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HEAT CAPACITY OF LIQUID BISMUTH

FIRST TECHNICAL REPORT

BY

HOWARD BELL
RALPH HULTGREN

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MATERIALS RESEARCH LABORATORY
INSTITUTE OF ENGINEERING RESEARCH
UNIVERSITY OF CALIFORNIA, BERKELEY

HEAT CAPACITY OF LIQUID BISMUTH(1)

by

Howard Bell(2) and Ralph Hultgren(3)

First Technical Report

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(1) Report based on a thesis by Howard Bell submitted in partial satisfaction of the requirements for the degree of Master of Science in Metallurgy to the University of California.
(2) Graduate Student, University of California, Berkeley.
(3) Professor of Metallurgy, University of California, Berkeley.

ABSTRACT

The true heat capacity of liquid bismuth was measured from within three tenths of a degree of the melting point (544.5°K) to 801.8°K by a method of mixtures using a liquid bismuth calorimeter. The results show a decrease in heat capacity with increasing temperature. This is in agreement with a trend which has been observed for the heat capacities of other liquid metals.

The results of the investigation are discussed in relation to the structure of the liquid. One conclusion reached is that there are associations similar to those found in the solid in the vicinity of the melting point which break up with increasing temperature.

INTRODUCTION

The prospect of extensive use of atomic power reactors has made urgent the problem of heat delivery from liquid coolants. The thermal diffusivity of a coolant is defined as the ratio of thermal conductivity to the product of specific heat and density. Liquid metals which are chemically stable at elevated temperatures and have a high thermal conductivity naturally play a major role in this field. As a result of its low melting point (544.5°K) and low absorption cross section for thermal neutrons, bismuth is a possible reactor coolant. One of the important heat transfer properties of liquid bismuth, specific heat, will be the subject of this investigation.

Knowledge of the heat capacity of liquids is also of interest since it may offer a sensitive measure of changes of structure. Some theories predict that atoms in the liquid, when just above the melting point, are associated in quasi-crystalline arrangements. An abnormal metal such as bismuth, in which the solid and liquid states differ markedly both in structure and physical properties, would be particularly subject to quasi-crystalline aggregations near the melting point, owing to the persistence in the liquid of forces acting on the atoms in the solid. These associations should be broken up by rising temperature, and this effect should be indicated by an anomalously high heat capacity.

In most cases measurements of the heat capacity of liquid metals lack sufficient accuracy to determine any definite trend. The usual procedure is to pass a straight line through the scattered results of heat content measurements, the slope giving a heat capacity which is constant with temperature[1]. Precise measurements of liquid heat capacity have been carried out on only a limited number of metals: lead, mercury, sodium, potassium, lithium[2], tin[3, 4], and indium[5]. In each case the heat capacity was determined directly and found to decrease with increasing temperature. In several cases Cp reached a minimum at a temperature somewhat above twice the melting point, and increased thereafter.

Direct measurements of the heat capacity of liquid bismuth have been carried out by Förster and Tschentke[6], Carpenter and Harle[7], and Person[8]. Förster and Tschentke found a decrease in Cp from the melting point to 690°K and increasing values thereafter but had considerable scatter, while Carpenter and Harle found decreasing Cp in the range 544. 5° - 640°K and Person reports a constant value of 7. 59 cal/deg. g-atom. Heat capacity values have also been determined from heat content data. Umino[9] reported a constant value of 7. 80, while Wüst and Meuthen[10] found a linear increase with temperature from 7. 1 at 544°K to 8. 76 at 1273°K.

The present investigation is designed to accurately determine the heat capacity of liquid bismuth directly. The results should be an important contribution to the thermodynamic knowledge of bismuth and offer further evidence as to whether or not decreasing heat capacity is a characteristic of liquid metals. Data in the vicinity of the melting point should also offer an insight to the structural changes occurring during the melting phenomena.

APPARATUS

A liquid-metal solution calorimeter has been adapted for these measurements. This apparatus has been described in detail elsewhere[12, 13]; therefore only a brief description will be given here.

The core of the apparatus is the liquid-bismuth bath, which consists of about 621 grams of liquid bismuth contained in a thin-walled molybdenum crucible. The crucible rests upon three sharp points of insulating refractory and is surrounded by a cylindrical nickel-plated copper jacket which weighs about ten kilograms. The jacket is heated by three series-connected Nichrome heating elements wound on an alundum tube at the sides and on ceramic disks at both ends of the jacket. A sensitive resistance-thermometer temperature controller makes it possible to prevent externally caused temperature drifts or fluctuations in the copper jacket either before or during a run. It is therefore possible to obtain constancy of the calorimeter temperatures to within less than ±0.001°C prior to making a run. A series of nickel radiation shields provide insulation from the rest of the apparatus.

The bath temperature is measured by a copper-constantan thermocouple extending into the center of the liquid bismuth inside a molybdenum protection tube. The jacket temperature is measured by a similar couple located in a vertical hole near the jacket wall ending at a point opposite the crucible. The couples have a common constantan leg making it possible to switch the leads appropriately to measure either temperature separately or the difference between the two. The jacket temperature is also measured by a platinum---platinum plus ten percent rhodium couple.

