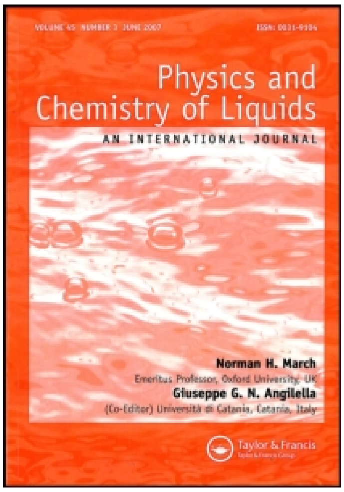

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Thermodynamic Properties of Liquid Na-Tl

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To cite this Article Gray, P. , Cusack, N. E. , Tamaki, S. and Tsuchiya, Y.(1980) 'Thermodynamic Properties of Liquid Na-Tl', Physics and Chemistry of Liquids, 9: 4, 307 — 321
To link to this Article: DOI: 10.1080/00319108008084783
URL: http://dx.doi.org/10.1080/00319108008084783

Phys. Chem. Liq., 1980, Vol. 9, pp. 307–322
0031-9104/80/0904-0307$04.50/0

Thermodynamic Properties of Liquid Na-Tl

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(*Received January 29, 1980*)

New measurements of the free energy and entropy of mixing and associated thermodynamic properties of liquid Na-Tl alloys at three temperatures are reported. A thermodynamic model is developed and fitted to these with success but the failure of the model to fit the properties of Na-Ga is reported. The problems involved in fitting thermodynamic models are discussed.

1 INTRODUCTION

The objects of this paper are: to report some new experimental measurements of the thermodynamic properties of the liquid Na-Tl system; to discuss the problem of fitting chemical thermodynamic models; to extend a model already discussed by Bhatia and Hargrove (1974);[1] to apply the extended model to Na-Tl and also to the properties of Na-Ga reported previously[2] (Tamaki and Cusack, 1979).

The compilation by Hultgren *et al.*[3] (1973) and the periodical literature records several previous measurements over various composition ranges and at certain temperatures using both EMF and calorimetric methods. Consistency of results is fair[3] and will be referred to below. The present work exploited the properties of Na β-alumina, a superionic conductor, to make a concentration cell in which the EMF was measured from the liquidus temperature to 903 K and the thermodynamic properties calculated at $T = 593$, 743 and 893 K with the Na concentration in the range $0.05 < c < 0.85$.

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2 EXPERIMENT AND RESULTS

In a previous paper[2] on Na-Ga (Tamaki and Cusack, 1979) the EMF cell using β-alumina was described and the same method was used here. The cell voltage and temperature were measured with a digital voltmeter (Schlumberger Solartron 7055). The Na and Tl were of purities 99.99 and 99.999 at. % respectively.

