Title

GIBBS ENERGIES, ENTROPIES, AND HEATS OF FORMATION FROM DROP CALORIMETRY: THE SILVER-LEAD SYSTEM

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Pierre-Hubert Sommelet

(Master's Thesis)

September, 1965

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GIBBS ENERGIES, ENTROPIES, AND HEATS OF FORMATION FROM DROP CALORIMETRY: THE SILVER-LEAD SYSTEM

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September 10, 1965

ABSTRACT

A thermodynamic study was made of silver-lead alloys by use of a diphenyl-ether drop calorimeter.

Corrections for deviation from equilibrium of the final solid state were derived and applied so that heats of formation of liquid alloys and two phase alloys could be calculated. By the use of the Oelsen technique,[1] Gibbs energies and entropies were also found. Corrections for non-equilibrium were of considerable importance.

I. INTRODUCTION

Drop calorimetry is usually applied to one-component systems for the purpose of determining heat contents, heat capacities and latent heats of fusion and transition.

Drop calorimetry may also be applied to measuring heats of reactions which occur during cooling in the calorimeter. An ideal case is provided by a simple eutectic system of metals A and B which are completely immiscible in each other in the solid state.

Let x be the atomic fraction of metal B

$$x = x_B$$

The alloy has the formula

$$A_{1-x}\ B_x$$

Dropping the alloy from a temperature T in the liquid range to room temperature, the liquid alloys on freezing and cooling dissociate into two solid phases composed of pure A and pure B. We have the reaction (1).

$$A_{1-x}\ B_{x(\ell,T)} = (1-x)\ A_{(s,298)} + xB_{(s,298)} \qquad (1)$$

We measure ΔHc_1 in this reaction

$$\Delta Hc_1 = -(H_T - H_{298})$$

With the pure A metal dropped in similar conditions we measure ΔHc_2 in the reaction (2)

$$(1-x)\,A_{(\ell,\ T)} = (1-x)\,A_{(s,\,298)} \tag{2}$$

with

$$\Delta Hc_2 = -(H_T - H_{298})_A \quad (1-x)$$

With the pure B metal we measure ΔHc_3 for the reaction (3)

$$x\,B_{(\ell,T)} = x\,B_{(s,\,298)} \tag{3}$$

with

$$\Delta Hc_3 = -x\,(H_T - H_{298})_B$$

The sum of reactions (2) + (3) - (1) gives

$$(1-x)\,A_{(\ell,\,T)} + xB_{(\ell,\,T)} = A(1-x)\,B_{x(\ell,\,T)}$$

and

$$\Delta H_T = \Delta Hc_2 + \Delta Hc_3 - \Delta Hc_1$$

the heat of formation of the liquid alloy from liquid components. From a set of experiments, dropping each sample from various temperatures between 298 and a temperature T where both A and B are liquid, to 298°K, we have ΔH as a function of temperature for each composition. Oelsen, Schürmann and Heynert have applied data such as these to the relation

$$\frac{d\left(\frac{\Delta G}{T}\right)}{d\left(\frac{1}{T}\right)} = \Delta H$$

so that the Gibbs energy of formation may be obtained by integration:

$$\int_{298}^{T} d\left(\frac{\Delta G}{T}\right) = \int_{298}^{T} \Delta H \ d\left(\frac{1}{T}\right)$$

that is to say

$$\frac{\Delta G_T}{T} = \frac{\Delta G_{298}}{298} + \int_{298}^{T} \Delta H \ d\left(\frac{1}{T}\right)$$

since the alloy separates into two pure components at 298°K,

$$\Delta G_{298} = 0$$

and

$$\frac{\Delta G}{T}[x, T] = \int_{298}^{T} \Delta H[x, T] \ d\left(\frac{1}{T}\right)$$

the values for ΔH, at a given composition, being plotted versus $\frac{1}{T}$, a graphical integration is easily performed. ΔG can be found as a function of temperature at each composition. ΔS_T may be deduced from ΔH_T and ΔG_T.

II. THE SILVER-LEAD SYSTEM AND THE OELSEN TECHNIQUE

This simple eutectic system, with negligible solubility of silver in lead and a small solubility of lead in silver (2.8% maximum solubility at 900°K, 0.8% at the eutectic temperature, none at 300°K) seems to be suited to this method and to the Oelsen technique.

The phase diagram is well established including temperature of liquidus and solidus, and the solid solubility of Pb in Ag (Hansen 1958). The liquidus determined in the present research by changing of slope in the heat content versus temperature curve at a given composition agrees perfectly with the reported phase diagram (Fig. 1).

The Oelsen technique assumes that the alloy is at equilibrium at both temperature T, the initial temperature, and 300°K, the final temperature for the drop. The alloy was maintained 24 hours at temperature T to obtain initial equilibrium. Analysis of the final product by X-rays show that there were small fractions of lead retained in the silver-rich phase after the drop. It was necessary to correct for this deviation from equilibrium. During the drop we have the reaction (4).

$$Ag_{1-x}\,Pb_{x(\ell,T)} = \frac{1-x}{1-x_f}\,Ag_{1-x_f}\,Pb_{x_f}(\alpha, 298) + \frac{x-x_f}{1-x_f}\,Pb_{(s,298)} \qquad (4)$$

$-\Delta H_4 = (H_T - H_{298})$ alloy is the quantity measured in the calorimeter.

x being the molar fraction of lead in the liquid alloy.

x_f being the molar fraction of lead in the α phase at 298°K

(in metastable equilibrium).

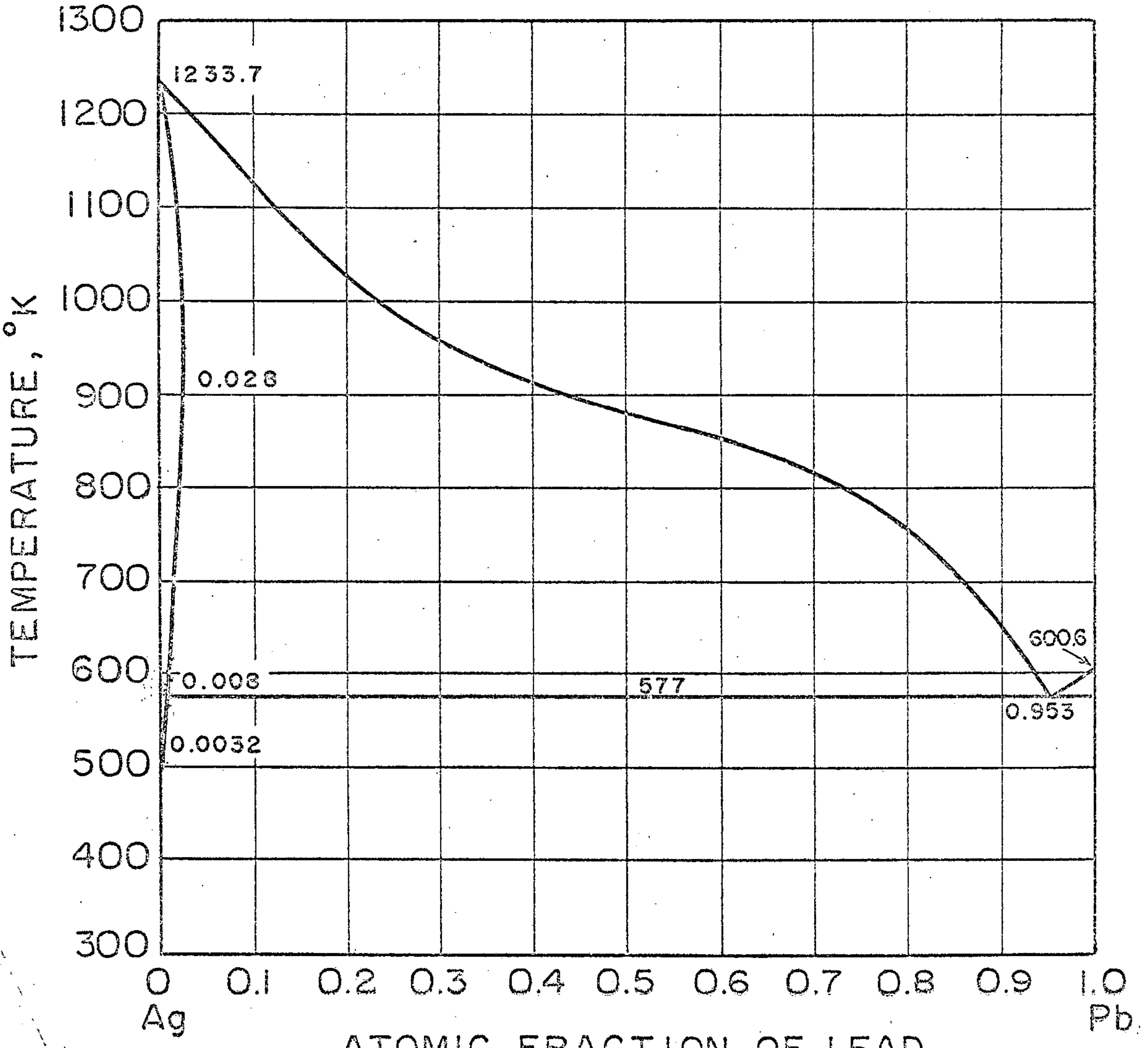

FIG. I PHASE DIAGRAM OF Ag-Pb SYSTEM.

