[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO]

The Solubility of Copper in Liquid Lead Below 950°

BY O. J. KLEPPA[1] AND J. A. WEIL

The lead-rich region of the copper–lead phase diagram has been studied by a solubility method. The shape of the liquidus curve between 950° and the eutectic temperature (326°) has been determined. From the data obtained, the differential heat of solution (relative partial molal heat content) and the excess (non-ideal) partial molal entropy of mixing have been calculated for copper at very low concentrations in liquid lead.

Introduction

For a study of the thermodynamic properties of the binary system copper–lead, exact knowledge of the phase diagram is of great value. Unfortunately, the existing data for the lead-rich part of the diagram, which lies between the eutectic point and the invariant temperature (monotectic) at which a second liquid phase appears, are meager and contradictory. For the composition of this end of the monotectic, at 954°, Bornemann and Wagenmann[2] give 7.35 wt. % (20.6 atomic %) copper, while Nishikawa[3] gives 13 wt. % (32.8 atomic %) copper. Only one point has been reported[2] which indicates the shape of the liquidus curve between the monotectic and eutectic temperatures. The eutectic composition at 326° has been reported by Heycock-Neville[4] to be 0.06 wt. % (0.195 atomic %) copper. A summary of available data, up to 1936, for the system copper–lead is given by Hansen.[5]

In this work the copper–lead phase diagram in the lead-rich region has been studied and the shape of the equilibrium curve has been determined. In a later communication it will be shown how solubility measurements of the type presented in this paper may be used for more complete thermodynamic calculations.

Experimental Procedure

Since the use of cooling curve methods was impracticable for the study of this region of the copper–lead phase diagram, the authors developed a method especially useful for this type of work.

Metallic copper, in the form of a small tube, and a 2–3-g. rod of pure lead were placed in a Vycor glass reaction tube. Before sealing this tube it was evacuated, so that formation of oxides during heating was prevented. A chromel–alumel thermocouple was tied to the Vycor tube, with the bead of the couple in close contact with the part of the tube containing the metals.

Two such tubes were placed in a well-insulated furnace, one from each end of the furnace. The temperature of the furnace was controlled by a variable transformer, and fluctuations in the current were reduced by using a constant voltage transformer. During the runs, which lasted 20–300 hours, the temperature was frequently measured, and the run was terminated only after several hours of relatively constant temperature. The fluctuations in temperature during this final period were less than ±1° around 400°, and were of the order of ±2° around 900°. The potentiometer used to measure the e.m.f. of the thermocouple was sensitive to 0.01 millivolt. Stirring the liquid metals, by using a motor to oscillate the furnace slightly, was found to be unnecessary.

The runs were terminated by turning the specially constructed furnace upside down. Thus the equilibrium solution of copper in lead flowed into the head of the tube, while the excess copper was held in its initial position by a constriction in the Vycor tube. The furnace was then allowed to cool to room temperature.

After the melt had solidified, the head of the tube was broken off. The whole alloy was weighed, and then analyzed for copper by electrolysis. The amount of lead was calculated by difference. Because of the presence of the lead, sulfuric acid could not be used in the deposition. It was necessary to control closely the amount of nitric acid used, since an excess caused the deposition of copper to be very slow, while a deficiency of acid caused a deposition of metallic lead on the cathode. The analytical method was checked by the use of known samples, of composition similar to those of the experimental alloys. It was found that the analysis of the copper was good to 0.2 milligram.

Both the copper and the lead were subjected to semi-quantitative spectrographic analysis, and the largest amounts of impurities were found to be 0.01% Fe and 0.2% P in the copper, and 0.003% Fe in the lead.

The scattering of the experimental points is due to one or more of the following reasons. Errors because of incorrect temperature measurement are unlikely, since the thermocouples and standard cell were both checked, and were found to give correct readings. Fluctuations of the temperature were of some importance at the higher temperatures. The analytical work gave no difficulties. It is possible that some of the points which were too high in copper concentration were so because of the presence of small copper crystals which had fallen into the equilibrium solution. To see whether this type of difficulty might have shifted the whole liquidus curve by some constant factor, two of the runs were performed with very coarsely crystalline copper. These two points fell right on the curve made by the other points, so that no systematic error due to this effect is likely. Scattering due to non-attainment of equilibrium is unlikely, since the points at the lower temperatures fall on a smooth curve, and the greatest scattering is at the highest temperatures.