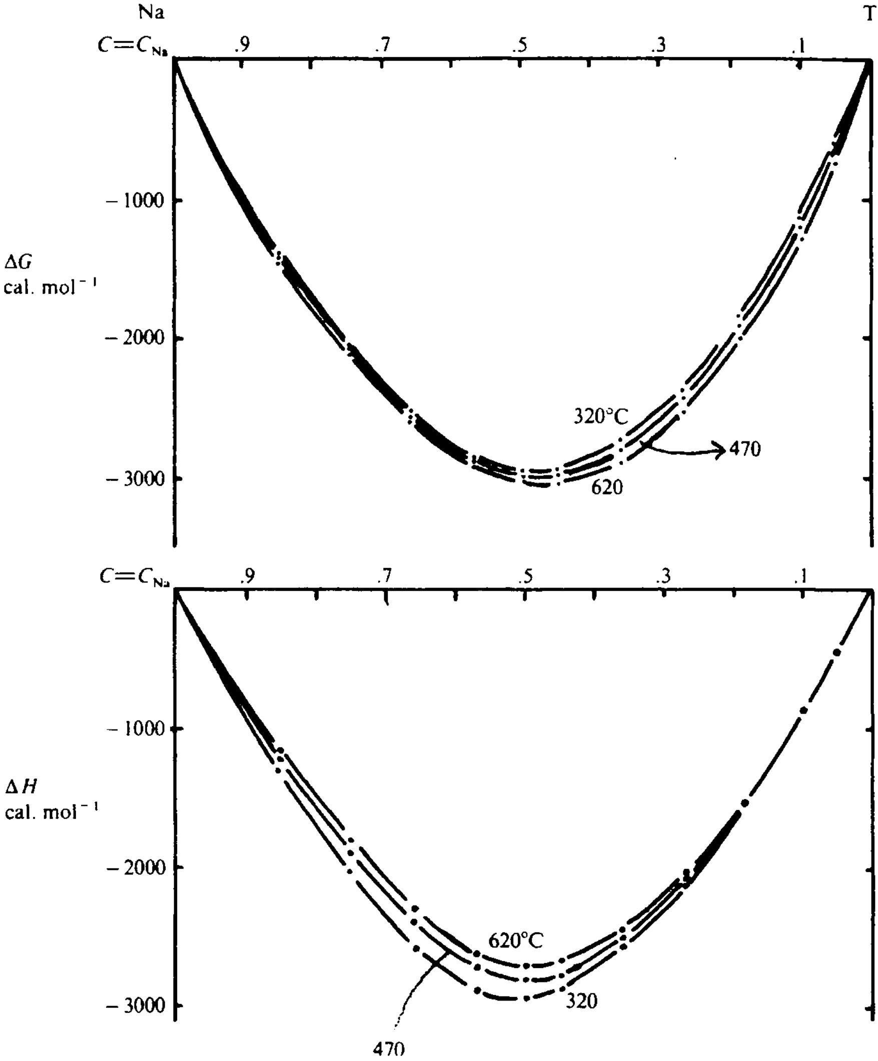

FIGURE 1 Measured values of ΔG and ΔH for Na-Tl. Note that pure Na, $c = 1.0$, is on the left

TABLE I

Observed Na-Tl cell voltage

	T°C							
$c = c_{Na}$	340	380	420	460	500	540	580	620
0.05	0.4840	0.4904	0.4972	0.5038	0.5100	0.5168	0.5238	0.5302
0.10	0.4102	0.4140	0.4181	0.4220	0.4260	0.4300	0.4340	0.4380
0.1864	0.3356	0.3365	0.3375	0.3387	0.3401	0.3417	0.3434	0.3452
0.27	0.2716	0.2710	0.2705	0.2702	0.2702	0.2703	0.2707	0.2711
0.36	0.2068	0.2055	0.2043	0.2034	0.2028	0.2023	0.2021	0.2019
0.45	0.1470	0.1458	0.1448	0.1439	0.1433	0.1429	0.1426	0.1424
0.50	0.1157	0.1148	0.1141	0.1135	0.1132	0.1130	0.1129	0.1128
0.57	0.0774	0.0771	0.0770	0.0772	0.0774	0.0778	0.0782	0.0787
0.66	0.0424	0.0429	0.0435	0.0440	0.0446	0.0452	0.0458	0.0465
0.75	0.0227	0.0233	0.0239	0.0244	0.0250	0.0255	0.0261	0.0267
0.85	0.0107	0.0100	0.0113	0.0117	0.0120	0.0123	0.0126	0.0130
0.95[a]	0.0032	0.0032	0.0033	0.0034	0.0035	0.0036	0.0037	0.0038

[a] Values for $c = 0.95$ are interpolated.

The values of $E(c, T)$ given in Table I were read from graphs drawn through the raw data points. We regard Table I as the experimental results. There are various ways of processing cell voltages to obtain thermodynamic quantities and some care is needed to avoid processing uncertainties which, though unavoidable, can at least be minimised.

The following equations were used; the notation is conventional as, for example, in Hultgren *et al.*[3] (1973).

$$\alpha(c) = -\frac{(zFE(c) + RT \ln c)}{(1-c)^2} \tag{1}$$

$$\beta(c) = \frac{-zE(\partial E/\partial T)_c}{(1-c)^2} \tag{2}$$

$$\Delta S = (1-c)\int_0^c \beta(c)dc \tag{3}$$

$$\Delta G = (1-c)\int_0^c \alpha(c)dc + RT\{c \ln c + (1-c)\ln(1-c)\} \tag{4}$$

$$\Delta\bar{G}_{Na} = -zFE(c) \tag{5}$$

$$\Delta\bar{G}_{Tl} = \frac{\Delta G}{1-c} - \frac{c}{1-c}\Delta\bar{G}_{Na} \tag{6}$$

