in the intermediate range an amminocupric tartrate ion is formed. This is reduced to the metal *via* the +1 state, the reactions being

$$\mathrm{Cu(NH_3)(Tart)^-} + \mathrm{NH_3} \longrightarrow \mathrm{Cu(NH_3)_2(Tart)} + e;\ E^0 = -0.04\ \text{v.}$$

and

$$\mathrm{Cu(Hg)} = \mathrm{NH_3} + \mathrm{Tart^{=}} \longrightarrow \mathrm{Cu(NH_3)(Tart)^-} + e;\ E^0 = +0.20\ \text{v.}$$

The solubility of +2 copper in M hydroxide is $2.18 \times 10^{-3}\ M$.

Gelatin severely distorts the waves of all these species, especially at concentrations above 0.001%. Great stress is laid on the caution that should be observed in its use if polarographic data are to be considered to represent the true electrochemical behavior of substances in solution.

NEW HAVEN, CONNECTICUT RECEIVED MARCH 30, 1949

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

A Thermodynamic Study of Liquid Metallic Solutions. I. The System Lead–Gold

BY O. J. KLEPPA

Introduction

In a detailed experimental study of the thermodynamic properties of binary liquid alloy systems, there are two general ways of approach. One method is to evaluate the activity of a volatile component (Hg, Zn, Cd, Mg) from vapor pressure measurements. The other method depends on measuring the electromotive force in reversible galvanic cells of the type

$$\mathrm{A(l)/A^{n+}/(A + B)(l)}$$

where A denotes the baser (more electropositive) metal, B the other metal.

If carried out over a sufficiently large composition and temperature range, both methods will give us, in principle, all the data required for a complete evaluation of the thermodynamic properties (*i. e.*, free energy, entropy and heat of mixing) for the mixture, using the pure components as reference states. Both methods have also found extensive application at moderately high temperatures during the past twenty to twenty-five years.[1]

It has not, however, so far been possible to tie the results of these researches in with any existing theory of solutions.[2] This paper is the first report on a series of investigations started in order, if possible, to arrive at a clearer understanding of the factors governing the properties of such liquid metallic solutions.

Experimental Method.—The system lead–gold is well suited for application of the electromotive force method.

Measurements of the electromotive force, E, of various liquid alloy compositions *versus* pure liquid lead immediately give us the relative chemical potential μ_{Pb} in the mixture through the relationship $\mu_{\mathrm{Pb}} - \mu_{\mathrm{Pb}}{}^0 = -2FyE$ where Fy is the faraday constant. The superscript^0 in this paper refers to the pure component.

The temperature gradient of the electromotive force, $\mathrm{d}E/\mathrm{d}T$, will give the relative partial molar entropy $\Delta\bar{S}$ in the mixture in a similar way, through the relationship

$$\Delta\bar{S} = \bar{S} - S^0 = 2Fy(\mathrm{d}E/\mathrm{d}T)$$

These quantities are thus directly available from measurements. Through the equation

$$\mu - \mu^0 = \bar{L} - T\Delta\bar{S}$$

we can also immediately calculate the relative partial molar heat content, $\bar{L}_{\mathrm{Pb}}$, for lead in the mixture.

A knowledge of the partial molar properties for one of the components over the whole concentration range makes possible a calculation of the same properties for the other component by (graphical) integration of the Gibbs–Duhem–Margules equation

$$x_1\mathrm{d}\bar{Y}_1 + x_2\mathrm{d}\bar{Y}_2 = 0$$

where $\bar{Y}_1$ is any partial molar quantity for component 1, x_1 is the corresponding mole fraction (or here atomic fraction).

