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Authors
Hultgren, Ralph
Sommelet, Pierre.

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Ralph Hultgren and Pierre Sommelet

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The Magnitude of Some of the Errors in Determining Heats
of Formation of Liquid Alloys by Drop Calorimetry;
the Silver-Lead System

By Ralph Hultgren and Pierre Sommelet [*]

Department of Materials Science and Engineering and Lawrence
Radiation Laboratory, University of California, Berkeley

If a sample undergoes a phase change while cooling in a drop calorim-
eter, the heat liberated during the phase change is included in the meas-
ured enthalpy. To take a simple example, if a liquid alloy at temperature,
T, freezes to pure solid elements at the final temperature, T_o, the heat
of formation at T is readily obtained by subtracting the enthalpies of the
component elements at T from the measured enthalpy of the alloy.

Oelsen, Schürmann, and Heynert[1] showed that if the entire enthalpy
versus temperature curve were measured, so that heats of formation were
calculable at all temperatures between T_o and T, the heats could be inte-
grated to determine entropies and Gibbs energies of formation, which
therefore could be determined "by calorimetry alone". Shortly afterward
Oelsen, Rieskamp, and Oelsen[2] described a new drop calorimeter in which
temperature of sample and the amount of heat evolved were measured
simultaneously. With this instrument the entire enthalpy versus tempera-
ture curve could be measured quickly and conveniently in one experiment.

However, as is often the case, rapidity and convenience are not ob-
tained without loss of some accuracy. It is our purpose to examine one
source of error which we think is insufficiently appreciated by many
calorimetrists. We shall not consider the formidable difficulty of meas-
uring a representative temperature of a rapidly cooling sample with large
and changing temperature gradients, nor the less serious tendency to
supercooling which makes too large the derived entropies.

The source of error which we will consider is the non-equilibrium
freezing of alloys. Foundrymen are quite familiar with the fact that equi-
librium is far from attained in most alloys in the "as cast" condition.
Highly segregated phases are commonly found and phases not in equilibri-
um at the composition of the casting commonly appear.

The magnitude of the effect on enthalpy of these deviations from equi-

librium is very difficult to estimate. We therefore decided to experimen-
tally determine it in a rather favorable system, the silver-lead system[3]
shown in Fig. 1. The equilibrium state at room temperature deviates
negligibly from the pure elements. Segregation is possible only in the
Ag-rich α phase.

Enthalpies were measured in a diphenyl ether drop calorimeter, a modification of one described elsewhere[4]. Samples were sealed into an evacuated quartz capsule, which was sus-pended in a furnace by a platinum wire. The sample was dropped into the
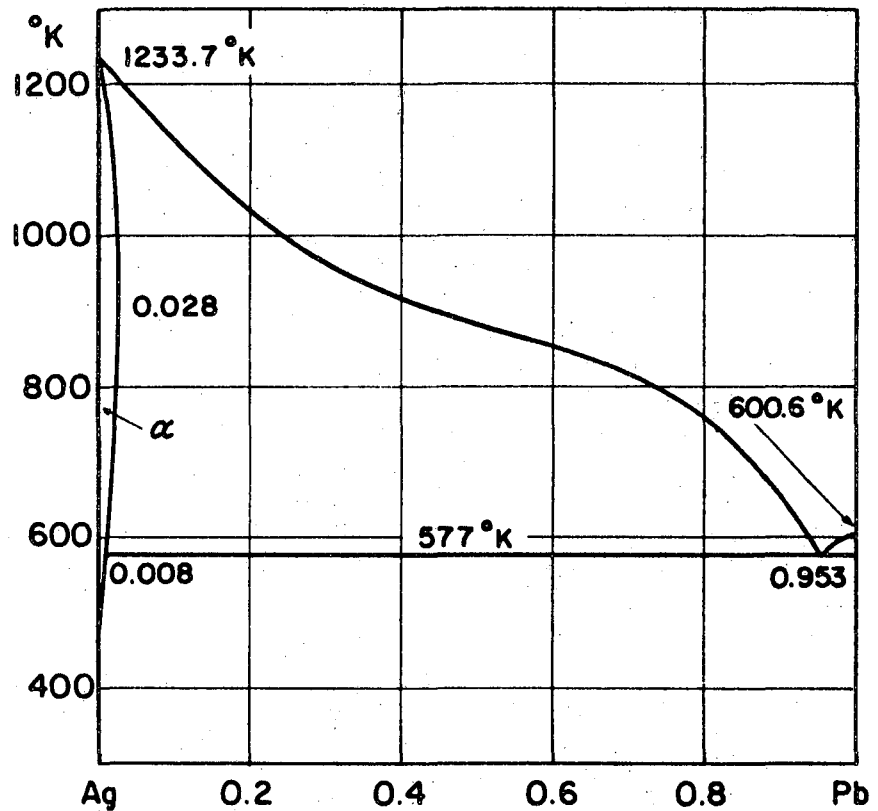
Fig. 1. The Silver-Lead System

