A Thermodynamic Study of Liquid Metallic Solutions. II. The System Tin–Gold

BY O. J. KLEPPA

Introduction

In an earlier communication dealing with the liquid system lead–gold[1] the author has pointed out the importance of gathering more information on liquid metallic mixtures. The present paper is the second report on a series of investigations which were started in order to secure more data on the thermodynamic properties of such solutions.

Experimental Method

The system tin–gold is as well suited as the system lead–gold for an investigation by the electromotive force method. This method was discussed in some detail in the previous paper. Here it shall only be stated that it is based on the possibility of constructing a reversible galvanic cell, which in the present case takes the form

$$\text{Sn(l)}/\text{Sn}^{++}/(\text{Sn} + \text{Au})\text{(l)}$$
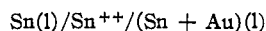
By measuring for such cells the electromotive force, E, and its temperature gradient, dE/dt over a sufficiently wide composition and temperature range, we shall be able to secure all the information required for a complete thermodynamic description of the mixture.

Experimental Procedure

The equilibrium phase diagram for gold–tin[2] shows that liquid alloys with a concentration of gold up to about 80 atomic per cent. can be investigated at temperatures low enough so that Pyrex apparatus can be used. However, due to the volatility of tin(II) chloride (b. p. 603° at 1 atm. pressure), which should be present in the electrolyte in an amount of a few per cent., it was decided not to use the open H-shaped cells which have found extensive application in this type of work. Instead, a closed cell type introduced by Seltz and Dunkerley[3] was adopted. The cell is shown in Fig. 1. It will be noticed that the sealing of the two charging tubes prevents the escape of the volatile chloride from the cell. The composition of the electrolyte was about 95% of the lithium chloride–potassium chloride eutectic and about 5 weight per cent. tin(II) chloride.

The electrolyte was first melted in the cell and degassed by heating for some time at 600–650°. Weighed amounts totalling 3–4 g. of gold and tin and of pure tin, respectively, were then introduced and melted down in their separate halves of the cell. This was then closed by sealing off the two charging tubes. From this time the cell was treated and the runs carried out in a manner similar to the procedure adopted in the case of the lead–gold system. However, in order to change the alloy composition it was now necessary to open the cell by means of a hand torch and reseal after introduction of the weighed amounts of gold or tin.

It was found in the present system that the electromotive forces were slightly less reproducible than for lead–gold, the precision dropping to 0.2–0.3 mv. for alloys high in gold. But in all cases this slight scattering represented

(1) O. J. Kleppa, THIS JOURNAL, 71, 3275 (1949).
(2) M. Hansen, "Aufbau der Zweistofflegierungen," Berlin, 1936.
(3) H. Seltz and F. J. Dunkerley, THIS JOURNAL, 64, 1392 (1942).

only a small fraction of one per cent. of the total electromotive force.

The possible presence of gold in the reference electrodes was checked after the completion of the runs by spectrographic means. In all cases it was found that the amount of gold was less than 0.001% and in some cases gold was totally absent. The alloy electrodes were analyzed by conventional analytical methods and showed no change in composition within the analytical error.

The tin used in the present investigation was the analytical reagent supplied by Mallinckrodt Chemical Works. Spectrographic analysis showed the presence of the following impurities.

Impurity	Amount, %
Pb	<0.04
Fe	< .01
Cu, Sb	< .004
Bi	< .002

The gold was "fine gold" (99.9% Au) supplied by Baker and Company.

Experimental Results

The measured electromotive forces for each alloy composition were plotted *versus* temperature. In the range between 500 and 600° it was never possible to detect any change in slope of these curves, and a graphical determination of the temperature gradient in this range was accordingly quite simple. From the same set of curves were obtained the electromotive forces at one common reference temperature, 600°. At temperatures below 500° a slight decrease in the slope was detected for a few alloy compositions. We shall return to this point below under "Discussion." The experimental results for a total of thirteen runs and the corresponding activities and "entropy fractions"[1] are recorded in Table I. It should be noted that "entropy fractions" *smaller* than the atomic fractions correspond to partial molar entropies *larger* than for ideal mixtures.