$$\Delta H = \Delta G + T\Delta S \tag{7}$$

$$S_{cc} = \frac{-RT}{zF}\frac{1-c}{\partial E/\partial c} \tag{8}$$

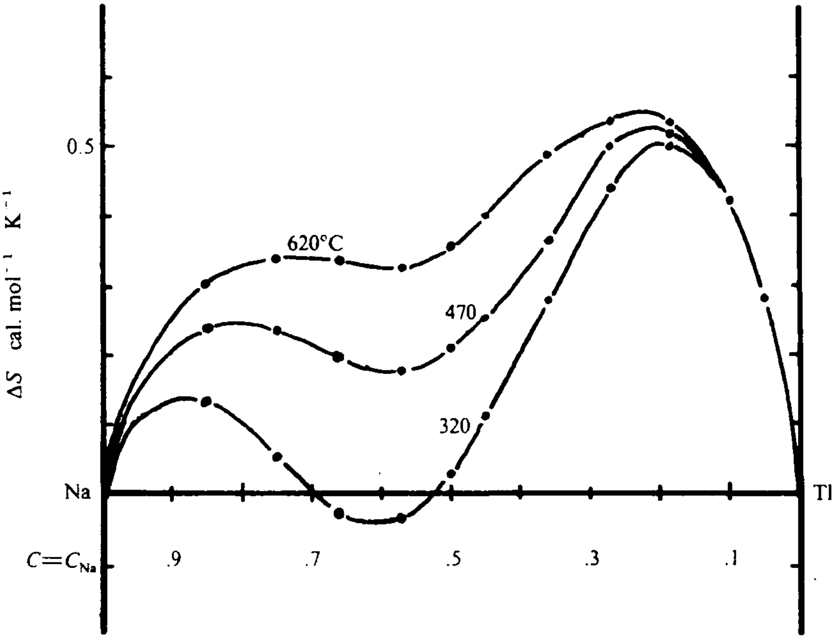

FIGURE 2 Measured value of ΔS for Na-Tl.

In these equations, $z = 1$ for Na and ΔG, ΔS, ΔH refer to 1 mole of alloy. First, $\beta(c)$ was evaluated from $(\partial E/\partial T)_c$ and fitted as a function of c at three chosen temperatures. ΔS was then found from Eq. 3. $\alpha(c)$ was calculated and Eq. 4 used to obtain ΔG. $\Delta\bar{G}_{\text{Na}}$ and $\Delta\bar{G}_{\text{Tl}}$ then come from Eq. 5 and 6 and ΔH from Eq. 7. From the numerator of $\alpha(c)$, which is zero for $c = 1$, $\partial E/\partial c$ was calculated in order to find S_{cc} from Eq. 8. All this can conveniently be done in one computer run.

The results are shown in Figures 1 to 4 and Table II. Figure 5 compares our data with others'.

3 THERMODYNAMIC MODELS IN GENERAL

The Pauling electronegativities of Na and Tl are 0.9 and 1.4 respectively. These phase diagram (Hansen 1958)[4] is fairly complex in the solid state and shows its most stable intermetallic compound, with composition NaTl, melting at 305°C. Few marked features are known in the electronic properties of the liquid state. $(\partial\rho/\partial T)$, where ρ is resistivity, changes sign at 50% Na, being negative over the range $c = 0.5$ to 0.7 (Kitajima and Shimoji, 1977).[5] The electron density increases by a factor ~4 from Na to Tl assuming valencies 1 and 3. The number of free electrons per Tl atom is however not very

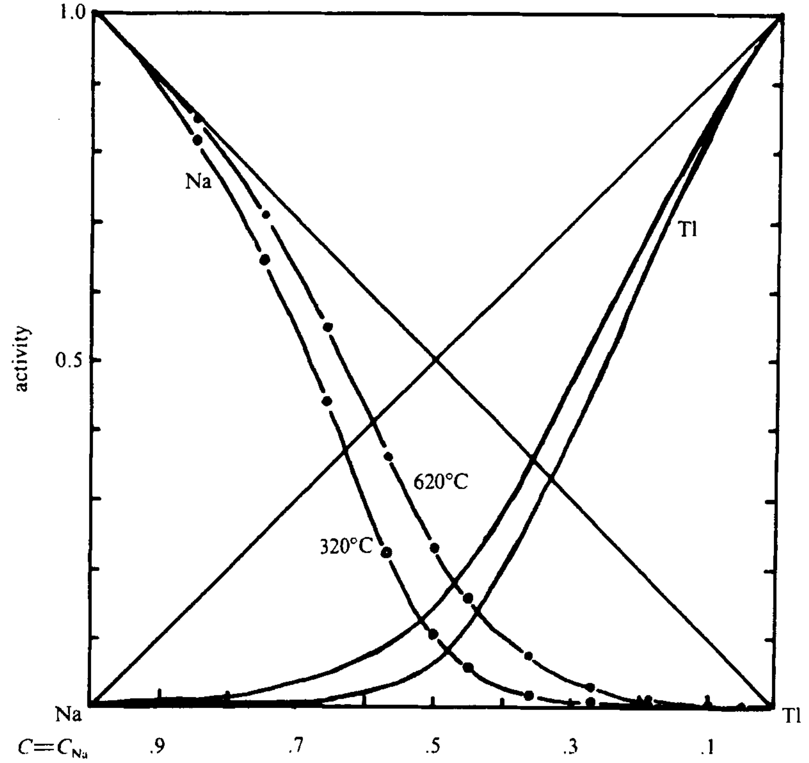

FIGURE 3 Measured activities in Na-Tl.

