[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Heat Content of Lead from 0 to 900°, and the Heat of Fusion[1]

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The heat content, relative to 0°, of a sample of 99.9% pure lead was measured at ten temperatures up to 900°, using a container of stainless steel type 446, a silver core furnace, and a Bunsen ice calorimeter. The heat of fusion and the heat capacity of the solid and liquid were derived from the data. The heat capacity, entropy, heat content and free energy are tabulated at intervals over the range 298 to 1200°K.

During the past several years this Laboratory has measured the thermal properties of a number of important heat transfer media. The values of heat capacity of liquid lead reported in the literature show very wide disagreement. The present paper reports precise measurements of this property up to 900°.

Experimental

A cast sample of NBS "standard sample" lead, believed to be purer than 99.9%, was used. A spectrochemical analysis of the sample after its use in the thermal measurements confirmed this order of purity. Of the 54 other metallic elements tested for, only the following were detected: bismuth, between 0.01 and 0.1%; sodium, less than 0.05% (if any); silver, aluminum, calcium, chromium, copper, iron, magnesium, silicon and tin, in trace amounts each less than 0.01%. As the specific heat of bismuth is almost the same as that of lead, the error its presence occasioned is no doubt entirely negligible.

The container for the lead was constructed of stainless steel type 446, as tests made elsewhere[2] indicate that high-chromium steels are only very slowly attacked by liquid lead at the high temperatures involved. The container was filled with and surrounded by helium during the measurements. Its heat capacity shows a marked transition in the region 500–700°, but the only effect this fact seems to have had on the net thermal values for lead was a poorer than average reproducibility in the runs at 500°.

The method, apparatus and correction procedures in measuring the relative heat content have been described in detail elsewhere.[3] The sample is heated in a silver core furnace to a temperature which is measured by a platinum resistance thermometer when not higher than 600°, but otherwise by a platinum–platinum-rhodium thermocouple. It is then dropped into an ice calorimeter, which measures the heat delivered in cooling to 0°. Repetition on the empty container at the same furnace temperature allows subtraction of the heat not contributed by the sample itself.

Results

In Table I is given the fully corrected mean measured heat for each furnace temperature, together with the average devation from the mean.[4] Each observed value listed is the mean of individual measurements whose number is given in parentheses. In each run on the sample, the mass of lead was 45.4857 g.

TABLE I

HEAT CONTENT MEASUREMENTS

Furnace temp. t, °C.[a]	Measured heat,[4] abs. joules With sample	Measured heat,[4] abs. joules Empty container	$H_t - H_0$, net for lead,[b] abs. joules g.$^{-1}$ Obsd.	$H_t - H_0$, net for lead,[b] abs. joules g.$^{-1}$ Calcd. − Obsd.
100.00	1417.9 ± 1.4 (4)	832.1 ± 1.4 (3)	12.88	0.00
200.00	2933.7 ± 1.7 (3)	1740.0 ± 1.7 (4)	26.24	.00
300.00	4545.6 ± 1.1 (3)	2723.5 ± 3.0 (5)	40.06	.00
350.00	6445.0 ± 0.4 (3)	3243.8 ± 2.0 (4)	70.38	− .08
400.00	7314.8 ± 4.6 (4)	3785.2 ± 1.6 (3)	77.60	+ .06
500.00	9107.3 ± 7.0 (6)	4915.3 ± 4.1 (5)	92.16	+ .10
600.00	11244.8 ± 1.0 (3)	6388.1 ± 1.9 (5)	106.77	− .07
701.2	13238.8 ± 3.5 (3)	7725.5 ± 3.0 (3)	121.21	− .03
795.7	14967.4 ± 1.1 (3)	8846.3 ± 3.5 (3)	134.57	− .02
895.3	16754.3 ± 1.4 (3)	10000.1 ± 2.2 (5)	148.49	+ .02

[a] International Temperature Scale of 1948. [b] Lead is liquid above 327.4°.

