while the energy to bind six water groups is an equal amount greater than the cobaltous value. The ammoniation energy of calcium ion, based largely on the iodide, is a few tens of kilocalories lower than that of magnesium, while the hydration energy of strontium ion seems 50 kcal. larger than that of cobaltous ion, primarily because of the binding energy for the first two water groups, the last four being bound with much the same energy as in the cobaltous case.

All of these cases share the circumstance in common of a shift in crystal type between the unsolvated and solvated salts. Thus, with the halides, the anhydrous salts are generally of the layer lattice types, and the hexammine is of the fluorite type. Since the Madelung constant of the latter structure is much higher than the former, one obtains a smaller difference in lattice energies than would be the case if there were no change in structure type. Professor W. H. Zachariasen has pointed out to us that in the layer-structure lattices there exists a dipole energy component not allowed for in the electrostatic calculation, and of the order of magnitude of the repulsion correction (about 10% of the lattice energies involved here). This cancels out between two layer-lattice crystals but remains as a correction when the two crystal types differ. Such a correction, of the order of 30–40 kcal., would put the ammonia and water binding energies (for six groups) in the order expected from evidence of general chemical behavior.

The anomaly of the energy for binding the first two pyridines seems even more marked with these comparisons, the value being as great as for six water groups, and little different from six ammonia groups, while the latter is a stronger Lewis base. Here one might suggest that some strain factor operates, related to the geometry of the flat ring molecule, and leading to a crystal spacing considerably greater than is appropriate to the true lattice energy. Such a factor would need to be independent to a large extent of the crystal structure type, to give the concordance found between the calculations for the binding energy with both nitrate and chloride. Extended further, such a factor might also account for the discrepancy between the water and pyridine binding energy difference from the heats of solution of the dihydrates, and from the lattice energy calculations.

The comparative data in Table VI offer a possible explanation of another phenomenon, long known, which has led to considerable speculation. This is the very ready extraction of uranyl nitrate from aqueous solution into various immiscible organic solvents. It has been shown[1] that the form so extracted is a tetrahydrated molecule, in line with other evidence on the role of $MX_2 \cdot 4S$ entities in the phenomenon of 2–1 salt solubility in organic solvents. If the assumptions of Table VI were true, that the several uranyl nitrate hydrates were of the fluorite structure, an explanation of the phenomenon would be ready to hand, namely, that the extractability is a function of the weakness with which the water is held in the 5th and 6th coördination positions, and the ease of replacement of these waters by anions. This explanation would be further substantiated by the cupric nitrate numbers, since although cobaltous nitrate hydrates are completely insoluble in diethyl ether, and uranyl nitrate is very soluble, cupric nitrate displays a significant solubility before hydrolysis sets in to precipitate the copper. Since the existing crystallographic data on uranyl nitrate hexahydrate[12] are not compatible with a fluorite structure, it is possible that (providing the lower hydrates are fluorite-like) the binding of the last two groups may be closer to that for the other salts than appears in Table V. There also exists the possibility, although less probable, that the Madelung constant of the structure is at least as high as that of the fluorite structure, or that the lower nitrates themselves may have a structure with a smaller Madelung constant than the fluorite constant, in which case the binding energy for the last water groups could be even smaller than that calculated. Although the numerical value is therefore quite uncertain, this possible answer to the problem of the relative extractabilities seems more in accord with the evidence as a whole[18] than postulation of specific complex formation dependent on 5f electron orbitals.[19]

[18] L. I. Katzin, *Nature*, **166**, 605 (1950).

[19] E. Glueckauf and H. A. C. McKay, *ibid.*, **165**, 594 (1950); **166**, 606 (1950).

CHICAGO 80, ILLINOIS

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

A Thermodynamic Study of Liquid Metallic Solutions. IV. Approximate Thermodynamic Data from the Phase Diagram for the Systems Copper–Bismuth, Copper–Lead and Copper–Thallium

BY O. J. KLEPPA

RECEIVED MARCH 22, 1952

For the systems copper–bismuth and copper–thallium some new data have been presented on the solubility of copper in the low-melting metal. Some comments have been presented on earlier attempts at obtaining thermodynamic data for liquid metal mixtures from the phase diagram. The methods do not take into account the entropy deviations frequently found in such mixtures. A new method has been described which, for certain types of phase diagrams, makes it possible to separate the calculated partial molal free energies (along the liquidus) into approximate heat and entropy terms. The method has been applied to the systems copper–lead, copper–bismuth and copper–thallium. The calculated heat data have been compared with calorimetric data where such data are available.