TABLE I

EXPERIMENTAL RESULTS, ACTIVITIES, a, AND "ENTROPY FRACTIONS," X'

Run	Weighed in X_{Sn}	E, mv., 600°	$\Delta E/\Delta T$, mv./100 deg. 500–600°	a_{Sn}	X'_{Sn}
2	0.8125	11.16	0.96	0.7415	0.800
3	.6815	27.65	2.02	.4794	.626
4	.5302	63.30	2.60	.1858	.547
5	.4426	93.90	3.25	.0823	.470
6	.3596	131.7	6.0	.0301	.248
7	.2589	189.8	9.25	.0064	.115
8	.9026	4.52	0.49	.8867	.893
9	.2223	217.5	~13.0	.0031	.05
10	.4982	72.18	2.71	.1467	.533
11	.5091	69.00	2.60	.1597	.547
12	.6085	41.50	2.23	.3316	.596
13	.2941	166.55	7.95	.0119	.158
14	.548	56.25	2.50	.2241	.560

TABLE II

COMPUTED ACTIVITIES, "ENTROPY FRACTIONS" AND HEAT CONTENT DATA AT ROUND FIGURE ATOMIC FRACTIONS

Reference state for gold is the hypothetical undercooled liquid gold.   Figures in parentheses are obtained by extrapolation.

X_{Sn}	a_{Sn}, 600°	a_{Au}, 600°	X'_{Sn}, 500–600°	X'_{Au}, 500–600°	$\bar{L}_{Sn}$, cal.	$\bar{L}_{Au}$, cal.	ΔH, cal.
1.000	1.000	0.000	1.000	0.000	0	(−7100)	0
.900	0.885	.001	0.895	.047	− 19	−6747	− 692
.800	.718	.0035	.780	.106	− 144	−5940	−1303
.700	.518	.0096	.645	.191	− 380	−5193	−1824
.600	.313	.025	.592	.223	−1105	−3803	−2184
.500	.149	.063	.535	.252	−2217	−2415	−2316
.400	.051	.152	.365	.346	−3413	−1421	−2217
.300	.013	.321	.164	.534	−4397	− 882	−1937
.200	.002	.603	.07	.709	−6167	− 282	−1459
.100	(.0003)	.844	(.02)	.883	−7284	− 78	− 799
.000	.000	1.000	.000	1.000	(−8300)	0	0

Based on this set of experimental data the activities and "entropy fractions" for round figure atomic fractions were determined graphically from the smooth curve drawn through the experimental points.   These quantities are given in the second and fourth columns of Table II.   In the same table will also be found activities and "entropy fractions" for gold, with reference to the hypothetical, undercooled liquid gold.   These data have been obtained from the data for tin by graphical integration of the Gibbs–Duhem–Margules equation in the usual way.   A plot of activities and "entropy fractions" for both components will be found in Fig. 2.   Finally, there are
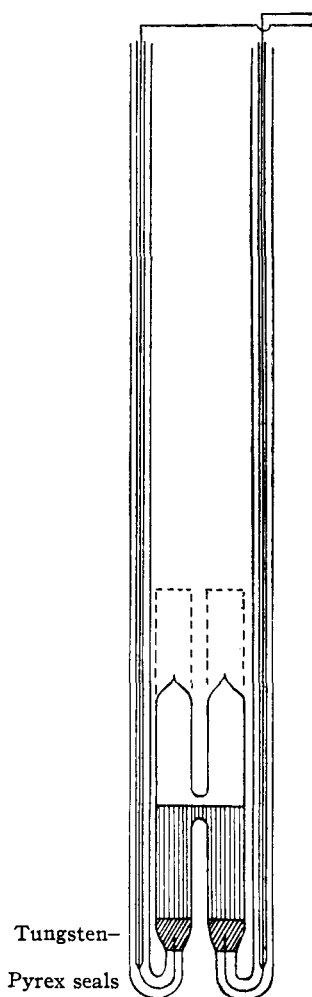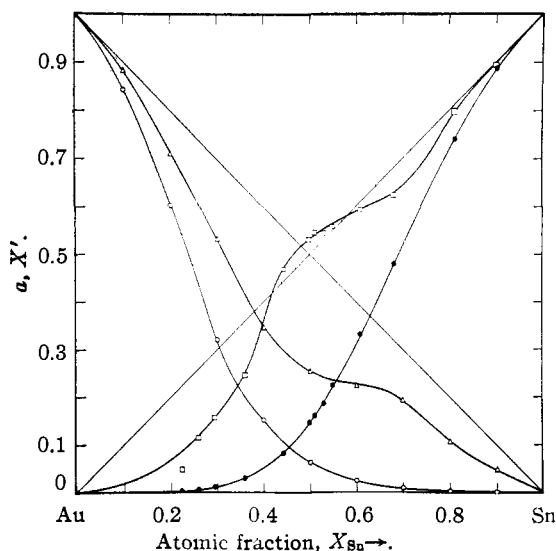

Fig. 1.—Pyrex cell, closed type.