It should, however, be noted that in the case of lead–gold, where it was not possible to extend the measurements into the gold-rich region beyond an atomic fraction of gold of 0.79, the calculation of the partial molar properties for gold in the mixtures is associated with some uncertainty. This uncertainty is carried through in any calculation of the integral thermodynamic properties Y through the equation

$$Y = x_1\bar{Y}_1 + x_2\bar{Y}_2$$

Experimental Procedure

The type of cell used in this investigation was similar to the H-shaped cell extensively applied by H. Seltz and co-workers.[3] However, as the study of the lead–gold system required measurements up to 800–850°, temperatures at which Pyrex will no longer stand up, the cells were made from fused silica. Although extended heating at the highest temperatures caused some devitrification of the cell walls, it was found that these silica cells in general stood up quite well to the attack of the electrolyte used. This consisted of a eutectic mixture (m. p. 360°) of lithium

---

(1) A fairly complete bibliography is recently given by John Chipman, *Discussions Faraday Soc.*, **4**, 23 (1948).

(2) J. H. Hildebrand, "Solubility," Reinhold Publishing Corp., New York, N. Y., 1936.

(3) H. Seltz, *Trans. Electrochem. Soc.*, **77**, 233 (1940).

chloride and potassium chloride with some 5 wt. per cent. of lead chloride added.

The electrolyte was first melted down in the cell and degassed by heating to 700–800° for a short period of time. Weighed amounts (totaling 3–4 g.) of gold and lead, and of pure lead only, were then melted down in their separate halves of the cell, before the cell was placed in a larger silica tube heated in an electric tube furnace. To prevent temperature fluctuations, the silica tube contained a lead "bath" protected by a chloride melt, into which the cell was immersed.

Tungsten leads, protected from the electrolyte in the cell by close fitting alundum thermocouple tubes, were then inserted, the system closed off and evacuated. The assembled system is shown in Fig. 1.

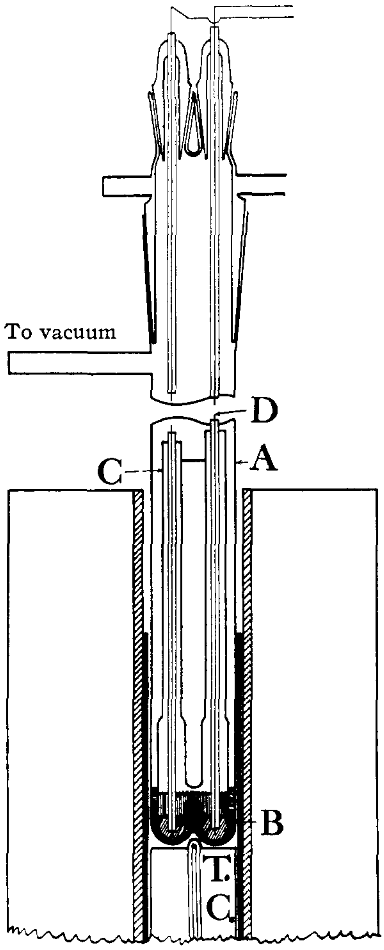

Fig. 1.—Experimental arrangement: A, outer silica tube; B, lead bath; C, silica cell; D, tungsten leads; T. C. thermocouple.

By using a constant voltage transformer for control of the power input it was possible to maintain constant temperature in the system to ± 1° over a period of many hours.

The temperature was measured by a chromel–alumel thermocouple in contact with the outside bottom of the silica tube (see Fig. 1, T.C.). It was found in separate experiments that this thermocouple showed a practically constant amount of 2° less than the actual temperature of the lead-bath (in the temperature range used); the reported temperatures are corrected for this difference. The Chromel–Alumel thermocouples were checked at the melting points of lead, antimony and silver.

The electromotive forces, both for cell and thermocouple, were measured by a Rubicon (type B) potentiometer which could be read easily to 0.005 mv.