Let us consider the reaction:

$$(1-x)Ag_{(s,298)} + \frac{x_f}{1-x_f}(1-x)Pb_{(s,298)} = \frac{1-x}{1-x_f} Ag_{1-x_f}Pb_{x_f(\alpha,298)} \quad (5)$$

with the heat $\frac{1-x}{1-x_f}\Delta H_{\alpha, x_f, 298}$. $\Delta H_{\alpha, x_f, 298}$ is the heat of formation of the α phase of composition x_f at 298°K. Subtracting (4) from (5) we get (6).

$$(1-x)Ag_{(s,298)} + xPb_{(s,298)} = Ag_{1-x}Pb_{x}\ (\ell, T) \quad (6)$$

and the heat involved here is

$$\Delta H = (H_T - H_{298})\text{ alloy} + \frac{1-x}{1-x_f}\Delta H_{\alpha, x_f, 298}$$

ΔH is the heat of formation of the liquid alloy at T°K from pure solid silver and pure solid lead at 298°K. Since, as will be discussed later, $(1-x_f)$ will vary from 0.995 to 0.98 but will be so close to 1 that it can be assumed to be equal to 1 without significant error,

$$\Delta H = (H_T - H_{298})\text{ alloy} + (1-x)\Delta H_{\alpha, x_f, 298}$$

The problem resolves into what value to use for $\Delta H_{\alpha, x_f, 298}$.

From the phase diagram we are able to calculate $\Delta H_{\alpha, x_e, T_e}$, x_e being the composition of the α phase at the eutectic temperature T_e. The solubility of silver in lead being practically equal to 0 we have, for the partial molar free energy of lead at all points on the solvus line,

$$\Delta \overline{G}_{Pb} = 0$$

and

$$G_{Pb} = \overline{G}_{Pb}$$

thus

$$\left[\frac{d(G_{Pb}/T)}{dT}\right] dT = \left[\frac{\partial(\overline{G}_{Pb}/T}{\partial T}\right]_x dT + \left[-\frac{\partial(\overline{G}_{Pb}/T)}{\partial x}\right]_T dx$$

$$\frac{d(G_{Pb}/T)}{dT} - \left[\frac{\partial(\overline{G}_{Pb}/T)}{\partial T}\right]_x = \frac{\left[\overline{H}_{Pb} - H_{Pb}\right]}{T^2}$$

Hence for the partial molar heat of formation of the α phase we have the equation:

$$\frac{\Delta\overline{H}_{Pb}}{T^2} = \left[\frac{\partial(\overline{G}_{Pb}/T)}{\partial x}\right]_T \frac{dx}{dT}$$

If Henry's law is assumed,

$$\left[\frac{\partial(\overline{G}_{Pb}/T)}{\partial x}\right]_T = \frac{R}{x}$$

and

$$\frac{R}{x} \cdot \frac{dx}{dT} = \frac{\Delta\overline{H}_{Pb}}{T^2}$$

or

$$\frac{d \ln x}{dT} = \frac{\Delta\overline{H}_{Pb}}{RT^2}$$

If we consider the solubility curve on the phase diagram (Fig. 2) we determine graphically the value of $\frac{dx}{dT}$

at $T_e = 577°K$

$x_e = 0.008$

we have

$$\frac{dx}{dT} = 8.22 \times 10^{-5} \text{ g-atom/deg.}$$

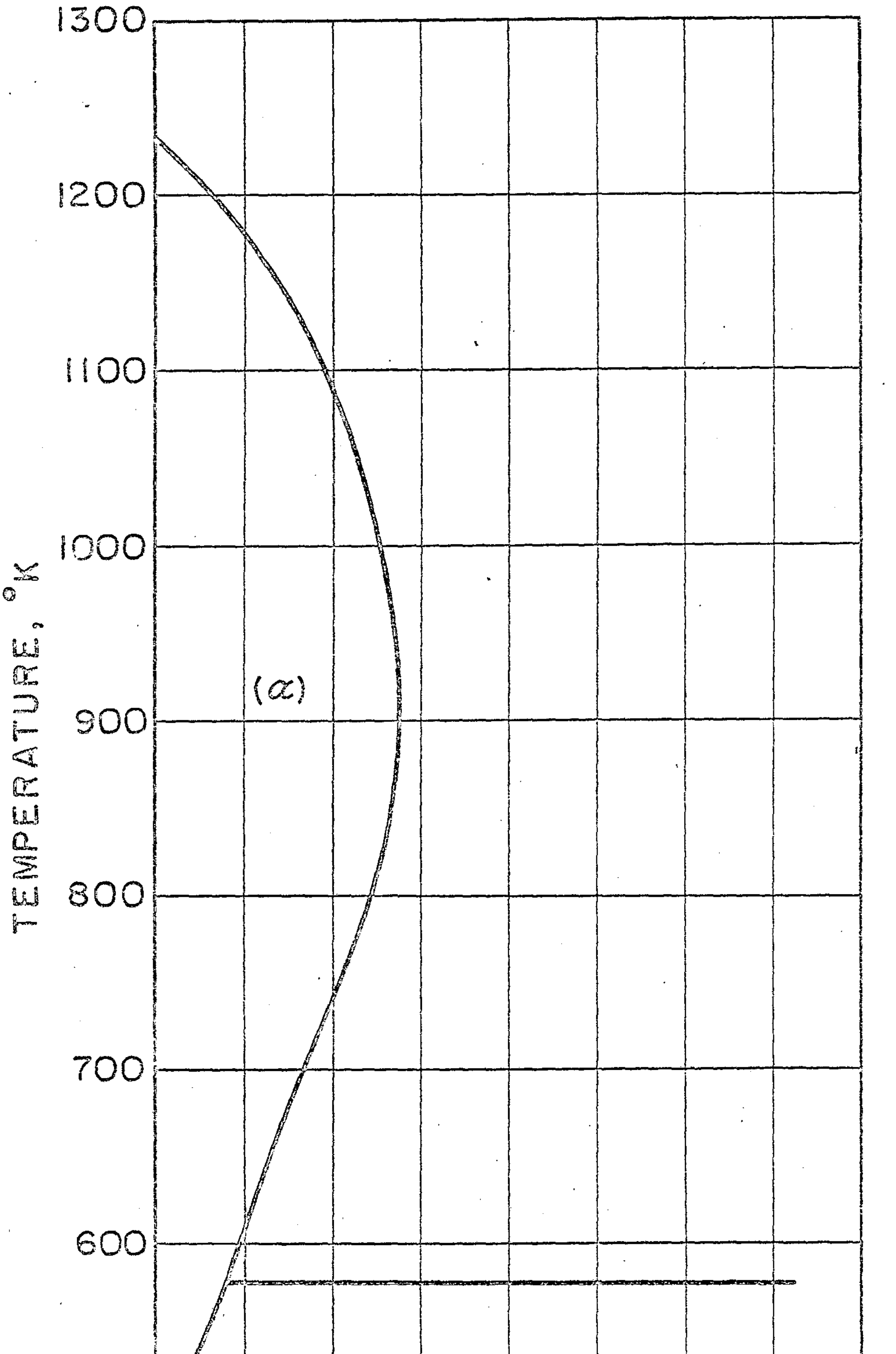

FIG. 2 SOLUBILITY CURVE FOR
Ag - RICH α-PHASE.

thus we have

$$\Delta\overline{H}_{Pb,\ T_e} = 6800 \text{ cal/mole}$$

with the assumption of Henry's law:

$$\Delta\overline{H}_{Ag} = 0$$

and

$$\Delta H_{\alpha,\ x_e,\ T_e} = x_e\ \Delta\overline{H}_{Pb} = 54 \text{ calories.}$$

If we then assume that Kopp's law and Henry's law are both approximately obeyed at the small concentrations in the α phase, we have ΔH_α at various temperatures at the solubility limit.

$$\Delta H_{\alpha,\ x_\alpha,\ T} = 6800\ x_\alpha \text{ calories}$$

$$\Delta H_{\alpha,\ x_f,\ 298} = 6800\ x_f \text{ calories}$$

But we have to consider one other factor which can introduce error. The lead in solution in silver at 298°K is in metastable equilibrium and prenucleation has set in as shown by broadening of the X-ray lines. This results in a strain energy which is not negligible. It can be found as described in the experimental section.

Each of the experimental heat contents must be corrected to take account of the heat of formation of α phase plus its strain energy in order to obtain heats of formation referred to the pure elements. These values can be integrated as described previously to obtain Gibbs energies and entropies of formation.

Integration can be conveniently begun at the eutectic temperature where liquid, alpha and $Pb_{(s)}$ are in equilibrium. For each of these phases at T_e, referred to $Ag_{(s)}$ and $Pb_{(s)}$

$$\Delta\overline{G}_{Pb} = 0$$

while the partial quantity for Ag can be estimated assuming Raoult's law for the α phase which has a solubility limit $x_\alpha = 0.008$.