Tungsten–

Pyrex seals

Fig. 2.—Activities, a and "entropy fractions," X', in system tin–gold: ●, a_{Sn}, 600°; □, X'_{Sn} 500–600° (experimental); ○, a_{Au}, 600°; △, X'_{Au} 500–600° (computed).

given in the last three columns of Table II the calculated values for the relative partial molar heat contents $\bar{L}_{Sn}$ and $\bar{L}_{Au}$ as well as for the integral heat of mixing, ΔH.   These quantities are plotted in Fig. 3.

The possible error in all the computed data is of the same order of magnitude as indicated for the system lead–gold.

Comparison with Earlier Data

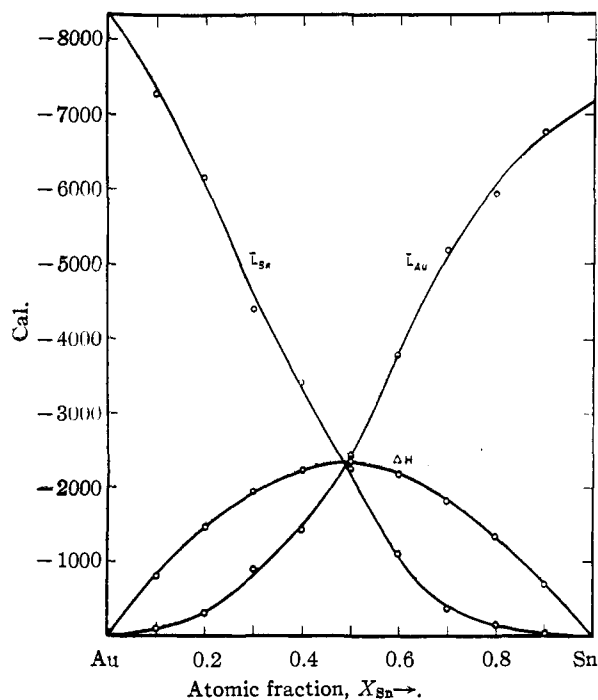Reported calorimetric measurements of the heat of formation of the intermetallic compound

Fig. 3.—Partial molar and integral heats of mixing in system tin–gold.

AuSn make possible a comparison of the thermal data obtained in this investigation with earlier work. Biltz, Rohlffs and Vogel[4] measured the difference between the heat of solution (in a solution calorimeter operated at 90° with bromine–potassium bromide, etc., as solution agents) of the solid compound AuSn and that of the same uncombined mixture. For the heat of formation from the pure solids at this temperature they give

$$\Delta H = -4._1 \text{ kcal./g. atom } (^1/_2\text{AuSn})$$

They give the average error of 12 separate determinations as ±7%. Kubaschewski[5] measured the heat of fusion of the same compound and found for one g. atom ($^1/_2$AuSn)

$$\Delta H_f = 3.06 \pm 0.08 \text{ kcal.}$$

The heats of fusion of gold and tin at their melting points have been determined quite accurately. If, therefore, the specific heats of the substances involved are known or can be estimated without too much uncertainty, we should be able to compute the heat of mixing for the liquid equiatomic mixture—with reference to pure liquid tin and undercooled liquid gold of the same temperature. Weibke and Kubaschewski[6] have carried out this computation, and give for this heat of mixing at 600°

$$\Delta H \cong -3._3 \text{ kcal.}$$

(4) W. Biltz, G. Rohlffs and H. U. v. Vogel, Z. anorg. allgem. Chem., **220**, 113 (1934).

(5) O. Kubaschewski, Z. physik. Chem., **A192**, 292 (1943).

(6) F. Weibke and O. Kubaschewski, "Thermochemie der Legierungen," Berlin, 1943.

The corresponding value from the present investigation is

$$\Delta H = -2.3 \text{ kcal.}$$

The possible error involved in our value is estimated to be less than 10%, and the agreement is thus not very satisfactory. It is believed, however, that the uncertainties involved in the data which form the basis for Weibke and Kubaschewski's computations may account for most of this discrepancy.