certain. The marked minimum in the magnetic susceptibility at the equiatomic composition in the solid is reduced in the liquid to a relatively minor departure from linear composition dependence. This was shown by Uemura *et al.*[6] (1978) who gave arguments concluding that the electron density of states at E_F is about 7% above the free electron value on liquid NaTl with a possible though, not certain, inference that the atoms are not distributed randomly at this composition.

The minima in ΔG, ΔH and S_{cc} occur at ~50 at % Na and this evidence of greatest heat of mixing and smallest concentration fluctuation *may* be connected with the stability of the solid with this composition. Arguments of this kind have been expanded into chemical thermodynamic models with considerable success by, for example, Bhatia and Hargrove[1] (1974; Te-Tl, Mg-Bi, Cu-Sn, Ag-Al) but with less success by Tamaki and Cusack[2] (1979; Na-Ga). An essential concept in these arguments is the cluster or complex which is a group of atoms, $A_\mu B_\nu$, assumed to form in the liquid with a lifetime much longer than that of the same group in an ideal mixture but very short compared with that of a stable molecule in a molecular fluid. The

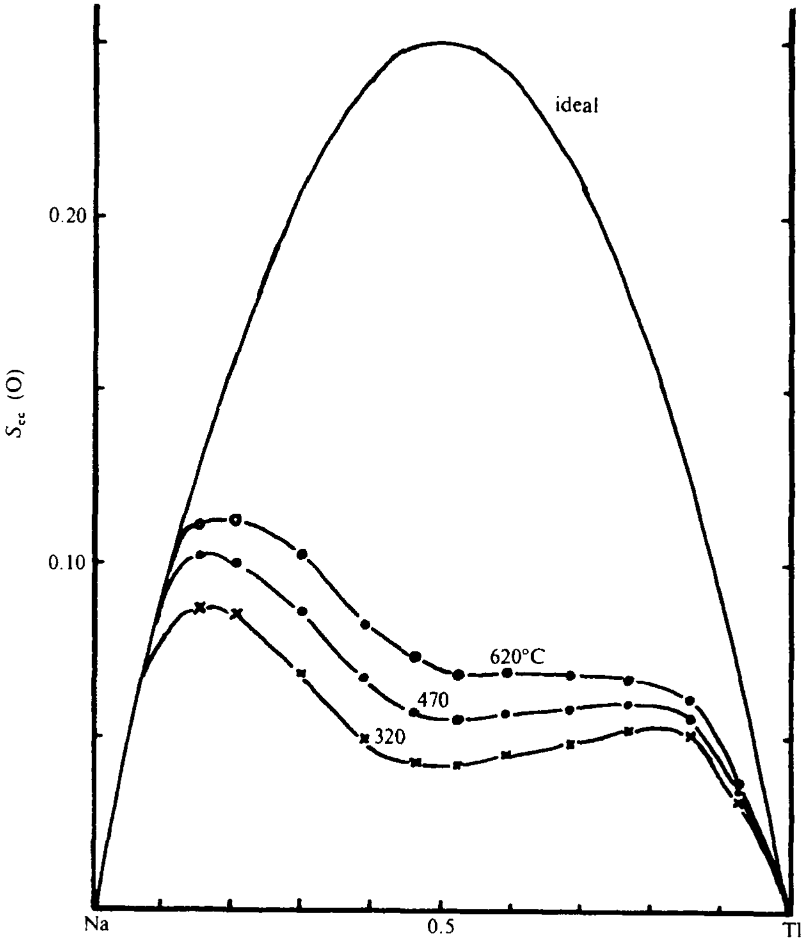

FIGURE 4 Measured values of S_{cc}.

