq. (7) the experimental value of ΔS is independent of T and ΔS_{hs} is expected to be only very weakly T dependent. The term $\chi(\partial\phi/\partial T)_p$ contributes only about 0.5% to ΔS, so $(\partial\chi/\partial T)_p$ must be constant. Independent confirmation of this result for one particular concentration, $c = 0.85$, is provided by the work of Alblas *et al.*[4]. These authors investigated the variation with temperature of the small angle structure factor $S(0)$ and fitted a Flory–Huggins type model to the results. Their fitted interchange parameter was found to vary linearly with T in the range 80 to 190°C, but the relative change in its value over a given temperature range was about twice the relative change we find for χ.

But it is the parameter $\omega(c)$ which is of more interest in connection with *ab initio* calculations of the change in free energy of such systems, its product with the volume function $\phi(c)$ giving directly the internal energy change ΔU for Na–Cs. One important and easily calculated part of this is the zero temperature free electron gas term. In terms of the molar volumes it is given by

$$\Delta U_{eg} = \text{const.}(V^{-2/3} - c_1 V_{\mathrm{Cs}}^{-2/3} - c_2 V_{\mathrm{Na}}^{-2/3}) \text{ per mole}$$

where const. $= 0.3(\hbar^2/m_e)(3\pi^2)^{2/3}N_A^{5/3}$ and N_A = Avogadro's No. This contribution turns out to be an order of magnitude greater than ΔU and of opposite sign, the ratio $\Delta U_{eg}/\Delta U$ ranging from about -17 at $c = 0.05$ to -10 at $c = 0.95$. The importance of an accurate knowledge of $V(c)$ is evident; it is required also, either directly or indirectly, in the calculations of other contributions to the energy of mixing—exchange, correlation, Madelung etc. terms—each of which is expected to be large compared with ΔU or ΔH; cf. calculations for $\mathrm{Na_{0.5}K_{0.5}}$, Umar *et al.*[5]. It will be interesting to see whether or not similar calculations of these quantities for Na–Cs using the volume data of I result in the concentration variation of ΔU implied by Figure 1.

That part of the entropy change which is due to the change in entropy of the free electron gas is also readily calculated. Following Silbert *et al.*[6], a sufficiently accurate approximation for this calculation is

$$\Delta S_{eg} = \text{const.}(V^{2/3} - c_1 V_{\mathrm{Cs}}^{2/3} - c_2 V_{\mathrm{Na}}^{2/3}) \text{ per mole where}$$
$$\text{const.} = N_A^{1/3} m_e(\pi k_b/\hbar)^2 T/(3\pi^2)^{2/3}.$$

ΔS_{eg} is found to be only ~ 1% of $\Delta S'$ whose origins must therefore be sought elsewhere.

5 HARD SPHERE DIAMETERS

With ΔS_{hs} determined by the parameter fitting procedure and ΔS_{gas} calculable from $V(c)$ Eq. 5 can be used to determine $(\Delta S_\eta + S_\sigma)$. Within the validity of the proposed model this sum is an experimental quantity. Its two terms are expressible as functions of the hard sphere diameters σ_1 and σ_2 by

$$\Delta S_\eta/R = -(\zeta - 1)(\zeta + 3) + C_1(\zeta_1 - 1)(\zeta_1 + 3) + C_2(\zeta_2 - 1)(\zeta_2 + 3) \tag{8a}$$

$$S_\sigma/R = c_1 c_2 (\sigma_1 - \sigma_2)^2\{(x_1 + x_2)(\zeta^2 - \zeta - \ln\zeta) + 3x_1(\zeta - 1)\} \tag{8b}$$

(Umar *et al.*[7]; Yokoyama *et al.*[8])