Thermocouple emf's are measured on a shielded White double potentiometer in connection with a moving coil reflecting galvonometer, meter scale and telescope. The sensitivity is such that a scale deflection of one mm. corresponds to a change of about 0.015 microvolt (0.00024° C) in the reading of the differential couple between the jacket and crucible.

The upper part of the apparatus contains the dispenser unit from which specimens are ejected one at a time into the bath. Specimens are solid pellets of pure bismuth with diameters of 5-1/2 mm. or less. A thermocouple measures the specimen temperature prior to the drop.

Previous investigations[3, 4, 5] have found that the cold samples which are dropped into the bath can cause too low a temperature reading if they come into close contact with the thermocouple. To prevent error from this source a tantalum funnel was placed inside the crucible to act as a baffle.

The units of the apparatus are supported in a vacuum-tight, water-cooled shell, which is evacuated to a pressure of 10^{-7} atmospheres during the runs.

SAMPLE

The bismuth used for both the bath and the pellets was supplied by Consolidated Mining and Smelting Co. This bismuth was 99.9999% pure. A spectrographic analysis found only a trace of iron to be present as impurity.

EXPERIMENTAL PROCEDURE

In preparing for the series of runs, bismuth was melted into a molybdenum crucible. This step was carried out in an argon atmosphere to prevent oxidation of the bath. After the bath had cooled to room temperature it was removed from the furnace and placed inside the calorimeter. Crucible and contents were then raised to temperature.

A run consisted of dropping a small bismuth pellet, initially at room temperature, into the bath of liquid bismuth. Previous to making a drop, readings of both the jacket temperature and the difference in temperature between the jacket and crucible were taken. These readings were made for a period of approximately twenty minutes to insure that steady-state conditios, in which the temperatures were constant to within ±0.001°C, existed in the calorimeter. The temperature of the specimen was recorded just prior to its being dropped into the bath. After a drop, readings of the differential and jacket temperatures were taken at frequent intervals until temperature uniformity had been attained within the crucible.

The heat transfer coefficient between the jacket and crucible was determined from measurements of the rate of return to steady-state conditions within the calorimeter after the reaction period. For the small differences of temperature involved (~ 1°C) the valid assumption was made that the net heat transfer between jacket and crucible followed Newton's law. The heat transfer correction for the reaction period was then evaluated using established methods based on Newton's law of heat transfer.

The amount of heat absorbed by the bismuth pellet was first calculated from the compiled heat content of bismuth[11]. The heat content was later recalculated, taking the heat content at the melting point to be 4200 kcal/mole, by graphically integrating the experimentally determined heat capacity curve. The calculations were repeated until a self-consistent set of heat content and heat capacity values were obtained.

The method of calculation used for the corrected temperature change of the liquid bismuth was that described by Orr, Goldberg, and Hultgren[12] in their work with liquid tin. Corrections were made for the heat capacity of the molybdenum crucible and thermocouple protection tube, the tantalum funnel, the copper-constantan thermocouple, and its asbestos covering by using the respective Cp values found in the literature[13]. A typical calculation of the heat capacity is shown on the Sample Calculation Sheet in the Appendix.

THERMOCOUPLE CALIBRATION

The copper-constantan thermocouple that measured the initial temperature of the specimen was calibrated against a Bureau of Standards calibrated platinum---platinum plus ten percent rhodium couple. The Cu-constantan thermocouple that measured the bath temperature was calibrated at the melting point of bismuth, which was taken to be 544.5°K. The couple was found to read 1.17° too high. The correction was assumed to be constant for all measurements.

EXPERIMENTAL DATA

The experimentally determined heat capacities are presented in Table I. In each of the runs, Newton's law was obeyed during the return of the crucible to the jacket temperature.

The heat content at the melting point was assumed to be 4200 cal/g-atom, a value in agreement with that reported by several investigators[11]. The heat contents at other temperatures were obtained from the values of Cp determined in this investigation. The selected values of heat contents and heat capacities are listed in Table II.

Figure 1 shows the plot of Cp versus temperature obtained in this investigation together with the data reported by other investigators.

TABLE I

Experimentally Determined Heat Capacity Data for Liquid Bismuth

Run No.	T, °K	Cp cal/deg. g-at.	Run No.	T, °K	Cp cal/deg. g-at.
21	801.7	6.69	8	577.4	7.13
20	801.8	6.72	7	577.4	7.13
19	755.2	6.83	2	558.5	7.22
18	755.3	6.76	1	558.5	7.21
17	698.1	6.79	11	545.9	7.32
16	698.1	6.86	10	546.6	7.29
			12	545.4	7.28
6	653.4	6.92	13	545.4	7.33
5	653.4	6.92	9	546.6	7.30
4	606.3	7.03	15	544.8	7.34
3	606.8	6.92	14	545.2	7.27

