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Berkeley, California

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VAPOR PRESSURE OF LEAD AND ACTIVITY MEASUREMENTS ON LIQUID LEAD-TIN ALLOYS BY THE TORSION EFFUSION METHOD

Donald Thomson Hawkins

(M. S. Thesis)

January, 1966

I. INTRODUCTION

The object of this investigation was to determine Gibbs energies

of formation in the liquid lead-tin system from measurements of the

activity of lead as a function of composition. The lead-tin system was

chosen because the Gibbs energy values in the liquid region have not

been resolved. Three previous investigations have been reported in

the literature. Predel[1] measured the vapor pressure of lead over lead-

tin alloys. His results show a considerable scatter about a chosen

curve. Voronin and Evseev[2] also measured vapor pressures of lead

over a series of alloys. Their data show a large negative deviation

from Raoult's Law at high lead compositions and a large positive devi-

ation at low lead compositions. All other investigations, including the

present one, show a positive deviation at all compositions. Atarashiya

et al.[3] measured partial molar Gibbs energies of tin by an equilibrium

method involving the H_2-H_2O partial pressures in equilibrium with Sn

and SnO_2, and Pb-Sn alloys and SnO_2. Since the final composition of

their samples is not certain, their measurements are also subject to

doubt. Therefore, the present investigation was undertaken in an

attempt to determine definitely Gibbs energy values in the liquid.

Activity measurements are commonly made either by electromotive

force measurements or by measurements of the equilibrium vapor pres-

sures over the alloys and over the pure metal. Electromotive force

measurements on the lead-tin system are of doubtful value because

lead and tin have very little difference in electropositivity. Vapor

pressure measurements are very well suited to this system because of the large difference between the vapor pressures of lead and tin, e. g. , at 1000°K the vapor pressure of lead is 1. 6 × 10^{-5} atmospheres, while that of tin is only 7. 3 × 10^{-11} atmospheres.[4,10]

A secondary object of this investigation was to ascertain whether surface depletion of the sample, which was found by Roy and Hultgren[5,6] to be a severe effect in solid Fe-Mn alloys, had any effect in liquid phases. Roy and Hultgren found that the vapor pressure of Mn decreased with time, indicating a loss of the volatile component from the surface of the sample which was not replenished due to slow diffusion rates. One would expect diffusion to be more rapid in a liquid than in a solid, so that this effect may not be observed.

In a system such as Pb-Sn, equilibrium vapor pressures are so low in the practical range of temperatures that they must be measured indirectly. In this investigation, the method chosen is that of torsion effusion. The torsion effusion method is a modification of the well known Knudsen method. It consists of measuring the recoil force exerted by the vapor effusing through small orifices into a surrounding vacuum. In the conventional Knudsen method the vapor is allowed to effuse through an orifice for a measured length of time at constant temperature. The weight loss is then measured, and the pressure can be calculated from the relation:

$$P = \frac{m}{a} \sqrt{\frac{2\pi RT}{M}} \tag{1}$$

where P = pressure in atmospheres

     m = mass of vapor effusing per second

     a = area of orifice in cm^2

     R = the gas constant

     T = the absolute temperature

     M = molecular weight of the effusing vapor

The torsion method differs from the Knudsen method in that the container is suspended on a wire. The vapor effuses through two orifices placed on opposite sides of the container so that there is a torque exerted on the suspension wire.

The torque is directly proportional to the pressure and to the angular rotation if the elastic limit of the wire is not exceeded. The vapor pressure can be calculated from the angle of torque and the cell geometry by the following relation:

$$P = \frac{2 D \phi}{a_1 q_1 + a_2 q_2} \tag{2}$$

where P = pressure

     D = torsion constant of the wire

     ϕ = angle of rotation

     a_1 and a_2 = areas of the orifices

     q_1 and q_2 = distances of the orifices from the axis of rotation

The only corrections are those needed for the thicknesses of the effusing orifices since the derivation of equations (1) and (2) assume infinitely thin orifices. Searcy and Freeman[7,8] and Schulz and Searcy[9]

have calculated correction factors to compensate for the effects of finite orifice thickness on the force exerted by the effusing vapors. The corrected torsion equation becomes

$$P = \frac{2 D \phi}{f_1 a_1 q_1 + f_2 a_2 q_2} \tag{3}$$

where f_1 and f_2 are the correction factors.

The torsion constant of the wire may be calculated from measurements of the period of oscillation when weights of known moment of inertia are suspended from the wire.

$$D = \frac{4 \pi^2 (I_1 - I_2)}{t_1^2 - t_2^2} \tag{4}$$

where I_1 and I_2 = moments of inertia of the weights

t_1 and t_2 = periods of oscillation with the weights.

II. EXPERIMENTAL

Materials

Pure lead was obtained from the American Smelting and Refining Co., which also supplied the results of chemical and spectrographic analyses. The lead was 99.999+% pure; maximum impurities were Mg: <1 ppm, Fe: <1 ppm, Cu: <1 ppm. The tin used in this study, obtained from Vulcan Detinning Co., was 99.999% pure; maximum impurities were Pb: 0.0005%, and Fe: 0.0002%.

Alloy Preparation

For measurements on pure lead the surface of the specimen was filed to remove surface oxides; the sample was then washed with acetone and dried.

A series of 8 Pb-Sn alloys was made by melting the cleaned metals together at 370°C in evacuated pyrex tubes and quenching in water. In all cases the weight of the alloy equaled the sum of the weights of the constituent metals within 0.1 mg. so the alloy composition was taken to be the weighed composition. Table I gives the compositions of the alloys.

TABLE I

Composition of Alloys

Alloy	x_{Pb}	Alloy	x_{Pb}
1	0.879	8	0.397
2	0.737	5	0.282
3	0.657	6	0.176
4	0.514	7	0.091

Apparatus

The apparatus, which is shown in Figure 1, has been described in detail previously.[5,6] The furnace chamber consists of a stainless steel chamber (A) which is water-cooled by copper tubes (B) soldered to the outside of the shell. A pipe (C) leads to an oil diffusion pump and mechanical forepump through a liquid nitrogen trap. A hole in the center of the top plate (D) leads to the suspension system. The temperature is measured with a chromel-alumel thermocouple (P) imbedded in a tantalum "dummy cell" (E). Two pairs of copper tubes (F) serve both as power conductors to the furnace and as conduits for water cooling of the furnace. Heating is accomplished by ten tungsten hair pins (H) 0.060" in diameter which carry the current between two copper discs (G) insulated with mica. A set of three molybdenum radiation shields (I) surrounds the furnace chamber. Power is controlled by a 7 KVA powerstat and is stepped down by twelve 0.575 KVA transformers in parallel, each with a maximum output of ten volts. Temperature control is achieved by a Leeds and Northrup controller actuated by the signal from the thermocouple. The maximum temperature of this investigation was 1105°K. The pressure in the system was maintained below 2×10^{-5} mm Hg.

