Solubility of Tin and Germanium in Liquid Sodium: The Sodium–Tin Partial Phase Diagram

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The solubility of tin (up to 6·9 atom %) and of germanium (up to 1·0 atom %) in liquid sodium has been determined by thermal analysis and electrical-resistance methods. The compound NaGe precipitates from dilute solutions of germanium in sodium. Partial molar enthalpies and entropies of solution in sodium for tin (with respect to $Na_{15}Sn_4$) and germanium (with respect to NaGe) are 46·8 and 44·3 kJ mol^{-1} and 50·7 and 29·7 J K^{-1} mol^{-1} respectively. A simple thermochemical cycle is used to demonstrate that metallic tin and lead dissolve exothermically in liquid sodium but that carbon dissolves endothermically; the cycle is also used to derive solvation energies for the elements Pb, Sn, and C which increase in the order Pb < Sn < C. The sodium–tin phase diagram is augmented over the range 0—6·9 atom % Sn.

DETERMINATION of the solubility of tin and germanium in liquid sodium forms part of a wider study of the solvent properties of the latter. Of the carbon-group elements, the first and last members have widely different solubility in liquid sodium. Significantly, these elements are the least and most metallic, respectively, of the group. Lead is the most soluble, data for which we have reported previously.[1] Existing data for tin and germanium are sparse. The phase diagram for Na–Sn is augmented by the present work. Interest is concentrated on sodium-rich mixtures of tin and germanium which, unlike those of lead, show no eutectic adjacent to the sodium axis.

EXPERIMENTAL

Apparatus for determining the solubility of solid elements in sodium by thermal and resistance methods has been described previously.[1] Solutions of tin (B.D.H., 99·96%) and of germanium (Koch–Light, 99·999%) in liquid sodium were prepared *in situ* by weighing in the appropriate quantities under an argon atmosphere and subsequently heating to 400 °C. A total of 13 solutions of tin (up to 6·9 atom %) and eight solutions of germanium (up to 1·0 atom %) in sodium were investigated. An electromagnetic pump was used to achieve homogeneity of the solutions. Simultaneous measurements of resistance and temperature with time were made as the solutions cooled. The temperature at which saturation with solute or a change of phase occurred was shown by abrupt changes in resistance and also by a change in the rate of loss of heat.

RESULTS AND DISCUSSION

The solubility of tin and of germanium in liquid sodium, together with that of lead for comparison, is shown as a function of temperature in Figure 1; the curves are of the same general shape for all three elements. In each case solubility increases non-linearly with increasing temperature. Tin and lead, however, are much more soluble than germanium. At 290 °C, for example, the solubilities are 6·55, 2·05, and 0·28 atom % for lead, tin, and germanium, respectively. Higher up this group of elements, solubility decreases even further to a value of 0·6 × 10^{-6} atom % for carbon.[2] The solubility of silicon in sodium is not known but is expected to lie between that of germanium and carbon.

Close examination of the solubility data for tin reveals that a linear relation holds between $\ln x$ (x = mole fraction of solute) and reciprocal absolute temperature for dilute solutions (<3·60 atom % Sn) but deviations from linearity occur at higher concentrations. This behaviour parallels that for solutions of lead in liquid sodium where the relation is linear only below 0·55 atom % Pb.[1] Solutions of germanium are not entirely analogous since a linear relation holds over the entire concentration range examined. The solubility

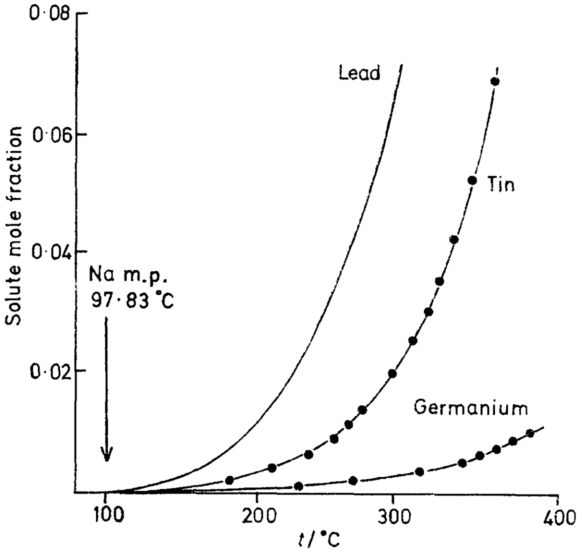

FIGURE 1 Solubility of germanium, tin, and lead in liquid sodium

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[1] P. Hubberstey and R. J. Pulham, *J.C.S. Dalton*, 1972, 819.
[2] B. Longson and A. W. Thorley, *J. Appl. Chem.*, 1970, **20**, 372.

of germanium is very small, however, necessarily making its determination less accurate than for tin and lead. Consequently any slight anomalies, though present, could be hidden.