In a period of two to three days some 100–200 independent measurements of both temperature and electromotive force were carried out at 8–15 different temperatures. When the required data for one alloy composition had been obtained in this way, nitrogen was admitted into the system and additional weighed amounts of gold or lead were added to the alloy electrode. The experiment was then continued for another two to three days until the required data for the new composition had been recorded. After 2 or 3 such consecutive runs, the cell was removed from the system, and the alloy and reference electrodes removed from the cooled off cell for analysis.

It was found that the electromotive force measurements at moderately high temperatures (< 700°) could be reproduced to ±0.02–0.03 mv. At temperatures above 700°, however, scattering increased and the precision dropped to ±0.1–0.2 mv. When measurements were carried out above 850°, it was no longer found possible to get consistent results over any prolonged period of time. This prevented extension of the measurements to alloys richer in gold than about 80 atomic per cent.

The possible presence of gold in the reference electrodes was checked after completion of the runs by spectrographic methods. In all cases, except one, it was found that the gold content was less than 0.02%. This amount is quite negligible compared with other sources of error. In one case, however, 0.31% gold was found in the reference electrode, indicating accidental contamination of the reference electrode by transfer of metal from the alloy side to the pure metal side of the cell. The results of these runs are not reported.

Analysis by conventional analytical methods of the alloy electrodes showed, within the analytical error, no change in composition. The compositions reported are based on weighed-in amounts.

The lead used in this investigation was "Baker's Analysed" with a total of foreign non-volatile matter of 0.02%. 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 *vs.* temperature. Over a range of 200–300°, there was never a detectable change in the slope of any of these curves, and a graphical determination of the temperature gradient of the electromotive force was, therefore, simple. From the same set of curves the electromotive forces for the various compositions at one reference temperature, 600°, were obtained. As most of the experiments were performed at 450–700°, it was decided to use 600° as a reference temperature also for alloys which would not be liquid at this temperature (alloys with less than 32 atomic per cent. lead). This involved an extrapolation of the data for these alloys from higher temperatures, making use of the simultaneously determined temperature gradient of the electromotive force. The reference state for gold in all data reported below is the hypothetical undercooled liquid gold.

The experimental results for the various runs and the corresponding activities a_{Pb} and "entropy fractions"[4] x'_{Pb} are recorded in Table I.

Based on this set of experimental data, the electromotive forces and their temperature gradients for round figure atomic fractions were de-

---

[4] For an explanation of the term "entropy fraction," see below.

TABLE I

Run	Atomic fraction of lead	E. m. f., mv., at			a_{Pb} 600°	$\Delta E/\Delta T$ mv./100°	x'_{Pb}	Temp. range, °C.
		600°	700°	800°				
2	0.9665	1.40			0.9623	0.12	0.973	450–700
3	.9345	2.75			.9294	.27	.940	450–700
4	.9008	4.25			.8932	.35	.922	450–700
5	.8205	8.81			.7911	.83	.825	450–700
6	.7393	14.14			.6866	1.26	.746	450–700
7	.6715	18.86			.6056	1.66	.680	450–700
8	.6311	22.91			.5438	2.10	.614	450–700
9	.6054	25.19			.5118	2.32	.583	450–700
10	.5935	25.84			.5030	2.35	.579	450–700
11	.5687	28.70			.4661	2.60	.547	450–700
12	.5078	35.15			.3927	3.49	.445	500–700
13	.4247	45.80			.2959	4.68	.337	500–700
14	.3336	60.25	66.50		.2015	6.25	.234	600–700
15	.2702	74.25	82.45		.1389	8.20	.149	600–780
19	.2135	91.2	101.3	111.4	.0885	10.1	.096	750–830
21	.3697	53.20			.2431	5.56	.275	550–650
22	.3031	65.00	72.10		.1771	7.10	.192	620–700
23	.2502	78.0	86.4	94.8	.1254	8.4	.142	700–800

TABLE II[a]