The suspension system is enclosed in a pyrex tube (J). The torsion filament (Q) is suspended from a brass rod (R). On the lower end of the filament are suspended a galvanometer mirror (K), an aluminum damping disk (L) and a chuck (M) for holding the crucible
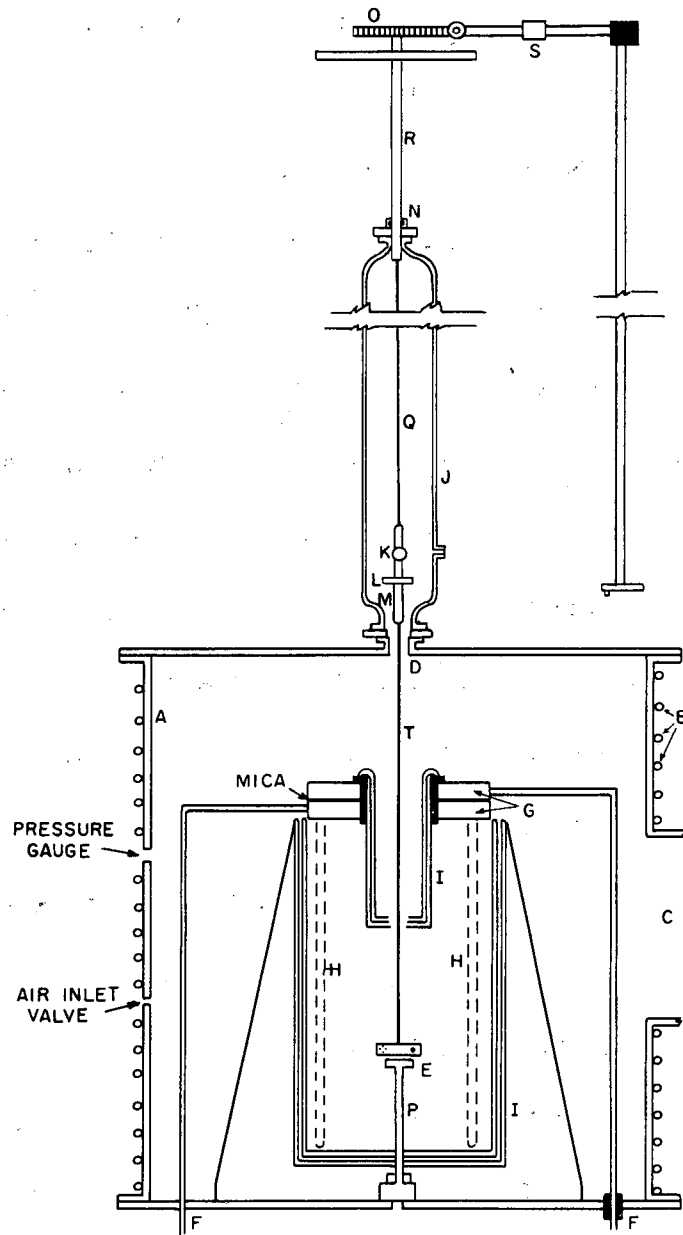
FIG. I EXPERIMENTAL APPARATUS.

MUB-8949

Fig. 1.   Experimental apparatus.

assembly. A sealastic fitting (N) at the top of the pyrex tube allows rotation of the rod, fiber, and mirror without loss of vacuum. A reduction gear (O) and revolution counter (S) are mounted on top of the suspension system. The gear has a 360 to 1 ratio which permits measurement of a 0.01 degree interval. A light source and scale are placed about 5 feet away. A null point method was used which eliminated the necessity of calibration of the scale.

The suspension filament used was a 3 X 1 mil tungsten ribbon. Roy[6] found ribbons superior to circular wires. In the present investigation it was found difficult to obtain a reliable torsion constant with circular wires, thus confirming this observation. Residual distortion with these ribbons was less than 1.5 cm. on the scale (approximately 7 cm. = 1 degree of rotation); runs with more distortion than this were not considered in the analysis of the data. The torsion constant of the wire was 1.002 dyne-cm.

The crucible was held by friction on the end of an 0.080" diameter tantalum rod (T) which was fastened to the chuck below the damping disk. The crucible was about $\frac{1}{4}$ inch above the dummy cell. High purity (<100 ppm impurities), nonporous (density at least 1.90 gm/cm^3) graphite (National grade ZTG) obtained from Union Carbide Corp. was used as a crucible material. Graphite was chosen because of its resistance to reaction with both lead and tin and its ease of fabrication. The crucible design is shown in fig. 2.
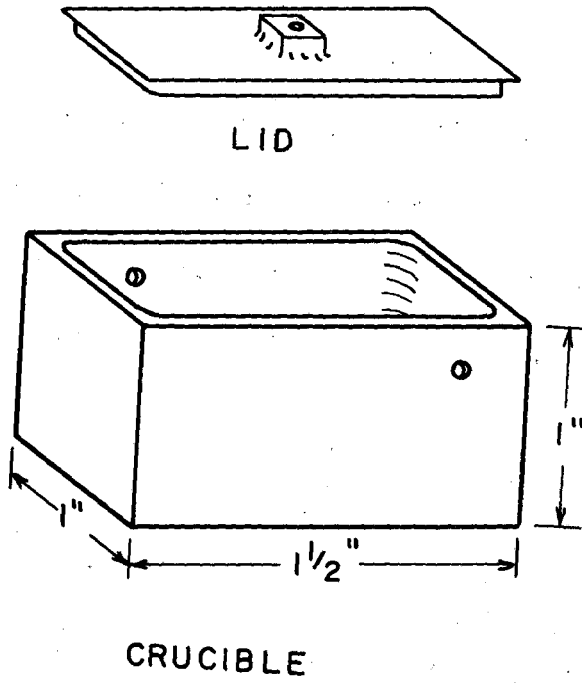
LID

CRUCIBLE

1"

1"

1½"

FIG. 2   CRUCIBLE DESIGN.

MUB-8950

Fig. 2. Crucible design.

The chromel-alumel thermocouple was calibrated in place by inserting a standard Pt-Pt + 10% Rh thermocouple inside the crucible and measuring the temperatures read by both thermocouples. The maximum correction was 13°C.

The hole diameters were measured with a travelling microscope, and wall thicknesses were measured with a micrometer. Table II gives the hole sizes of the various crucibles along with the correction factors of Schulz and Searcy. When these values are inserted into

TABLE II

Crucible Dimensions

Crucible	Hole Area (cm^2)		Wall thickness (cm)		Schulz-Searcy Correction Factor	
	Front	Rear	Front	Rear	Front	Rear
1	2.29×10^{-3}	2.17×10^{-3}	0.1699	0.1704	0.301	0.294
2	7.85×10^{-3}	7.95×10^{-3}	0.1661	0.1478	0.447	0.477

equation (3) and the proper unit conversions applied, the torsion equations for the two crucibles used in this study become

$$P = 1.0255 \times 10^{-5} \phi \quad \text{(for crucible 1)}$$

$$(5)$$

$$P = 1.8926 \times 10^{-6} \phi \quad \text{(for crucible 2)}$$

where P is in atmospheres and ϕ is in degrees.