Activities of Gold from the Phase Diagram

Because of a certain but so far undetermined amount of solid solubility of tin in gold,[2] the evaluation of activities from the phase diagram in the gold rich region is not possible. In the temperature range covered in the present investigation, the situation is further complicated by the possible presence of the intermediary solid phase (β) with about 12 atomic per cent. tin.

Discussion

The liquid system tin–gold may in some respects serve as a prototype for liquid mixtures where strong intermetallic compounds exist in the solid state. We should expect that the liquid mixtures in such cases will show signs of the strong interaction between the components. This interaction is amply illustrated by the low activities and large heat of mixing found in the present system. However, very interesting features of this system will not easily be observed if one's attention is limited to activities and heat of mixing only. The unusual shape of the curves for the "entropy fraction" (Fig. 2) should indicate that it might be worthwhile to investigate the entropy problem for this system somewhat more in detail.

A preliminary and qualitative discussion of the factors affecting the entropy of mixing was given by the author in the paper on lead–gold. We shall first focus our attention on one of these factors only, namely, on the contribution to the entropy of mixing of the short range order in the mixture. The factors contributing to the large positive entropy deviation will be discussed separately later.

Hildebrand[7] has introduced into solution theory the term "regular solution" in order to classify a mixture which shows an ideal entropy of mixing but a non-ideal heat of mixing ($\Delta H \gtrless 0$). The ideal entropy of mixing presupposes a random distribution of the atoms and accordingly the lack of any short range order.

Guggenheim[8] and Rushbrooke[9] have criticized the assumption of random distribution of the atoms in those mixtures which show a non-zero heat of mixing. They instead treat such solu-

(7) J. H. Hildebrand, Proc. Nat. Acad. Sci., **13**, 267 (1927).

(8) E. A. Guggenheim, Proc. Roy. Soc. (London), **A148**, 304 (1935).

(9) G. S. Rushbrooke, ibid., **A166**, 296 (1938).

tions by use of the so-called "quasi-chemical" method of statistical thermodynamics, and arrive at expressions for the deviation of free energy, heat and entropy of mixing from that of an ideal solution.

Without going into the details of their model or treatment, we shall confine ourselves to quote the final expressions given by Guggenheim[10]

$$A - A_{\text{ideal}} = X_A X_B \lambda (1 - X_A X_B (2\lambda/ZRT))$$
$$E - E_{\text{ideal}} = X_A X_B \lambda (1 - 2X_A X_B (2\lambda/ZRT))$$
$$S - S_{\text{ideal}} = -X_A^2 X_B^2 (2\lambda^2/ZRT^2)$$

In these expressions A, E and S are Helmholtz free energy, internal energy and entropy of mixing, X_A and X_B are mole fractions of components A and B, respectively, while Z is coördination no., which is assumed to be the same in the mixture as in the pure components. The single new parameter λ is given by

$$\lambda = N(2W_{AB} - W_{AA} - W_{BB})$$

where W_{AB}, W_{AA} and W_{BB} are the potential energies of the AB, AA and BB nearest neighbor interactions or bonds while N is Avogadro's number. As we are dealing with a process taking place in the condensed phase we can disregard the negligible difference between H and E, and can now clearly see the effect of a non-zero heat of mixing on the entropy. A positive or negative ΔH corresponds on the atomic scale to a difference between the strength of the AB bond and half the sum of the AA and BB bonds. If the AB bond is much stronger (large negative values for λ and ΔH), there will be a tendency toward formation of a larger number of such bonds than corresponds to random distribution. On the other hand, in the case of a weak AB bond (ΔH positive) there will be a surplus of AA and BB bonds compared with random distribution. For sufficiently large positive values of ΔH this will lead first to cluster formation and eventually to segregation into two liquid phases. In both cases we thus get a certain short range order in the mixture. This will cause a corresponding reduction in the entropy of mixing as given by the formula above.

We might try to get some idea of the order of magnitude of this effect. If we disregard second order terms (λ small compared with ZRT) and the small difference between ΔH and ΔE, we have

$$\Delta H = H - H_{\text{ideal}} \cong X_A X_B \lambda$$

We can thus establish the order of magnitude of λ by simply dividing ΔH for a certain composition by $X_A X_B$. Let us for simplicity choose ΔH at equiatomic composition, $\Delta H_{0.5}$. Thus, we get

$$\lambda \cong 4 \Delta H_{0.5}$$

Hence

$$\Delta S - \Delta S_{\text{ideal}} \cong -\frac{2R}{Z} X_A^2 X_B^2 \left(\frac{4 \Delta H_{0.5}}{RT}\right)^2$$

(10) A printing error occurs in Guggenheim's expression for the entropy deviation. It has been corrected here. We have also introduced mole fractions throughout.