1	2	3	4	5	6	7	8	9	10
	600° C.		600° C.						
x_{Pb}	$\mu_{Pb} - \mu^0_{Pb}$ cal.	$\Delta\bar{S}_{Pb}$, cal. deg.$^{-1}$	a_{Pb}	a_{Au}	x'_{Pb}	x'_{Au}	$\bar{L}_{Pb}$, cal.	$\bar{L}_{Au}$, cal.	ΔH, cal.
1.000	0	0	1.000	0.000	1.000	0.000	0	(?)	0
0.900	− 205	0.18	0.889	.036	0.913	.045	− 48	−400	− 84
.800	− 460	.42	.767	.087	.809	.093	− 93	−123	− 99
.700	− 780	.71	.638	.150	.699	.144	− 160	75	− 90
.600	−1170	1.08	.509	.229	.581	.204	− 227	198	− 57
.500	−1655	1.60	.385	.322	.447	.280	− 258	243	− 8
.400	−2250	2.32	.273	.429	.311	.375	− 225	234	+ 50
.300	−3065	3.28	.171	.553	.192	.484	− 198	232	+103
.200	−4450	5.0	.077	.716	.081	.637	− 85	203	+145
.100	(−6500)	(8.5)	.023	.879	.014	.860	+1000	38	+134
.000	....	..	.000	1.000	.000	1.000	(?)	0	0

[a] The values in parentheses are based on extrapolation. The reference state for gold is the hypothetical undercooled liquid gold.

termined by graphical interpolation of the smooth curve drawn through the experimental points. The corresponding chemical potentials and partial molar entropies are recorded in columns 2 and 3, Table II.

In column 4 of this table are given the activities of lead at 600°, while column 5 gives the corresponding activities of gold, calculated by graphical integration of the atomic ratios *versus* activity coefficients. Columns 6 and 7 give, in a similar way, the "entropy fractions" for lead and gold, respectively.

The author, in another communication,[5] has suggested the use of the "entropy fraction" to indicate the deviations of the partial molar entropies from those of an ideal solution.

The entropy fraction x'_i is defined by the relationship

$$\Delta\bar{S}_i = -R \ln x'_i$$

It will be seen that this quantity is related to the partial molar entropy in the same manner as the activity is related to the chemical potential. If x' is different from x, the ratio of the two (x'/x) gives a numerical measure for deviations from the ideal partial molar entropy. The quantity (x'/x) might be termed "entropy fraction coefficient" and is particularly useful in graphical integrations involving the partial molar entropy. Like the chemical potential, the partial molar entropy goes numerically to infinity when x goes to zero, while the activity coefficient and (x'/x) of course remain finite. This has been made use of in the computation of the data of column 7.

Plots of activities and "entropy fractions" for both components are given in Fig. 2.

Columns 8, 9 and 10 finally give the calculated values for relative partial heat contents $\bar{L}$ and for the integral heats of mixing ΔH. These quantities are plotted in Fig. 3.

Limits of Error in Computed Data.—The limits of error in the basic data of Table II (columns 2 and 3) are estimated to generally less than ±1% for the chemical potentials and to ±2–3% for the partial molar entropies. This estimation

---

[5] O. J. Kleppa, *Discussions Faraday Soc.*, **4**, 109 (1948).