III. EXPERIMENTAL RESULTS

Pure Lead

Experimental data for pure lead are given in Table III. The third law method has been used in evaluating the results. Values of P were calculated for each measurement from equation (5). Values of the Gibbs energy function for liquid and gaseous lead were taken from Hultgren et al.[10] For each measurement, a value of $\Delta H^{\circ}_{v, 298}$ was calculated from the relation:

$$\Delta H^{\circ}_{v, 298} = -T \Delta \left(\frac{G^{\circ}_T - H^{\circ}_{298}}{T} \right) - RT \ln P \qquad (6)$$

Taking the average of all $\Delta H^{\circ}_{v, 298}$ values gave the selected value of 46620 ± 170 cal/gm-atom.

Both crucibles 1 and 2 were used with pure lead in order to ascertain if there was any dependence of vapor pressure on hole diameter. Measurements with crucible 1 are in excellent agreement with those using crucible 2, showing that no hole size dependence is present. Crucible 2 alone was used for the alloys.

Lead-Tin Alloys

Values of the activity of lead were calculated from the relation:

$$a_{Pb} = \frac{P_{Pb}}{P^{\circ}_{Pb}} \qquad (7)$$

where P_{Pb} is the vapor pressure of lead over the alloy and P°_{Pb} is the

TABLE III.

Experimental Data for Pure Lead

T, °K.	log P(atm)	$-\Delta\left[\dfrac{G^{\circ}_T - H^{\circ}_{298}}{T}\right]$ cal/gm-atom-degree	$\Delta H^{\circ}_{v,298}$ cal/gm-atom	Deviation from Average
950	-5.2758	24.81	46502	-117
952	-5.3079	24.80	46731	110
953	-5.2915	24.80	46708	88
955	-5.2758	24.80	46737	117
958	-5.1914	24.79	46505	-114
961	-5.1666	24.78	46532	-87
963	-5.1666	24.78	46619	-0
965	-5.1788	24.78	46779	159
966	-5.1101	24.76	46601	-18
970	-5.0996	24.75	46641	21
975	-5.0239	24.74	46534	-85
976	-5.0153	24.74	46544	-76
981	-4.9987	24.73	46697	77
984	-4.9307	24.72	46524	-95
986	-4.9307	24.71	46609	-10
989	-4.8716	24.71	46483	-136
991	-4.9034	24.70	46712	92
996	-4.8535	24.69	46710	90
998	-4.8091	24.69	46601	-18
1000	-4.7888	24.68	46592	-27
1001	-4.7785	24.68	46591	-28
1002	-4.7934	24.68	46706	86
1002	-4.7883	24.68	46672	52
1002	-4.7544	24.68	46527	-92
1005	-4.7883	24.67	46812	192
1005	-4.7687	24.67	46722	102
1008	-4.7101	24.66	46581	-38
1012	-4.6697	24.65	46569	-50
1015	-4.6401	24.65	46569	-50
1015	-4.6623	24.65	46662	42
1015	-4.6855	24.65	46780	160
1016	-4.6330	24.64	46572	-47
1017	-4.6437	24.64	46668	48
1021	-4.5767	24.63	46528	-91
1022	-4.6090	24.62	46714	94
1024	-4.5926	24.62	46729	109
1027	-4.5439	24.61	46627	7
1027	-4.5676	24.61	46738	118
1029	-4.5161	24.61	46587	-32
1031	-4.5298	24.60	46732	112
1035	-4.4652	24.60	46556	-23
1036	-4.4418	24.60	46541	-78
1038	-4.4418	24.59	46621	1
1042	-4.3966	24.58	46574	-45
1047	-4.3707	24.57	46663	43
1048	-4.3574	24.57	46633	13
1048	-4.3555	24.57	46635	15
1050	-4.3482	24.56	46678	58
1052	-4.3405	24.56	46732	112
1053	-4.3319	24.56	46733	113
1054	-4.3096	24.56	46670	50
1057	-4.2680	24.54	46581	-38
1059	-4.2205	24.54	46438	-181
1062	-4.2414	24.53	46661	41
1065	-4.1702	24.53	46446	-173
1066	-4.2137	24.52	46691	71
1069	-4.2037	24.52	46773	153
1071	-4.1431	24.51	46553	-66
1071	-4.1927	24.51	46796	176
1075	-4.0874	24.50	46442	-177
1076	-4.0996	24.50	46546	-73
1077	-4.1133	24.50	46667	47
1079	-4.1165	24.49	46748	128
1080	-4.0844	24.49	46633	13
1081	-4.0517	24.49	46514	-105
1082	-4.0354	24.49	46476	-143
1083	-4.0736	24.49	46709	89
1085	-4.0187	24.48	46512	-107
1090	-3.9726	24.47	46485	-134
1092	-3.9800	24.47	46607	-12
1095	-3.9347	24.46	46498	-121
1098	-3.9434	24.46	46669	49
1100	-3.9027	24.45	46538	-81
1101	-3.8853	24.45	46493	-126
1102	-3.8867	24.45	46542	-77
1105	-3.8620	24.45	46543	-76

Average $\Delta H^{\circ}_{v,298}$ = 46620 cal/gm-atom

Average Deviation = 81 cal/gm-atom

Standard Deviation = 95 cal/gm-atom

vapor pressure of pure lead. The vapor of lead is assumed to be ideal.
From each value of a_{Pb} values of $\Delta\overline{G}_{Pb}$ and $\Delta\overline{G}_{Pb}^{xs}$ were calculated:

$$\Delta\overline{G}_{Pb} = RT \ln a_{Pb} \tag{8}$$

$$\Delta\overline{G}_{Pb}^{id} = RT \ln x_{Pb} \tag{9}$$

$$\Delta\overline{G}_{Pb}^{xs} = \Delta\overline{G}_{Pb} - \Delta\overline{G}_{Pb}^{id} \tag{10}$$