Introduction

It is well known that the electromotive force and the vapor pressure methods, which are most commonly used for the study of the thermodynamic properties of metallic mixtures, are subject to serious limitations in their application. In recent years attention has therefore been given to the use of the binary equilibrium phase diagram for obtaining thermodynamic data for liquid metallic mixtures. The systems that are especially well suited for investigation are those of a simple eutectic type.

In general, these calculations are limited to systems where the corresponding data are known for the terminal solid solutions. Unfortunately, this condition is very seldom fulfilled. However, for a considerable number of systems the solid solubility is negligible, which makes the calculations particularly simple.

The methods adopted are based on the following two well-known principles: (1) For the liquid and solid phases in equilibrium the chemical potentials (activities) for each component are the same in both phases. If the solid solubility is negligible, the solid may be considered as a pure (one-component) phase. In this case the equilibrium condition is simply that the chemical potential of this component is the same in the two phases.

(2) If one neglects solid solubility and difference in specific heat between the pure solid and liquid metal, the chemical potential at the liquidus, referred to the pure undercooled liquid metal of the same temperature, will be given by

$$\mu - \mu^\circ = \frac{\Delta H_f}{T_m}(T - T_m) \qquad (1)$$

Here ΔH_f is the heat of fusion, T_m is the melting temperature for the pure metal, and T is the liquidus temperature.

The equilibrium information relating to the liquid mixture provided by the phase diagram is restricted to the temperatures and compositions along the liquidus. In order to have the computed quantities referred to one common temperature, one is forced to make at least one assumption regarding the temperature dependence of the quantities involved. The assumption most commonly adopted is that the solution is "regular,"[1] and that accordingly the entropy of mixing is independent of temperature and equal to the ideal (random) entropy of mixing

$$\Delta S = -R[x \ln x + (1 - x) \ln (1 - x)] \qquad (2)$$

Here x and $(1 - x)$ are the mole fractions of the two components, while R is the gas constant.

This simple assumption is adopted by Scheil[2] and by Chipman[3] in papers discussing the derivation of thermodynamic data from the phase diagram. On the basis of this assumption Scheil develops a general method for the calculation of heats of mixing from binary phase diagrams. It is found, however, that certain of the heats of mixing calculated by Scheil do not agree with data obtained from electromotive force measurements or from direct calorimetric experiments. Thus he calculates for the heat of mixing of an equi-atomic mixture of copper–bismuth, $\Delta H_{0.5} = 860$ cal./g. atom, while the calorimetric measurements of Kawakami[4] indicate a value of about 1600 cal. at 1200°. Similarly Scheil finds for the system zinc–tin $\Delta H_{0.5} = 500$ cal., while Kawakami[5] gives 870 cal. In this latter case the calorimetric results are in excellent agreement with the e.m.f. data reported by Taylor.[6] Scheil is unable to account for this large discrepancy, and suggests that the accepted phase diagram, which is the work of several investigators, may be in error. Actually the discrepancy undoubtedly arises from his assumption with respect to the entropy of mixing. This is clear from a closer examination of Taylor's data, which show that for the system zinc–tin at about 500° there is a positive entropy deviation at equi-atomic composition of 0.5_6 cal./deg. g. atom (about 40% more than ideal). One may attempt to estimate the error involved in Scheil's results by taking this entropy difference into account. In his calculations the "true" ΔH will be reduced by an amount of approximately $T(\Delta S - \Delta S_{\text{ideal}})$, where for T we take the liquidus temperature for the equi-atomic composition, about 600°K. With these values we find for the "true" heat of mixing $\Delta H_{0.5} \cong \Delta H_{\text{Scheil}} + 330 = 830$ cal., which is in good agreement with Kawakami. In general we may expect the Scheil–Chipman method of calculation to yield low values for ΔH if the entropy deviation is positive, and high values if the deviation is negative. If on the other hand calorimetric data for the heat of mixing are available, the method may be used for estimation of entropy deviations. For the copper–bismuth system the data quoted above indicate a positive entropy deviation of the order of 0.7 cal./deg. g. atom at 1100°K.