For most metallic liquids at moderately high temperatures we expect a type of packing similar to that of the corresponding solid. Thus $Z \cong 10$, and we have

$$\Delta S - \Delta S_{\text{ideal}} \cong -6.4 \, X_A^2 X_B^2 \, (\Delta H_{0.5}/RT)^2$$

We are now in a position to get approximate values for the contribution to the entropy of mixing of the short range order at equiatomic composition, a measure for which is $|\Delta H_{0.5}/T|$.

$|\Delta H_{0.5}/T|$	1	2	(3)
$(\Delta S - \Delta S_{\text{ideal}})_{0.5}$	-0.1	-0.4	(-0.9)

In order to further illustrate the effect, we shall investigate how the "entropy fraction" is affected. In Fig. 4 are accordingly plotted the "entropy fractions" *versus* mole fraction for these same values of $|\Delta H_{0.5}/T|$. The entropy fractions have been computed from

$$\ln \left(\frac{X_B'}{X_B}\right) = \frac{2}{Z} \left(\frac{4 \Delta H_{0.5}}{RT}\right)^2 X_B X_A^2 (2X_A - X_B)$$

which formula can easily be derived from the expression for $\Delta S - \Delta S_{\text{ideal}}$ above. As before we take $Z \cong 10$.
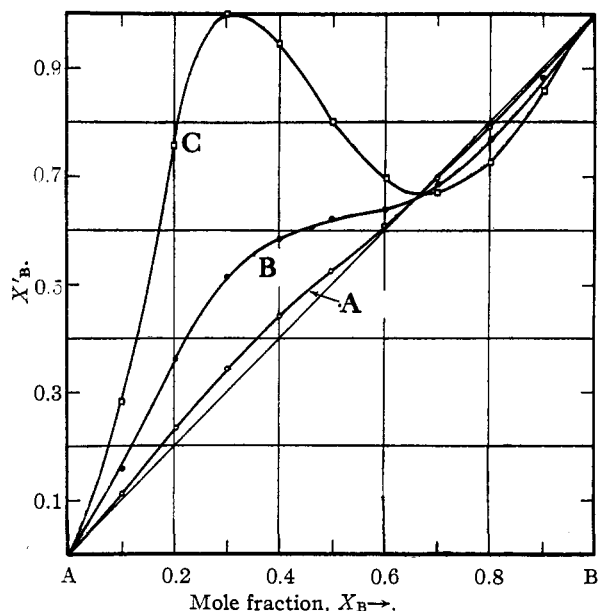

Fig. 4.—"Entropy fraction" *versus* mole fraction from quasi-chemical theory: A, $|\Delta H_{0.5}| = T$; B, $|\Delta H_{0.5}| = 2T$; C, $|\Delta H_{0.5}| = 3T$.

The curves given in Fig. 4 illustrate quite well the importance of $|\Delta H_{0.5}/T|$ for the partial molar entropy. They also throw some light on the problem of why the effect has not previously been verified for liquid metallic mixtures. Most such systems which have been the subject of detailed investigation, have had a ratio of $|\Delta H_{0.5}/T|$ of unity or less. The negative contribution of the short range order to the entropy of mixing has accordingly been very small, and has escaped detection. However, in the system tin–gold, which

we are presently discussing, we have a value of $|\Delta H_{0.5}/T|$ at 600° of about 2.6 and should accordingly expect a very marked effect.

If we return to the "entropy fraction" curves given in Fig. 2, we immediately recognize that the pattern of these curves is the same as of those given in Fig. 4. However, it is obvious that the short range order effect is superimposed on some other effect or effects which tend to give positive entropy deviations. We shall come back to this problem later.