Figure 3 gives the experimental data for each of the alloys as a
function of temperature. The selected values at 1050°K are given in
Table IV. In analyzing the data, runs in which the deflection was less
than 5 degrees have been disregarded as they showed abnormal scat-
ter, and gave misleading results.
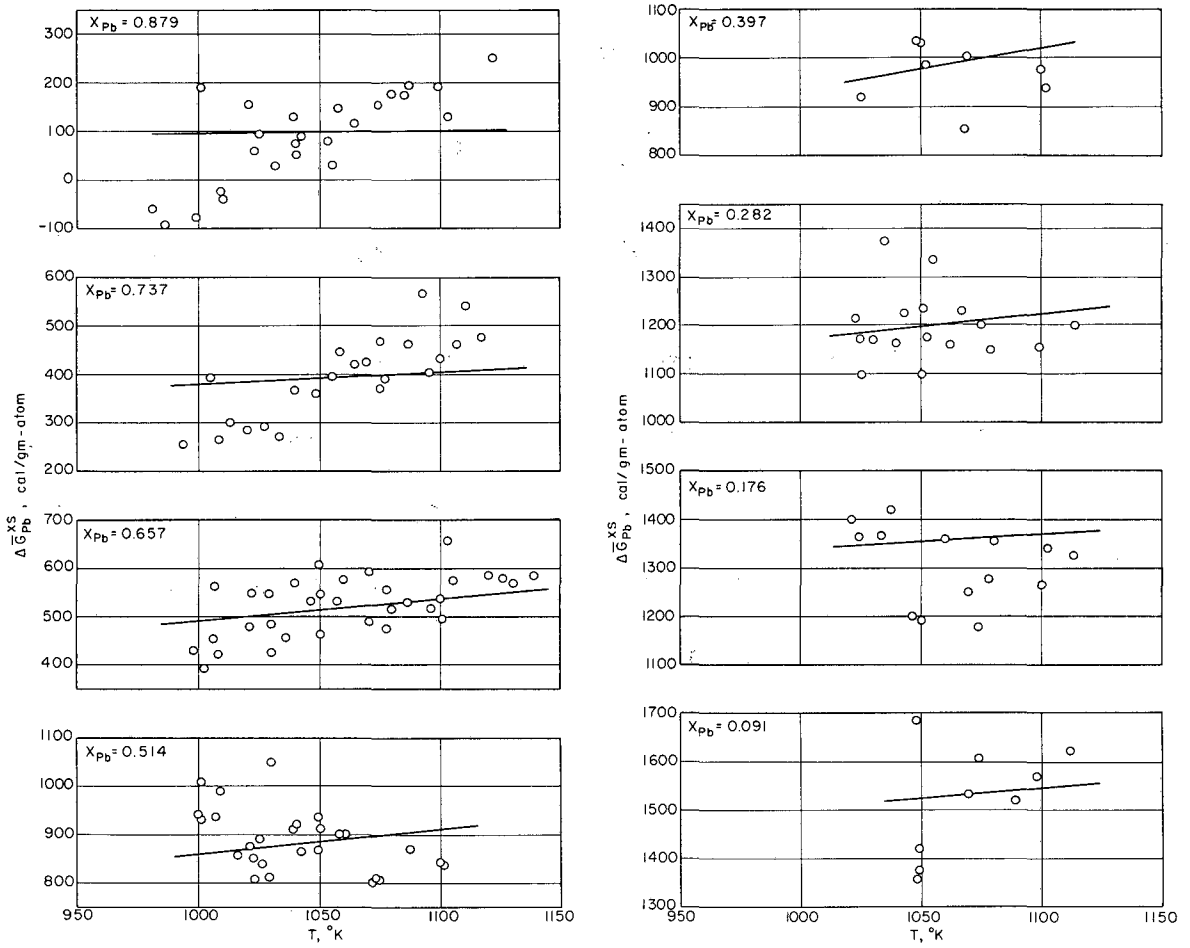
FIG. 3 EXPERIMENTAL VALUES OF $\Delta\bar{G}_{Pb}^{xs}$ FOR LIQUID LEAD-TIN ALLOYS.

MUB-8951

Fig. 3. Experimental values of $\Delta\bar{G}_{Pb}^{xs}$ for liquid lead-tin alloys.

TABLE IV

Experimental Data for Pb-Sn Alloys at 1050°K

$$P^{\circ}_{Pb} = 4.613 \times 10^{-5} \text{ atm.}$$

Alloy No.	x_{Pb}	$P \times 10^5$ (atm.)	a_{Pb}	$\Delta \bar{G}^{xs}_{Pb}$	α_{Pb}
				(cal/gm-atom)	
1	.879	4.253	.922	100	6849
2	.737	4.101	.889	390	5636
3	.657	3.889	.843	520	4422
4	.514	3.621	.785	884	3743
8	.397	2.929	.635	980	2695
5	.282	2.311	.501	1200	2328
6	.176	1.555	.337	1355	1996
7	.091	1.015	.220	1525	1846

IV. DATA INTERPRETATION AND DISCUSSION

Pure Lead

Table III shows no dependence of $\Delta H^{\circ}_{v, 298}$ on temperature, thus indicating the absence of systematic error. The uncertainty of ± 170 cal/gm-atom has been assigned based on the deviations given in Table III. This value is approximately two times the standard deviation of the measurements.

Many other measurements have been made on the vapor pressure of lead.[10] The present investigation is in excellent agreement with the most reliable of these. The value of $\Delta H^{\circ}_{v, 298}$ previously selected by Hultgren et al.[4] is 46600 cal/gm-atom, only 20 cal/gm-atom lower than the value found in this investigation.

Lead-Tin Alloys

From the values of $\Delta \bar{G}^{xs}_{Pb}$ given in Table IV values of α_{Pb} were calculated:

$$\alpha_{Pb} = \frac{\Delta \bar{G}^{xs}_{Pb}}{(1-x_{Pb})^2} \tag{11}$$

Figure 4 is a plot of this quantity as a function of x_{Sn}. From this plot and the Gibbs-Duhem relationship it is possible to calculate activities, activity coefficients, partial molar Gibbs energies, excess partial molar Gibbs energies, integral Gibbs energies, and excess integral Gibbs energies for both components as a
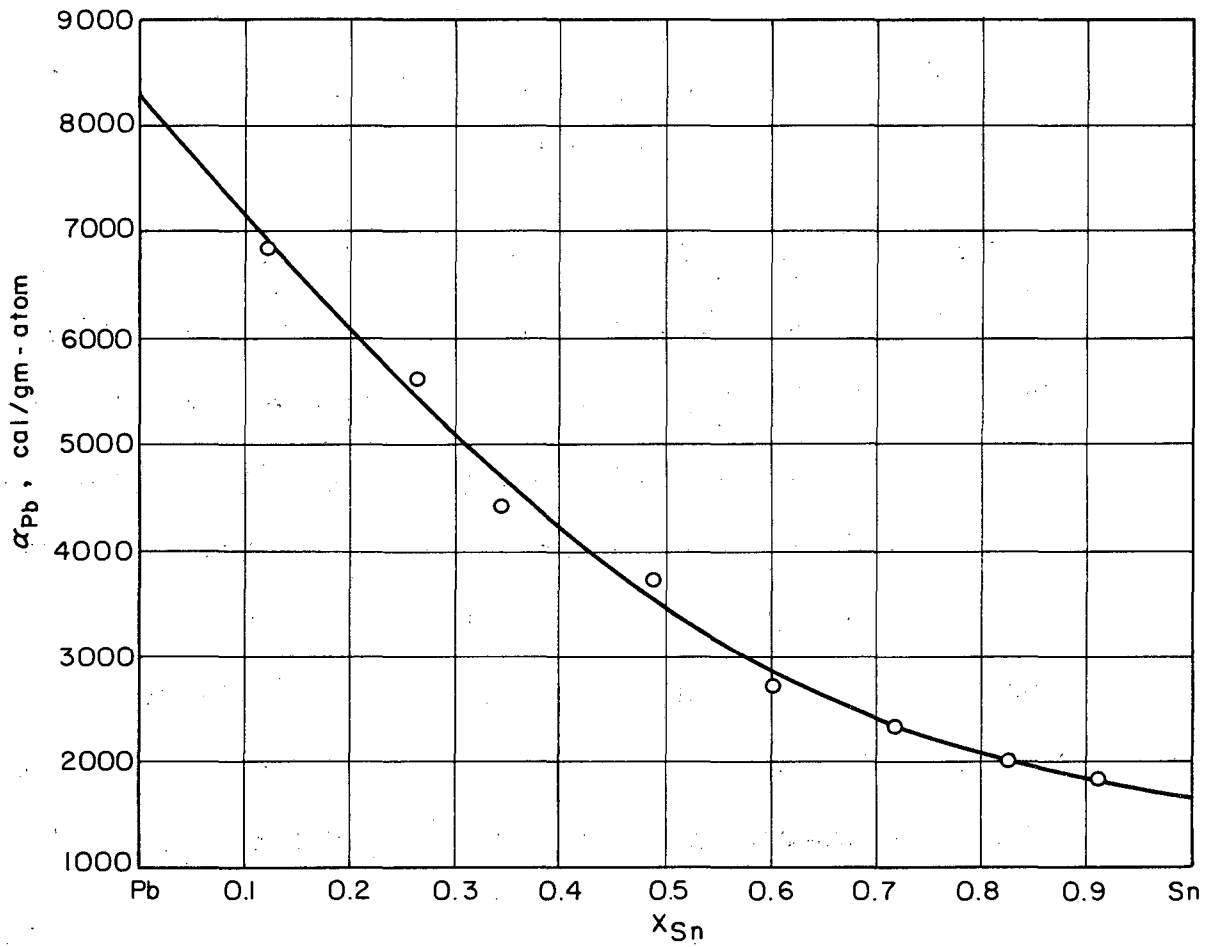
FIG. 4 EXPERIMENTAL VALUES OF α_{Pb} FOR LIQUID LEAD - TIN ALLOYS AT 1050 °K.

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Fig. 4. Experimental values of α_{Pb} for liquid lead-tin alloys at 1050 °K.

function of composition. The Gibbs-Duhem relationship in terms
of the alpha function is:

$$\Delta \bar{G}_{Sn}^{xs} = -x_{Sn} x_{Pb} \alpha_{Pb} + \int_{x_{Pb}=0}^{x_{Pb}} \alpha_{Pb} dx_{Pb} \tag{12}$$

1050°K was chosen as the temperature of tabulation.

Kleppa[11] has measured heats of formation of Pb-Sn alloys
from $x_{Sn} = 0.04$ to $x_{Sn} = 0.96$ at 623°K and 723°K. He found the
heats to be independent of temperature, thus indicating the validity
of the Kopp-Neumann Law of additive heat capacities for this sys-
tem. Several other measurements of heats of formation have been
made, but those of Kleppa are to be preferred.[4] Taking Kleppa's
values of ΔH, and assuming Kopp's Law holds up to 1050°K, values
of ΔH, ΔS, and ΔS^{xs} can be calculated. A plot of the Q-function:

$$Q = \frac{\Delta H}{x_{Pb} x_{Sn}} \tag{13}$$

yields values of $\Delta \bar{H}_{Pb}$, and hence $\Delta \bar{H}_{Sn}$, $\Delta \bar{S}_{Pb}$, $\Delta \bar{S}_{Pb}^{xs}$, $\Delta \bar{S}_{Sn}$, and
$\Delta \bar{S}_{Sn}^{xs}$.

$$\Delta \bar{H}_{Pb} = (1-x_{Pb})^2 \left[Q + x_{Pb} \frac{dQ}{dx_{Pb}} \right] \tag{14}$$

The thermodynamic properties of the system are thus completely
determined. Tables V and VI give values of the partial molar
quantities for both Pb and Sn, and the integral quantities for Pb-Sn
alloys, respectively. Figures 5, 6, 7 and 8 give values of the

TABLE V

Partial Molar Quantities for Liquid Alloys at 1050°K

A. Pb Component $Pb_{(\ell)}$ = Pb (in alloy)$_{(\ell)}$

x_{Pb}	a_{Pb}	γ_{Pb}	$\Delta\overline{G}_{Pb}$	$\Delta\overline{G}^{xs}_{Pb}$	$\Delta\overline{H}_{Pb}$	$\Delta\overline{S}_{Pb}$	$\Delta\overline{S}^{xs}_{Pb}$
1.0	1.000	1.000	0	0	0	0.000	0.000
0.9	0.931	1.035	- 148	72	20	0.160	-0.049
0.8	0.899	1.124	- 222	243	70	0.279	-0.165
0.7	0.872	1.246	- 285	459	143	0.408	-0.301
0.6	0.829	1.382	- 391	675	234	0.595	-0.420
0.5	0.757	1.514	- 581	865	343	0.880	-0.497
0.4	0.656	1.641	- 879	1033	472	1.286	-0.535
0.3	0.529	1.764	-1327	1185	629	1.863	-0.529
0.2	0.380	1.899	-2020	1338	823	2.708	-0.491
0.1	0.204	2.043	-3314	1490	1065	4.171	-0.405
0.0	0.000	2.195	- ∞	1640	1360	∞	-0.267

B. Sn Component $Sn_{(\ell)}$ = Sn (in alloy)$_{(\ell)}$

x_{Sn}	a_{Sn}	γ_{Sn}	$\Delta\overline{G}_{Sn}$	$\Delta\overline{G}^{xs}_{Sn}$	$\Delta\overline{H}_{Sn}$	$\Delta\overline{S}_{Sn}$	$\Delta\overline{S}^{xs}_{Sn}$
0.0	0.000	6.816	- ∞	4004	1500	∞	-2.385
0.1	0.346	3.458	-2215	2589	1118	3.175	-1.401
0.2	0.430	2.151	-1760	1598	834	2.471	-0.728
0.3	0.471	1.571	-1569	942	615	2.080	-0.312
0.4	0.517	1.293	-1375	537	446	1.734	-0.087
0.5	0.578	1.156	-1144	302	312	1.387	0.010
0.6	0.650	1.084	- 897	169	207	1.051	0.036
0.7	0.729	1.042	- 658	86	122	0.743	0.035
0.8	0.814	1.017	- 431	35	57	0.465	0.021
0.9	0.904	1.004	- 212	8	15	0.216	0.007
1.0	1.000	1.000	0	0	0	0.000	0.000