cluster is supposed to be characterised by the small numbers (μ, ν) and to influence by its existence the partial radial distribution functions and therefore also the thermodynamic properties which can be calculated from these in principle. Without knowledge of any spatial distribution functions, one way of proceeding[1,7] (Bhatia and Hargrove, 1974; McAllister and Crozier, 1974) is to treat these clusters as unstable molecules with Gibbs free energy of formation $g(T)$ per mole. There is no certainty that any clusters forming in the liquid will have resemblances either to crystal structures because there is no imposition of long range order; or to free molecules in a gas phase because the effective interatomic forces will have been modified. Consequently

TABLE II

Thermodynamic properties of liquid Na–Tl alloys at 480°C

c_{Na}	$\Delta\bar{G}_{Na}$ cal mol^{-1}	$\Delta\bar{G}_{Tl}$ cal mol^{-1}	ΔG cal mol^{-1}	$\Delta\bar{S}_{Na}$ cal mol^{-1} K^{-1}	$\Delta\bar{S}_{Tl}$ cal mol^{-1} K^{-1}	ΔS cal mol^{-1} K^{-1}	ΔH cal mol^{-1}
0.1	−9962	−239	−1211	2.43	0.20	0.42	−896
0.2	−7596	−646	−2036	0.70	0.49	0.53	−1636
0.3	−5726	−1269	−2606	−0.16	0.77	0.49	−2238
0.4	−4802	−2155	−2926	−0.38	0.88	0.37	−2644
0.5	−2650	−3327	−2989	−0.18	0.70	0.26	−2792
0.6	−1530	−4690	−2794	0.22	0.22	0.22	−2630
0.7	−817	−6001	−2372	0.35	0.00	0.24	−2191
0.8	−409	−7217	−1771	0.27	0.23	0.27	−1571
0.9	−168	−8606	−1012	0.13	1.07	0.23	−841

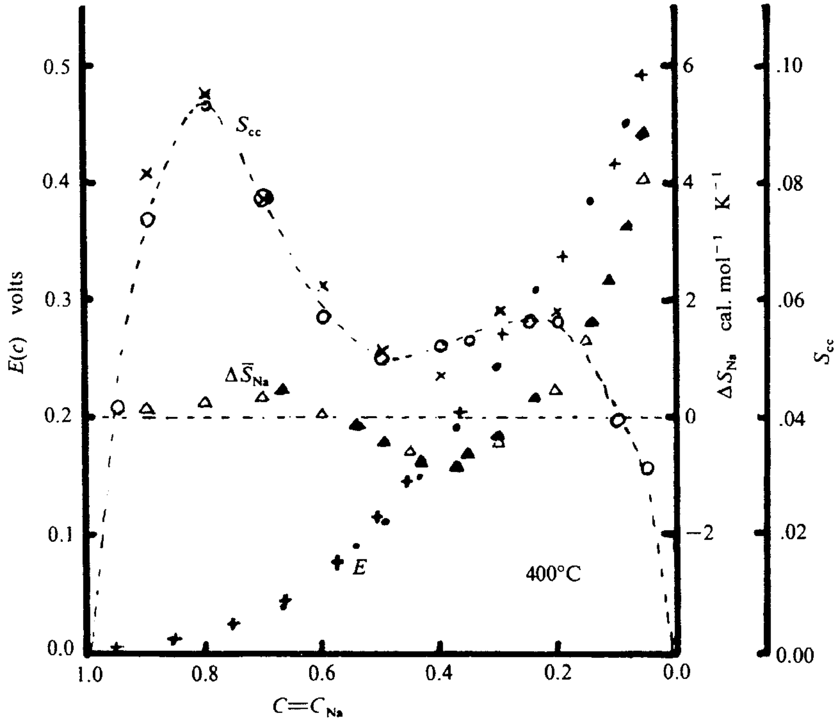

FIGURE 5 Literature comparisons. + $E(c)$ present work; ● $E(c)$ from Ref. 10. ⊙ S_{cc} present work; × S_{cc} computed from data in Ref. 3. △ $\Delta \bar{S}_{Na}$ from present work; ▲ $\Delta \bar{S}_{Na}$ from Ref. 10. All data refer to 400°C.

the nature of any clusters suggested by thermodynamic results are not necessarily to be inferred from other known structures.

A first attempt to discuss Na-Ga in these terms was by Tamaki and Cusack[2] (1979) and a more general one is given below. Bhatia and Hargrove[1] (1974) set the matter out very clearly and we will therefore adopt their notation and definitions. Their N can later be put equal to unity to represent 1 mole of alloy. A modification of their model will first be given.

