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BY THE TORSION EFFUSION METHOD

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ABSTRACT

The torsion effusion method has been used to measure the vapor pressure of lead over pure lead and eight lead-tin alloys ranging from 9.1 to 87.9 at. % lead in the temperature range 950° -1125°K. The resulting $\Delta H_{V, 298}^{\circ} = 46627 \pm 200$ cal/gm -atom for pure lead is in excellent agreement with previous work. Derived $\Delta \bar{G}_{Pb}^{xs}$ values for the alloys were smoothed and correlated with previous heat of formation data to obtain entropies for the liquid alloys. Values for the tin component were calculated by Gibbs-Duhem integration.

No surface depletion was found for these liquid alloys, in contrast to previous measurements on solid Fe-Mn alloys.

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INTRODUCTION

The activities and Gibbs energies of the liquid lead-tin system are rather uncertain, although the heats of formation have been well determined by Kleppa¹. Vapor pressure determinations of a_{Pb} by Voronin and Evseev² disagree with those of Predel³. Elliott and Chipman⁴ measured emf values for the ternary Pb-Sn-Cd system. From the resulting a_{Cd} measurements, they were able to calculate a_{Pb} and a_{Sn} values for the binary Pb-Sn system at the compositions $x_{\text{Sn}} = 0.33$ and 0.67 . Atarashiya, Uta, Shimoji, and Niwa⁵ determined a_{Sn} from H_2 - H_2O equilibrium measurements, but their results are subject to doubt because of uncertainty of the final state.

To resolve these differences, measurements of the activity of Pb were made using a torsion-effusion apparatus. Among other advantages, this apparatus rapidly detects errors from surface depletion, which may reduce the apparent vapor pressure of the more volatile component. This

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effect was shown to cause serious errors in measuring a_{Mn} for solid Fe-Mn alloys⁶. A second objective of this investigation was to determine if surface depletion caused similar errors in a representative liquid alloy system.

EXPERIMENTAL

99.999+% Pb was obtained from the American Smelting and Refining Co. and 99.999% Sn from Vulcan Detinning Co. Eight Pb-Sn alloys were prepared by melting together weighed amounts of the pure metals in evacuated pyrex tubes and quenching the melts in water. Loss of weight in preparation was less than 0.02% in all cases.

The effusion cells were made from high purity, non-porous graphite. Graphite was chosen because of its resistance to reaction with Pb and Sn and because it can be accurately machined with precision orifices. Two cells were used with overall dimensions as shown in Figure 1. The orifices of cells 1 and 2 were, respectively, 1 mm and 1.5 mm in diameter.

The cell was suspended on a tungsten torsion filament 1×3 mils in cross-section, 50 cm long, with a torsion constant of 0.9688 dyne - cm/radian.

The apparatus has been fully described elsewhere^{6,7}. A vacuum of better than 2×10^{-5} torr was maintained during the measurements. The temperature was controlled and measured by a calibrated chromel-alumel thermocouple.

The vapor pressure is given by equation (1):

$$P = \frac{2D\phi}{f_1 a_1 q_1 + f_2 a_2 q_2} \quad (1)$$

where D is the torsion constant; ϕ is the angle of twist, a_1 and a_2 are the orifice areas, q_1 and q_2 are the distances of the orifices from the axis of rotation, and f_1 and f_2 are the corection factors determined by Freeman and Searcy⁸ to account for orifice thickness.

The appropriate quantities for the cells used are:

	cell 1	cell 2
a_1	0.008223 cm ²	0.01733 cm ²
a_2	0.007469 cm ²	0.01667 cm ²
q_1	1.482 cm	1.448 cm
q_2	1.489 cm	1.474 cm
f_1	0.46553	0.55123
f_2	0.45127	0.56745

So that, for cell 1,

$$P = 3.12188 \times 10^{-6} \phi$$

and, for cell 2,

$$P = 1.18548 \times 10^{-6} \phi$$

where P is in atmospheres and ϕ is in degrees.

