The Sodium–Lead Phase Diagram

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The sodium–lead phase diagram has been determined up to 7·8 atom % lead by thermal and resistance methods. A eutectic occurs at 0·10 atom % lead and 97·32 °C. The partial molar enthalpy and entropy of solution of lead in liquid sodium is 7·07 kcal (29·6 kJ)/g atom and 5·52 cal (23·1 J)/°C/g atom respectively.

THE determination of the sodium–lead phase diagram at low lead concentrations not only forms part of a wider study of the solvent properties of liquid sodium but was a prerequisite to the reaction of alkyl halides with sodium–lead alloys. Although the phase diagram has been the subject of several investigations, sodium-rich solutions have been largely ignored. A critical review[1] showed that precise location of the liquidus was not feasible below 6·6 atom % lead due to lack of data. This paper describes the determination of the phase diagram for solutions containing up to 7·8 atom % lead using both resistance–temperature and thermal analytical methods. The relative merits of the techniques are also compared.

EXPERIMENTAL

Apparatus and Procedure.—The apparatus (Figure 1) was based on that described[2] for measuring the resistance of homogeneous liquid-metal solutions. The alloy was drawn from a steel reservoir, A, and forced by a miniature electromagnetic pump, P, through a double-steel capillary R across which the resistance was measured, and returned to the reservoir below the liquid level. Since no head of metal is involved, dense liquids can be circulated and mixed efficiently. A well, W, was inserted in the reservoir for a chromel-alumel thermocouple additional to that, T, welded to the capillary. As an alternative to the Kelvin-Wheatstone bridge used previously,[2,3] the total resistance, R, was determined by comparing the voltage drop, V_T, across the capillary section with that, V_S, across a standard resistance (0·001 Ω) when passing a constant current of 3 A through both. The current and potential leads were of silver and were attached to the steel discs, D, (Figure 1) as before.[3] The resistance of the liquid inside the capillary was calculated from $R(\Omega) = V_T/V_S \times 10^{-3}$ and the equation[3] for parallel conductors. The current was generated by a constant-current/voltage power supply (type 1412·2, Solartron Electronic Group). Potential differences were measured by a Vernier potentiometer (type 5590B, H. Tinsley) in conjunction with a galvanometer (Type 5656, H. Tinsley). Thermocouple e.m.f.s were measured to ± 1 μV (*i.e.* ±0·025 °C). In addition to measurements by potentiometer, the potential difference across the capillary and from the thermocouples was fed into potentiometric chart recorders (Types 700 and 700T, Telsec Instruments) to provide a continuous record of changes in both potential and temperature with time, and facilitate subsequent intercorrelation of all three parameters.

The cleaned[3] cell was weighed and baked out at 300 °C under 10^{-3} Torr in an air oven (Laboratory Thermal Equipment) which was equipped with a fan for internal air circulation and could be controlled to ±0·5 °C at 300 °C. The temperature was decreased by 10° steps and the resistance of the empty cell determined. This allowed subsequent compensation for any irregularity in the resistance of the steel. The cell was removed to an argon-filled glove box and charged with purified[3] sodium (100 g). The resistance of the filled cell was then determined, with the pump running, from 300 to 120 °C. Spontaneous cooling was then allowed and measurements of temperature, from both thermocouples, and resistance were made with time. The thermocouples were calibrated at the freezing point, 97·83 °C, of sodium,[4] a process lasting an hour, during which time the temperature fluctuated by no more than ±0·05 °C. The cell was removed to the glove box and charged with a weighed quantity of lead (Koch–Light, 99·999%). No further purification other than removal of surface film was deemed necessary. The cell was reheated to 330 °C and the liquid metals were mixed by means of the pump. The resistance of the liquid metal was redetermined at fixed temperatures until near the expected liquidus when spontaneous cooling was allowed. The cooling rate varied from 0·8 at 200 to 0·35 °C/min at 100 °C. Simultaneous measurements of resistance and temperature with time were made and repeated at higher lead concentrations. Confirmation that the solutions were initially homogeneous was obtained from the smooth increase in resistance at constant temperature of the liquid with increasing lead content.

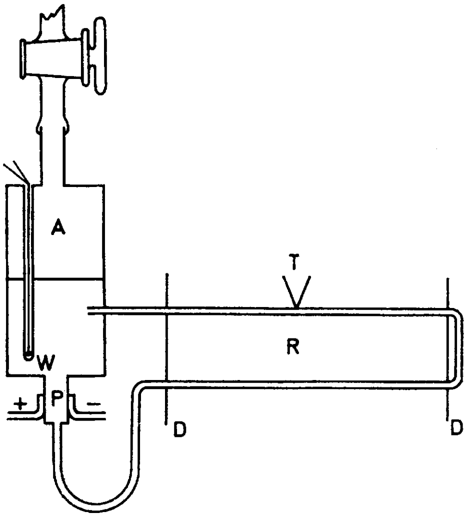

FIGURE 1 Apparatus

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[1] M. Hansen, 'Constitution of Binary Alloys,' McGraw-Hill, 1958, 2nd edn.