Thermodynamic quantities derived from solubilities of germanium and tin in sodium are probably most meaningful for very dilute solutions where solute–solute interactions are minimised. Linear $\ln x$ against $(1/T)$ relations at low concentrations were used, therefore, to derive the thermodynamic data in Table 1. The gradient and intercept of such plots are a measure of the partial molar enthalpy, $H_{(soln.)}$, and entropy, $S_{(soln.)}$, of solution in liquid sodium of 1 g-atom of the solute element from the precipitating phase according to equation (1). The Table includes published data for

$$\ln x = \frac{-H_{(soln.)}}{RT} + \frac{S_{(soln.)}}{R} \qquad (1)$$

solutions of carbon (with a probable but assumed reference state of Na_2C_2),[2] germanium,[3] tin,[4] and lead[1] for comparison. There is generally good agreement between the various estimates of partial quantities for germanium and tin in sodium, particularly in view of the differences in methods employed. The partial molar enthalpy of solution is positive for all four systems so that solubility increases with increasing temperature. It is noticeable that the value of $H_{(soln.)}$, determined in this way, for carbon is much larger than those for the other elements. Also, whereas $H_{(soln.)}$ values for germanium and tin are similar, that for lead is much smaller. This last feature may be reconciled with the eutectic which occurs only in the lead system and which generates disproportionately high solubilities at low temperatures.[1] The effect is to increase $H_{(soln.)}$ and decrease $S_{(soln.)}$.

TABLE 1

Thermodynamic quantities for solutions of Group IV elements in liquid sodium

Element	$H_{(soln.)}$ / kJ g-atom^{-1}	$S_{(soln.)}$ / J K^{-1} g-atom^{-1}	Composition atom %	T/K
Carbon (Na_2C_2 ref. state)	104·5		0·00—0·10	873—1 223 [a]
Germanium	44·31	29·51	0·00—0·99	371—653
(NaGe ref. state)	40·19	22·08	0·28—4·00	573—823 [b]
Tin	46·75	50·71	0·00—3·60	371—594
($Na_{15}Sn_4$ ref. state)	45·00	45·08	0·01—0·88	373—533 [c]
Lead ($Na_{15}Pb_4$ ref. state)	29·58	23·09	0·10—0·52	371—443 [d]

[a] Ref. 2. [b] Ref. 3. [c] Ref. 4. [d] Ref. 1.

The increase in solubility from carbon to lead is a trend seen in most Groups of the Periodic Table and is generally attributed to a balance between the difference in electronegativity between sodium and the solute and the difference in their atomic size. As is seen from equation (1), solubility is determined by $H_{(soln.)}$, $S_{(soln.)}$, and T. The contributions from the two parts of this equation are of the same order of magnitude. The $H_{(soln.)}$ term, which at infinite dilution is equivalent to the enthalpy of solution of the element relative to the precipitating phase, can be used to extricate to some extent the role of size and electronegativity factors by referring to a thermochemical cycle of the type shown below for tin:

$$\begin{tikzcd}
Na_4Sn(s) \arrow[r, "H_{(soln.)}"] & 4Na(l) + Sn(l,\ in\ Na) \\
4Na(s) + Sn(s) \arrow[u, "\Delta H^{\ominus}"] \arrow[d, "4\Delta H_f"'] & \\
4Na(l) + Sn(s) \arrow[r, "\Delta H_s"] \arrow[uur, "H_{(solute)}"] & 4Na(l) + Sn(g) \arrow[uu, "U_{(solvn.)}"']
\end{tikzcd}$$