Hence

$$\Delta\overline{G}_{Ag} = RT \ln (1-x) = -9 \text{ cal/g. atom}$$

For any phase or combination of phases with total composition x at 577°K, the integral Gibbs energy will be

$$\Delta G_{577} = (1-x)\, \Delta\overline{G}_{Ag} + x\, \Delta\overline{G}_{Pb} = -9\,(1-x)$$

Hence

$$\frac{\Delta G_T}{T} = \frac{\Delta G_{577}}{577} + \int_{577}^{T} \Delta H \; \alpha\left(\frac{1}{T}\right) = \frac{-9}{577}\,(1-x) - \int_{577}^{T} \frac{\Delta H}{T^2}\, dT \qquad (7)$$

III. EXPERIMENTAL

Heat content measurements were made using a diphenyl ether Bunsen type drop calorimeter (Fig. 3). Details of the design of the calorimeter will be given in a forthcoming publication.[2]

The experimental procedure will be described only briefly here. The encapsulated sample is suspended by a wire in a platinum-wound vertical tube furnace and heated to a given temperature, which is measured by a Pt - Pt + 10% Rh thermocouple, then dropped into the calorimeter. Heat from the specimen enters a surrounding chamber containing liquid and solid diphenyl ether at its melting point, 300.0°K, melting some of the solid isothermally. The resulting increase in volume is measured by displacement of mercury from the bottom of the diphenyl ether chamber into a horizontal calibrated capillary tube or into a weighed beaker depending on the amount of heat involved. The heat effect is calculated from the measured volume change using the calibration factor determined by Jessup[3] and confirmed by separate calibrating runs using platinum as a secondary standard.

Silver from Cominco Products, Inc. and lead from American Smelting and Refining Company both having a purity stated by the suppliers to be 99.999+ % were used in the study. The amount of silver and lead in each sample was calculated in advance in order to obtain 1.2 cc in one case or 1.4 cc in the other of alloys at 10 different compositions: 0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, 0.95 g-atom fraction of lead. Samples of pure lead and pure silver were prepared

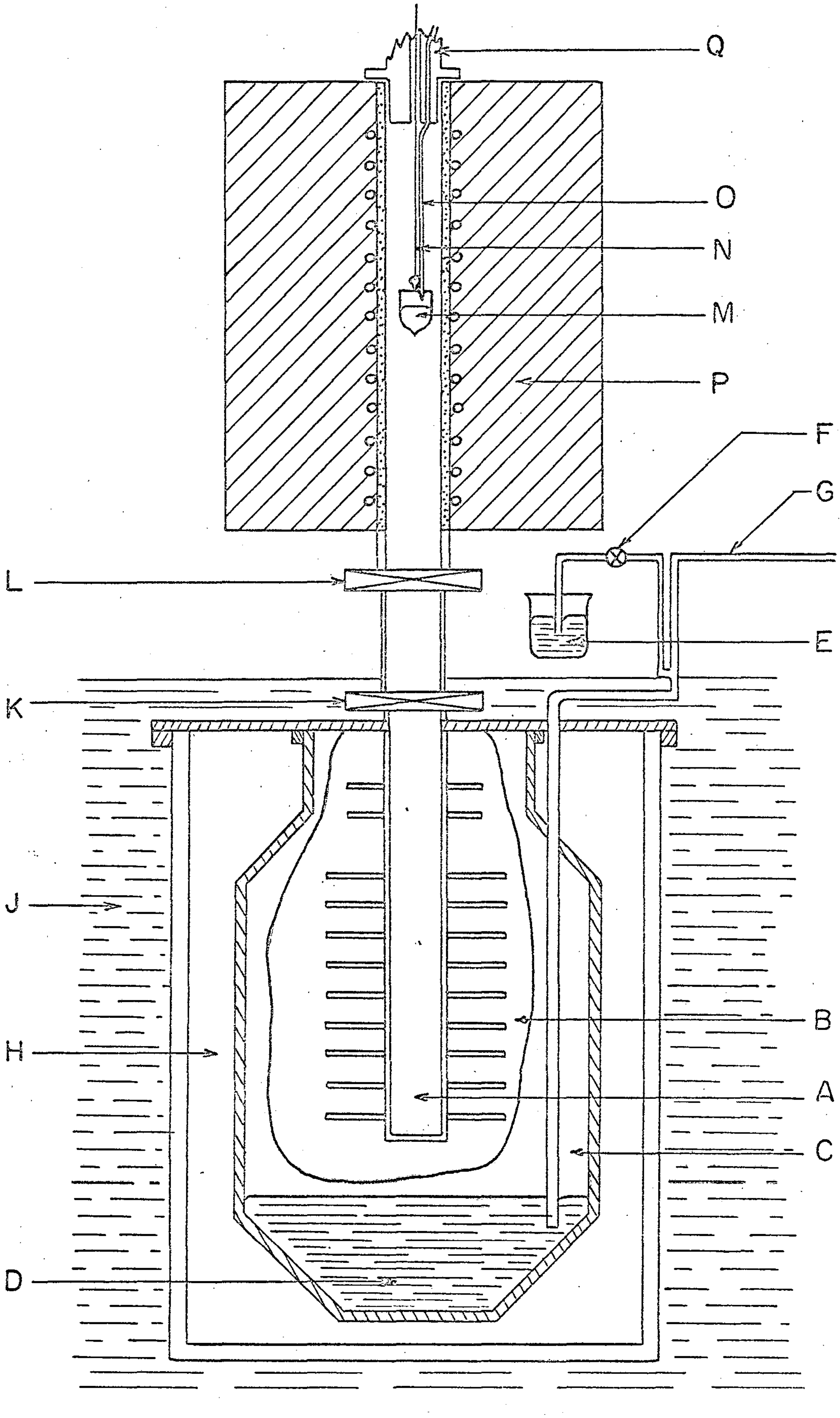

FIG. 3 DIPHENYL ETHER CALORIMETER.

Schematic Drawing of the Diphenyl Ether Calorimeter

A: Calorimeter well
B: Solid diphenyl ether
C: Liquid diphenyl ether
D: Mercury
E: Mercury reservoir
F: Stopcock
G: Calibrated capillary
H: Insulating air space
J: Constant temperature bath
K: Lower gate
L: Upper gate
M: Encapsulated sample
N: Platinum suspension wire
O: Thermocouple
P: Platinum wound furnace
Q: Dropping system

in identical conditions. They were sealed under vacuum in silica capsules. Three different shapes of capsules were used: cylindrical, truncated-conical, and spherical. The alloy of high lead content wetted the silica, causing the capsules to crack from contraction in volume of the alloy on freezing. The spherical shape was found to be the most successful for reducing capsule failure, when filled less than half full.

The sample and capsule weights and the composition of the alloys are recorded in Table I. Correction for the heat contents of silica capsules and heat loss accompanying the drops were determined by dropping capsules of the 3 different shapes, containing the same volume of platinum (to obtain a comparable emissivity) throughout the measured temperature range. Tabulated heat data for platinum[4] were used to determine the heat contents of the capsules minus heat loss during the drop. The measured heat contents of the alloy were corrected for the small difference between the calorimeter temperature 300°K and the standard reference temperature 298.15°K using $Cp_{298.15} = 6.07$ for silver and $Cp_{298.15} = 6.32$ for lead.[4]

Calculations were made using the 1961 International Atomic weights.[5]

Table I

Weights and Compositions of the Samples, Weights of the Capsules

Sample #	Shape	Lead/gm.	Silver/gm.	Capsule/gm.	Composition atom. fract. of Pb
1	cyl.		14.6240	2.9343	0.0000
2	cyl.	1.3719	13.6010	3.0299	0.0499
3	cyl.	3.8079	11.1879	2.9367	0.1505
4	cyl.	5.9081	9.2338	3.2863	0.2498
5	cyl.	7.7513	7.5218	3.2925	0.3491
6	cyl.	9.3957	5.9948	3.1249	0.4493
7	cyl.	10.8759	4.6322	3.0750	0.5500
8	cyl.	12.1873	3.4133	2.9773	0.6502
9	cyl.	13.3730	2.3254	3.0279	0.7496
10	cyl.	14.4406	1.3270	2.9400	0.8499
11	cyl.	15.4541	0.4003	2.9241	0.9526
12	cyl.	15.9040		2.9484	1.0000
13	conical	12.1905	3.4144	3.0255	0.6503
14	conical	13.3744	2.3193	3.1565	0.7497
15	conical	14.4397	1.3298	2.9025	0.8497
16	spher.		10.3552	2.8424	0.0000
17	spher.	0.9788	9.7139	2.8149	0.0498
18	spher.	5.5363	5.3769	2.5275	0.3489
19	spher.	5.5380	5.3728	2.2759	0.3492
20	spher.	9.5534	1.6635	2.3019	0.7493
21	spher.	9.5515	1.7266	2.7843	0.7427
22	spher.	11.0386	0.2887	2.6222	0.9521
23	spher.	11.3611		2.7803	1.0000
24	spher.	11.3586		2.8975	1.0000
25	spher.	11.3646		2.4436	1.0000

IV. CALCULATIONS

For each sample composition a Y function,

$$Y = \frac{H_T - H_{298.15}}{T - 298.15}$$

was calculated at each temperature of measurement. These results have been plotted versus temperature, for the ten alloys, pure silver, and pure lead. Figure 4 gives an example for the composition $x_{Pb} = 0.35$.