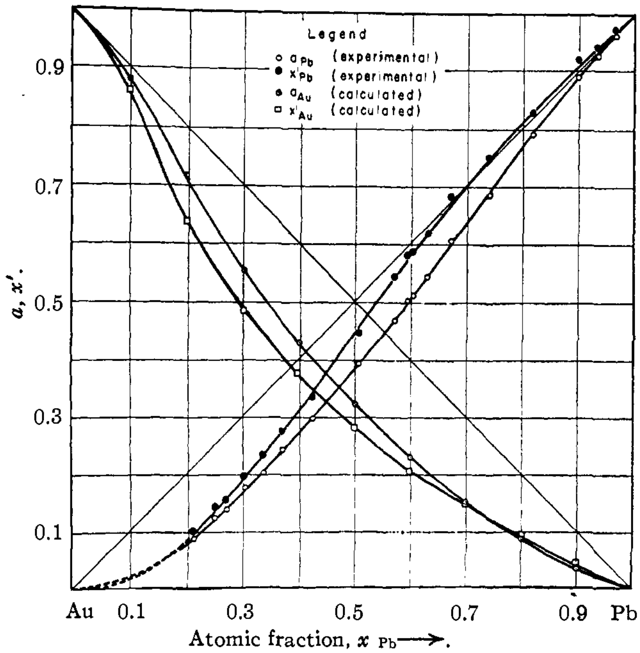

Fig. 2.—Activities and "entropy fractions" in the system Au (l)-Pb (l).

is based primarily on the reproducibility of the measurements, the temperature fluctuations during the experiments and on the possible error involved in the graphical interpolations.

These errors cannot seriously affect the calculated values for the activity and "entropy fraction" for lead. However, the relative partial molar heat content, $\bar{L}_{Pb}$, is derived as a difference between two large numbers, and may accordingly be associated with a considerably greater uncertainty.

In the subsequent calculations of the activities and "entropy fractions" for gold more serious error may also be involved, because of the required extrapolation of the data for lead into the most gold-rich region (bracketed values in columns 2 and 3) and the uncertainty associated with the graphical integration. What is said above about the uncertainty in the partial molar heat content, is even more the case for $\bar{L}_{Au}$ than for $\bar{L}_{Pb}$.

Comparison with Other Data.—Unfortunately, there are no calorimetric data available for the system lead–gold. These would have represented a very desirable check on the thermal data. However, by comparison with the equilibrium phase diagram, we have an independent method for determination of the chemical potential of gold in the liquid alloys rich in gold.

The phase diagram in this system was worked out by Vogel.[6] From his data we find that the liquid in equilibrium with the solid solution of lead in gold at 600° has an atomic fraction of lead of 0.314. As the solid solubility of lead in gold is probably of the order of 0.05% or less at 600°[7] we can neglect it in our calculations without introducing any appreciable error.

The equilibrium condition is then simply

$$\mu'_{Au}\ (\text{solid}) = \mu_{Au}\ (\text{in solution})$$

We must accordingly calculate the chemical potential of pure solid gold at 600°, referred to pure liquid undercooled gold of the same temperature. This immediately also gives the chemical potential of gold in the solution.

For the process Au(l) = Au(s) K. K. Kelley[8] gives $\Delta H = -3030$ cal. at the melting point of gold (1336°K.). In the lack of data for the specific heat of undercooled liquid gold, we make the reasonable assumption that $\Delta C_P = 0$ and find for the considered process

$$\mu'_{Au(s)} - \mu^0_{Au(l)} = 2.268T - 3030$$

whence

$$\log a_{Au} = 0.4957 - (662.3/T)$$

At 600° we calculate $a_{Au} = 0.546$ while this investigation gives $a_{Au} = 0.538$ for $x_{Pb} = 0.314$. In view of the assumptions made and the possible error involved in our computations of the activities of gold in the solutions, this agreement must be considered quite satisfactory.