The last column of Table I refers to the values calculated from the empirical equations derived by least squares to fit the observed values of heat content. These equations, in abs. joules g.$^{-1}$ at t, °C., are

$$H_t(\text{solid}) - H_0(\text{solid}) = 0.12649t + 2.349(10^{-5})t^2 \quad (0 \text{ to } 327.4°) \qquad (1)$$

$$H_t(\text{liquid}) - H_0(\text{solid}) = 17.76 + 0.152721t - 7.466(10^{-6})t^2 \quad (327.4 \text{ to } 895°) \qquad (2)$$

Differentiation gives the heat capacity (in abs. joules g.$^{-1}$ deg. C^{-1} at t, °C.)

$$C_p(\text{solid}) = 0.12649 + 4.70(10^{-5})t \; (0 \text{ to } 327.4°) \qquad (3)$$

$$C_p(\text{liquid}) = 0.15272 - 1.493(10^{-5})t \; (327.4 \text{ to } 895°) \qquad (4)$$

TABLE II

THERMODYNAMIC FUNCTIONS OF LEAD. (CAL. DEG.$^{-1}$ G.-ATOM^{-1})

T, °K.	$C_p°$	$S°$	$\frac{H^0 - H^0_{298.16}}{T}$	$-\left(\frac{F^0 - H^0_{298.16}}{T}\right)$
298.16	6.32	15.49	0	15.49
300	6.33	15.529	.039	15.490
325	6.38	16.038	.525	15.513
350	6.44	16.513	.945	15.568
375	6.50	16.959	1.314	15.645
400	6.56	17.381	1.640	15.741
425	6.62	17.780	1.931	15.849
450	6.68	18.160	2.193	15.967
475	6.73	18.523	2.430	16.093
500	6.79	18.870	2.647	16.223
525	6.85	19.202	2.846	16.356
550	6.91	19.522	3.029	16.493
575	6.97	19.831	3.199	16.632
600	7.02	20.128	3.357	16.771
600.6 (s)	7.03	20.135	3.361	16.774
600.6 (l)	7.32	22.034	5.260	16.774
650	7.28	22.612	5.415	17.197
700	7.25	23.151	5.548	17.603
750	7.21	23.650	5.660	17.990
800	7.17	24.114	5.756	18.358
850	7.14	24.548	5.838	18.710
900	7.10	24.955	5.909	19.046
950	7.06	25.337	5.971	19.366
1000	7.03	25.699	6.024	19.675
1050	6.99	26.041	6.071	19.970
1100	6.95	26.365	6.112	20.253
1150	6.92	26.673	6.148	20.525
1200	6.88	26.967	6.179	20.788

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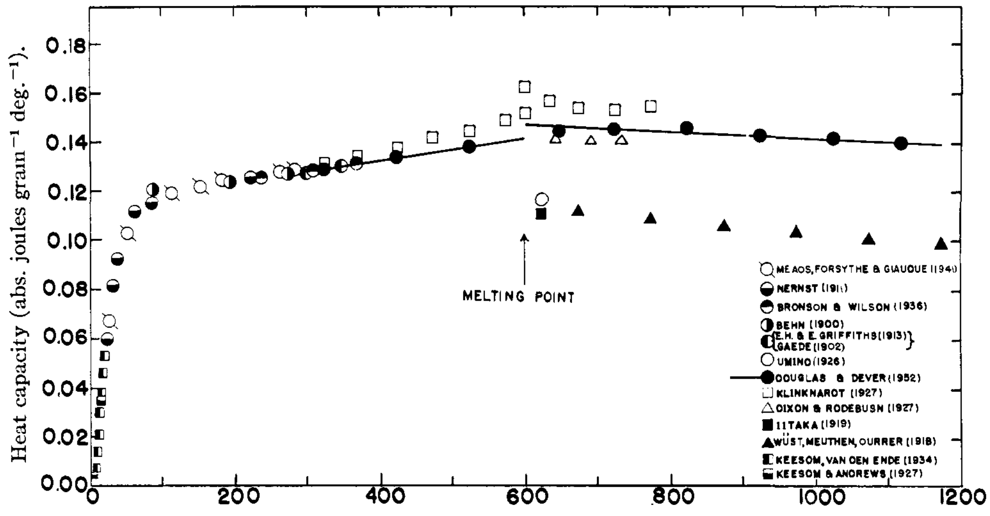
(1) This work was supported by the Atomic Energy Commission.

(2) "Liquid Metals Handbook," 2nd Edition, U. S. Govt. Printing Office, Washington, D. C., 1952.

(3) D. C. Ginnings, T. B. Douglas and A. F. Ball, *J. Research Natl. Bur. Standards*, **45**, 23 (1950).

(4) Each average deviation from the mean has been adjusted to the basis of an infinite number of observations by multiplying by the factor $\sqrt{n/(n-1)}$, where n is the number of observations actually made at that temperature.



Temperature (° K.).