TABLE VI

Integral Quantities for Liquid Alloys at 1050°K

$$(1-x)Pb_{(\ell)} + xSn_{(\ell)} = Pb_{(1-x)}Sn_{x(\ell)}$$
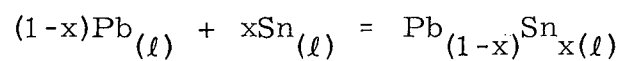
x_{Sn}	ΔG	ΔH	ΔS	ΔG^{xs}	ΔS^{xs}
0.1	-355	130	0.462	323	-0.184
0.2	-530	223	0.717	514	-0.278
0.3	-671	285	0.910	604	-0.304
0.4	-784	319	1.051	620	-0.287
0.5	-863	327	1.134	583	-0.244
0.6	-890	313	1.145	514	-0.192
0.7	-859	274	1.079	416	-0.135
0.8	-748	211	0.913	296	-0.081
0.9	-522	120	0.611	156	-0.035
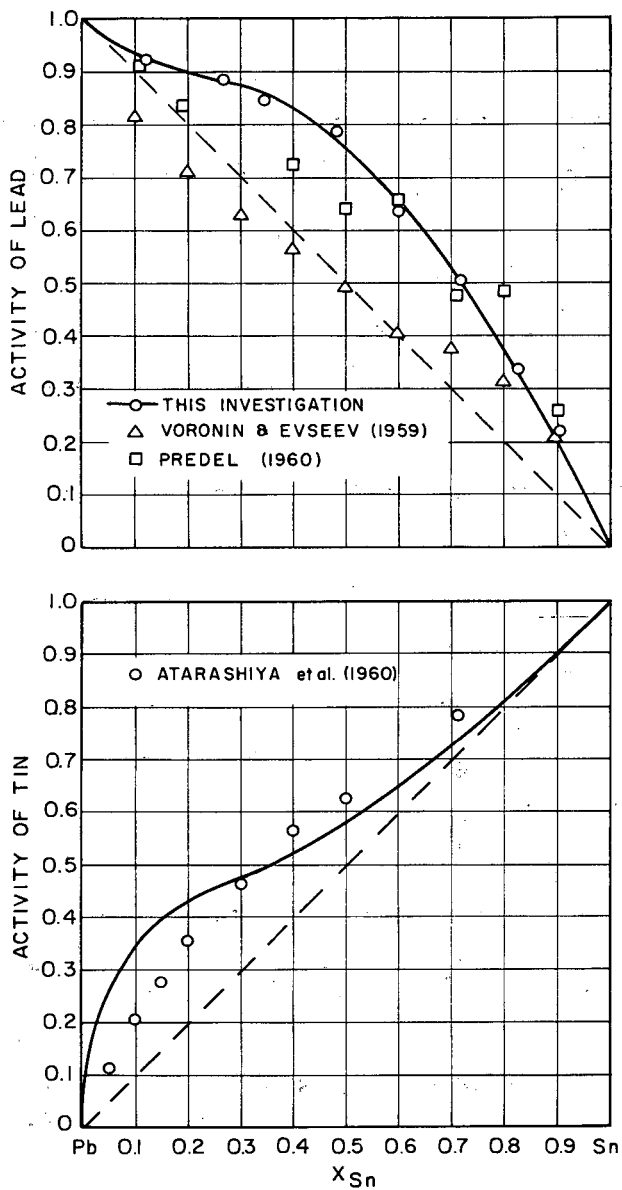
FIG. 5   ACTIVITY VALUES FOR LIQUID LEAD -TIN
ALLOYS AT 1050°K.

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Fig. 5.   Activity values for liquid lead-tin alloys at 1050°K.
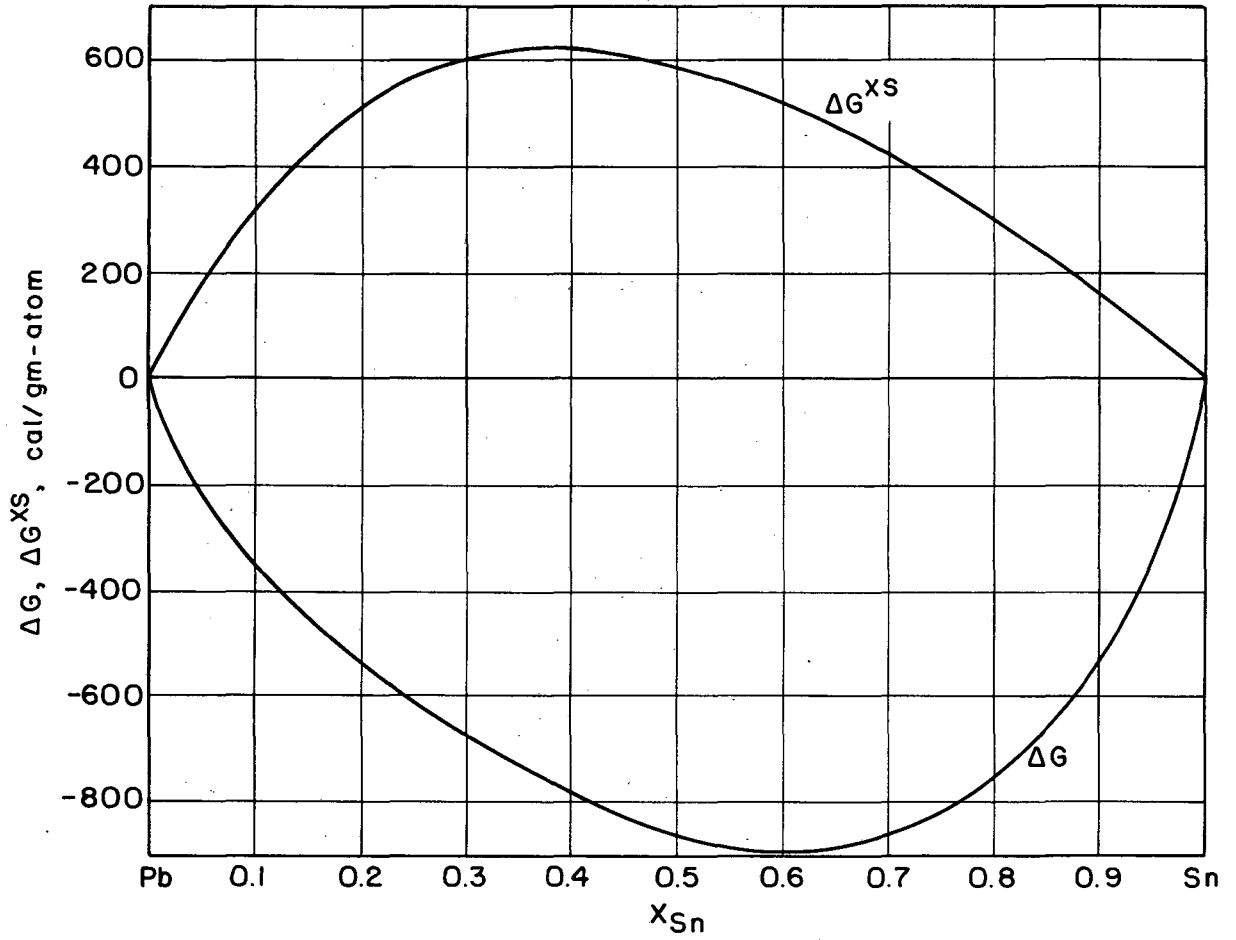
FIG. 6 INTEGRAL GIBBS ENERGY VALUES FOR LIQUID LEAD-TIN
ALLOYS AT 1050°K.