Experimental Results

Table I gives some values for the concentration of copper in solution at various temperatures. They were taken from Fig. 1, which is a plot of the atomic per cent. of copper *versus* the absolute temperature T. In Fig. 2 is plotted the logarithm of atomic per cent. of copper against $1/T$. On the former graph there are plotted a few points, obtained by other investigators, to provide a basis for comparison.

TABLE I

T, °K.	600	700	800	900	1000	1100	1200
At. % Cu	0.20	0.60	1.56	3.36	6.59	12.17	25.46

Discussion

From Fig. 1 it is seen that the solubility of copper in liquid lead is small, ranging from 0.2 atomic per cent. at the eutectic temperature to about 33% at the monotectic, 954°. As is also seen from Fig. 1, the data obtained check very well with the previously reported value of the eutectic composition[4] at 326°. The upper part of the liquidus curve is in accord with that obtained by Nishikawa[3] and also by Bogitch.[6] This point and the shape of the curve do not agree with that suggested by Bornemann and Wagenmann.[2]

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(1) Norwegian Defense Research Establishment, Lillestrom, Norway.

(2) K. Bornemann and K. Wagenmann, *Ferrum*, **11**, 291, 309 (1913–1914).

(3) M. Nishikawa, *Suiyokwai-Shi* (*Japan*), **8**, 239 (1933).

(4) C. T. Heycock and F. H. Neville, *Trans. Roy. Soc. London*, **A 42**, 189 (1897).

(5) M. Hansen, "Aufbau der Zweistofflegierungen," Berlin, 1936.

(6) B. Bogitch, *Compt. rend.*, **161**, 416 (1915).

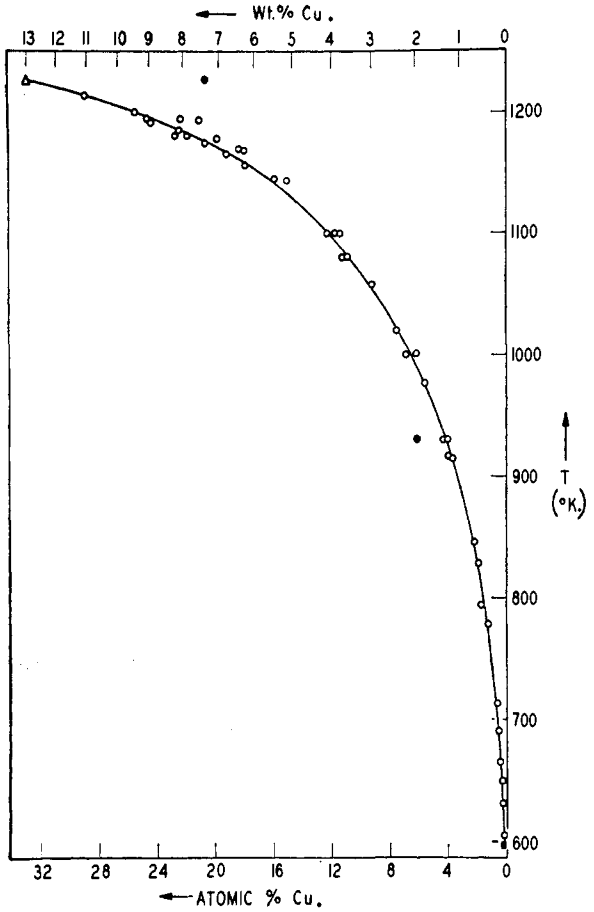

Fig. 1.—△, Nishikawa and Bogitch; ●, Bornemann-Wagenmann; ■, Heycock-Neville; ○, Kleppa-Weil.

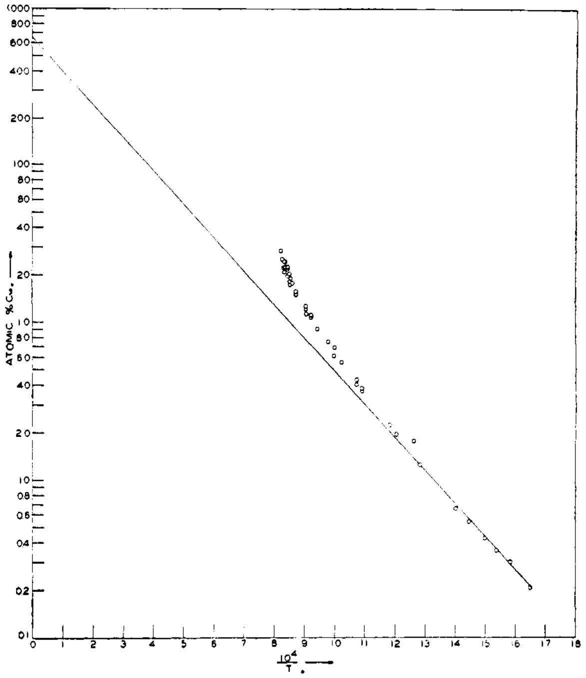

Fig. 2.