Using smoothed values of the Y functions for the alloy and for the pure components, the heat values were obtained from the expression,

$$(\Delta H_T - \Delta H_{298.15})_{alloy} = (H_T - H_{298.15})_{alloy} - (H_T - H_{298.15})_{elements}$$
$$= (T-298.15)\left[Y - \left\{xY_{Pb} + (1-x)\,Y_{Ag}\right\}\right]$$

at even intervals of temperature (every 50°), at the melting point of silver, at the liquidus temperature, and at the melting point of lead. Figure 5 shows $(\Delta H_T - \Delta H_{298.15})_{alloy}$ for the composition $x_{Pb} = 0.75$.

At each temperature $(\Delta H_T - \Delta H_{298.15})_{alloy}$ was plotted versus composition as shown in Figure 6 for the eutectic temperature $T_e = 577°K$. It is gratifying to note that all the curves form straight lines in the two phase region, as they should. The fluctuation is small, showing a high degree of self consistency. Heats of formation from $Ag_{(s)}$ plus $Pb_{(s)}$ can now be obtained by adding $\Delta H_{298.15}$ to the plotted curves. $\Delta H_{298.15}$ would be zero if the final solid phases were pure $Ag_{(s)}$ and pure $Pb_{(s)}$.

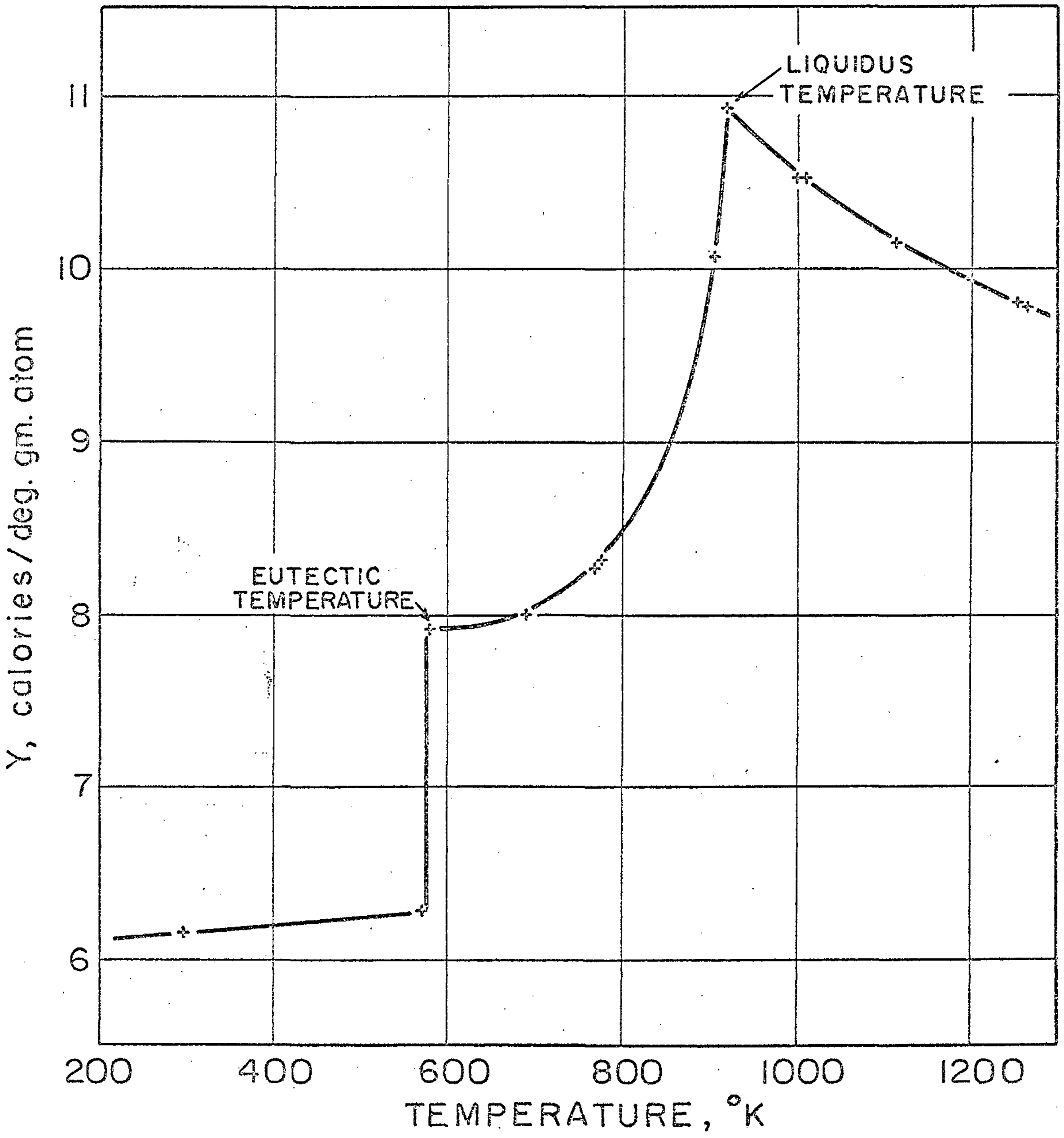

FIG. 4 Y FUNCTION AT $X_{Pb} = 0.35$.

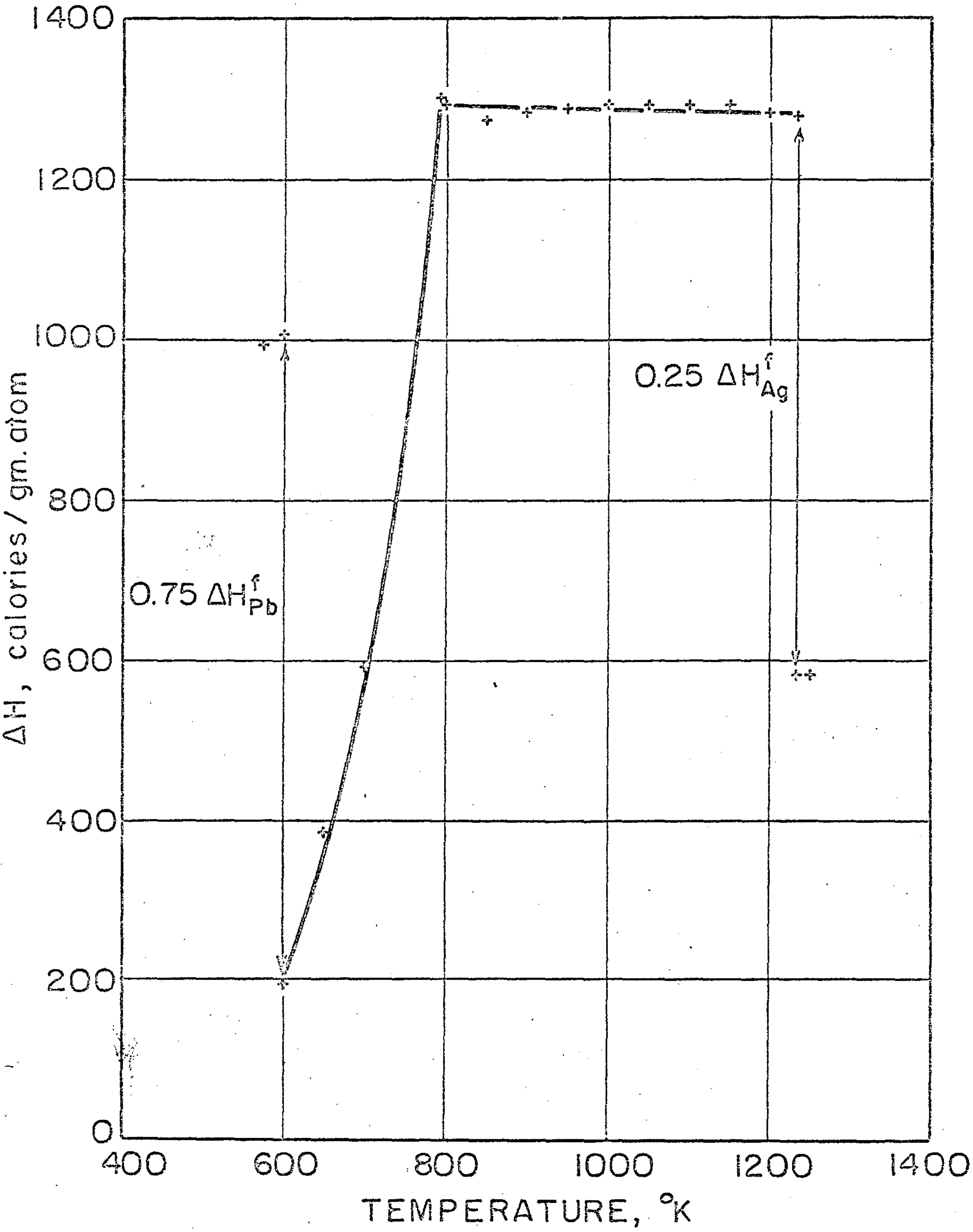

FIG. 5 HEAT OF MIXING AT X_{Pb} = 0.75.