[2] C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1971, 1395.

[3] C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1969, 1482.

[4] G. W. Thomson and E. Garelis, 'Physical and Thermodynamic Properties of Sodium,' Ethyl Corporation, Detroit, 2nd edn.

RESULTS AND DISCUSSION

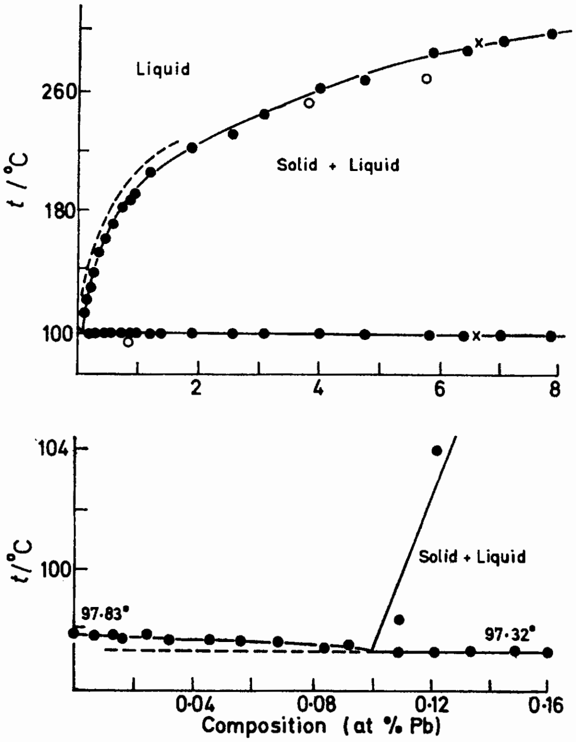

FIGURE 2 *Upper diagram:* The sodium–lead phase diagram for compositions up to 8 atom % lead; filled circles, this work; open circles, ref. 7; crosses, ref. 5; and broken line, ref. 8

Lower diagram: The sodium–lead phase diagram for compositions up to 0·16 atom % lead

Although the phase diagram can be derived directly from the observed changes in potential, it was expedient to calculate and use the resistance of the alloys for this purpose since this was also required in a separate investigation. The variation of the resistance with temperature was determined for 37 solutions of lead (up to 7·83 atom %) in sodium. A cooling curve was also constructed for each of these solutions. The phase diagram, shown in the upper diagram of Figure 2, was derived from abrupt changes in the temperature dependence of resistance curves and from thermal arrests in the (temperature–time) curves. A eutectic occurs adjacent the sodium axis and thereafter the liquidus rises steeply and smoothly to 300 °C at 8 atom % lead. The results agree well at 6·6 atom % lead with that of Mathewson[5] whose data extend to higher concentrations. This overlap renders the liquidus complete up to 20 atom % lead. The liquidus, as determined by Mathewson using a thermal method, has been corroborated by Hubberstey[6] using an e.m.f. technique, over the concentration range 7·8—14·6 atom % lead. Kurnakow[7] studied the entire composition range by a thermal method. The results for low concentrations only are shown in the upper diagram of Figure 2 and fall near our line. When taken in their entirety, however, they give rise to a steeper curve than indicated by our results. The solubility of lead in liquid sodium over the temperature range 119—244 °C has been determined[8] by a method which involved filtration from a solution saturated with lead and subsequent analysis of the liquid. The liquidus, as derived from the solubility, is shown as the broken line and covers the range 0·06—2·43 atom % lead. This is higher than we find and the method so used was inherently incapable of detecting the eutectic or establishing the hypoeutectic liquidus. The eutectic horizontal occurs at 97·32 ± 0·05 °C compared with 97 °C reported by Matthewson[5] who, although observing a lower temperature than 97·83 °C, the freezing point of sodium, was unaware of the eutectic composition. The region in which this occurs, from zero to 0·16 atom % lead, is shown in the lower diagram of Figure 2. The liquidus falls from the melting point of sodium almost linearly with increasing concentration of lead to a eutectic composition of 0·100 ±0·005 atom % lead; thereafter, the liquidus rises steeply with increasing lead content. The eutectic pause could be detected only for hypereutectic solutions. For hypoeutectic compositions, the eutectic temperature was inseparable from the liquidus. Consequently this section of the eutectic horizontal is shown as a broken line in lower diagram Figure 2. The extent of solid solubility, x_s (atom fraction), of lead in sodium was less than 0·01 atom % when calculated from the depression, ΔT, of the freezing point, T(K), produced by a concentration x_1 (atom fraction) of lead dissolved in the liquid