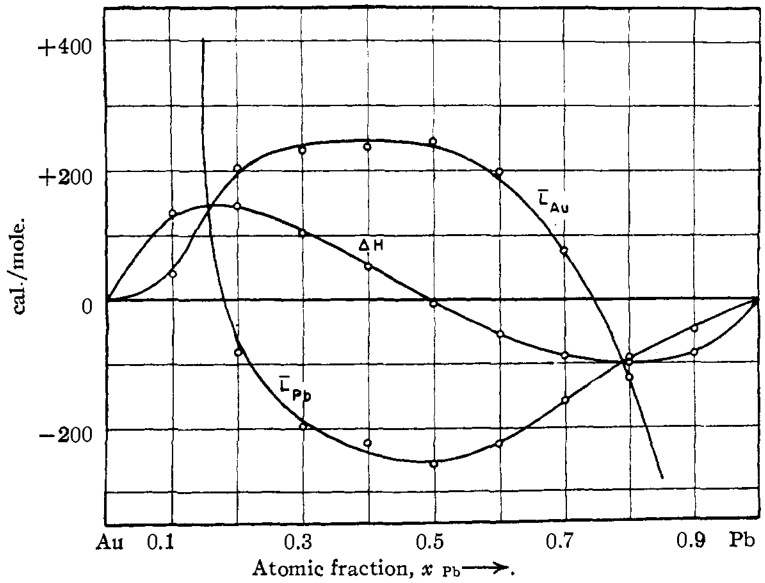

Fig. 3.—Relative partial molar and integral heats of mixing in the system Au (l)-Pb (l).

---

(6) R. Vogel, *Z. anorg. allgem. Chem.*, **45**, 11 (1905).

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

(8) K. K. Kelley, U. S. Bureau of Mines Bull. **393** (1936).

Thermodynamic Properties of Au_2Pb.—By further study of the phase diagram for lead-gold, it will be seen that between the temperatures 420 and 254°, various liquid mixtures are in equilibrium with solid Au_2Pb, and that between 254 and 215° other mixtures are in equilibrium with solid $AuPb_2$.

We shall use our thermodynamic data for the liquid extrapolated to the appropriate temperatures to calculate the free energy of formation ΔF for $Au_2Pb(s)$, with reference to the pure liquid metals of the same temperatures. In these calculations it is assumed that there is no change in the partial molar entropies in the liquid with temperature. At equilibrium conditions

$$\mu'_{Pb} \text{ (in } Au_2Pb) = \mu_{Pb} \text{ (in solution)}$$
$$\mu'_{Au} \text{ (in } Au_2Pb) = \mu_{Au} \text{ (in solution)}$$

For the process

$$2Au(l, \text{ undercooled}) + Pb(l) = Au_2Pb(s)$$

we then have

$$\Delta F = 2\,\mu_{Au} + \mu_{Pb}$$

The results of these calculations are recorded in Table III.

TABLE III

Atomic fraction, x_{Pb}	Equil. temp., °K.	$-\Delta F$ (Au_2Pb)	$-\Delta F/T$	$10^3 \times 1/T$
0.4382	696	4223	6.067	1.437
.4880	681	4268	6.267	1.468
.5381	656	4327	6.615	1.524
.5885	628	4407	7.017	1.592
.6390	593	4495	7.580	1.686
.6694	565	4526	8.010	1.769
.6899	548	4541	8.226	1.824

The data in the first two columns are taken from Vogel,[6] ΔF is calculated from the equation above after the appropriate extrapolation of our experimental data has been carried out. In Fig. 4, $\Delta F/T$ is plotted *versus* $1/T$ in the usual way, and from the slope we find

$$\Delta H = -6000 \pm 300 \text{ cal.}$$

Hence, for the entropy of formation at 692°K.

$$\Delta S = (\Delta H - \Delta F)/T = -2.6 \pm 0.5$$

In the lack of data for the specific heat of undercooled liquid gold and Au_2Pb, we shall not try to evaluate the standard heat of formation of Au_2Pb at room temperature.

Discussion

The thermodynamic properties of the liquid mixture of gold and lead can be summarized as follows. The heat of mixing is small (±100 cal.). The considerable deviation of the solution from Raoult's law can be attributed largely to an anomalously high entropy of mixing.