Approximate Thermodynamic Data from Solubility Measurements.—In the present paper a method of calculation is presented, which permits a separation of the free energy of mixing into approximate heat and entropy terms. The method is restricted to simple eutectic phase diagrams with a steep liquidus displaced toward one extreme in composition. The suggested method should be particularly useful for metal mixtures which can not be investigated by the e.m.f. and vapor pressure methods.

In a recent communication the author[7] has illustrated how solubility measurements may be used in order to evaluate the differential heat of solution (relative partial molal heat content) at high dilution, $\bar{L}_i^0 = \lim \bar{L}_i$, as $x_i \rightarrow 0$, as well as the corresponding excess partial molal entropy, $\Delta\bar{S}_i^{x0} = \lim (\Delta\bar{S}_i + R \ln x_i), x_i \rightarrow 0$. In the original derivation of these relationships it was not specifically stated that the derivation presupposes that $\bar{L}^0$ and $\Delta\bar{S}^{x0}$ (and accordingly ΔH and ΔS) are independent of temperature within the limited temperature range involved in the actual determination of these quantities. In order to apply these data to calculations involving other temperatures and compositions, we are forced to make additional assumptions. In the absence of specific heat data for the liquid mixture we first extend the above assumption to cover the whole temperature range covered by the actual phase diagram. As deviations from the Neumann–Kopp rule for the specific heat may be expected in metallic mixtures,[8] this is a serious limitation. However, the assumption is frequently an improvement compared to the regular solution hypothesis, $\overline{\Delta S^x} = 0$.

In order to apply the experimentally determined data for $\bar{L}^0$ and $\overline{\Delta S^{x0}}$ to a discussion of the properties of non-dilute solutions, we have to make at least one additional assumption regarding the dependence of these quantities on concentration.

---

[1] J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes," 3rd edition, Reinhold Publishing Corp., 1950.

[2] E. Scheil, *Z. Elektrochem.*, **49**, 242 (1943).

[3] J. Chipman, *Discussions Faraday Soc.*, **4**, 23 (1948).

[4] Masuo Kawakami, *Sci. Rep. Tôhoku Imp. Univ. I*, **19**, 521 (1930).

[5] Masuo Kawakami, *ibid.*, **17**, 915 (1927).

[6] N. W. Taylor, THIS JOURNAL, **45**, 2865 (1923).

[7] O. J. Kleppa and J. A. Weil, *ibid.*, **73**, 4848 (1951).

[8] O. J. Kleppa, *ibid.*, **72**, 3346 (1950).

It is well known that for a number of binary systems the integral heat of mixing can be given by the approximate equation

$$\Delta H = x(1 - x)\bar{L}^0 \qquad (3)$$

At a given temperature $\bar{L}^0$ is a constant. For systems where this expression is applicable we have the simple parabolic dependence of $\bar{L}$ on concentration

$$\bar{L}_1 = x_2^2\bar{L}^0 \qquad (4)$$

This expression is well known from Hildebrand's regular solution theory, and may be expected to hold to a good approximation if the atomic volumes of the two liquid metals are not very different. In the general case, however, one may expect some energetic asymmetry in a binary system. For many such systems it has been demonstrated, particularly by Hildebrand and co-workers, that the energetic asymmetry may be taken into account by use of a volume fraction expression for the excess free energy. Hildebrand has also shown that for a number of liquid metallic systems, the deviation from the ideal may be represented to be a better approximation by a volume fraction expression than by a mole fraction expression.[1] If this is the case, it may be assumed that the integral heat of mixing can be expressed by the van Laar[9] relation

$$\Delta H = \alpha x(1 - x)/(V_1V_2V_m) \qquad (5)$$

Here α is a constant, while V_1, V_2 and V_m are the molar volumes of the pure components and of the mixture, respectively. The constant α may be determined from the experimental $\bar{L}^0$. If V_1 is the atomic volume of the solute component in the solubility experiment, we have

$$\alpha = V_1V_2^2\bar{L}^0 \qquad (6)$$

and get

$$\Delta H = x(1 - x)(V_2/V_m)\bar{L}^0 \qquad (7)$$

For the purpose of the present discussion only a small error is introduced if we assume

$$V_m = x_1V_1 + x_2V_2 \qquad (8)$$

In this case we get for the dependence of the relative partial molal heat contents on concentration

$$\bar{L}_1(\text{solute}) = \bar{L}^0\vartheta_2^2 \qquad (9a)$$

$$\bar{L}_2(\text{solvent}) = \bar{L}^0\vartheta_1^2(V_2/V_1) \qquad (9b)$$

Here ϑ_1 and ϑ_2 are the volume fractions $x_1V_1/(x_1V_1 + x_2V_2)$ and $x_2V_2/(x_1V_1 + x_2V_2)$. According to these expressions we should obtain a maximum for the (positive) heat of mixing at compositions richer in the smaller atom than the equi-atomic mixture. The author has shown that this is actually found for many liquid metallic systems, although exceptions from the rule are known.[10]