Fig. 1.—Heat capacity of lead.

The melting point of lead was not determined by the authors. Mellor[5] and Kelley[6] both listed 327.4° as the best representative value, and those of ten investigators are said to agree with this value within ±0.5°. At this temperature, combination of equations 1 and 2 gives 23.03 abs. joules g.$^{-1}$ for the heat of fusion. The values of eight investigators, which average 1.3% higher, vary over a range of about 25%.[6]

Based on their own low temperature heat capacity measurements, a table of thermodynamic functions of lead from 15 to 300°K. was given by Meads, Forsythe and Giauque.[7] They found 15.51 cal. g.-atom^{-1} deg.$^{-1}$ for the entropy at 298.16°K. Using instead Kelley's[8] more recently recalculated value of 15.49 ± 0.05, and equations 1 and 2, the thermodynamic functions of Table II were computed.[9]

Discussion

Figure 1 affords a comparison of the smoothed heat capacity values of lead given by equations 3 and 4, with those calculated from successive heat content differences in Table I, as well as with the values found by other investigators.[7,10–21]

Several checks on the accuracy of the furnace and ice calorimeter used to measure the values reported in this paper have been afforded by comparison with the values on a number of pure substances measured also in other precise calorimeters at the National Bureau of Standards. In comparison with the unusually accurate results of Osborne, Stimson and Ginnings,[22] who used an adiabatic calorimeter, the same apparatus that was used to measure lead gave for water *mean* heat capacities 0.05 ± 0.12% higher over the range 0 to 25°, and 0.02 ± 0.02% higher over the range 0 to 250°.[23] Over the common temperature range of measurement, 0 to 100°, it has usually given higher heat capacities, but by not more than 0.2%, than those given for the same substances by the present NBS low-temperature adiabatic calorimeters.

Compared with the authors' values for the heat capacity of solid lead, the values found by Bronson and Wilson[11] and those by Griffiths and Griffiths[13] agree within 0.15% on the average, whereas Meads, Forsythe and Giauque,[7] whose measurements extend up to 300°K., found at this temperature a value 1.4% higher than that in Table II.[24] The present results on solid lead are based on heat content measurements covering only three temperature intervals (of 100° each), and the heat capacity near the bottom of the range of measurement must be assigned an enhanced uncertainty. Nevertheless, the resulting mean heat capacity between 273 and

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[5] J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. 7, Longmans, Green and Co., Inc., New York, N. Y., 1922–1937, p. 531.

[6] K. K. Kelley, *U. S. Bur. Mines Bulletin*, **476**, U. S. Govt. Printing Office, Washington, D. C., 1949, p. 92.

[7] P. F. Meads, W. R. Forsythe and W. F. Giauque, THIS JOURNAL, **63**, 1902 (1941).

[8] K. K. Kelley, *U. S. Bur. Mines Bull.*, **434**, 50 (1948).

[9] 0°C. = 273.16°K., 1 cal. = 4.1840 abs. joules, and the at. wt. of Pb = 207.21.

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[11] H. Bronson and A. J. C. Wilson, *Can. J. Research*, **14A**, 181 (1936).

[12] U. Behn, *Ann. Physik*, [4] **1**, 257 (1900).

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[20] W. H. Keesom and J. N. van den Ende, *Koninkl. Ned. Akad. Wetenschap.* (*Proc.*), **34**, 210 (1934).

[21] W. H. Keesom and D. H. Andrews, *Comm. Phys. Lab.*, Univ. Leiden, no. 185a (1927).

[22] N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 197 (1939).

[23] The precision is expressed as the probable error of the mean. The sample masses of water and lead actually used were such that the total mean heat capacity of the water sample was about five times that of the lead sample over each of these two temperature intervals.

[24] The heat capacity of mercury at 298.16°K. as recently reported by R. H. Busey and W. F. Giauque, THIS JOURNAL, **75**, 806 (1953), is 0.4% higher than the corresponding value of T. B. Douglas, A. F. Ball and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **46**, 334 (1951). Substantially the same respective calorimeters were used as for lead.

373°K. is 6.38 ± 0.01[23] cal. g.-atom^{-1} deg.$^{-1}$; and with this the values of Meads, Forsythe and Giauque, which increase almost linearly from 6.183 at 200° to 6.418 at 300°K., obviously cannot be made to agree by any plausible extrapolation.