calorimeter chamber which was surrounded by another chamber contain-
ing liquid plus solid diphenyl ether at 300°K, the melting point of diphenyl
ether. The heat given off by the sample melted some of the solid causing
an expansion which was measured by the amount of mercury displaced.
From this result it was possible to calculate the heat of formation at the
initial temperature, T. A number of drops were made at suitable initial
temperatures between T and T_o, so that enthalpies were found as a func-
tion of temperature. This is laborious, but it certainly avoids the
sources of error mentioned in the continuous cooling process.

Experimental. Alloys were prepared from about 11-16 grams of 99.999%

pure silver and lead, which were melted into the spheroidal capsules to make them less than half full. Larger lead-rich samples wetted the quartz and caused the capsules to break during freezing. Numerous platinum samples were used for calibration, the value of Jessup[5], 18.91 cal/g of Hg, was confirmed. From the total enthalpy of capsule plus sample was subtracted the enthalpy of the empty capsule. In measuring this, a small amount of platinum foil was placed in the empty capsule so the emissivity and therefore the loss of heat during the drop would be more comparable. The experimental results are given in Table 1. The dependence of the enthalpy on temperature for a typical composition is shown in Fig. 2.

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TABLE 1

Experimental Results

</div>

x_{Pb}	$T, °K$	H_T-H_{300}	x_{Pb}	$T, °K$	H_T-H_{300}
0	1500.0	11162	0.15	1257.5	9242
0	1255.0	9220	0.15	1114.5	8112
0	1257.0	9228	0.15	1004.5	6245
0	1239.8	9113	0.15	903.1	4727
0	1226.2	6286	0.15	776.0	3365
0	1117.5	5427	0.25	1254.0	9339
0	1000.0	4592	0.25	1256.9	9331
0	901.7	3883	0.25	1115.2	8203
0	689.5	2433	0.25	1003.4	7365
0	580.7	1736	0.25	902.8	5385
0	570.0	1639	0.25	776.1	3665
0.05	1256.5	9176			
0.05	1257.7	9197	0.35	1253.1	9362
0.05	1242.5	9053	0.35	1258.1	9399
0.05	1180.4	8120	0.35	1116.9	8302
0.05	1115.5	6985	0.35	1004.9	7444
0.05	1222.8	8811	0.35	1000.5	7384
0.05	1115.4	6243	0.35	903.2	6076
0.05	1000.0	4875	0.35	776.7	3972
0.05	901.4	4086	0.35	775.9	3942
0.05	776.1	3079	0.35	689.9	3118
0.05	690.1	2500	0.35	580.5	2226
0.05	581.2	1775	0.35	568.9	1692
0.05	570.3	1642	0.45	1255.5	9352
0.05	1198.3	8655	0.45	1257.1	9395
0.05	1303.9	9537	0.45	1116.2	8268
			0.45	1003.4	7438
0.15	1254.6	9216	0.45	902.4	6634