The theoretical basis for the use of volume fraction expressions for metallic mixtures is still unsatisfactory. The expressions are advanced here as semi-empirical relations, and as far as possible their use should be justified by agreement with experiment. A more comprehensive discussion of the problem of energetic asymmetry in liquid metallic mixtures will be presented in a later communication.

When an assumption has been made regarding the dependence of the heat of mixing on composition, the corresponding excess partial molal entropies for the solute may be calculated by the following procedure: (1) For temperatures and compositions along the liquidus the appropriate free energy is obtained from (1). (2) The heat term, $\bar{L}_1$, is calculated from (4) or alternatively from (9a). Thus

$$\overline{\Delta S}_1{}^x = R \ln x_1 + \bar{L}_1/T - (\Delta H_f/T_m)(1 - T_m/T) \qquad (10)$$

In this expression $\Delta H_f/T_m$ is the entropy of fusion for component 1.

If the binary system in question has a liquid miscibility gap, we are unable in this way to arrive at free energy (and entropy) data for the unstable mixtures. We may to some extent overcome this difficulty by assuming a smooth behavior for the partial molal entropy in the unstable region (see, *e.g.*, broken lines, Figs. 3b and 4b).

Finally it should be mentioned that it is of course also possible to start the computations by an assumption regarding the dependence of the excess entropy on concentration. By this method one would obtain the corresponding heat data indirectly through combination with the free energy from the liquidus.

Application to the Systems Copper-Lead, Copper-Bismuth and Copper-Thallium

Experimental Data.—Because of the low vapor pressures of the components, these systems do not lend themselves too well to investigation by the vapor pressure method. Also, the relatively small difference in electrochemical character between copper on the one hand, and lead, bismuth and thallium on the other, indicate that the systems are unsuitable for attack by the electromotive force method. We shall, instead, try to obtain some information by the outlined solubility method.

In the earlier communication dealing with the solubility of copper in liquid lead,[7] details were presented on the experimental method used. In the present paper solubility data are reported for copper in liquid bismuth and thallium. The determinations were carried out as for copper-lead, with the necessary modifications in analytical procedure:

Copper-Bismuth.—The equilibrium alloy was dissolved in nitric acid and bismuth precipitated by ammonium carbonate after neutralization with ammonia. In order to remove all copper from the precipitate, this was redissolved on the filter paper and the procedure repeated two times. All filtrates were gathered and copper determined by electrolysis.

Copper-Thallium.—The equilibrium alloy was dissolved in nitric acid and thallium precipitated by a mixture of ammonium chloride and ammonia. In the filtrate all chlorides were removed by evaporating to dryness with sulfuric acid. The copper was determined by electrolysis.

The experimental results are presented in Fig. 1. At temperatures above those of the actual solubility measurements the liquidus has been taken from reference 11 (Cu-Bi) and from M. Hansen[12] (Cu-Tl). In the figure the logarithm of the atomic fraction, log x_{Cu}, is plotted *versus* $1/T$. By comparison with the earlier data for copper-lead, it will be found that the systems are very similar, the solubility of solid copper in the three liquid metals increasing in the order $(x_{Cu})_{Bi} > (x_{Cu})_{Pb} > (x_{Cu})_{Tl}$.

It will be observed, however, that the scattering of the experimental points is somewhat greater for the systems now investigated than for copper-lead. This is probably due in part to the more cumbersome and less accurate analytical procedure required for these systems, partly also to the

---

[9] J. J. van Laar, "Thermodynamik der einheitlichen Stoffe und binärer Gemische," Groningen, 1935.

[10] O. J. Kleppa, THIS JOURNAL, 73, 385 (1951).

[11] "Metals Handbook," A.S.M., 1948 edition.