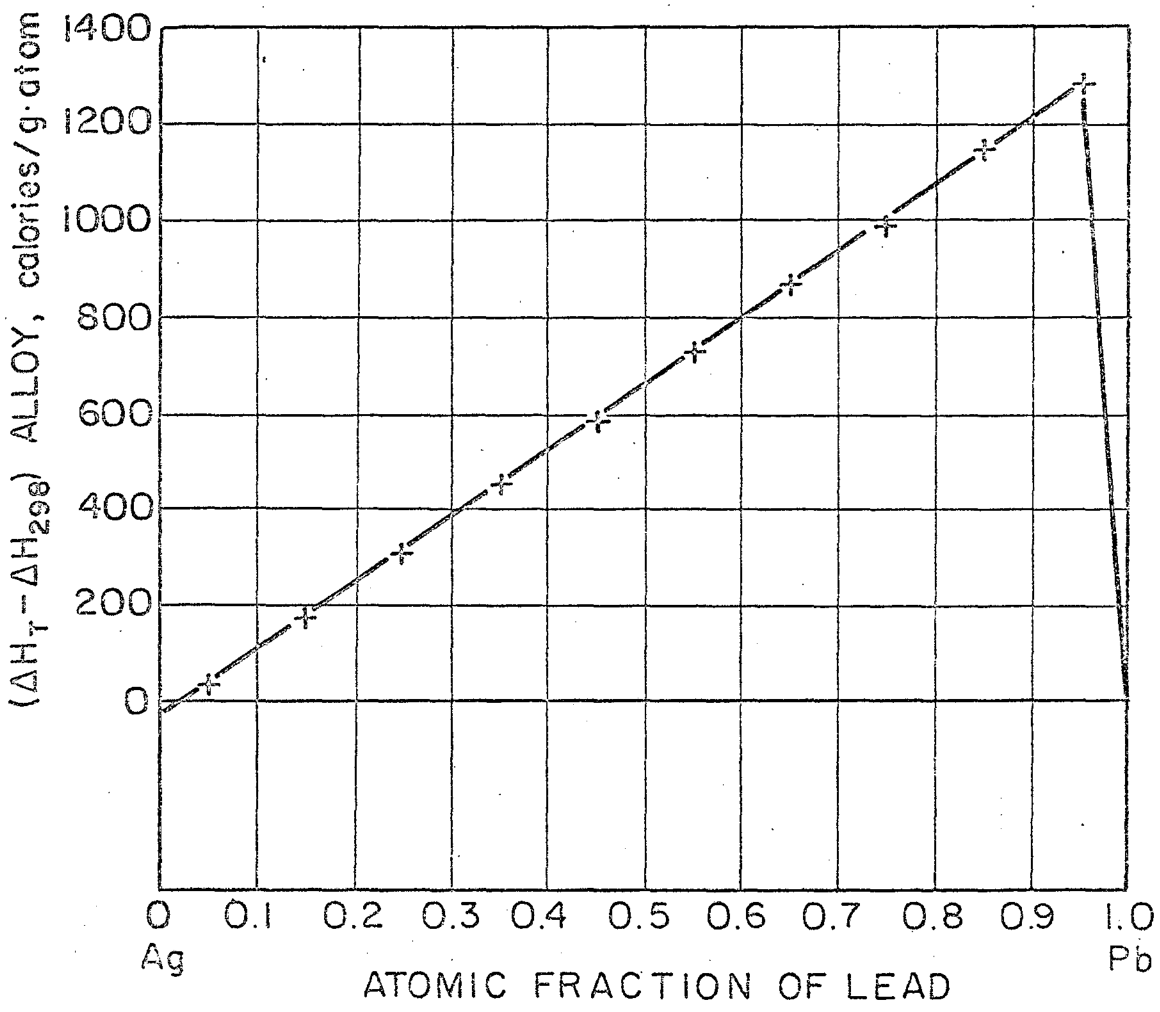

FIG. 6 EXPERIMENTAL DATA FOR $(\Delta H_T - \Delta H_{298})$ AT 577 °K.

However, the alpha (silver-rich) phase is not pure but contains a small amount, x_f, of lead. Therefore,

$$\Delta H_{298.15} = \frac{1-x}{1-x_f} (\Delta H_{\alpha, x_f} + E_{x_f})$$

where ΔH_{α_f} is the heat of formation of the alpha phase of the final product; E_{x_f} is the strain energy; and $\frac{1-x}{1-x_f}$ is the proportion of the alpha phase in the final product.

From the phase diagram, it was calculated (page 9)

$$\Delta H_{\alpha, x_e, T_e} = 54 \text{ cal/g. atom}$$

From the curve of Figure 6

$$(\Delta H_{577} - \Delta H_{298})_{x=0.008} = -20 \text{ cal/g. atom}$$

Hence

$$\Delta H_{\alpha, x_f, 298.15} + E_{x_f} = +74 \text{ cal/g. atom}$$

Lattice constants of the alpha phases in the final products were determined from back reflection X-ray studies. They showed for these alloys quenched from 577°K $x_f = 0.0077$, practically equal to $x_e = 0.008$. If Kopp's law is assumed, then $\Delta H_{\alpha, x_f, 298.15} = 54$ and $E_{x_f} = +20$ cal/g. atom which is reasonable.

For other drop temperatures in the two phase region, the correction was found in a similar manner. $\Delta H_{\alpha, x_f}$, for the alpha phase in equilibrium with the liquid at temperature T was estimated as

$$\Delta H_{\alpha, x_f} = 6800 x_f$$

The corrections are shown in Table II. The X-ray analysis was done

Table II

Correction, as a Function of the Temperature of the Drop for Each Composition, in calories

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	80	68	55	52	45	36	28	20	12	2
600	82	70	57	55	48	46	29	20	12.5	2
650	90	75	60	60	55	56	31	21	13	2
700	100	85	70	65	65	66	33	22	13.5	2
750	110	100	87	70	70	70	35	23	13.5	2
800	120	110	95	85	75	75	37	24	13.5	2
850	130	110	100	90	80	65	38	24	13.5	2
900	130	115	100	85	75	58	38	24	13.5	2
950	125	115	97	85	71	58	38	24	13.5	2
1000	125	115	97	85	71	58	38	24	13.5	2
1050	125	110	97	85	71	58	38	24	13.5	2
1100	125	110	97	85	71	58	38	24	13.5	2
1150	125	110	97	85	71	58	38	24	13.5	2
1200	125	110	97	85	71	58	38	24	13.5	2
1234	125	110	97	85	71	58	38	24	13.5	2
1250	125	110	97	85	71	58	38	24	13.5	2

by taking the reflection of the K - α radiation of copper on the (333) + (511) planes. The diffraction angle for this reflection in pure silver is fairly large (78.4°), which enables us to know the interplanar spacing with good accuracy, $\frac{da_o}{d\theta}$ being very small at large angles. The analysis was done on a pure silver sample used as a standard and on various samples, which had been run in the calorimeter at the temperatures tabulated in Table III. The samples were spark polished and etched in nitric acid to expose undeformed α. The lattice constant and hence the composition x_{α_f} were determined from the values reported by Hultgren and Chiswick[6] and Raub and Polaczek-Wittek.[7]

It remains to consider the correction from samples dropped from the liquid state. x_{α_f} was determined for these samples in the same way and found frequently to be smaller than for alloys dropped from the two phase region because of the influence of retrograde solubility of Pb in the alpha phase. Thus the correction is the same for a given composition for all temperatures in the liquid state, slightly smaller than the correction in the two phase region as shown in Table I.

Values of ΔG_T were obtained from graphical integrations of the Gibbs-Helmholtz equation from 577° to T°K as shown in Equation 7.

The heats of fusion of lead and silver have been determined from the results for the pure metals. The heat of fusion of lead found in this research, 1140 ± 10 cal./g. atom, is in good agreement with the value of 1140 cal./g. atom reported by Douglas and Dever.[8] For silver a value of 2760 ± 10 cal./g. atom has been found, which is about 150 cal.

Table III

X-Ray Analysis

Sample	Composition x_{Pb}	Temperature	a, Å	Pb (at. %) in α phase
Ag	0.00		4.0856	0.00
AgPb-1	0.05	1257	4.0961	1.33
AgPb-3	0.25	1257	4.0950	1.20
AgPb-5	0.45	1257	4.0952	1.22
AgPb-7	0.65	1257	4.0932	0.96
AgPb-4	0.35	576	4.0910	0.77
AgPb-6	0.55	776	4.1018 4.0965	2.05 1.38

higher than the values of Cavallaro,[9] Oelsen,[10] and Wittig,[11] but 95 calories less than Kelley's[12] value. From the measured entropies of fusion the values for ΔG were referred to both liquid silver and liquid lead. The complete thermodynamics of the liquid alloys were then evaluated at 1250°K.

Integral Functions

The experimental values of ΔH have been used to determined the Q values, where

$$Q = \frac{\Delta H}{x(1-x)}$$

From the plot of Q vs. x (Fig. 7), smoothed values of ΔH were obtained. The plot of $\Delta G_{1250^\circ K}$ vs. x (Fig. 9) was found to be perfectly symmetrical. The curve is represented by a power equation of the type

$$\Delta G = a\,[x(1-x)]^{n}$$

where $n = \frac{2}{3}$ $a = 3580$ cal./g. atom

Values of ΔS were calculated from ΔG and ΔH. The integral quantities are plotted in Figure 9.