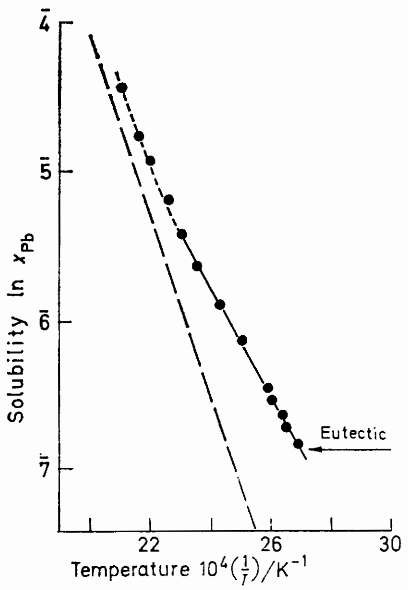

FIGURE 3 The solubility of lead in liquid sodium

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[5] C. H. Mathewson, *Z. anorg. Chem.*, 1906, **50**, 171.

[6] P. Hubberstey and A. W. Castleman, *J. Electrochem. Soc.*, in the press.

[7] N. S. Kurnakow, *Z. anorg. Chem.*, 1900, **23**, 439.

[8] G. J. Lamprecht, L. Dicks, and P. Crowther, *J. Phys. Chem.*, 1968, **72**, 1439.

using the equation[9] $\Delta T = RT^2(x_1 - x_s)/L_f$, where L_f is the latent heat of fusion[4] (622·2 cal or 2·603 kJ/g atom) of sodium and R is the molar gas constant. The eutectic horizontal is extended accordingly in the lower diagram of Figure 2. Although early reports of a depression in the freezing point of sodium from 97·69 to 97·39 °C by 0·04 atom % lead[10] and of 0·21 °C by 0·14 atom % lead[11] are not in precise agreement with our results, neither investigation was extensive.

The partial molar enthalpy $\Delta\bar{H}_{Pb}$ and entropy $\Delta\bar{S}_{Pb}$ of solution of lead in liquid sodium was determined from the solubility of the metal, of which the hypereutectic liquidus, upper diagram of Figure 2, is a measure, using the equation $\ln x = \Delta\bar{H}_{Pb}/RT + \Delta\bar{S}_{Pb}/R$, where x is the mol fraction of lead dissolved in sodium at temperature T K. The relationship between $\ln x$ and $1/T$ is shown in Figure 3. There is a linear relationship commencing at the eutectic and extending over low concentrations which is superceded by a shallow curve as the concentration of lead increases. Thus, the enthalpy of solution is independent of the lead concentration only below 0·5 atom %. The enthalpy and entropy of solution as derived from the gradient and intercept of the linear portion of the curve are 7·07 kcal (29·58 kJ)/°C/g atom and 5·52 cal (23·09 J)/°C/g atom^{-1} respectively. These values are lower than the 12·03 kcal/g atom and 16·06 cal/°C/g atom^{-1}, respectively obtained by Lamprecht *et al.*[8] who reported a linear relationship (dashed line, Figure 3) extending from 0·06 to 2·43 atom % lead. Also the solubility is generally lower at any temperature than we find (Figure 3) and appears to fall below the minimum possible, as given by the eutectic composition for lead in liquid sodium.

Comparison of Methods.—The liquidus points are located more sharply by resistance measurements than by thermal analysis. Precipitation of a solid sodium-lead compound abruptly reduces the resistance whereas the heat evolved is small and barely perceptible in cooling curves obtained from thermocouples T and W (Figure 1). The eutectic temperature is more accurately determined, however, using thermocouple W even though both thermal pause and resistance change are enhanced as remaining liquid is replaced by solid. At this point, the large volume of metal in the reservoir holds the temperature constant (±0·05 °C) for a long time (50 min) whilst losing latent heat of fusion. For the same reason, thermocouple W is always better for determining thermal arrests than thermocouple T, which is used essentially to measure the temperature of resistance changes. Thus, by combining the methods, the temperature of most phase changes was determined with precision.

[1/1883 *Received*, 14*th October*, 1971]

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[9] C. Wagner, 'Thermodynamics of Alloys,' Addison-Wesley Press, Cambridge, Mass., 1952.

[10] C. T. Heycock and F. H. Neville, *J. Chem. Soc.*, 1889, **55**, 666.

[11] G. Tammann, *Z. phys. Chem.*, 1889, **3**, 441.