TABLE 1 (continued)

x_{Pb}	$T, °K$	H_T-H_{300}	x_{Pb}	$T, °K$	H_T-H_{300}
0.45	776.0	4256	0.75	775.0	5113
			0.75	689.1	3955
0.55	1254.6	9236	0.75	580.4	2822
0.55	1256.7	9222			
0.55	1116.2	8192	0.85	1254.2	8442
0.55	1002.9	7370	0.85	1256.2	8417
0.55	903.9	6562	0.85	776.2	5007
0.55	900.8	6557	0.85	689.4	4170
0.55	778.3	4567	0.85	580.2	2992
0.55	580.3	2528			
			0.95	1253.7	8020
0.65	1255.4	9051	0.95	689.0	3982
0.65	1256.7	9040	0.95	579.5	3133
0.65	1116.5	8037	0.95	568.8	1784
0.65	1000.1	7210			
0.65	902.2	6462	1.00	1256.0	7815
0.65	776.5	4854	1.00	1116.8	6825
0.65	689.3	3745	1.00	1000.3	6014
0.65	569.0	1723	1.00	902.9	5283
			1.00	776.2	4398
0.75	1255.2	8772	1.00	689.6	3694
0.75	1256.7	8772	1.00	689.9	3766
0.75	1119.1	7798	1.00	589.1	1912
0.75	1004.1	6955	1.00	571.2	1773
0.75	902.2	6225			

If H_T-H_{300} for the components in the elementary state[6] is subtracted from the measured enthalpy, the quantity obtained is $\Delta H_T-\Delta H_{300}$, the uncorrected heat of formation of the alloy at temperature, T. If equilibrium at 300°K were attained by the alloy in its final state in the calorimeter, ΔH_{300} would, of course, be zero; it is the value ΔH_{300} which is the error caused by non-equilibrium freezing of the alloy.
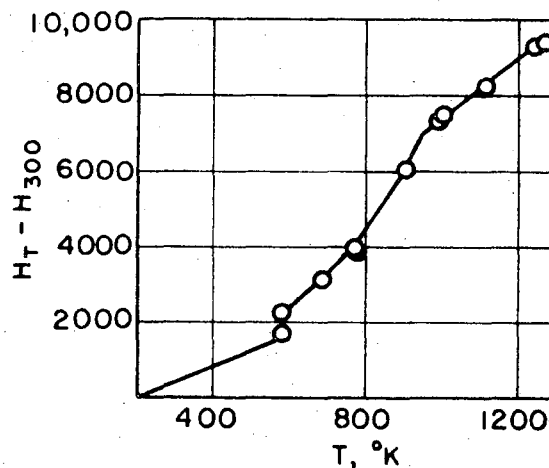

Fig. 2. Heat Content of Alloy, $x_{Pb} = 0.35$ (cal/g-atom)

A number of alloys which had been dropped in the calorimeter were examined by back-reflection X-ray diffraction. In each case the Pb-rich phase gave sharp lines from which a lattice constant was calculated which

agreed with that of pure lead within experimental error. For the Ag-rich phase, however, the lines were somewhat broadened and the lattice constant was larger than that of pure silver. From the known dependence of lattice constant on composition[7] x_{Pb} can be found.

The samples dropped from 577°K, just above the eutectic temperature, all yielded lattice constants near 4.0910Å, compared with 4.0856Å for pure silver. This corresponds with x_{Pb} = 0.0077, closely agreeing with the phase diagram value, x_{Pb} = 0.008. Thus there was virtually no precipitation of Pb from this phase during cooling in the calorimeter. For drops from higher temperatures, the amount of Pb retained in solution increased to a maximum of x_{Pb} = 0.015 at 900°K, where the maximum in the retrograde solubility curve is x_{Pb} = 0.028. From higher temperatures, the lead content in the residual Ag-rich phase fell off to x_{Pb} = 0.014.

The heat of formation of the solid solution of Pb in Ag was calculated from the solid solubility curve, which has been determined with precision[7]. At the eutectic temperature, x_{Pb} = 0.008 and ΔH = 54 cal/g-atom was calculated. Assuming Henry's law, $\Delta H = 6750 x_{Pb}$ would give an approximately correct heat of formation at all compositions.