4 A PARTICULAR THERMODYNAMIC MODEL

i) The model of Bhatia and Hargrove is not essentially altered in this section but generalised to allow the components to have different volumes. The interaction term has also been symmetrised. There seems no justification for either asymmetry or equal volumes in Na-Tl or Na-Ga. The molar volumes of the pure liquids differ by a factor of about 2 and they are incorporated

In Eq. (13) and (14), $n = \sum_i n_i$ is the total number of moles present in the pseudo-binary mixture, and the primes denote differentiation with respect to c.

Since the A_j are defined by

$$G_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n'} = G_i^{(0)} + RT\ln\left(\frac{n_i}{n}\right) + A_i, \tag{15}$$

where the differentiation is carried out holding $n_k(k \neq j)$ constant, the A_j appropriate to the model described by Eq. (9) may be calculated in a straightforward way. When these are inserted in Eqs. (13) and (14), the general equations for S_{cc} and chemical equilibrium are found to be

$$S_{cc}^{-1} = \sum_{i=1}^{3} n_i\left(\frac{n_i'}{n_i}\right)^2 - n\left(\frac{n_i}{n}\right)^2 + n\left(\frac{n'}{n} - \frac{V'}{V}\right)^2$$
$$+ \frac{1}{2VRT}\sum_{i\neq j=1}^{3}\sum \chi_{ij}(v_i + v_j)n_i n_j\left(\frac{n_i'}{n_i} - \frac{V'}{V}\right)\left(\frac{n_j'}{n_j} - \frac{V'}{V}\right), \tag{16}$$

where

$$S_{cc} = RT/(\partial^2 G/\partial c^2)_{T,p,N}$$

has been used, and

$$\frac{\phi_1^{\mu}\phi_2^{\nu}}{\phi_3} = K\exp\left\{-(\mu + \nu - 1) + \frac{n\delta}{V} - Z\right\} \tag{17}$$

where

$$\delta = \mu v_1 + \nu v_2 - v_3$$

is the volume by which the complex $A_\mu B_\nu$ is smaller than that of its constituent particles, $K = \exp(-g/RT)$ is the usual equilibrium reaction constant, and

$$Z = \frac{1}{2VRT}\left\{\chi_{12}(v_1 + v_2)(\nu n_1 + \mu n_2 - n_1 n_2\delta/V) + \chi_{13}(v_1 + v_3)(\mu n_3 - n_1 - n_1 n_3\delta/V)\right.$$
$$\left. + \chi_{23}(v_2 + v_3)(\nu n_3 - n_2 - n_2 n_3\delta/V)\right\} \tag{18}$$

ii) It is of interest to study the limiting behaviour of Eq. (16) for several reasons. In the limit of high temperature, and when the tendency of A and B atoms to form a compound is very weak ($K \to \infty$), the form of S_{cc} should approximate to that for the binary regular solution. In fact, however, some terms due to the volume effects remain:

$$S_{cc} = \frac{c(1-c)}{1 + c(1-c)\left\{\left[\dfrac{v_1 - v_2}{cv_1 + (1-c)v_2}\right]^2 - \dfrac{\chi_{12}}{RT}\dfrac{v_1 v_2 (v_1 + v_2)}{(cv_1 + (1-c)v_2)^3}\right\}} \tag{19}$$

In the special case $v_1 = v_2$, the usual regular solution result is recovered.

If A and B tend to form a highly stable compound, an analytic solution for S_{cc} may be obtained, for as $K \to 0$ either n_1 or n_2 vanishes; thus the pseudo-binary mixture contains either compound and pure A only, or compound and pure B only.

The final form of S_{cc}, which is now an explicit function of c only (i.e., it does not depend on an n_3 which satisfies Eq. (17)) may be put in the compact form

$$\begin{aligned} \mu^2 S_{cc}^{-1} &= \frac{1}{x(1-(\mu+v)x)(1-(u+\nu-1)x)} \\ &\quad + \frac{\left(\dfrac{v_3}{v_2} - 1\right)^2}{(1-(u+\nu-1)x)\left(1 + \left(\dfrac{v_3}{v_2} - (u+\nu)\right)x\right)^2} \\ &\quad - \frac{\chi_{23}}{RT}\frac{\dfrac{v_3}{v_2}\left(\dfrac{v_3}{v_2} + 1\right)}{\left(1 + \left(\dfrac{v_3}{v_2} - (\mu+v)\right)x\right)^3}; \; x = \frac{c}{\mu}, 0 < x \le \frac{1}{\mu+\nu}. \end{aligned} \tag{20}$$

Equation (20) also applies for the range $c \ge \mu/\mu + \nu$, with μ replaced by ν, subscript 2 replaced by 1 everwhere, and $x = (1-c)/\nu$. This limiting form of S_{cc} consists of two peaks, touching at stoichiometric composition $c = \mu/\mu + \nu$, where $S_{cc} = 0$. It is particularly useful because it shows immediately how important the effects of different molar volumes are likely to be in a system where $K \neq 0$, and also because reliable estimates of χ_{13} and χ_{23} may be obtained by fitting the peak heights using Eq. (20), for systems with small K.