Any discussion trying to explain the properties of this mixture should perhaps be focused on the entropy of mixing rather than on the heat (energy) of mixing.[9] Unfortunately, the factors contributing to entropy deviations in metallic mixtures are even less understood than those deciding energetic deviations. Although theories exist which try to account for entropy deviations due to one single factor only, no attempt has been made so far to get a more complete understanding of their concerted effect. Among the single factors which, although not mutually independent, undoubtedly may play a role in the determination of the entropy of mixing are the following:

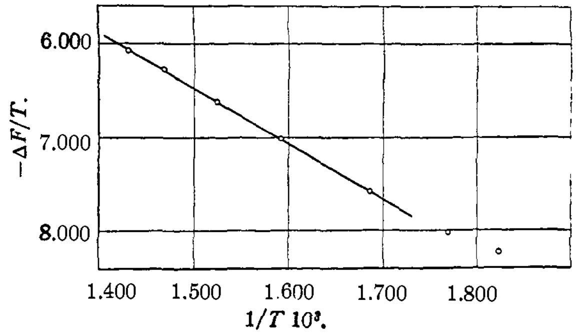

Fig. 4.

Factor	Effect on ΔS	Reference
Short range order	Neg.	Fowler and Guggenheim[10]
Net volume change $\Delta V > 0$	Pos.	Scatchard[11]
on mixing $\Delta V < 0$	Neg.	
Diff. in space req. of each component	Pos.	Hildebrand[12]
Change in sp. heats on mixing	Pos. or neg.	...
Change in coördination no. on mixing	Pos. (?) or neg.	...

The only one of these factors on which we have any decisive information in the case of the gold–lead system, is the difference in space requirement of the gold atom and lead atom, respectively.

At the melting point the atomic volume of liquid lead is 19.4 cm.[3] per g. atom, while the corresponding figure for gold is 11.5 cm.[3] If a correction is introduced for the thermal expansion between the melting points and our reference temperature 600°, the difference between the two would be still greater.

It is found, however, that the formulas derived to correct the entropy of mixing for a difference in volume of the two components are quite unable to account for a positive deviation of our order of magnitude.[12]

If data had been available for the net volume change on mixing, the formulas derived by Scatchard[11] might perhaps have explained the excess entropy of mixing. However, without density measurements on liquid lead–gold mixtures, we

---

[9] A more complete discussion of the factors causing anomalous entropies of mixing in liquid metallic mixtures will be given in a later communication in this series.

[10] R. Fowler and E A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, 1939.

[11] G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

[12] J. H. Hildebrand, *J. Chem. Phys.*, **15**, 225 (1947).

shall not be able to bring the discussion to a conclusion on this point.

Acknowledgments.—The author is indebted to Mr. R. Fryxell and Mr. L. Howell for carrying out the analytical work involved in this investigation, and to Dr. N. H. Nachtrieb and Dr. T. Rosenqvist for frequent and stimulating discussions during the progress of the research. This work was supported by grants from Union Carbide and Carbon Corp. and from Norges Teknisk-Naturvitenskaplige Forskningsråd.

Summary

The chemical potentials and partial molar entropies of mixing for lead in liquid lead–gold mixtures have been determined by the electromotive force method for compositions up to 79 atomic per cent. gold.

From these data have been calculated for both components activities at 600°, "entropy fractions," and relative partial and integral molar heats of mixing. It was found that the deviation of this mixture from Raoult's law can be largely attributed to a non-ideal entropy of mixing.

The heat and free energies of formation for $Au_2Pb(s)$ from liquid lead and undercooled liquid gold at about 400° were calculated using information from the established equilibrium phase diagram of Au–Pb and from this investigation.

CHICAGO, ILLINOIS RECEIVED APRIL 6, 1949

[CONTRIBUTION FROM GOESSMANN CHEMISTRY LABORATORY, UNIVERSITY OF MASSACHUSETTS]

Composition of Ferric Thiocyanate at High Concentrations

BY STANLEY E. POLCHLOPEK[1] AND J. HAROLD SMITH

Several recent investigations[2-5] have established by a variety of methods that in dilute solution the composition of the ferric thiocyanate complex is $FeSCN^{++}$. Møller[6] used conductivity measurements to identify complexes such as $Fe(SCN)_2^+$ and $Fe(SCN)_4^-$, in more concentrated solutions. In an earlier study Schlesinger and VanValkenburg[7] had concluded that $Fe(SCN)_6^{\equiv}$ was responsible for the red color of ferric thiocyanate solutions on the basis of boiling point elevation and freezing point depression data and absorption spectra.