In these expressions $\zeta_i = 1/(1 - \eta_i)$ and the packing fraction of i is $\eta_i = \sigma_i \pi^3/6\Omega_i$; for the alloy $\zeta = 1/(1 - \eta)$ and $\eta = \pi(c_1\sigma_1^3 + c_2\sigma_2^3)/6\Omega$; finally

$$x_1 = (\sigma_1 + \sigma_2)/(c_1\sigma_1^3 + c_2\sigma_2^3)$$

and

$$x_2 = \sigma_1\sigma_2(c_1\sigma_1^2 + c_2\sigma_2^2)/(c_1\sigma_1^3 + c_2\sigma_2^3)^2.$$

Equations 8, with the sum of the left hand sides set equal to $(\Delta S_\eta + S_\sigma)$(expt.) cannot be solved explicitly for both σ_1 and σ_2; but by choosing a diameter for sodium lying within the range of values determined from previous *ab initio* calculations (Table I of Visser *et al.*[2]) it is possible to find the corresponding caesium diameter with considerable precision. The accuracy of the result depends on the reliability of $(\Delta S_\eta + S_\sigma)$(expt.) which is only a small fraction of the total entropy change. After all sources of error involved in its computation are considered it is concluded that the packing and misfit of the hard spheres in this model together contribute between 0 and 5 % of the total entropy of mixing over the whole concentration range, i.e. $(\Delta S_\eta + S_\sigma)$ is almost certainly positive, has a roughly parabolic variation with c, and reaches a peak value of not more than 0.3 $\text{JK}^{-1}\,\text{mol}^{-1}$. To determine the hard sphere diameter ratio the criterion adopted was that fitted diameters should reproduce the values of $(\Delta S_\eta + S_\sigma)$ in Table I to within ±100 % over the whole concentration range. Calculations were carried out for sodium diameters in the range 3.15 to 3.45 Å but no pair of concentration independent diameters could be found which satisfied this criterion. Improved agreement between $(\Delta S_\eta + S_\sigma)$ calculated from Eq. 8 and the experimental results was obtained by allowing the diameter of each component to decrease by up to about 0.7 % as its mole fraction in the alloy decreases from unity to zero, but was still unsatisfactory when the $\sigma_i(c)$ were chosen to be simple linear or quadratic functions of c. However, a dramatic improvement resulted on choosing a simple cubic variation of the form shown in Figure 5(A). The