[12] M. Hansen, "Aufbau der Zweistofflegierungen," Berlin, 1936.

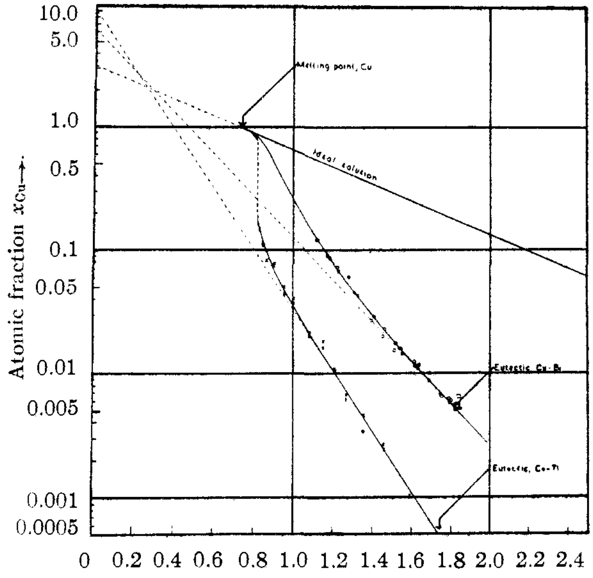

Fig. 1.—Solubility of Cu(s) in Bi(l), respectively: O, Cu in Bi; ×, Cu in Tl; □, Cu in Bi, Heycock and Neville.

somewhat less satisfactory control of furnace temperature during these runs.

By extrapolation of the experimental data for the two systems we find for the eutectic composition of copper–bismuth alloys, x_{Cu} = 0.0048, and for copper–thallium alloys, x_{Cu} = 0.0005. Earlier investigations[13] give for the eutectic composition of copper–bismuth x_{Cu} = 0.0065, while no information was found on the composition of the copper–thallium eutectic. By extrapolation we also determined the composition of the thallium-rich phase at the copper–thallium monotectic temperature, 962° (three-phase equilibrium of solid copper and two liquids) to be $x_{Cu} \simeq 0.20$.

In Fig. 1 we have also drawn the limiting straight lines of the solubility curves, and from their slopes and the intercepts at $1/T = 0$, we find $\bar{L}$ and $\Delta\bar{S}^{x°}$. The entropy of fusion for copper has been taken to be 2.30 cal./deg. g. atom, the melting point 1356°K. The purity of the metals used in these investigations ranged from 99.7% (Cu) to better than 99.9%, as determined by semi-quantitative spectrographic analysis.

System	$\bar{L}^0_{Cu}$, kcal./g. atom	$\Delta\bar{S}^{x0}_{Cu}$, cal./deg. g. atom	Remarks
Cu-Pb	6.6	1.4	Ref. 7
Cu-Bi	4.6	1.4	...
Cu-Tl	8.1	2.0	...

Computed Thermodynamic Data. Discussion.—In Figs. 2a, 3a and 4a the calculated heat data for the three systems under consideration have been plotted. Plots are given for the partial molal heat contents of both components as well as for the integral heats of mixing. In Figs. 2b, 3b and 4b the corresponding excess partial entropies for copper have been given. In all cases the calculations have been carried out using one of the two alternatives: I, validity of equation (3); II, validity of equation (9a, b). In these calculations we have taken the volume ratio for bismuth–copper to be 3.00, for lead–copper 2.75 and for thallium–copper 2.65.

For the systems copper–bismuth and copper–lead we have included in Figs. 2 and 3 the experimental values for the integral heat of mixing at 1200° reported by Kawakami.[4] For the first of these systems we have also given Scheil's curve for ΔH.