So far as the present measurements indicate, the heat capacity of solid lead increases uniformly with temperature above 273°K. It is noteworthy that the values of Meads, Forsythe and Giauque increase at almost exactly the same rate between 200 and 300°K. One is led to wonder whether the discrepancy between the two sets of values is due to a different state of the lead. Prior to their measurements they had crystallized theirs over a period of several days, whereas the sample of the present investigation had previously been melted and recrystallized rapidly. However, the heat content values on the solid for any one furnace temperature (of which the first was 300°) showed no trend with time, and it is difficult to believe that this metal could be held for a total of several hours at temperatures as near its melting point without the occurrence of thorough annealing.

In this connection, heat content measurements were made in this Laboratory a few years ago on samples of highly pure sodium following very slow and afterwards very rapid crystallization.[3] The mean capacity after the latter treatment was found to be different by the following percentages: 0–59°, 0.4 ± 0.15% higher; 0–40°, 0.25 ± 0.15% and 0.5 ± 0.2% lower.[23] This evidence, of course, is largely inconclusive.

The heat capacity of lead in the liquid state has been found to decrease with temperature over a considerable range just above the melting point. This has been found true of numerous other liquid metals, alloys, and salts. One such material may be the liquid eutectic alloy of lead and bismuth (45% Pb), for which the authors recently obtained an average heat capacity between 150 and 800° of 0.142 abs. joule g.$^{-1}$ deg.$^{-1}$, and an indication from the less precise results that the heat capacity may decrease with temperature by 0.01–0.02% per deg. The heat capacity of liquid lead, which according to equation 4 averages over the same temperature range 2–3% higher (per g. or per g. atom), decreases 0.01% per deg.

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[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Lithium Fluoride: Heat Content from 0 to 900°, the Melting Point and Heat of Fusion[1]

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Using an ice calorimeter and a silver-core furnace, the relative heat content of lithium fluoride was measured from 0 to 900°. The melting point was found to be 848 ± 1°. The derived heat capacity of the solid is believed accurate in general to ±0.5%, and that of the liquid over the 42° range of measurement, to ±1.5%. The heat capacity–temperature curve, which is in good agreement with recently reported values from −254 to −1°, possesses a point of inflection at approximately 450°. The values of entropy and free energy also were calculated.

The alkali halides, because of their structural simplicity and high stability, have been studied extensively for many years, with a relatively high degree of success in coördinating and explaining their properties. Yet much of this work has been handicapped by a lack of accurate data at high temperatures. The measurements reported here extend thermal values for lithium fluoride to 50° above its melting point.

Experimental

Sample.—The lithium fluoride was obtained from the Harshaw Chemical Co., Cleveland, Ohio, in the form of single crystals of approximately 1 cc. each. A spectrochemical analysis of the original sample showed the metallic impurities to be a few thousandths of 1% each of calcium, magnesium, sodium and nickel, plus traces of aluminum, chromium, iron and silicon. After the measurements in a nichrome container had been completed, similar analyses revealed in addition a few hundredths of 1% of chromium and a few thousandths of 1% of aluminum, manganese and silicon. The constancy of temperature during melting and freezing, described later, is in accord with these analyses.

Calorimetric Procedure.—The method and apparatus have been described in detail previously.[2] Briefly, the sample in a container is heated in a furnace to a known temperature and is then dropped into an ice calorimeter that measures the heat evolved in cooling sample and container to 0°. Adequate time, as determined by special tests, was allowed for equilibration, with particular attention to those runs in which the furnace temperature was only a few degrees above the melting point. The heat contributed by the container and that lost during the drop into the calorimeter were accounted for by similar measurements on the empty container, which was constructed of Nichrome V and, after filling with helium, was sealed by a gold gasket. The temperature of the furnace core, maintained highly uniform by a housing of silver 1/2 in. thick, was measured up to 600° by a platinum resistance thermometer and above 600° by a platinum-platinum-rhodium thermocouple. All measuring instruments were calibrated at the National Bureau of Standards, and very small corrections were applied for unavoidable inconsistencies in temperature and masses of container materials entering the calorimeter.

Melting Point.—A separate sample of lithium fluoride in a helium-filled Inconel container was suspended in the furnace. By maintaining the temperature of the latter constant to ±0.1° for successive periods of several min. each at approxi-

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[1] This work was sponsored by the U. S. Air Force, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] D. C. Ginnings, T. B. Douglas and A. F. Ball, *J. Research Natl. Bur. Standards*, **45**, 23 (1950); THIS JOURNAL, **73**, 1236 (1951).