5 NUMERICAL APPLICATION TO NaTl AND NaGa

A major difficulty with these thermodynamic models is the potentially large number of parameters. Apart from g and three χ_{ij}'s, μ and ν have to be chosen. Unless χ_{ij} is assumed to be constant, parameters may be needed to describe its concentration dependence. g and χ_{ij} will normally depend on temperature but this dependence may be regarded as determined experimentally if ΔG etc.

are fitted at several temperatures. Bhatia and Hargrove[1] obtained good model representations of ΔG and S_{cc} with two, or sometimes three, constant χ_{ij}'s by choosing the lowest values of μ and v in the appropriate ratio.

In NaTl it was not difficult to achieve quite good fits of the observed ΔG using only χ_{12} and g. Such fits deteriorated as the cluster size was increased above $\mu = 1 = v$. Good reproduction of S_{cc} and ΔS seemed unlikely with only one χ and ΔG was therefore fitted with Eq. 9, 17 and 18 by a Simplex minimisation method which gave the best values of g, χ_{ij}. This proved possible with an r.m.s. deviation of less than 0.6% and the Simplex calculation was consistent in arriving at the same parameter values from different initial values. The difference between the calculated and experimental values would not show in Figure 1.

S_{cc} was then calculated from Eq. 16 using the same parameters and compared with S_{cc} obtained in Section 2. The good agreement is shown in Figure 6. The parameters were:

NaTl Parameters

T°C	μ	v	g/RT	cal mol^{-1}	χ_{12}/RT	χ_{13}/RT	χ_{23}/RT
360	1	1	4.296	5400	−1.837	−0.321	−0.945
600	1	1	2.878	5000	−0.520	0.136	−0.527

Computations at other temperatures show that g and the χ_{ij}'s are closely linear functions of T.

To calculate ΔS from the model, approximate values of temperature derivatives of the parameters are obtained by fitting ΔG at 360° 380° and this gave satisfactory agreement with the entropy data using Eq. 21. This fit is also in Figure 6.

$$\Delta S = n_3 \frac{\partial g}{\partial T} - R \sum_i n_i \ln \phi_i - \frac{1}{2V}\left\{\frac{\partial \chi_{12}}{\partial T}(v_1 + v_2)n_1 n_2 + \frac{\partial \chi_{13}}{\partial T}(v_1 + v_3)n_1 n_3 + \frac{\partial \chi_{23}}{\partial T}(v_2 + v_3)n_2 n_3\right\} \tag{21}$$

On the other hand, an attempt to use the Simplex method to determine the temperature derivatives of the parameters by fitting the data directly with equation (21) failed, the reason apparently being that ΔS is linear in these quantities (whereas ΔG is a complex non-linear function of g and the χ_{ij} by virtue of Eq. (17)), and consequently the minimum sought by the Simplex is extremely wide and shallow. The good agreement obtained for the entropy may be taken as confirmation of the precision of the fit obtained to ΔG.