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Fig. 6. Integral Gibbs energy values for liquid lead-tin alloys
at 1050°K.
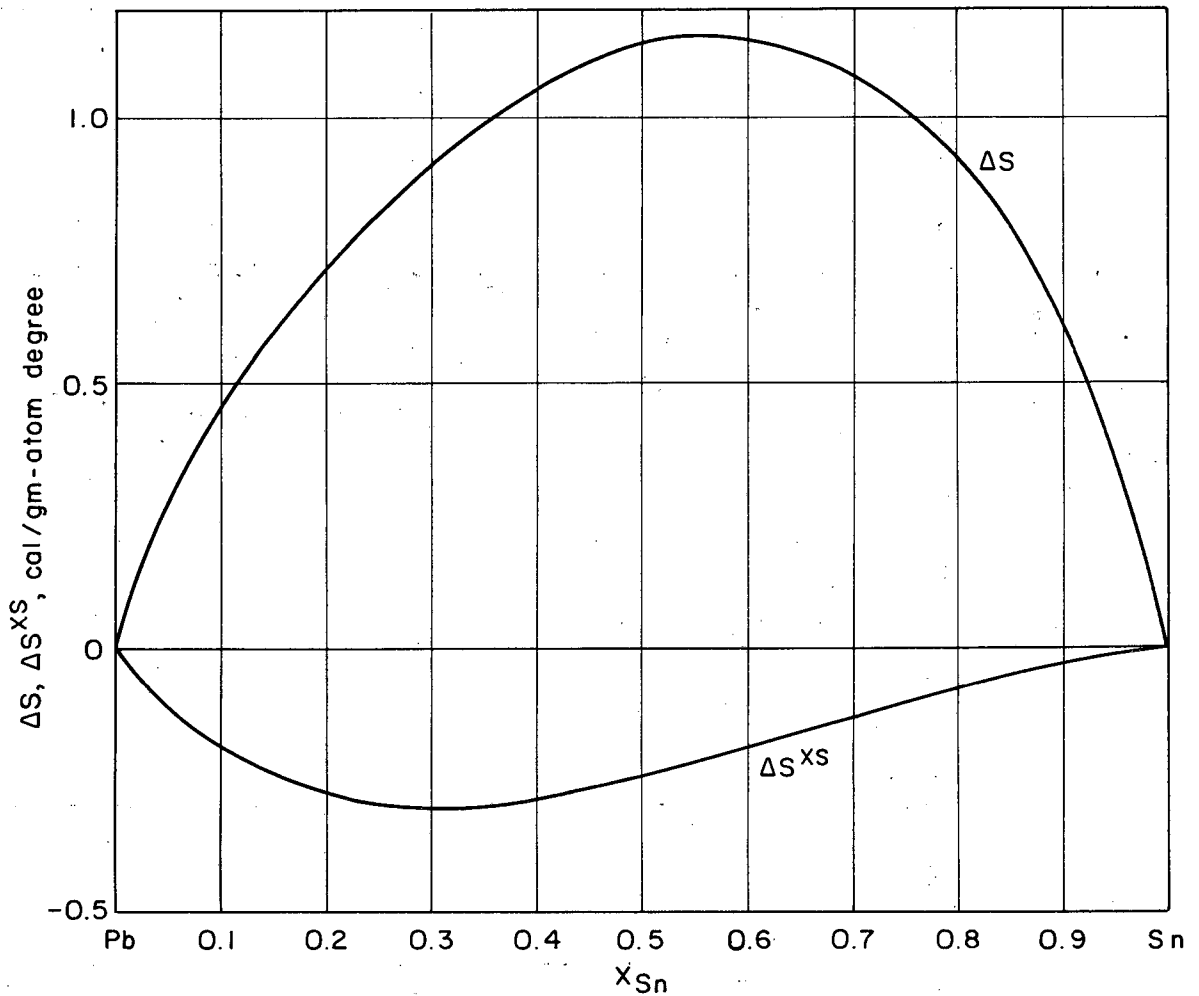
FIG. 7 INTEGRAL ENTROPY VALUES FOR LIQUID LEAD-TIN ALLOYS AT 1050 °K.

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Fig. 7. Integral entropy values for liquid lead-tin alloys at 1050°K.
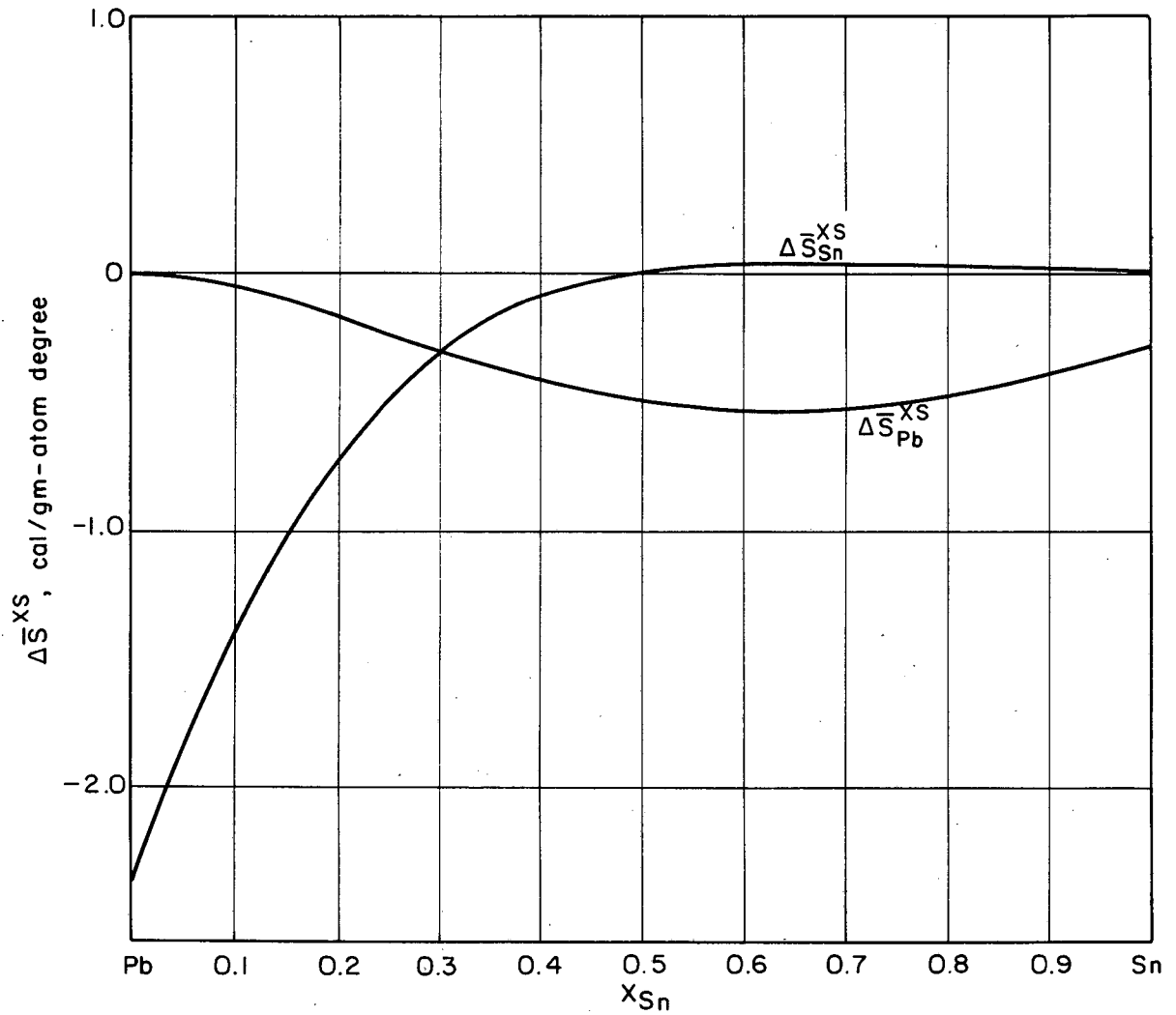
FIG. 8 EXCESS PARTIAL MOLAL ENTROPIES FOR LIQUID LEAD - TIN ALLOYS AT 1050°K.