It is possible to calculate the partial molal entropy of solution as well as the heat of solution for copper by finding the limiting slope (Fig. 2) as the copper concentration becomes very small. A suitable method was suggested by Zener[7] for the case of solid solutions, but may equally well be applied in the present case. If one considers an essentially pure solute in contact with its saturated solution, one knows that the equilibrium condition is simply that the chemical potential (partial molal free energy) for the solute is the same in the two phases. Thus

$$\Delta\bar{F} = \Delta\bar{H} - T\Delta\bar{S} \qquad (1a)$$

or

$$\Delta\bar{H} = T\Delta\bar{S} \qquad (1b)$$

The partial molal entropy appearing in this expression may be said to consist of two parts, the entropy of fusion, ΔS_f, and the differential entropy of solution (partial molal entropy of mixing). Similarly, $\Delta\bar{H}$ is the sum of the heat of fusion and the differential heat of solution (relative partial molal heat content). In other communications,[8] one of the authors has pointed out that metallic mixtures frequently show much larger entropies of mixing than the ideal. The partial molal entropy of mixing may therefore also be considered to be the sum of two terms, $\Delta\bar{S}_{mix}$ and $\Delta\bar{S}'$. Here $\Delta\bar{S}_{mix}$ is the ideal (random) partial molal entropy, given by the expression

$$\Delta\bar{S}_{mix} = -R \ln (x) \qquad (2)$$

where x is the mole fraction of solute. The term $\Delta\bar{S}'$ is the excess partial molal entropy, and undoubtedly arises from changes in the motion and possibly in the short range structure of solute and solvent atoms when the solution is formed from the liquid constituents. In the previous publications, this contribution to the entropy, in analogy with the solid state, was referred to as "vibrational entropy." Perhaps a better name, in the case of liquids, would be "kinetic entropy." We shall see below how this excess partial molal entropy for the solute may be estimated from the solubility measurements.

On introduction of (2) into equation (1b) we get

$$\Delta\bar{H} = T(\Delta S_f + \Delta\bar{S}') - RT \ln (x)$$

which can be rewritten as

$$\ln (x) = (\Delta S_f + \Delta\bar{S}')/R - \Delta\bar{H}/RT$$

$$x = \exp (\Delta S_f + \Delta\bar{S}')/R \exp (-\Delta\bar{H}/RT) \qquad (3)$$

Thus when one plots the logarithm of x *versus* $1/T$, one gets a curve, the slope of which is $-\Delta\bar{H}/R$.

It can be seen from equation (3) that when $1/T$ is zero, the concentration x equals $\exp (\Delta S_f + \Delta\bar{S}')/R$. The assumptions that $\Delta\bar{H}$ is constant and that there is a random distribution of solute atoms are not valid except at very low concentrations of the solute. It is thus seen that if the plot of log x *versus* $1/T$ is extended along the initial straight line, obtained at low copper concentrations (*i.e.*, below ~2 atomic per cent.), to the limit $1/T = 0$, the value of x found from the intercept should be a measure of the excess partial molal entropy at high dilution, provided the entropy of fusion is known. Similarly the slope of this straight line

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[7] C. Zener, "Thermodynamics in Physical Metallurgy," American Society for Metals, Cleveland, Ohio, 1950, p. 16 ff.

[8] O. J. Kleppa, THIS JOURNAL, **72**, 3346 (1950); *ibid.*, **73**, 385 (1951).

will give the differential heat of solution, if the heat of fusion is known.

From the limiting slope of our curve we determined $\Delta\bar{H}$ to be about 9700 cal./mole. It is known that the heat of fusion for copper at its melting point (1356° *K.*) is 3120 cal./mole.[9] If we assume this heat of fusion to be independent of temperature, we get a value of 6580 cal./mole for the differential heat of solution at high dilution. In a similar manner, if we assume the entropy of fusion, which at the melting point is 2.30 cal./degree mole, to be independent of temperature, we find from the intercept $x \cong 6.5$ that the excess partial molal entropy is about 1.4 cal./degree mole. If data for the specific heat of the undercooled liquid copper had been available, we might have been able to improve these values by taking into account the dependence of the heat and entropy of fusion on temperature. In the absence of such data, we are only able to estimate the direction of this correction. It is well known that, at the melting point, the specific heat, C_p, of the liquid metal is normally somewhat larger than for the corresponding solid.[10] If we assume ΔC_p to have the same sign at lower temperatures, this will lead to higher values for the calculated differential heat of solution and also for the excess partial molal entropy.