However, this is not the whole story as can be seen in Fig. 3. The samples were dropped from 577°K, a two-phase region consisting of a solid phase with x_{Pb} = 0.008 and a liquid phase with x_{Pb} = 0.953. Heats of formation versus composition should fall on a straight line. Indeed, the plot of the uncorrected
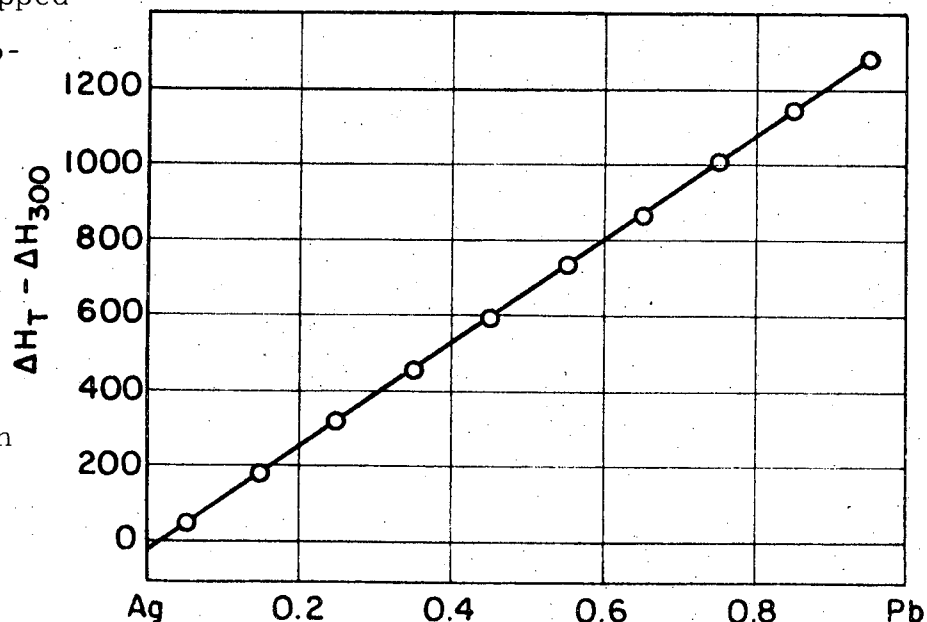

Fig. 3. Uncorrected Heats of Formation at 577°K (cal/g-atom).

values is gratifyingly straight. However, the uncorrected values should intersect 0 at x_{Pb} = 0.008, since a phase of this composition should arrive at 300°K without a chemical reaction. However, at this composition $\Delta H_T - \Delta H_{300}$ is very clearly -20; ΔH_{300} is 20 cal/g-atom more endothermic than ΔH_{577}. Since negligible precipitation of Pb has been found to occur, this heat effect must be due to pre-precipitation processes shown by the broadening of the X-ray lines.

The correction to be added to the measured value at x_{Pb} = 0.008 is therefore 74, not 54 cal/g-atom. Assuming this correction is also linear with composition

$$\Delta H_{corr} = 9250 x_{Pb} .$$

Applying these corrections, allowing for the proportion of Ag-rich phase actually present at 300°K, the corrections shown in Table 2 are found.

TABLE 2

Correction in cal/g-atom To Be Added to Measured Value
to Obtain Heat of Formation

T, °K	x_{Pb}									
	0.05	0.15	0.25	0.35	0.45	0.55	0.65	0.75	0.85	0.95
577	70	63	56	48	41	33	26	18	11	4
700	98	88	77	67	57	46	36	26	15	5
800	116	104	92	79	67	55	43	30	18	6
900	134	120	106	92	78	63	49	35	21	7
1000	116	111	98	85	72	59	46	33	20	7
1100	116	111	98	85	72	59	46	33	20	7
1200	116	111	98	85	72	59	46	33	20	7
1250	116	111	98	85	72	59	46	33	20	7

Corrections to the entropy will amount to as much as 0.2 eu, and corrections to ΔG will be exothermic, of the same order of magnitude as the endothermic corrections to ΔH. Thermodynamic quantities finally found for liquid Ag-Pb alloys are shown in Table 3.

Discussion. Even with a highly favorable system such as Ag-Pb, and without the errors of the continuous cooling method, corrections must be applied which are not negligible.

TABLE 3

Heats, Entropies and Gibbs Energies of Formation at 1250°K

x_{Pb}	ΔH cal/g-atom	ΔS cal/g-atom-deg	ΔG cal/g-atom
0.1	230	0.760	- 720
0.2	453	1.210	-1060
0.3	648	1.535	-1270
0.4	788	1.733	-1378
0.5	844	1.803	-1410
0.6	811	1.751	-1378
0.7	694	1.571	-1270
0.8	506	1.253	-1060
0.9	266	0.789	- 720

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