We mentioned previously that the temperature gradient of the electromotive force for a few runs was observed to change somewhat below 500°, while no change could be detected above 500°. In view of our discussion of the short range order effect and the importance of the ratio $|\Delta H_{0.5}/T|$, we should now be in a position to explain this phenomenon. The temperature gradient is proportional to the partial molar entropy. As we go from a higher to a lower temperature and assuming that ΔH is independent of temperature, the ratio $|\Delta H_{0.5}/T|$ increases, which means that the corresponding partial molar entropy decreases. We should thus expect that the temperature gradient of the electromotive force decreases somewhat as we go down in temperature. The extent to which this was actually observed during the present investigation is illustrated in Fig. 5, where plots are given for the measured electromotive forces for the four runs where the effect was
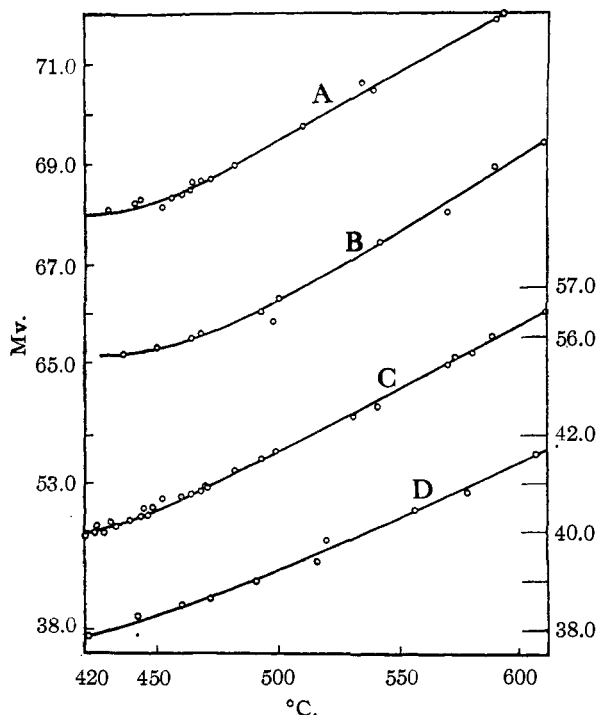

Fig. 5.—Electromotive force *versus* temperature for runs 10, 11, 12, 14: A, X_{Sn} = 0.498; B, X_{Sn} = 0.509; C, X_{Sn} = 0.548; D, X_{Sn} = 0.608.

detected. We shall at this point make a reservation regarding a quantitative use of Guggenheim's formulas in the present case. In our discussion so far we have tacitly assumed that the coördination number in the liquid mixture is the same as for each of the pure liquids, i. e., approximately 10. The four runs plotted in Fig. 5 are all of a composition close to the intermetallic compound AuSn, which gives rise to a maximum in the phase diagram.[2] Solid AuSn is known to have nickel arsenide structure.[11] In this structure each tin atom is surrounded by six gold atoms as nearest neighbors, and each gold atom is similarly surrounded by six tin atoms plus two other gold atoms at approximately the same distance. It might be expected that, at least immediately above the melting point of AuSn, this atomic arrangement should to some extent be retained, with loss on fusion primarily of the long range order of the solid state. We are thus led to assume in the liquid immediately above the melting point of AuSn (418°) an average coördination number of about 7. This is considerably lower than for pure liquid tin or gold, for which we have taken Z to be about 10.

With increasing temperatures above the melting point of the compound some increase in coördination number might very well take place simultaneously with the reduction in short range order. If this is really the case, it does, of course, discourage any attempt at evaluation from the experimental results of some special short range order parameter for the mixtures in question, as done, e. g., for α-brass by Guttman,[12] who used for this purpose the more refined quasi-chemical theory of Takagi.[13]

It should finally be mentioned that recent X-ray investigations of liquid tin–gold mixtures by Hendus[14] have given structural evidence for the presence of some degree of short range order. He suggests for this mixture that two kinds of atomic distributions are present. The atomic arrangement seemed in part to be like that of a compound, while the remainder was statistically distributed. With increasing temperature the distribution became more random. In structural language this expresses essentially the same as what we have presently deduced from entropy considerations.

It was pointed out above that the presence of a high degree of short range order is not generally found in simple binary liquid alloys. In fact, to the knowledge of the author, detailed experimental evidence for the effect of the local order on the entropy of mixing in liquid mixtures has not previously been recognized. This does not mean that such evidence is not reported in the literature. Thus, e. g., in the liquid systems

(11) L. Pauling, THIS JOURNAL, **69**, 542 (1947).

(12) Lester Guttman, A. I. M. E., Metals Tech., Tech. Publication 2330 (1948).

(13) Y. Takagi, *Proc. Phys.-Math. Soc. Japan*, **23**, 44 (1941).