By using the same effusion cell for pure lead and the alloy, it follows that

$$a_{\text{Pb}} = \frac{P_{\text{Pb, alloy}}}{P_{\text{Pb, pure}}} = \frac{\phi_{\text{Pb, alloy}}}{\phi_{\text{Pb, pure}}} \quad (2)$$

so that most systematic errors in the pressure measurements are eliminated in determining activities.

RESULTS

Individual measurements on pure Pb for both cells are given in

Table 1. Values of $\Delta H_{v,298}^{\circ}$ were calculated using tabulated Gibbs energy functions⁹. No trend was found with temperature or size of orifice indicating equilibrium was attained.

A single Knudsen measurement was made at 1047°K using cell 2. The weight loss of 0.2909 gm led to a calculated $P_{Pb} = 4.12 \times 10^{-5}$ atm, and $\Delta H_{v,298}^{\circ} = 46733$ cal/gm-atom, agreeing with the torsion measurements.

Measurements on the Pb-Sn alloys are shown in Figure 2 indicating a scatter of ± 100 cal/gm-atom.

Values were smoothed with respect to composition by a plot of $\frac{\Delta \bar{G}_{Pb}^{xs}}{x_{Sn}^2}$ versus x_{Sn} , with a temperature coefficient chosen to agree with Kleppa's¹ heats of formation. The resulting selected values are indicated in Figure 2 by the solid lines, which have slopes agreeing with the entropies given in Table 3 (see Discussion.) Reliable $\Delta \bar{S}_{Pb}^{xs}$ values could not be derived directly from this investigation due to the short range of temperature over which measurements were made.

DISCUSSION

The value of $\Delta H_{v,298}^{\circ}$ for pure Pb obtained in this study is in excellent agreement with previous investigations⁹.

In the Pb-Sn system, this study shows positive deviations from Raoult's Law at all compositions. The values of a_{Pb} are considerably higher than those measured by other investigators²⁻⁵. (Fig. 3). Values of $\Delta \bar{G}_{Sn}^{xs}$ were calculated by Gibbs-Duhem integration. From these results and Kleppa's¹ heats of formation, assuming Kopp's Law of additive heat capacities, the quantities of Tables 2 and 3 were derived.

During the measurements, the vapor pressures remained substantially constant with time, indicating that no surface depletion was occurring. 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 this effect.

ACKNOWLEDGMENT

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TABLE 1

Vapor Pressure of Lead

T, °K	P×10 ⁵ atm	$\Delta H_{V, 298}^{\circ}$ cal/gm-atom	T, °K	P×10 ⁵ atm	$\Delta H_{V, 298}^{\circ}$ cal/gm-atom
	Cell 1			Cell 2	
1029	2.653	46874	950	0.5299	46503
1035	3.153	46778	952	0.4921	46736
1038	3.309	46806	953	0.5110	46712
1047	4.058	46765	955	0.5299	46736
1052	4.558	46737	958	0.6435	46505
1061	5.682	46651	961	0.6813	46534
1063	5.713	46722	963	0.6813	46626
1071	6.618	46741	965	0.6624	46772
1074	7.493	46600	968	0.7760	46606
1080	8.211	46649	970	0.7949	46651
1087	9.428	46635	975	0.9463	46541
1094	10.99	46585	976	0.9652	46548
1097	11.30	46644	981	1.003	46699
1107	14.11	46555	984	1.173	46528
1109	14.36	46595	986	1.173	46618
1114	16.27	46517	989	1.344	46485
1125	20.17	46467	991	1.249	46718
			995	1.386	46691
			996	1.401	46714
Average $\Delta H_{V, 298}^{\circ} = 46666$					

Table 1 (Cont' d.)