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Fig. 8. Excess partial molal entropies for liquid lead-tin alloys at 1050°K.

activity, integral Gibbs energies, integral entropies, and partial molar excess entropies, respectively. Experimental points of this investigation are indicated on Figure 5. Those of Predel, Voronin and Evseev, and Atarashiya et al. have been referred to 1050°K using the entropies calculated in this study. These values are also indicated on Figure 5. Since the temperature differences are small, the uncertainty introduced by this procedure should be negligible.

The lines shown on the graphs of Figure 4 are the values of $\Delta\overline{G}_{Pb}^{xs}$ which are consistent with the values in Tables V and VI. It would be expected that partial molar entropies could be determined from the temperature coefficients of $\Delta\overline{G}_{Pb}^{xs}$, since

$$\frac{d\,\Delta\overline{G}_{Pb}^{xs}}{d\,T} = -\Delta\overline{S}_{Pb}^{xs} \qquad (15)$$

However, over the limited range in which the vapor pressures could be measured ($\sim 100°K$) the accuracy of this procedure is questionable. It would seem, that when reliable heat data are available, as in the present case, a better and more sound practice would be to combine the heat and Gibbs energy data to obtain the entropies. The maximum scatter on the plots in Figure 4 is ±100 calories in $\Delta\overline{G}_{Pb}^{xs}$.

In the absence of extensive Gibbs energy data, Hultgren et al.[4] postulated that Pb and Sn formed a regular solution. Their assumption was based on the fact that a plot of ΔH versus x was nearly a parabola. However, the solution is clearly not regular, since examination of Table VI and Figure 7 show that ΔS^{xs} is far from zero. Shaefer and

Hovorka[12] measured $\Delta\bar{G}_{Sn}$ by an e.m.f. method in the composition range x_{Sn} = 0.9 to 1.0. Since the use of the e.m.f. method is doubtful for the Pb-Sn system, as has been explained in Section I, it seems preferable to ignore their results.

In all measurements of this investigation, the pressure readings were substantially constant with time. This would indicate an absence of the surface depletion problem found by Roy[5,6] for the solid iron-manganese system. This is not surprising; liquids have more rapid diffusion rates than solids, and convection currents may greatly help to provide sufficient mixing so as to eliminate depletion.

At the beginning of each series of measurements, the samples were held at a temperature where the alloy was molten but where the vapor pressure of lead was sufficiently low so as to give no visible deflection on the scale. If this was not done, it was found that consistently high readings were obtained. The reason for this effect is that the alloy was not homogeneous. After heating for a length of time ($1\frac{1}{2}$ to 2 hours), diffusion and convection currents provided complete mixing of the alloy, and readings as shown on Figure IV were obtained.

There was a very slow drop in pressure with time due to bulk loss of lead from the sample. As the composition changed with x_{Pb} decreasing, the pressure also decreased. The maximum loss occurred at high temperatures and long vaporization times, and amounted to less than 2% Pb in all cases. In order to minimize this effect, later runs were made as rapidly as possible. A measurement at 1050°K,

the tabulation temperature, was made first, followed by measurements at 1100°, 1075°, 1025°, and 1000°K. In this fashion, it was usually possible to complete an entire run in approximately $1\frac{1}{2}$ hours. Correction of the points in Figure 3 to account for this effect has not been attempted because reliable heat data are available and have been used to calculate entropies.

V. CONCLUSION

The vapor pressure of pure lead was measured in the temperature range between 950° and 1105°K. The selected $\Delta H^{\circ}_{v, 298} = 46620 \pm 170$ cal/gm-atom agrees very well with previous measurements.

Vapor pressures of lead over liquid lead-tin alloys were determined over the entire composition range. From these measurements and the Gibbs-Duhem relation, Gibbs energy values for both components were calculated. Correlation with existing heat of formation data allowed determination of entropy values.

No surface depletion was found for these liquid alloys.

VI. ACKNOWLEDGEMENTS

VII. REFERENCES

1. B. Predel, Z. Metallk., 51, 381 (1960).

2. G. F. Voronin, and A. M. Evseev, Russ. J. Inorg. Chem., 33, 373 (1959).

3. K. Atarashiya, M. Uta, M. Shimoji, and K. Niwa, Bull. Chem. Soc. Japan, 33, 706 (1960).

4. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley, New York (1963).

5. P. Roy, and R. Hultgren, Trans. Met. Soc. AIME, 233, 1811 (1965).

6. P. Roy, Ph. D. Thesis, University of California, Berkeley, 1964.

7. R. D. Freeman, and A.W. Searcy, J. Chem. Phys., 22, 762 (1954).

8. R. D. Freeman, and A. W. Searcy, J. Chem. Phys., 22, 1137 (1955).

9. D. A. Schulz, and A. W. Searcy, J. Chem. Phys., 36, 3099 (1962).

10. R. Hultgren, R. L. Orr, and K. K. Kelley, Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys, (loose-leaf sheets), Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley, California, 1964 - present.

11. O. J. Kleppa, J. Phys. Chem., 59, 175 (1955).

12. R. A. Shaefer, and F. Hovorka, Electrochem. Soc. Reprint No. 87, 23, 287 (1945).