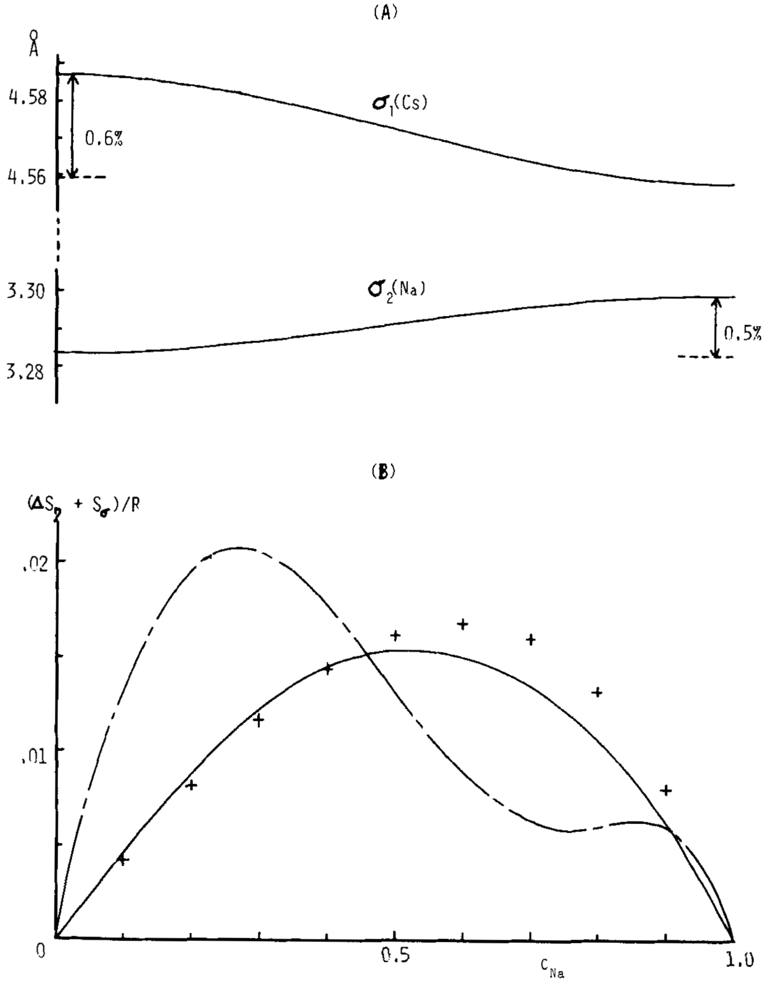

FIGURE 5 (A) Variation of hard sphere diameters with concentration (see text): $\sigma_1 = 4.587 - 0.028(3 - 2c)c^2$; $\sigma_2 = 3.284 + 0.016(3 - 2c)c^2$. (B) (Packing + misfit) contribution to entropy of mixing. + experimental. ——— calculated from diameters in (A). — — — — calculated from $\sigma_1 = 4.541$, $\sigma_2 = 3.30$ Å.

results are illustrated in Figure 5(B) for a pure sodium diameter of 3.3 Å; also shown is the best fit obtainable with concentration independent diameters.

From similar results obtained with other pure sodium diameters in the range 3.15 to 3.45 Å and also for data at 200°C it follows from this model that the ratio of the hard sphere diameters of the pure species σ_1/σ_2 must be very close to 1.390.

6 STRUCTURE FACTORS

The long wavelength limits of the Faber–Ziman structure factors are given in terms of $S_{cc}(0)$, the compressibility factor $\theta = RT\kappa_T/V$ and the dilatation factor $\delta = -(1/V)(\partial V/\partial c)_{T,p}$ by

$$a_{\mathrm{CsCs}}(0) = a_{11} = \theta - \frac{c}{1-c} + \left(\frac{1}{1-c} - \delta\right)^2 S_{cc}$$

$$a_{\mathrm{NaNa}}(0) = a_{22} = \theta - \frac{1-c}{c} + \left(\frac{1}{c} + \delta\right)^2 S_{cc}$$

$$a_{\mathrm{CsNa}}(0) = a_{12} = \theta + 1 - \left(\frac{1}{1-c} - \delta\right)\left(\frac{1}{c} + \delta\right) S_{cc}$$

(Bhatia and Thornton[9])

The variations of these factors with c are shown in Figure 6. To investigate further the observed large deviations from ideality in sodium-rich alloys we look for a possible separation into effects attributable to (i) the form of $V(c)$ for this alloy and (ii) the ion–ion interactions expressed by the parameter χ. Of course the latter are partially responsible for the former; nevertheless some insight may be gained by considering a hypothetical solution for which Eq. 6 is modified by putting $\chi = 0$, its change in Gibbs energy being

$$\Delta G' = -T\Delta S_{hs} + p\Delta V$$

Its properties depend on $V(c)$ and in particular its correlation function $S'_{cc}(0)$, obtained by evaluating $\partial^2 \Delta G'/\partial c^2$, is less than $S_{cc}(\text{ideal}) = c(1-c)$ for all c. The corresponding values of a'_{ij} calculated using S'_{cc} in the above Bhatia–Thornton formulae are also shown in Figure 6.

The deviations from ideality attributable to the separate volume effects and ion–ion interactions are conveniently summarized in the behaviour of the parameter (Bhatia *et al.*[10]) $A = a_{11} + a_{22} - 2a_{12}$.

It is easily shown that

$$S_{cc}(0) = S_{cc}(\text{ideal}) + c^2(1-c)^2 A$$

so that A measures the departure of $S_{cc}(0)$ from ideality. The behaviour of A' calculated from the a'_{ij} and of the quantity $A'' = A(\text{expt.}) - A'$ are shown in Figure 7. This figure expresses quantitatively for Na–Cs the qualitatively evident result that molar volume difference will not produce a sharp peak in S_{cc} in a purely hard sphere system and that some form of longer range ion–ion interaction must be involved. The latter completely dominates the departure from ideal behaviour in sodium-rich alloys despite the fact that the sodium–caesium reaction is only moderately endothermic.