Partial Molar Functions

From the Q values, the partial molar heat contents were calculated from the expression:

$$\Delta\overline{H}_{Ag} = x^{2}\left[Q - (1-x)\frac{dQ}{dx}\right]$$

and

$$\Delta\overline{H}_{Pb} = \frac{1}{x}\left[\Delta H - (1-x)\,\Delta\overline{H}_{Ag}\right]$$

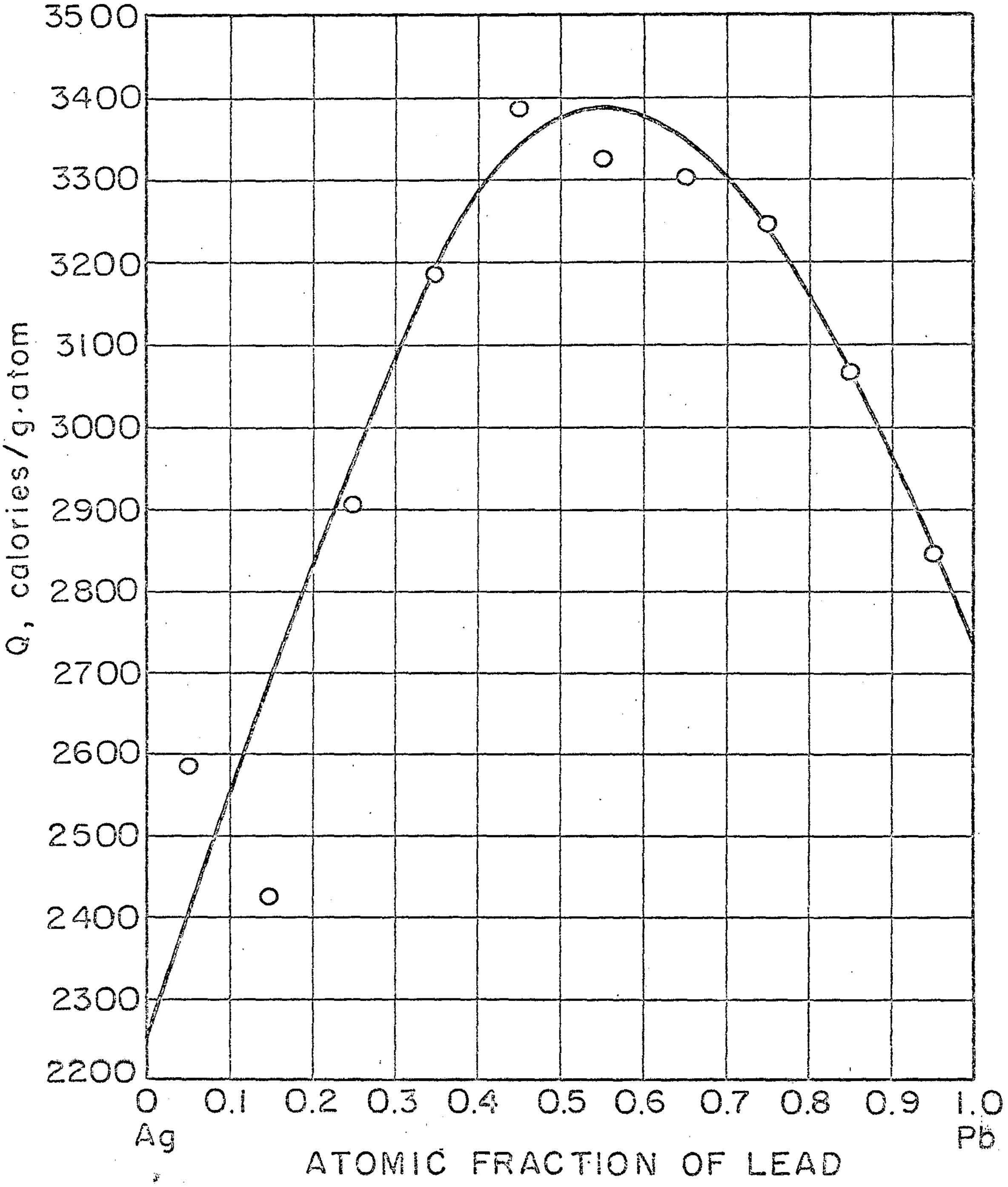

FIG. 7 Q FUNCTION AT 1250°K.

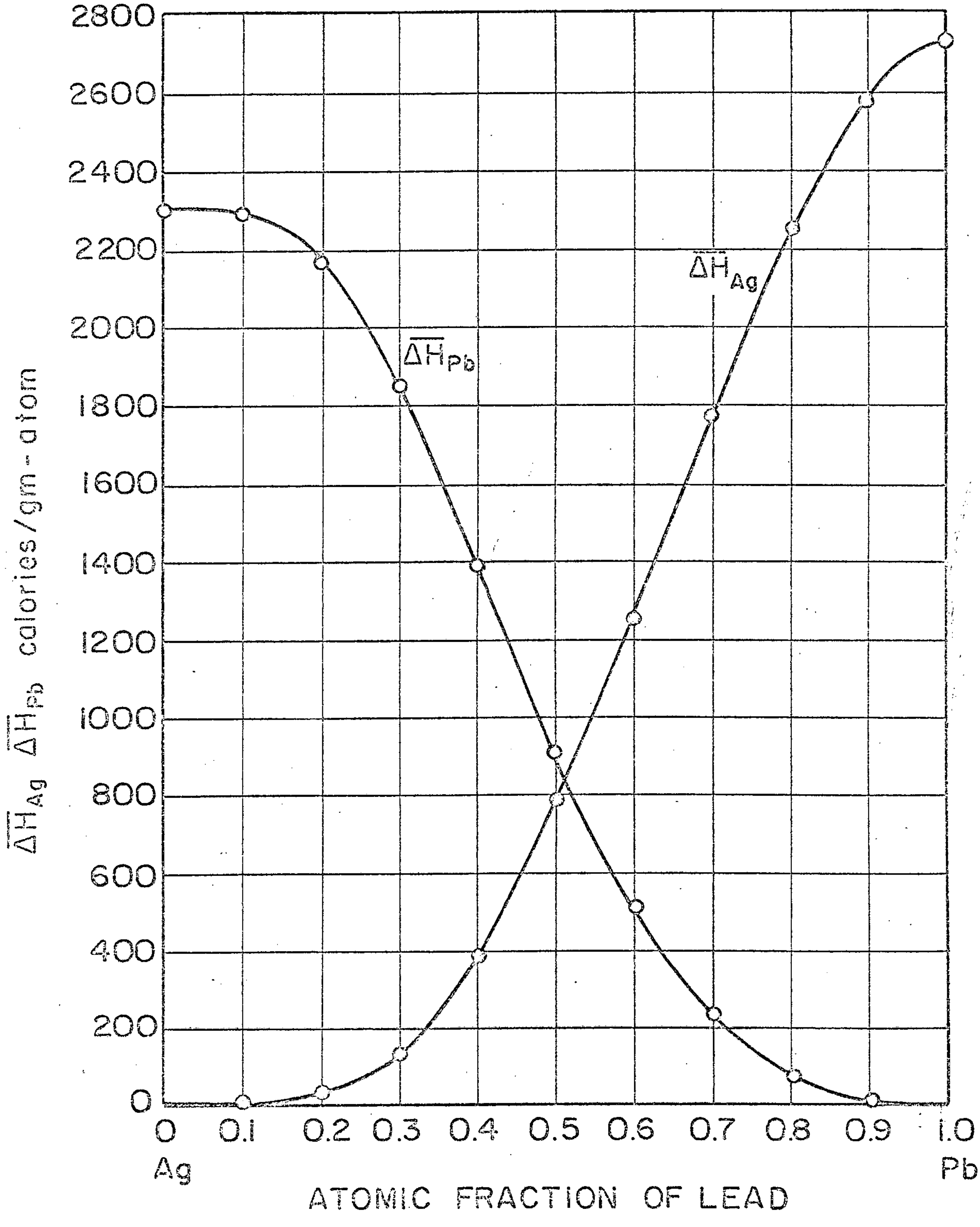

FIG. 8 RELATIVE PARTIAL MOLAR HEATS OF MIXING AT 1250°K.