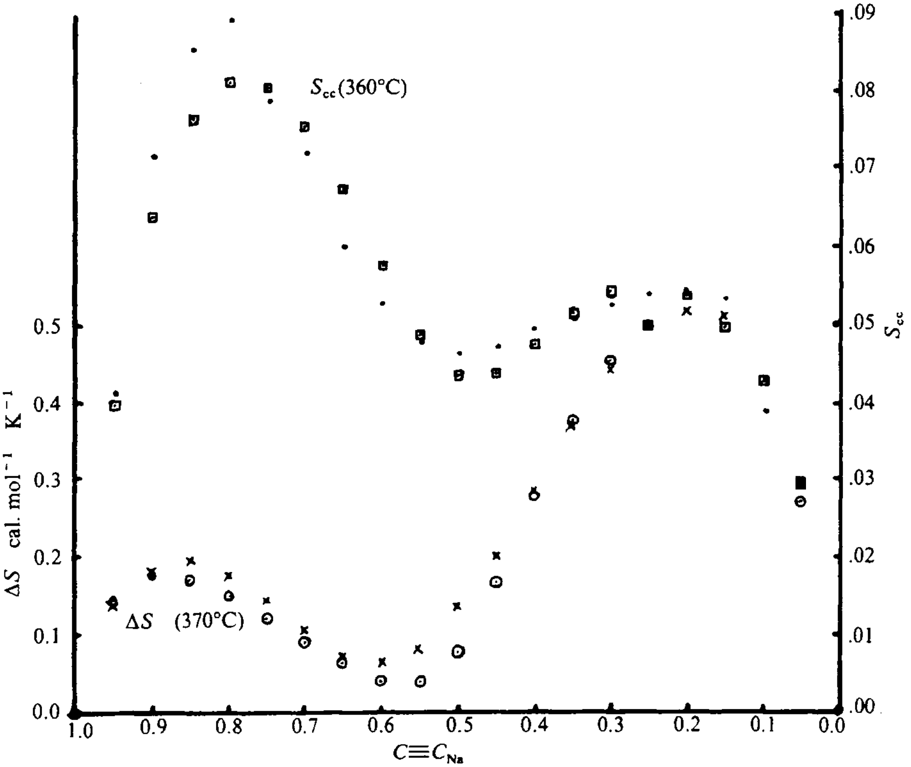

FIGURE 6 Comparison of calculated and experimental values of ΔS and $\bar{S}_{cc}$. ⊙ ΔS from model; × ΔS from experiment. ⊡ S_{cc} from model; ● S_{cc} from experiment.

The theory of the preceding section was unable to describe the data for Na-Ga satisfactorily. The precision of the best fit to ΔG was 10%, while that for the best fit to S_{cc} was 5%, but these could only be achieved with entirely different parameter sets (g, χ_{ij}).

Runs were made to determine whether cluster size was important, and also whether the model proposed here differed significantly from model (b) of Bhatia and Hargrove (1974).[1] For Na-Tl very little difference in the precision of fit was found for either test, but for Na-Ga the r.m.s. deviation of the fit to S_{cc} was three times larger in the model (b) case.

6 DISCUSSION AND SUMMARY

The work in reference 10 used pyrex glass and a molten salt as electrolytes, a technique which is limited to $T < 500$°C. The present work using β-alumina covered a wider temperature range and offers more data (Table I).

The agreement at 400°C, the temperature in Ref. 10, is very good (Figure 6), not only for the e.m.f. but also for $\Delta\bar{S}_{Na}$ which depends on dE/dT, a quantity more difficult to measure accurately and one which was formerly subject to considerable doubt.[10] We may therefore regard the experimental situation as satisfactory. However it is worth remarking on the sensitivity of S_{cc} to errors introduced by data processing; these could be $\pm 10\%$.

The numerical work shows that the Na-Tl results are well described by a model which postulates the formation of a single compound of equiatomic composition. The estimated free energy of formation has a reasonable value and the interchange energies are small enough to be compatible with the thermodynamic perturbation basis of the theory. n_3 had a maximum between 0.3 and 0.4 at $c = 0.5$ and fell as T rose. Thermodynamic model fitting does not of course determine the structures or the electronic situation in the postulated clusters; it merely contributes to the general discussion of the alloys.

The model failed with Na-Ga which suggests that the system may be more complicated than supposed with perhaps more compounds present in significant amounts. Na-Ga is being studied further both experimentally and theoretically.

To summarise therefore:

i) the experiment shows how Na-Tl mixtures depart from ideality and how this departure decreases as T rises. (Figure 4).

ii) S_{cc} and other measures of behaviour can be quantitatively fitted by a quasi-chemical thermodynamic model based on attractive forces, represented by free energy g, which form clusters of a certain stoichiometric composition, a proportion of which are dissociated.

iii) using the commonly adopted Flory formula—an assumption requiring examination elsewhere[11]—a generalised model is given for a system with components of differing partial molar volumes and a volume change on cluster formation. These formulae are more appropriate to some systems than others.

Acknowledgments

S. Tamaki is grateful to the Science Research Council for a Senior Visiting Fellowship at the University of East Anglia. N. E. Cusack benefitted greatly from a stay at Niigata University under the Monbusho-British Council scheme. The authors thank Mr. A. Rais (University of East Anglia) for help with some computing and Mr. Y. Matsuo and Mr. S. Iijima of the Research Division of the NGK Spark Plug Co. Ltd., Japan, for the β-alumina tubes. P. Gray wishes to express his indebtedness to NATO for a Senior Fellowship, to the University of Texas at Austin for its hospitality during 1979–80, and to Drs W. Grise, K. Mednick, J. C. Thompson, and J. Turner for helpful advice particularly in connection with computing.

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