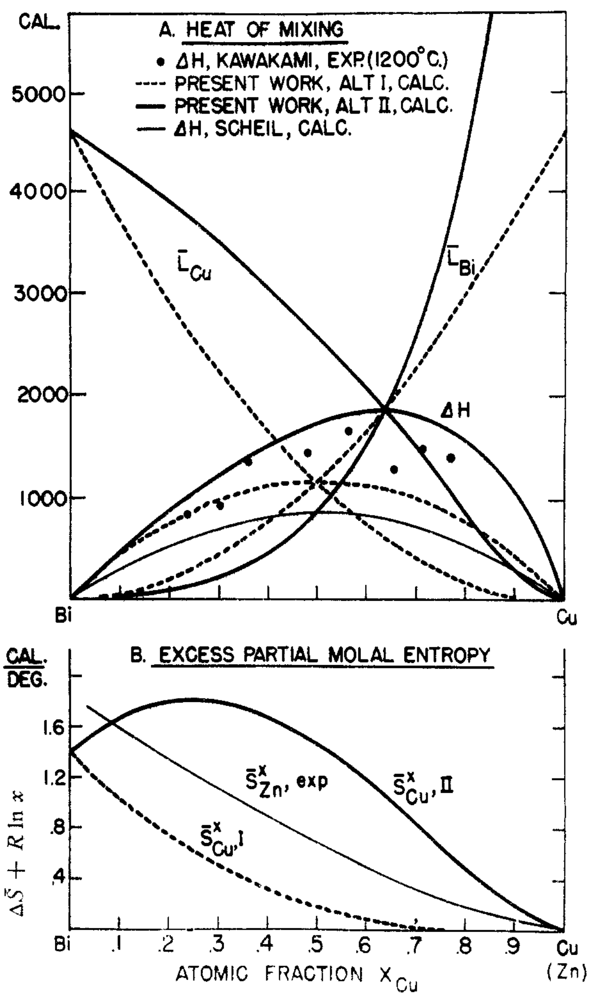

Fig. 2A.—Calculated and experimental heat data for the system Cu(l)–Bi(l). B.—Calculated excess partial molal entropies for copper in Cu(l)–Bi(l).

Heat of Mixing.—For the two systems where calorimetric data are available we find that all the experimental points fall between the two calculated curves (I and II). This should indicate that neither equation (3) nor (9a,b) adequately represents the concentration dependence of the heat of mixing. It appears that the volume fraction expression for ΔH is the better approximation for the copper–bismuth system, while the mole fraction curve gives a somewhat better fit for copper–lead. It will be seen that the unweighted mean of I and II for both systems would be in reasonable agreement with Kawakami's experimental data. As should be expected, we find that Scheil's curve for ΔH (Fig. 2) runs lower than either of the other curves.

For the system copper–thallium no calorimetric data are available in the literature.

Excess Entropy of Mixing.—Because of the large difference in volume between the (small) copper atoms on one side and the (large) thallium, lead and bismuth atoms on the other side, we anticipate

---

[13] C. T. Heycock and F. H. Neville, *J. Chem. Soc.*, **61**, 893 (1892).

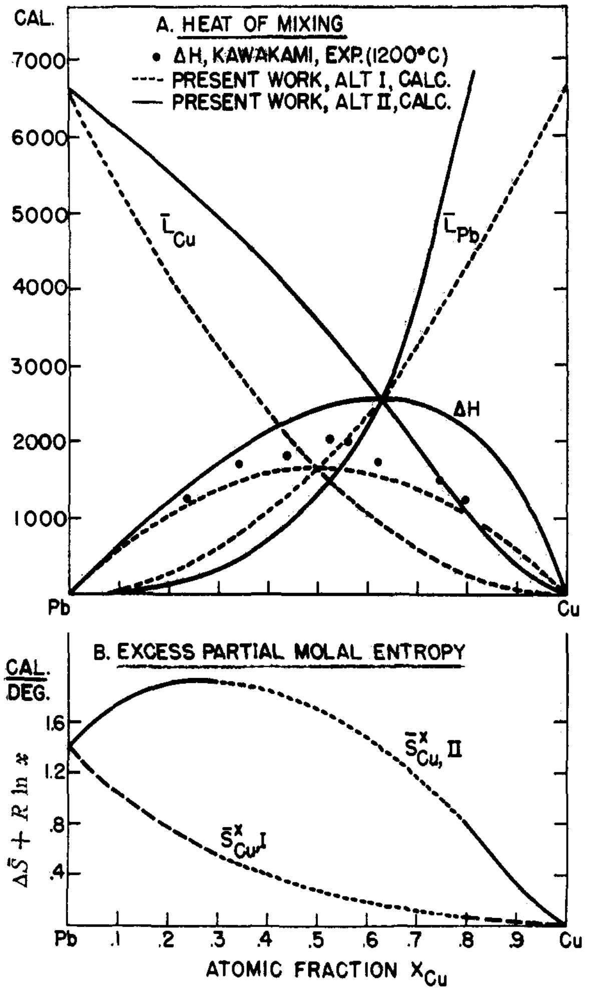

Fig. 3A.—Calculated and experimental heat data for the system Cu(l)–Pb(l). B.—Calculated excess partial molal entropies for copper in Cu(l)–Pb(l).

quite large excess entropies of mixing.[8] It turns out that alternatives I and II both lead to entropies larger than ideal. However, the mole fraction expression for ΔH yields relatively small excess entropies only.