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[9] K. K. Kelley, U. S. Dept. of the Interior, Bureau of Mines, Bull. 476 (1949).

[10] O. J. Kleppa, *J. Chem. Phys.*, **18**, 1331 (1950).

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[CONTRIBUTION FROM THE BATTELLE MEMORIAL INSTITUTE]

The Dissociation Pressures of Thorium Dihydride in the Thorium–Thorium Dihydride System[1a]

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Dissociation pressures have been measured in the thorium–hydrogen system for the range of compositions up to approximately $ThH_{1.90}$ at temperatures from 650–875°. The system resembles the Pd–H system in that the observed dissociation pressures are dependent on the solid-phase composition throughout the system.

Introduction

The reaction of thorium with hydrogen reported first by Winkler[2] in 1891, has been studied by numerous investigators.[2–6] Systematic pressure-composition studies of the Th–H system were made by Sieverts and co-workers,[7–9] using metal 96% pure and contaminated chiefly with thorium oxide.

The data of Sieverts and co-workers show that the Th–H system is similar to the Pd–H system, the most extensively investigated of the metal-hydrogen systems. They found the ability of thorium to absorb hydrogen to depend on the condition of the specimen, and noted hysteresis effects similar to those obtained with Pd–H.

No reference has been found in the literature to dissociation pressure studies in which pure metal was used. Since previous workers have noted that the absorption and desorption of hydrogen in the Th–H system are strongly influenced by the previous history of the metal, it was thought desirable to determine the dissociation pressure of the thorium–thorium hydride system, using the purest metal available.

Apparatus.—The hydride preparation and the pressure determinations were carried out in a modified Sieverts apparatus.

The thorium sample was contained in a double-walled, clear-silica reaction vessel which was connected to a full-length, open-end mercury manometer by a Picein wax seal. The system was evacuated with a Cenco Hyvac pump pumping through a Dry Ice–alcohol trap used to remove condensable vapors. An automatic Toepler pump was used to remove hydrogen from the system for measurement and analysis. A McLeod gage was used to check the tightness of the system and the degree of initial evacuation.

Hydrogen additions were measured with a 50-ml. gas buret graduated in 0.1-ml. divisions. Readings were estimated to the nearest 0.03 ml. Sample temperatures were measured with Pt, Pt-Rh (10%) thermocouple in conjunction with a Leeds and Northrup precision potentiometer. The thermocouple was calibrated at the gold point and tested for homogeneity before and after each run.

The heat input to the furnace was so adjusted that temperature fluctuations were only ±2°. All equilibrium pressures were read when the reaction bulb was at the exact temperature recorded, however, and it is believed that the probable error in sample temperature is less than ±1°, since equilibria were reached very rapidly in each case.

Pressures were estimated, with the aid of a magnifying lens, to ±0.3 mm. All readings were corrected for the thermal expansion of mercury. The fluctuation in pressure after reaching equilibrium was less than ±1.0 mm., and this probably represents the over-all precision of the pressure values. Atmospheric pressure was measured with a Taylor aneroid barometer, calibrated periodically against a mercury barometer.

The reaction bulb was heated by a heavily insulated platinum-wound tubular furnace 1.5 inch inside diameter and 18 inches long. A Foxboro controller was used to maintain the furnace at the desired temperature.

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(1) (a) This work was carried out under sponsorship of the Manhattan Engineering District and the Atomic Energy Commission, Contract No. W-7405-eng-72. (b) Battelle Memorial Institute, Columbus, Ohio.

(2) (a) C. Winkler, *Ber.*, **24**, 873 (1891); (b) C. Matignon, *Compt. rend.*, **131**, 891 (1900).

(3) C. Matignon and M. Delépine, *ibid.*, **132**, 36, 232 (1901).

(4) R. Schwarz and H. Deisler, *Ber.*, **52**, 1896 (1919).

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(6) R. Schwarz and E. Konrad, *Ber.*, **54**, 2122 (1921).

(7) A. Sieverts and E. Roell, *Z. anorg. allgem. Chem.*, **153**, 289 (1926).

(8) A. Sieverts and A. Gotta, *ibid.*, **172**, (1928).

(9) A. Sieverts, A. Gotta and S. Halberstadt, *ibid.*, **187**, 156 (1930).