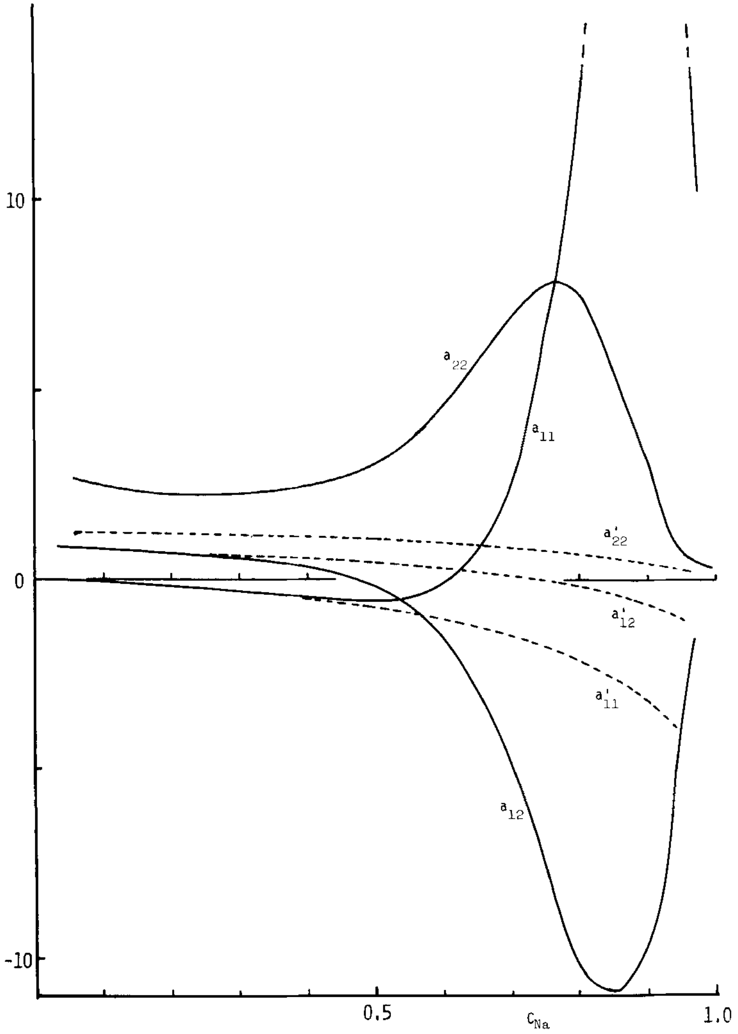

FIGURE 6 Structure factors $a_{ij}(0)$ for Cs–Na at 110°C, 1 bar. ——— observed ----- calculated for a hypothetical mixture for which $\Delta U = 0$.