The volume fraction expression for ΔH, on the other hand, gives very large excess entropies. For all three systems this expression leads to a maximum in the excess partial molal entropy for copper around $x_{\text{Cu}} = 0.3$. In this case the Gibbs–Duhem equation requires a minimum at the same composition in the corresponding quantity for the other component (Bi, Pb, Tl). As these excess partial molal entropies start out at zero for $x_{\text{Cu}} = 0$, negative deviations from the ideal would be obtained for mixtures weak in copper. This behavior is very uncommon, but a similar result has been obtained by the author for the system gold–lead.[14] It is again believed, however, that the correct values may be intermediate between the two extremes I and II, but probably closer to II.

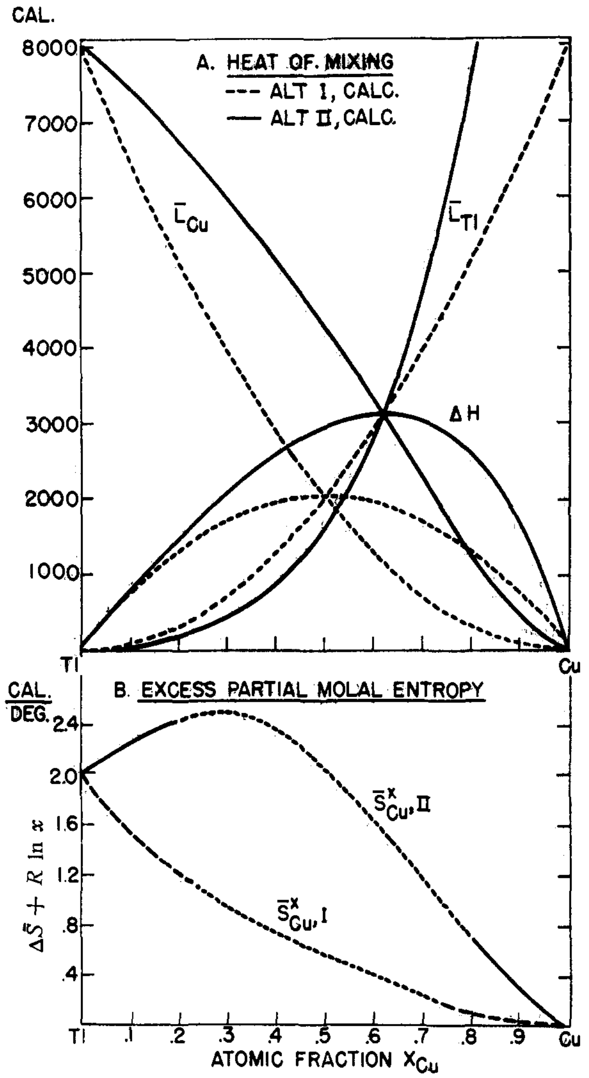

Fig. 4A.—Calculated heat data for the system Cu(l)–Tl(l). B.—Calculated excess partial molal entropies for copper in Cu(l)–Tl(l).

We have illustrated this by plotting in Fig. 2b the excess partial molal entropies for zinc in liquid zinc–bismuth mixtures.[15] As the copper atoms are smaller than the zinc atoms, we should expect the correct entropy values for copper–bismuth to be somewhat larger than the corresponding zinc–bismuth data.

Acknowledgments.—The experimental part of the present paper was carried out while the author was associated with the Norwegian Defense Research Establishment, Lillestrom, Norway. The author is indebted to Miss E. Aamodt for carrying out the analytical work involved in the solubility determinations. He also wishes to acknowledge the assistance offered by Messrs. L. J. Howell and Th. Holager in checking the purity of the metals used.

CHICAGO, ILLINOIS

---

(14) O. J. Kleppa, THIS JOURNAL, **71**, 3275 (1949).

(15) O. J. Kleppa, *ibid.*, **74**, 6052 (1952).