(14) H. Hendus, Z. *Naturforschung*, **2a**, 505 (1947).

zinc–antimony and cadmium–antimony, which were investigated some years ago by Seltz and DeWitt,[15,16] we also find the kind of strange behavior of the partial molar entropy which has been discussed above. However, the meaning of this behavior does not seem to have been realized by the authors at that time. It is in this connection interesting to note that the zinc–antimony and cadmium–antimony systems have stable intermetallic compounds which give rise to maxima in the phase diagram similar to that of the tin–gold system. But an important difference exists in the fact that these two systems show much smaller values for $|\Delta H_{0.5}/T|$, which in both cases is about 1. One is, therefore, led to assume that the lower coördination number of the intermetallic compounds and probably also in the mixture may play a more important part in these cases than in the case of the tin–gold system. It is suggested that X-ray structural investigations of these liquid mixtures may provide interesting evidence for the presence of a high degree of short range order.

It was pointed out above that the effect of the short range order on the entropy of mixing was superimposed on some other effect or effects, which tend to give a large positive entropy deviation. It also appears that this effect is somewhat stronger on the gold rich than on the tin rich side of the system. A similar effect was observed in the previously reported system gold–lead, and analogous behavior has later been found by the author in the systems gold–bismuth and gold–thallium,[17] with the gold–bismuth system showing the greatest positive deviation.

It should here be pointed out that similar positive entropy deviations, although varying in degree, have been observed in a number of previously investigated systems, while ideal entropies of mixing and slightly negative deviations have been found in a few cases only.[18,19]

Entropy Deviation and Changes in Volume.— The previous paper in this series pointed to the work by Scatchard[20] on the effect of a net volume change on the entropy of mixing. According to Scatchard the entropy of mixing should be changed on mixing according to the formula

$$\Delta S - \Delta S_{\text{ideal}} = \int_{V}^{V + \Delta V} (\partial S/\partial V)_T\, dV$$

where V is the volume of the unmixed components and ΔV the net change in volume, positive or negative. In first approximation $(\partial S/\partial V)_T$ can

(15) H. Seltz and B. J. DeWitt, THIS JOURNAL, **60**, 1305 (1938).

(16) H. Seltz and B. J. DeWitt, *ibid.*, **61**, 3170 (1939).

(17) O. J. Kleppa, unpublished.

(18) See, *e. g.*, J. Chipman, *Disc. Faraday Society*, **4**, 23 (1948), (Fig. 10).

(19) It is here referred primarily to systems which have been investigated by the electromotive force method, as this method seems far superior to the vapor pressure method for determination of entropies of mixing.

(20) G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

be assumed independent of volume and set equal to α/K, where α is the thermal coefficient of expansion and K is the isothermal compressibility at atmospheric pressure.

Only for a small number of systems are density data for liquid metallic mixtures available, notably through the work of Matuyama.[21]

Data for α and particularly for K, for these mixtures are generally lacking, but approximate values can sometimes be obtained from those of the pure components. It is thus found that the order of magnitude of α for liquid tin, lead, bismuth and cadmium ranges from 1.0×10^{-4} to 1.5×10^{-4} degree^{-1}, while the compressibilities for the same metals at their melting points range from 3.1×10^{-6} to 4.2×10^{-6} bar^{-1}.[22]

The order of magnitude of α/K can thus be established at $\cong 1$ cal./cc. degree. For alloys involving these metals we might thus expect approximate correlation between the net volume change on mixing in cc./g. atom and the entropy deviation in cal./degree g. atom.

In Table III are summarized such data as are available on net volume changes, taken from Matuyama, and on entropy deviations taken from three different investigators. It should be pointed out that the curves for entropy deviations and volume changes within any one system are generally not symmetrical, and that their maxima normally do not coincide. In Table III data for these quantities are given at equiatomic concentration, which composition may not coincide with the maximum deviations.