Here $\Delta H^{\ominus}$ is the standard enthalpy of formation of the precipitating phase, ΔH_f the enthalpy of fusion of sodium (2·60 kJ g-atom^{-1}), and ΔH_s the enthalpy required to atomise the solute element (a measure of its bond strength); $H_{(solute)}$ and $U_{(solvn.)}$ are the partial molar enthalpy of solution and solvation energy, respectively, of the element alone since the enthalpy change on mixing Na(l) with liquid sodium containing a small quantity of dissolved solute is negligible. The quantity $U_{(solvn.)}$ is a form of solvation energy which differs from the classical definition in that it refers to an initially neutral rather than a charged solute species; it is the energy associated with surrounding an atom of the element with sodium atoms and allows for possible, but uncertain, polymerisation of the solute or charge transfer between the solvent and solute. This term also reflects the effect of size and electronegativity on the solution of the element in sodium and is evaluated from the measured $H_{(soln.)}$ and the other terms in the cycle. Values of $U_{(solvn.)}$, $H_{(solute)}$, $H_{(soln.)}$, $\Delta H^{\ominus}$, and ΔH_s are presented in Table 2 for cycles involving tin, lead, and carbon respectively. Cycles for silicon and germanium cannot be completed since $\Delta H^{\ominus}$ is unknown for NaSi and NaGe.

Values of $U_{(solvn.)}$ are negative, *i.e.* energy is liberated on solvating all three atoms Pb, Sn, and C. The solvation energy, however, becomes progressively more negative as the group is ascended. Ostensibly this is due to the increasing electronegativity difference between the solute and sodium solvent and to their increasing disparity in size. In all probability the smallest and most electronegative solute, carbon, will exist as

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[3] P. Hubberstey and A. W. Castleman, jun., *J. Electrochem. Soc.*, 1972, **119**, 963.

[4] G. J. Lamprecht, P. Crowther, and D. M. Kemp, *J. Phys. Chem.*, 1971, **71**, 4209.

the anion. The quantity $H_{(\text{solute})}$ is the algebraic sum of ΔH_s and $U_{(\text{solvn.})}$. This is negative for Pb and Sn, in contrast to the positive value of 112 kJ g-atom^{-1} for the non-metal, carbon. The solution process for carbon is endothermic due presumably to the particularly large bond energy, as reflected by ΔH_s, which is only partly offset by solvation. Values of $H_{(\text{solute})}$ for Sn (—49·7) and Pb (—64·4 kJ g-atom^{-1}), as derived from the cycle, can be compared with those determined independently from e.m.f. measurements. Thus for Sn, values of —52·7 [5] and —58·5 kJ g-atom^{-1} (ref. 6) are reported and a value of —83·6 kJ g-atom^{-1} exists for Pb.[7] Although not identical, the values are in reasonable agreement, particularly for Sn. Of the terms in the cycle from which $H_{(\text{solute})}$ is calculated, values of $\Delta H^\ominus$ for Sn and Pb are most prone to uncertainty.

TABLE 2

Solvation energies, $U_{(\text{solvn.})}$, and enthalpies of solution, for some Group IV elements in liquid sodium

$\Delta H^\ominus$ / kJ mol^{-1}	$H_{(\text{soln.})}$ / kJ g-atom^{-1}	Ref. state	ΔH_s / kJ g-atom^{-1}	$H_{(\text{solute})}$ / kJ g-atom^{-1}	$U_{(\text{solvn.})}$ / kJ g-atom^{-1}	Ref. state
20·1 [a]	105·0	Na_2C_2	720 [b]	112·4	−607·4	Graphite
−86·3 [c]	47·0	$Na_{15}Sn_4$	301 [d]	−49·7	−305·7	Tin
−84·0 [e]	30·0	$Na_{15}Pb_4$	184 [f]	−64·4	−248·4	Lead

[a] G. K. Johnson, E. H. Van Deventer, J. P. Ackerman, W. N. Hubbard, D. W. Osborne, and H. E. Flotow, *J. Chem. Thermodynamics*, 1973, **5**, (1), 57. [b] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, 'Selected Values of Chemical Thermodynamic Properties,' Nat. Bureau Stand., 1952, circular 500, p. 585. [c] Ref. 5. [d] P. Pascal, *Nouveau Traite de Chimie Minerale*, 1963, **8**, 301, 302. [e] Ref. 7. [f] Footnote *b*, p. 653.