T, °K	P×10 ⁵ atm	$\Delta H_{V,298}^{\circ}$ cal/gm-atom	T, °K	P×10 ⁵ atm	$\Delta H_{V,298}^{\circ}$ cal/gm-atom
998	1.552	46600	1029	3.047	46591
1000	1.626	46596	1031	2.952	46742
1001	1.665	46593	1035	3.352	46652
1002	1.609	46705	1035	3.426	46607
1002	1.628	46682	1036	3.615	46539
1002	1.760	46527	1038	3.615	46624
1005	1.628	46814	1040	3.791	46611
1005	1.703	46724	1042	4.012	46578
1008	1.949	46586	1047	4.258	46666
1012	2.139	46574	1048	4.391	46644
1014	2.038	46759	1048	4.410	46635
1015	2.290	46567	1050	4.485	46684
1015	2.176	46671	1052	4.561	46736
1015	2.063	46778	1052	5.011	46540
1016	2.328	46577	1053	5.070	46557
1017	2.271	46670	1053	4.656	46735
1017	2.298	46647	1054	4.902	46669
1021	2.650	46532	1057	5.394	46594
1022	2.460	46726	1059	6.018	46447
1024	2.555	46735	1062	5.735	46673
1027	2.858	46636	1064	6.255	46572
1027	2.706	46748	1065	6.757	46450

Table 1 (Cont'd.)

T, °K	P×10 ⁵ atm	$\Delta H_{V,298}^{\circ}$ cal/gm-atom	T, °K	P×10 ⁵ atm	$\Delta H_{V,298}^{\circ}$ cal/gm-atom
1066	6.113	46704	1105	13.74	46534
1069	6.256	46778	Average $\Delta H_{V,298}^{\circ} = 46618$		
1071	7.192	46564	Average $\Delta H_{V,298}^{\circ}$ for all		
1071	6.416	46807	measurements		
1075	8.176	46454	= 46627 (± 200)		
1076	7.949	46555			
1077	7.703	46663			
1079	7.646	46761			
1080	8.233	46643			
1081	8.876	46522			
1082	9.619	46390			
1082	9.217	46482			
1083	8.441	46711			
1085	9.577	46520			
1090	10.65	46492			
1092	10.47	46609			
1095	12.49	46347			
1095	11.62	46503			
1098	11.39	46666			
1100	12.511	46542			
1101	13.02	46494			
1102	12.98	46540			

TABLE 2

Partial Molar Quantities for Liquid Alloys at 1050°KA. Pb Component $\mu_{\text{Pb}(l)} = \mu_{\text{Pb (in alloy)}(l)}$

x_{Pb}	a_{Pb}	γ_{Pb}	$\Delta\bar{G}_{\text{Pb}}$	$\Delta\bar{G}_{\text{Pb}}^{\text{xs}}$	$\Delta\bar{H}_{\text{Pb}}$	$\Delta\bar{S}_{\text{Pb}}$	$\Delta\bar{S}_{\text{Pb}}^{\text{xs}}$
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

TABLE 2 (Cont'd.)

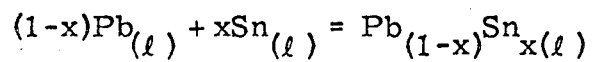
B. Sn Component

$\text{Sn}_{(l)} = \text{Sn (in alloy)}_{(l)}$

x_{Sn}	a_{Sn}	γ_{Sn}	$\Delta\bar{G}_{\text{Sn}}$	$\Delta\bar{G}_{\text{Sn}}^{xs}$	$\Delta\bar{H}_{\text{Sn}}$	$\Delta\bar{S}_{\text{Sn}}$	$\Delta\bar{S}_{\text{Sn}}^{xs}$
0.0	0.000	6.816	$-\infty$	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 3

Integral Quantities for Liquid Alloys at 1050°K



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

List of Figure Captions

Figure 1. Effusion Cell Design.

Figure 2. Experimental Values of $\Delta\bar{G}_{\text{Pb}}^{\text{XS}}$ for Liquid Lead-tin Alloys.

Figure 3. Activity Values for Liquid Lead-tin Alloys at 1050°K.