TABLE III

ENTROPY DEVIATIONS AND VOLUME CHANGE IN LIQUID ALLOY SYSTEMS

Sys-tem	$(\Delta S - \Delta S_{\text{ideal}})_{0.5}$ cal./deg. g. atom	$\Delta V_{0.5}$ Cc./g. atom	Temp., °C.	$\left\|\dfrac{V_1 - V_2}{V_1 + V_2}\right\|$
Bi–Cd	$+0.42^a$	$+0.1_8$	330	0.20
Bi–Pb	$\sim 0^b$	$+ .1_9$	305	.04
Bi–Sn	$\sim 0^c$	$+ .1_5$	282	.10
Cd–Pb	$+0.21^a$	$+ .1_0$	330	.16
Cd–Sn	$+0.28^a$	$+ .2_5$	302	.10
Cd–Zn	$\sim 0^a$	~ 0	420	.18
Sn–Zn	$+0.56^a$	$+0.2_0$	420	.27

[a] N. W. Taylor, THIS JOURNAL, **45**, 2865 (1923). [b] H. S. Strickler and H. Seltz, *ibid.*, **58**, 2084 (1936). [c] H. Seltz and F. J. Dunkerley, *ibid.*, **64**, 1392 (1942).

From this table it will be seen that the correlation between the volume change on mixing and the entropy deviation is relatively poor. This may, however, partly be due to the uncertainties involved in the accepted data. In particular, it will be seen that the systems bismuth–lead and bismuth–tin, which show nearly ideal entropies of mixing, both appear to have relatively large changes in volume. This last fact is in itself rather surprising, as it should be expected that, *e. g.*, lead and bismuth, which have only slightly

(21) Y. Matuyama, *Sci. Rep. Tohoku Imp. Univ.*, [1] **18**, 19 (1929).

(22) O. J. Kleppa, unpublished results.

different atomic volumes, should be able to mix in the liquid state without any appreciable volume change. The relative difference in volume between the two components may be illustrated by the data in the last column of Table III, which shows the ratio of the volume difference at the melting points, to the sum of the volumes for the systems under consideration. It would appear that these ratios, with a notable exception in the case of zinc–cadmium, show approximately as good a correlation with the entropy deviations as the actual experimental values for the volume change. In this connection it should be pointed out that the gold–lead and gold–tin systems which both show large positive entropy deviations also are mixtures of small atoms (gold) with a relatively large atom (tin, lead).

Entropy Deviations and Changes in Specific Heat. Vibrational Entropy Terms.—From the measurements of Bottema and Jaeger[23] it is known that the specific heat of the solid intermetallic compound AuSn over a limited temperature range is larger than should be expected from Kopp's rule. This might be expected to give some positive contribution to the entropy of mixing also for the liquid alloys of a similar composition. In the general case, however, the absence of the required specific heat data, and the complications introduced through the process of melting in two component systems will make impossible a quantitative estimation for liquid alloy systems of the contribution to the entropy of mixing from specific heat differences.

From a qualitative, atomistic point of view, on the other hand, it is not difficult to visualize a general reduction of the mean vibrational frequency when we mix two atoms of different size, due to the packing problems involved. We should thus expect that the positive contribution of vibrational entropy terms should become increasingly important as the difference in volume between the two components becomes larger. This leads us back to the mentioned qualitative correlation between volume difference and positive entropy deviation.

In this connection we may point to an interesting observation by Zener[24] with regard to the

(23) J. A. **Bottema** and F. M. Jaeger, *Proc. Acad. Amsterdam*, **35**, 916 (1932).

(24) C. **Zener**, A. S. M. Symposium on Thermodynamics and Physical Metallurgy, Cleveland, 1950.

partial molar entropy of the solute in the case of limited solid solubility in metals. Zener found in these cases a positive contribution of the vibrational entropy, and a rough correlation between large entropy deviations and small solid solubilities. Now it is well known that the most important single factor determining the extent of solid solubility is the relative difference in size of the solute and solvent atoms. Thus we have here a new and interesting correlation between the thermodynamic properties of solid and liquid alloys.

Summary

The activities and "entropy fractions" for tin in liquid tin–gold mixtures have been determined by the electromotive force method for compositions up to 78 atomic per cent. gold.

From these data have been computed for both components activities at 600°, "entropy fractions" and relative partial molar and integral heats of mixing. This system shows a very large negative deviation from Raoult's law, consistent with the presence of stable intermetallic phases which give rise to a maximum in the binary phase diagram.

The "entropy fraction" data for this system have been interpreted as evidence for the presence of a certain degree of short range order, which phenomenon has been discussed in a semi-quantitative way in terms of the "quasi-chemical" theory.

In spite of the negative contribution to the entropy of mixing due to the short range order, the system is found to show large positive entropy deviations. The possible effect of net volume changes and difference in volume between the two components on the entropy of mixing has been discussed. An interpretation of the results as due to vibrational entropy terms is suggested.