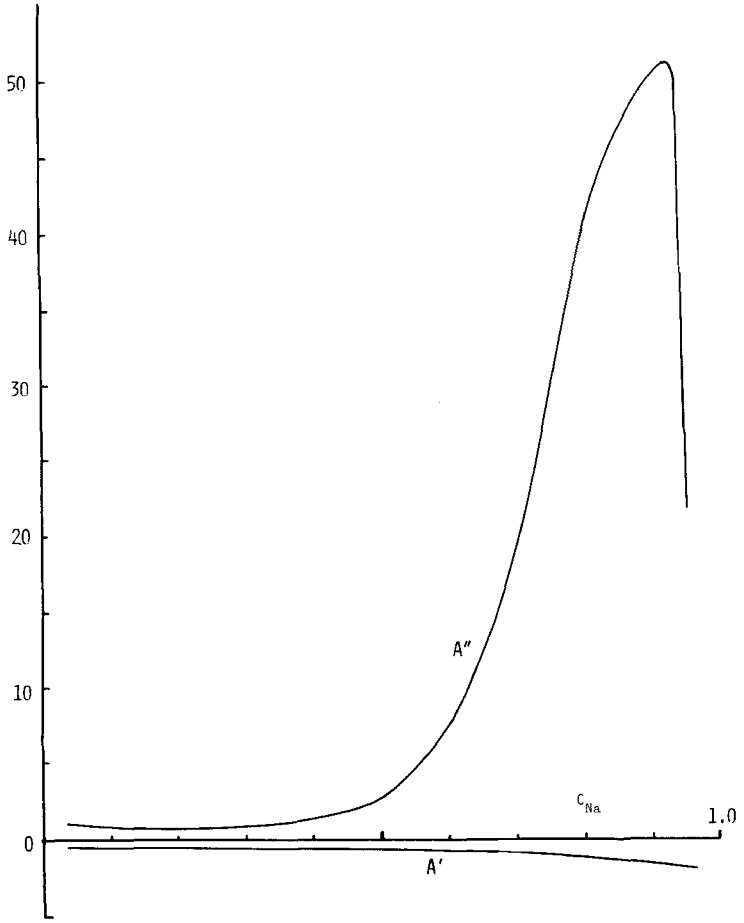

FIGURE 7 Contributions of ion-ion interactions as measured by A'' and of volume effects as measured by A' to deviations from ideality in Na-Cs at 110°C, 1 bar. For definitions of A'' and A' see text.

Acknowledgements

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References

1. F. E. Neale and N. E. Cusack, *J. Phys. F: Met. Phys.*, **12**, 2839 (1982).
2. E. G. Visser, W. van der Lugt, and J. Th. M. de Hosson, *J. Phys. F: Met. Phys.*, **10**, 1681 (1980).
3. A. B. Bhatia and N. H. March, *J. Phys. F: Met. Phys.*, **5**, 1100 (1975).
4. B. P. Alblas, J. Dijkstra, W. van der Lugt, and A. B. Bhatia, *Phys. Chem. Liq.*, **12**, 255 (1983).
5. I. H. Umar, A. Meyer, M. Watabe, and W. H. Young, *J. Phys. F: Met. Phys.*, **4**, 1691 (1974).
6. M. Silbert, I. H. Umar, M. Watabe, and W. H. Young, *J. Phys. F: Met. Phys.*, **5**, 1262 (1975).
7. I. H. Umar, I. Yokoyama, and W. H. Young, *Phil. Mag.*, **34**, 535 (1976).
8. I. Yokoyama, A. Meyer, M. J. Stott, and W. H. Young, *Phil. Mag. A*, **40**, 729 (1979).
9. A. B. Bhatia and D. E. Thornton, *Phys. Rev.*, **B2**, 3004 (1970).
10. A. B. Bhatia, W. H. Hargrove, and N. H. March, *J. Phys. C: Solid State Phys.*, **6**, 621 (1973).

Appendix

For the model calculations referred to in Section 3 the following polynomials were used:

χ is expressed in terms of a dimensionless parameter X by

$$X = \chi/RT = a_0 + a_1c + a_2c^2 + a_3c^3 + a_4c^4$$

for which the coefficients are given in the following table:

p(bar)	$T(K)$	a_0	a_1	a_2	a_3	a_4
1	383	1.825	−2.000	4.968	−5.657	2.444
1	473	1.523	−1.291	2.708	−2.700	1.061
200	383	1.800	−1.975	4.969	−5.660	2.444

The combined packing and misfit contribution to the entropy of mixing is given by

$$\Delta S_\eta + S_\sigma = 0.3569c - 0.0781c^2 - 0.1150c^3 - 0.1637c^4 \text{ JK}^{-1}\text{ mol}^{-1}$$

and the excess volume by

$$\Delta V = -11.249c + 9.438c^2 + 4.765c^3 - 2.957c^4 \text{ cm}^3\text{ mol}^{-1}$$