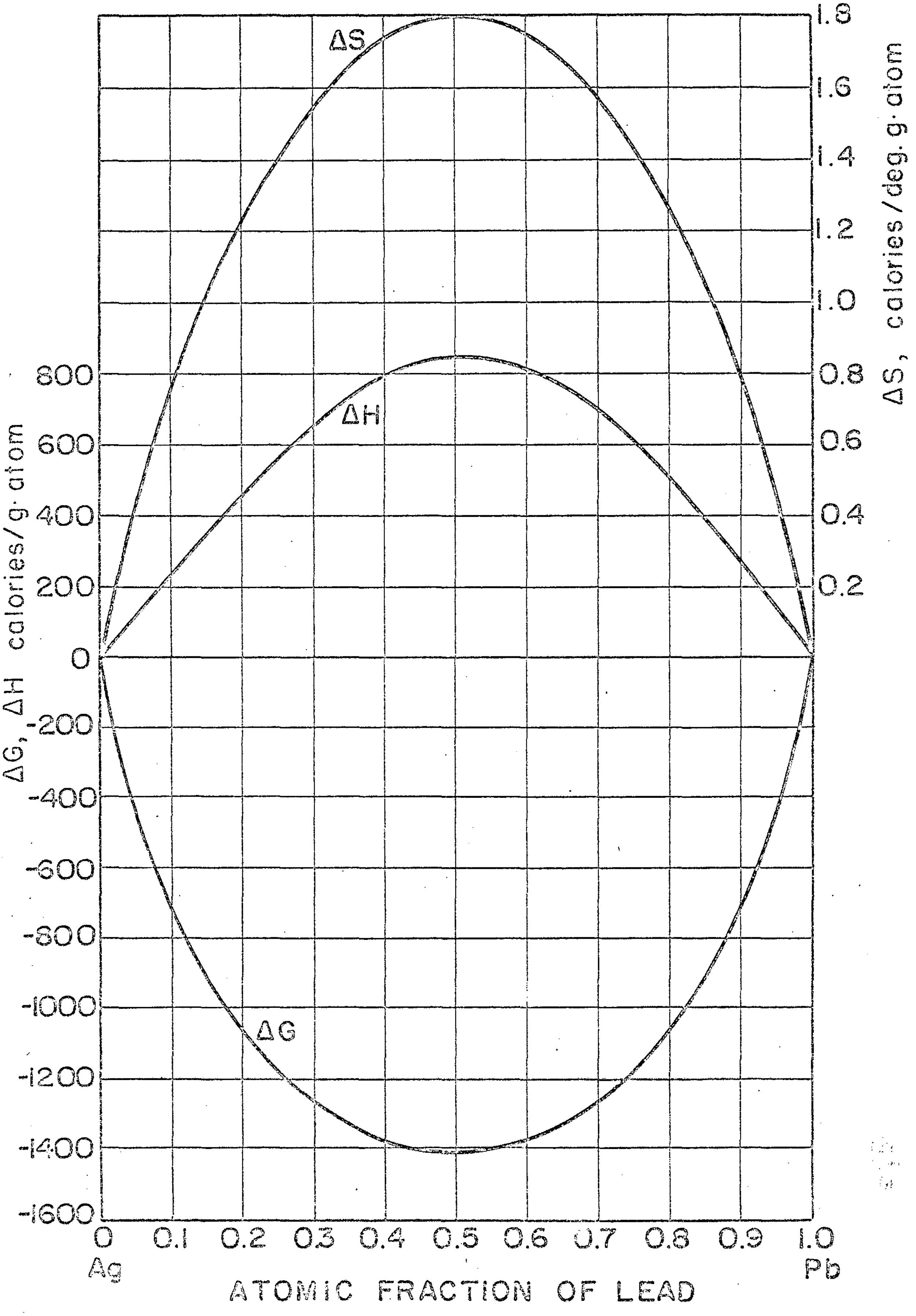

FIG. 9 GIBBS ENERGY, ENTROPY AND HEAT OF MIXING AT 1250 °K.

Values of $\frac{dQ}{dx}$ were obtained graphically from the Q plot. Both partial molar heat contents have been plotted in Figure 8.

The partial molar Gibbs energy for lead was deduced from the equation for ΔG, that is to say:

$$\begin{aligned}\Delta\overline{G}_{Pb} &= \Delta G + (1-x)\ \frac{d\Delta G}{dx}\\ &= a\,[\,x\,(1-x)\,]^{n} + (1-x)\ a\left[n\ [\,x\,(1-x)\,]^{n-1}\ (1-2x)\right]\\ &= a\,[\,x\,(1-x)\,]^{n}\ [1 + nx^{-1} - 2n]\end{aligned}$$

Then, $\Delta\overline{G}_{Ag}$ was obtained from the expression:

$$\Delta\overline{G}_{Ag} = \frac{1}{1-x}\ (\Delta G - x\ \Delta\overline{G}_{Pb})$$

The partial molar entropies were calculated from the partial molar Gibbs energies and enthalpies.

V. RESULTS

The experimental results are listed in Table IV and are shown plotted in Figure 10.

Table V lists smoothed values for heats, entropies and Gibbs energies of formation at 1250°K. Figure 9 shows these values.

Table VI gives the partial molar quantities for silver and Table VII for lead. The partial molar heats of formation for silver and lead have been plotted on Figure 8.

The average ΔCp values, calculated from the slope of a straight line through the ΔH versus T values in the liquid phase, are plotted versus composition in Figure 11.

From the tabulated values for $\Delta\overline{G}_{Ag}$ and $\Delta\overline{S}_{Ag}$ at 1250°K and values of $\Delta\overline{C}p_{Ag}$ obtained graphically from Figure 11, values of $\Delta\overline{G}_{Ag}$ with respect to liquid silver were calculated along the liquidus, using the relationships

$$\left(\frac{\partial \Delta\overline{G}_{Ag}}{\partial T}\right)_x = -\Delta\overline{S}_{Ag}$$

$$\left(\frac{\partial \Delta\overline{S}_{Ag}}{\partial T}\right)_x = \frac{\Delta\overline{C}p_{Ag}}{T}$$

From these quantities, values of $\Delta\overline{G}_{Ag}$ with respect to $Ag_{(s)}$ were obtained assuming the free energy of melting of silver to be given by:

$$\Delta G_{m,T} = (1234 - T)\,\Delta S_m$$

where

$$\Delta S_m = 2.237 \text{ cal./deg./g-atom}$$

Table IV

Experimental Results

x_{Pb}	Sample No.	T, °K	H_T-H_{300}
0	16	1500.0	11162
0	1	1255.0	9220
0	1	1257.0	9228
0	1	1239.8	9113
0	1	1226.2	6286
0	16	1117.5	5427
0	16	1000.0	4592
0	16	901.7	3883
0	16	689.5	2433
0	16	500.7	1736
0	16	570.0	1639
0.05	2	1256.5	9176
0.05	2	1257.7	9197
0.05	2	1242.5	9053
0.05	17	1180.4	8120
0.05	17	1151.5	6985
0.05	17	1222.8	8811
0.05	17	1115.4	6243
0.05	17	1000.0	4875
0.05	17	901.4	4086
0.05	17	776.1	3079
0.05	17	690.1	2500
0.05	17	581.2	1775
0.05	17	570.3	1642
0.05	17	1198.3	8655
0.05	17	1303.9	9537
0.15	3	1254.6	9216
0.15	3	1257.5	9242
0.15	3	1114.5	8112
0.15	3	1004.5	6245
0.15	3	903.1	4727
0.15	3	776.0	3365
0.25	4	1254.0	9339
0.25	4	1256.9	9331
0.25	4	1115.2	8203
0.25	4	1003.4	7365
0.25	4	902.8	5385
0.25	4	776.1	3665

x_{Pb}	Sample No.	T, °K	H_T-H_{300}
0.35	5	1253.1	9362
0.35	5	1258.1	9399
0.35	5	1116.9	8302
0.35	18	1004.9	7444
0.35	18	1000.5	7384
0.35	19	903.2	6076
0.35	19	776.7	3972
0.35	19	775.9	3942
0.35	19	689.9	3118
0.35	19	580.5	2226
0.35	19	568.9	1692
0.45	6	1255.5	9352
0.45	6	1257.1	9395
0.45	6	116.2	8268
0.45	6	1003.4	7438
0.45	6	902.4	6634
0.45	6	776.0	4256
0.55	7	1254.6	9236
0.55	7	1256.7	9222
0.55	7	116.2	8192
0.55	7	1002.9	7370
0.55	7	903.9	6562
0.55	7	900.8	6557
0.55	7	778.3	4567
0.55	7	580.3	2528
0.65	8	1255.4	9051
0.65	8	1256.7	9040
0.65	13	1116.5	8037
0.65	13	1000.1	7210
0.65	13	902.2	6462
0.65	13	776.5	4854
0.65	13	689.3	3745
0.65	13	569.0	1723

Table IV (continued)

Experimental Results

x_{Pb}	Sample No.	T, °K	H_T-H_{300}
0.75	9	1255.2	8772
0.75	14	1256.7	8772
0.75	20	1119.1	7798
0.75	20	1004.1	6955
0.75	21	902.2	6225
0.75	21	775.0	5113
0.75	21	689.1	3955
0.75	21	580.4	2822
0.85	10	1254.2	8442
0.85	15	1256.2	8417
0.85	15	776.2	5007
0.85	15	689.4	4170
0.85	15	580.2	2992

x_{Pb}	Sample No.	T, °K	H_T-H_{300}
0.95	11	1253.7	8020
0.95	22	689.0	3982
0.95	22	579.5	3133
0.95	22	568.8	1784
1.00	12	1256.0	7815
1.00	12	1116.8	6825
1.00	23	1000.3	6014
1.00	24	902.9	5283
1.00	25	776.2	4398
1.00	25	689.6	3694
1.00	25	689.9	3766
1.00	25	589.1	1912.
1.00	25	571.2	1773

Table V

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

Table VI

Partial Molar Enthalpies, Entropies and Gibbs Energies for Ag

x_{Pb}	$\Delta\overline{H}_{Ag}$	$\Delta\overline{S}_{Ag}$	$\Delta\overline{G}_{Ag}$
0.0	0.0	0.0	0
0.1	1.0	0.235	-293
0.2	25.2	0.444	-530
0.3	134.4	0.737	-787
0.4	384.8	1.165	-1072
0.5	786.7	1.757	-1410
0.6	1252.8	2.472	-1837
0.7	1771.4	3.336	-2398
0.8	2249.6	4.344	-3180
0.9	2577.6	5.709	-4559
1.0	2740.0	∞	$-\infty$