The Sodium–Tin Partial Phase Diagram.—The sodium–tin phase diagram for compositions below 22 atom % Sn is shown in Figure 2. Our results, depicted as filled circles, were derived from abrupt changes in resistance–temperature and temperature–time curves. They are concentrated in the range 0—6·9 atom % Sn and both span the gap between, and overlap at each end with, previously reported data. As seen in Table 1 data [4] for concentrations up to 0·88 atom % Sn are almost identical with ours. The liquidus is thus defined for dilute solutions of tin in sodium; it rises smoothly away from the sodium axis to subsequently merge with that obtained from previously reported data at higher concentrations. In this region, liquidus points derived from thermal data [8] are in good agreement with those calculated from electrochemical measurements.[5]

Unlike the system sodium–lead, no eutectic was detected adjacent to the sodium axis. The eutectic horizontal (Figure 2) occurred at 97·83 ± 0·05 °C [*cf.* 97 (ref. 8)]. Sodium–tin and -germanium are similar in this respect; complete solidification occurs within ±0·05 °C of the freezing temperature of pure sodium. The composition of any hidden eutectic is estimated, therefore, to be below 0·02 atom % Sn by using the formula relating depression of freezing point to eutectic composition and extent of solid solubility of tin in sodium.[1] In this calculation it was assumed that solid solubility is negligibly small. This is reasonable since solubility is very small in liquid sodium at the freezing point and solubility in solids is generally even smaller than in liquids.

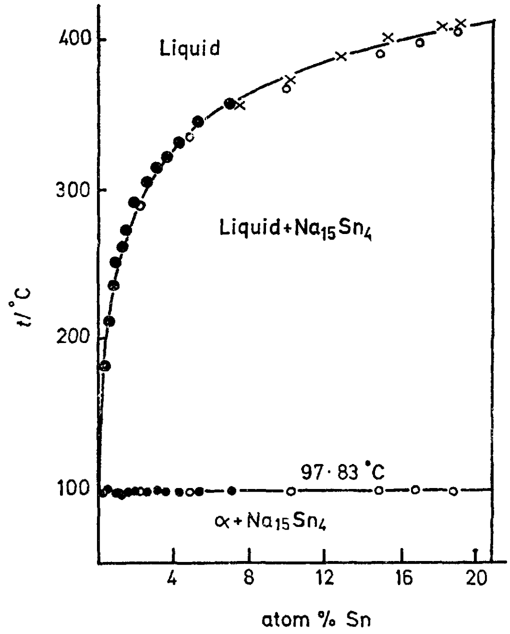

FIGURE 2 Sodium–tin partial phase diagram: (●), this work; (○), ref. 8; and (×), ref. 5

Solid Phases.—Solid phases which precipitate from dilute solutions of tin and lead in sodium are Na_4Sn (m.p. 408 °C) [8,9] and Na_4Pb (m.p. 386 °C) [10] respectively although these are more precisely designated $Na_{15}Sn_4$ [11] and $Na_{15}Pb_4$.[12] The solid which crystallises from dilute solutions of germanium in liquid sodium was established as NaGe. A homogeneous solution containing 3 atom % germanium was cooled from 600 to 20 °C. Crystallisation commenced near 500 °C (ref. 3) and was complete at 97·83 °C, the melting point of sodium. The solid mixture was extruded under an argon atmosphere through a die (0·1 mm diameter)

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[5] P. Hubberstey and A. W. Castleman, jun., *J. Electrochem. Soc.*, 1972, **119**, 967.

[6] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, 'Selected Values of Thermodynamic Properties of Metals and Alloys,' Wiley, London, 1963, p. 873.

[7] Ref. 6, p. 868.

[8] W. Hume-Rothery, *J. Chem. Soc.*, 1928, 947.

[9] M. Hansen, 'Constituion of Binary Alloys,' McGraw-Hill, 1958, p. 1004.

[10] Ref. 9, p. 997.

[11] W. B. Pearson, *Internat. Ser. Monographs Metallurgical Phys. and Phys. Metallurgy*, 1964, **4**, 768.

[12] Ref. 11, p. 766.

into a Lindemann capillary tube (0·3 mm diameter). The tube was then sealed and an *X*-ray diffraction powder pattern obtained of the compound still embedded in the matrix of solid sodium. By this means, it was not necessary to remove excess of sodium and contamination of the product was reduced. After accounting for sodium lines, the pattern observed was identical to that reported for the compound NaGe [13] [m.p. 489 °C (decomp.), *in vacuo*].[14]

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[13] W. B. Pearson, *Internat. Ser. Monographs Metallurgical Phys. and Phys. Metallurgy*, 1967, **8**, 977.

[14] R. Schafer *and* W. Klemm, *Z. anorg. Chem.*, 1961, **312**, 214.