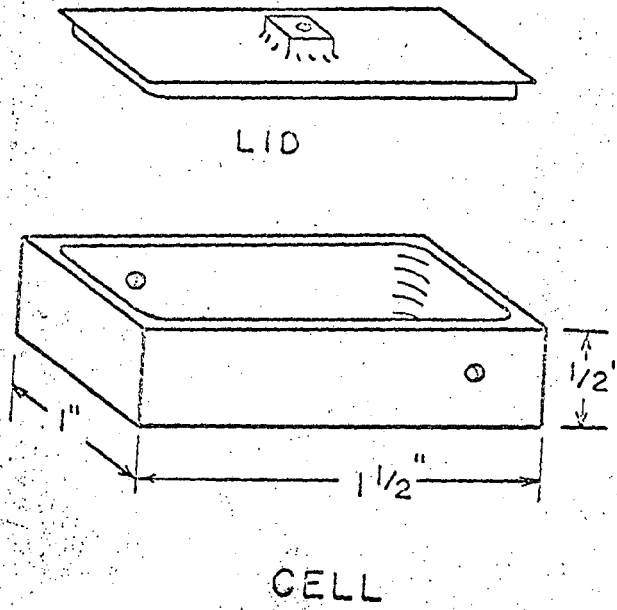


FIG. I. EFFUSION CELL DESIGN.