Table VII

Partial Molar Enthalpies, Entropies and Gibbs Energies for Pb

x_{Pb}	$\Delta\overline{H}_{Pb}$	$\Delta\overline{S}_{Pb}$	$\Delta\overline{G}_{Pb}$
0.0	2295	∞	$-\infty$
.1	2290	5.483	-4559
.2	2164	4.275	-3180
.3	1846	3.395	-2398
.4	1392	2.584	-1837
.5	902	1.850	-1410
.6	517	1.271	-1072
.7	232	0.815	- 787
.8	70	0.480	- 530
.9	9	0.242	- 293
1.0	0	0.000	0

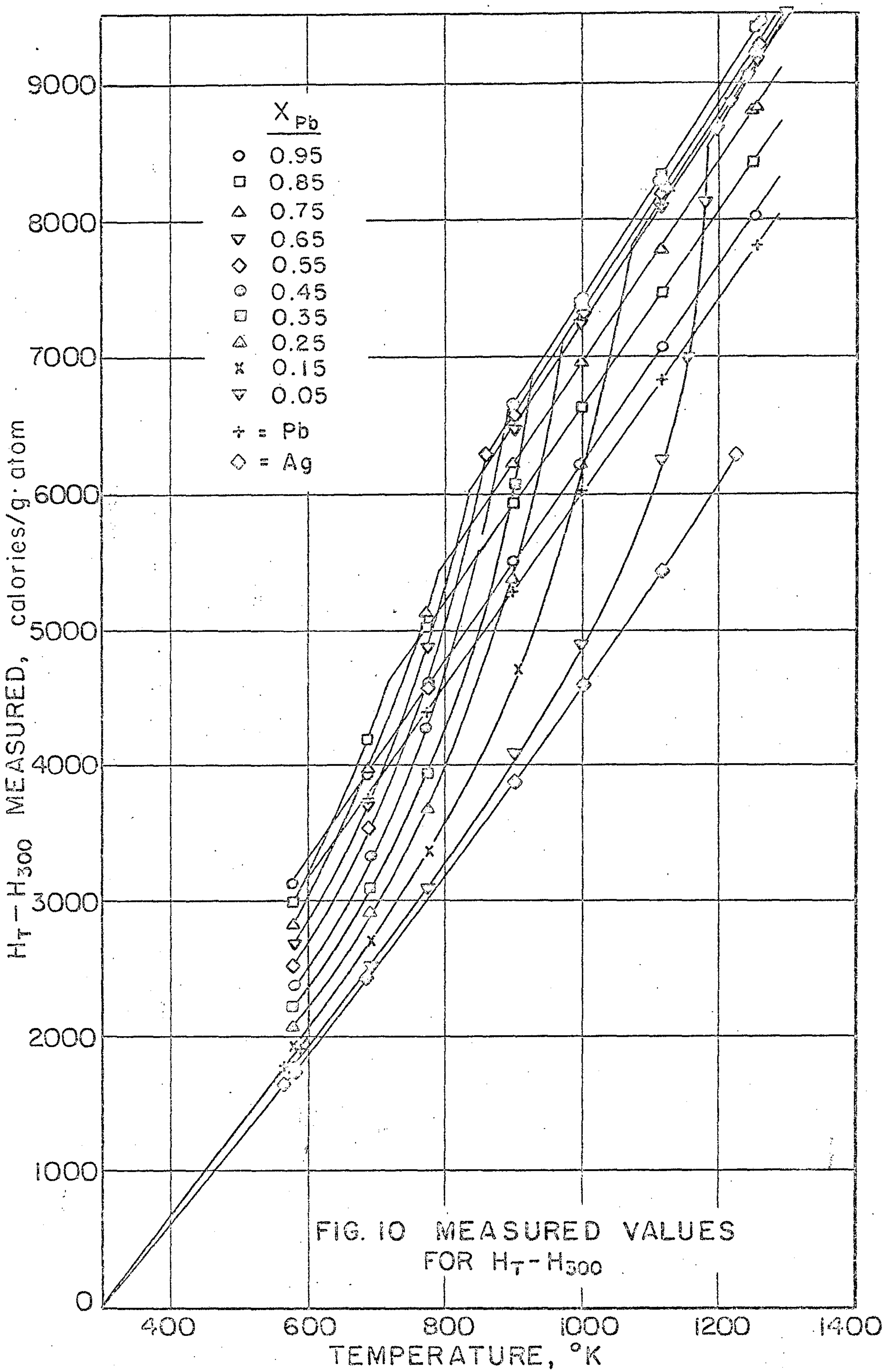

FIG. 10 MEASURED VALUES FOR $H_T - H_{300}$

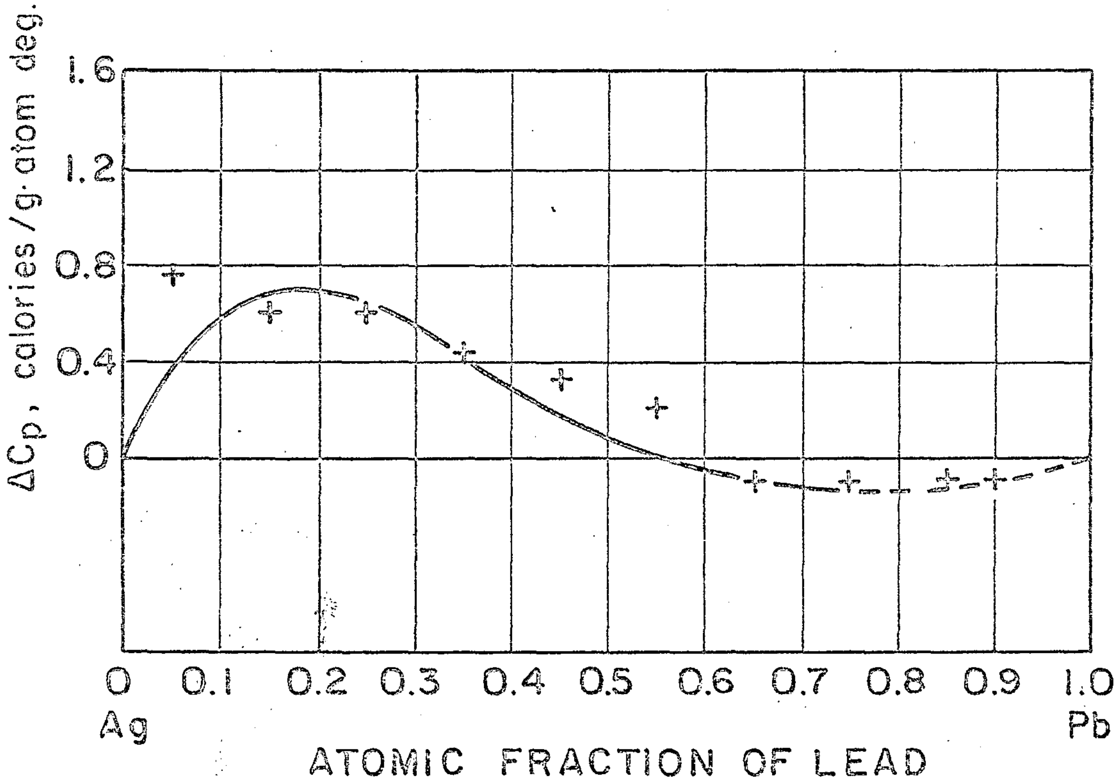

FIG. 11 INTEGRAL ΔC_p VALUES.

All these values agree well within ± 20 calories with the values for $\Delta\overline{G}_{Ag}$ which would be calculated assuming Ag to obey Raoult's law in the α phase, up to 0.7 atomic fraction of lead. For .8 and .9 we have a slight disagreement which can be due to several factors: the uncertainty in the liquidus temperature, the increased uncertainty in the values of ΔG_m for Ag and the large temperature interval over which the integration is performed. Both components show positive deviations from Raoultian behaviour at all compositions and the system is characterized throughout by positive heats and excess entropies of formation. The present results are in good agreement with the free energy values obtained by vapor pressure measurements by Aldred and Pratt,[13] within ± 20 calories, but are about 80 to 100 calories more negative at 1000°K than the values calculated from e.m.f. measurements of Eremenko[14] $x_{Pb} = 0.44$ to 0.91, 720° to 1050°K, and of Terpilowski[15] $x_{Pb} = 0.05$ to 0.93, 773°K to 1273°K. The $\Delta\overline{H}_{Ag}$ for $x_{Pb} = 1.0$ given by Kleppa from solution calorimetry at 723°K is tangent to the present ΔH curve at this temperature[16].

The measurements suggest, as pointed out by Aldred and Pratt, that these liquid alloys must show anomalously large positive deviations from Kopp-Neumann behavior. This observed positive energy of formation may be partly due to a misfit energy arising from the large atom size disparity of the components. The mixing of atoms of differing size and valency may be expected through the influence on the vibrational frequency to result in positive excess specific heats, positive contribution to the enthalpies and excess entropies.

VI. CONCLUSIONS

Even in this very favorable system, the use of drop calorimetry to obtain heats of formation is subject to considerable error unless corrections are made for nonequilibrium in the final state. When the corrections are made, reliable values of entropies and Gibbs energies of formation may be derived in the method recommended by Oelsen. The continuous measurement during cooling suggested by Oelsen[1] will probably not yield reliable values because of nonequilibrium during cooling and in the final state.

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