It has been the purpose of this investigation to study the formation of higher ferric thiocyanate complexes at high concentrations by means of the spectrophotometer, using the method developed by Job[8] and modified by Vosburgh and Cooper.[9] Gould and Vosburgh[5] used this method of continuous variations and found the 1:1 complex at low concentrations, but the method has never been applied to high concentrations of ferric thiocyanate probably because of the very intense color of a concentrated solution. This intense color made necessary the use of very thin absorption cells and the development of a technique for handling these cells.

Experimental

Ferric nitrate and potassium thiocyanate were selected as reactants to avoid the formation of other complexes. The ferric nitrate solutions were standardized against sulfato-ceric acid; the potassium thiocyanate solutions were standardized against silver nitrate. Potassium nitrate solutions were used to maintain constant ionic strength whenever possible. The determinations on 0.1 and 0.25 *M* solutions were made with the potassium thiocyanate solutions brought to the ionic strength and *p*H of the ferric nitrate. Check determinations were made without bringing the potassium thiocyanate to the *p*H of the ferric nitrate and it was found that the absorption maxima remained the same as with the *p*H adjusted potassium thiocyanate. In 1.0 *M* solutions it was not possible because of solubility considerations to bring potassium thiocyanate to the same ionic strength as the ferric nitrate and only the *p*H was adjusted. In the 2.0 *M* solutions studied neither the *p*H nor the ionic strength were adjusted. It should be noted that with the high acidity of the thiocyanate solution measurements of optical density had to be made immediately because of the instability of these solutions.

Absorption spectra were determined for solutions in which the ratio of iron(III) to thiocyanate ranged from 1:1 to 1:6 at 0.1 and 0.25 *M* concentrations. These spectra were determined by keeping the volume of the iron(III) solution constant and increasing the volume of thiocyanate. In order that the final volume of ferric thiocyanate be the same for each determination after mixing the components a potassium nitrate solution of the same ionic strength and *p*H was added each time in appropriate volume.

The absorption measurements were taken with a Beckman D. U. Quartz Spectrophotometer. The band widths used in the determinations ranged from 0.8 mμ of spectrum at a wave length of 400 to 4 mμ of spectrum at a wave length of 600 mμ according to data supplied by the manufacturer. The absorption cells used in these measurements were made from "special grade, colorless" microscope slides (A. H. Thomas Co.). Two thin slips of a plastic sheet (or thin cover glasses) were sandwiched between the microscope slides in such a manner that the plastic or glass separators were at both ends of the cell and the center area could be filled with liquid. The cells were clamped at both ends with spring back metal paper clamps. The

[1] From a thesis submitted in June, 1948, by Stanley E. Polchlopek to the Graduate School of the University of Massachusetts in partial fulfilment of the requirements for the degree of Master of Science.

[2] Bent and French, THIS JOURNAL, **63**, 568 (1941).

[3] Edmonds and Birnbaum, *ibid.*, **63**, 1471 (1941).

[4] Frank and Oswalt, *ibid.*, **69**, 1321 (1947).

[5] Gould and Vosburgh, *ibid.*, **64**, 1630 (1942).

[6] Max Møller, "Studies on Aqueous Solutions of Ferric Thiocyanate," Dana Bogtrykerri, Copenhagen, 1937.

[7] Schlesinger and Van Valkenburg, THIS JOURNAL, **53**, 1212 (1931).

[8] Job, *Ann. chim.*, (10) **9**, 113 (1928).

[9] Vosburgh and Cooper, THIS JOURNAL, **63**, 437 (1941).