MUB-8950

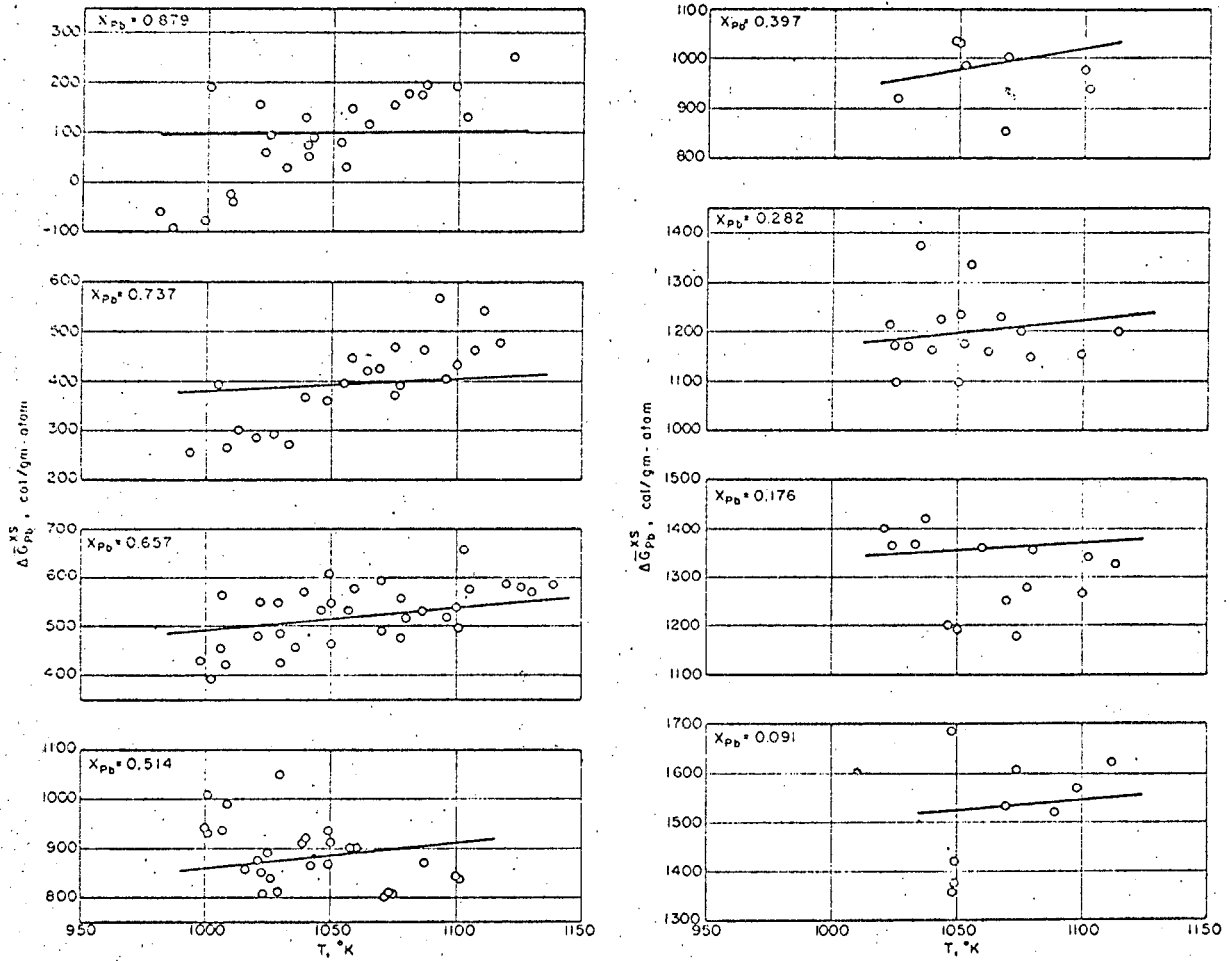


FIG. 2 EXPERIMENTAL VALUES OF ΔG_{Pb}^{XS} FOR LIQUID LEAD-TIN ALLOYS.

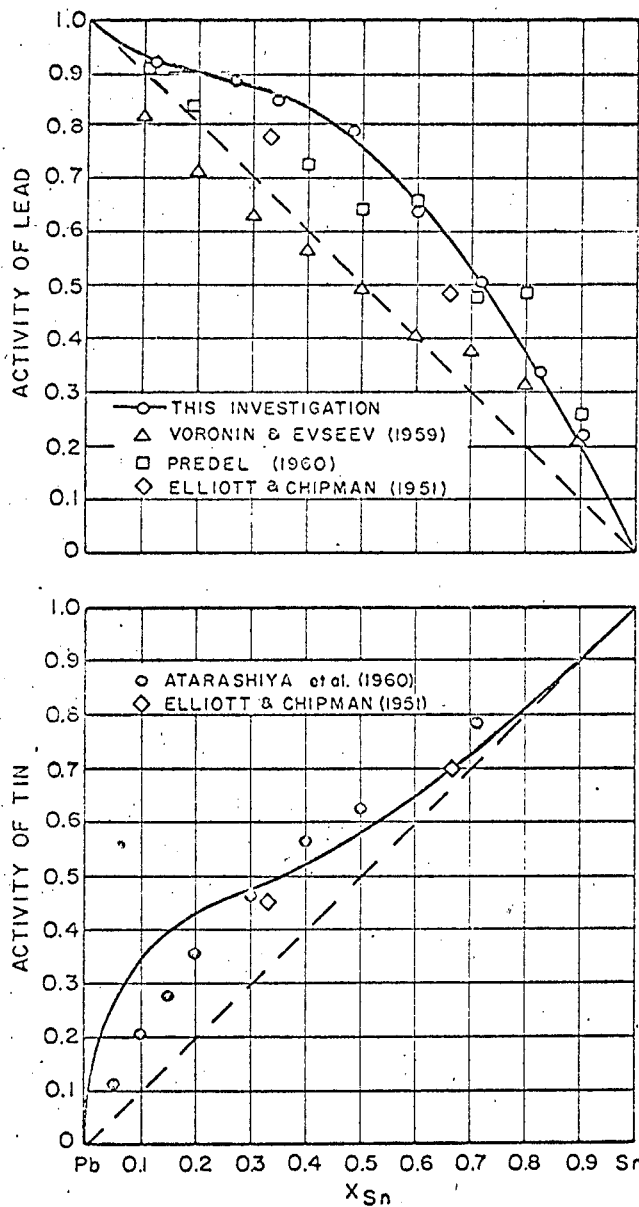


FIG. 3 ACTIVITY VALUES FOR LIQUID LEAD-TIN ALLOYS AT 1050°K.

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