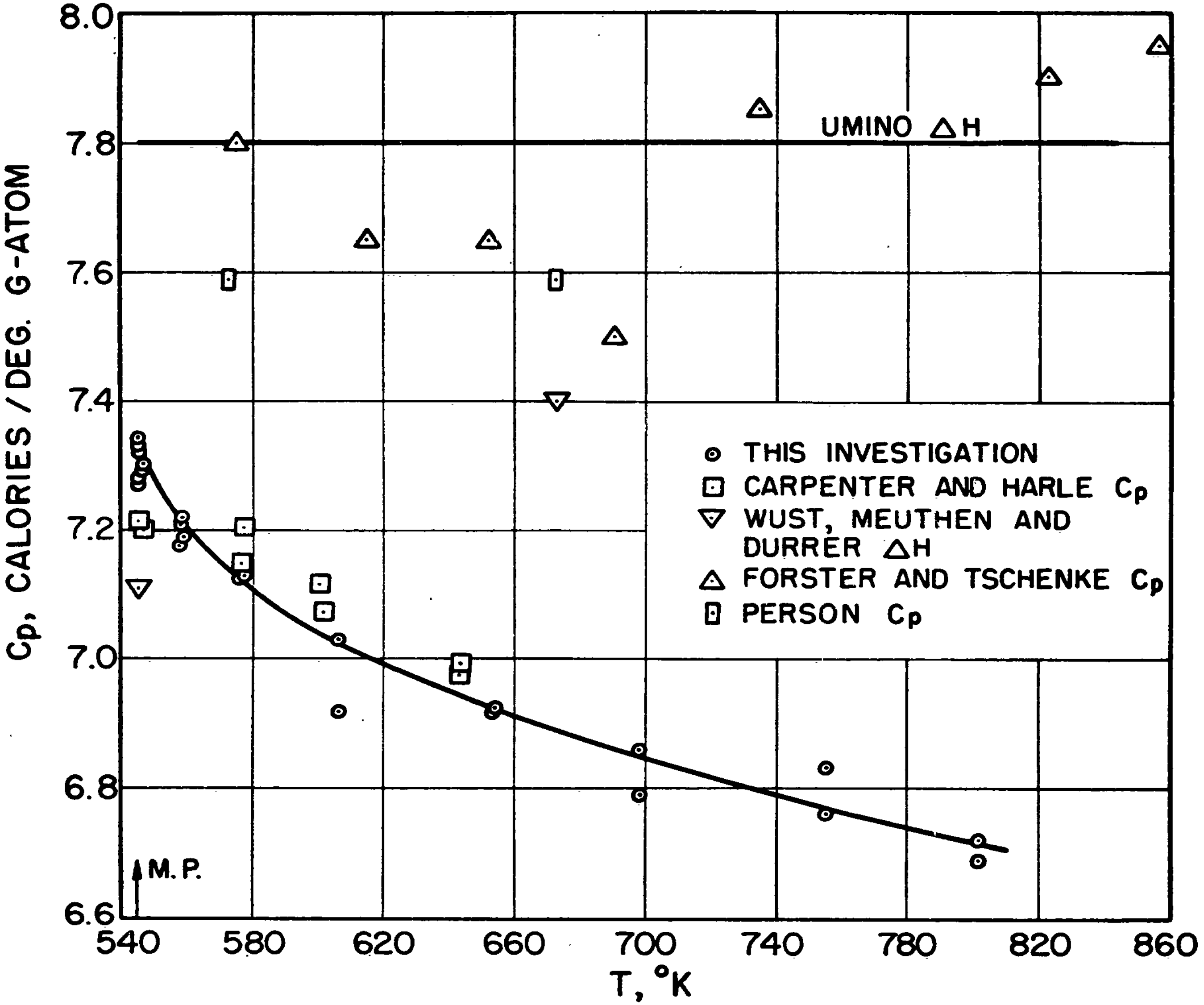

FIG. I HEAT CAPACITY OF LIQUID BISMUTH.

TABLE II

Selected Data for Liquid Bismuth

T, °K	Cp cal/deg. g-at.	H_T-H_{298} cal/g-at.
544.5 (m. p.)	----	4200
550	7.27	4240
600	7.04	4597
650	6.93	4946
700	6.85	5290
750	6.78	5631
800	6.72	5969

NOTE: Heat content values are based on 4200 cal/g-at. at 544.5°K, which is selected from the literature[11].

DISCUSSION OF RESULTS

The close agreement between the measured values and the results of Carpenter and Harle confirms the decreasing heat capacity of liquid bismuth with increasing temperature. The failure of Person and of Förster and Tschentke to obtain either the correct trend or absolute values is believed to be due to errors in accounting for over-all convective and radiative heat losses. The fact that the data of Umino and of Wust, Meuthen and Durrer disagree with the measured values is not surprising, since most heat-content data are too inaccurate to obtain even average values of Cp.

The anomalously high heat capacity of liquid bismuth just above the melting point adds credence to the belief that residual aggregates similar to the solid exist in that region. The dissolution of these associations with increasing temperature would account for the high Cp within a few degrees of the melting point. Bublik and Buntar[14] have interpreted their electron diffraction patterns as indicating that in this region liquid bismuth has a structure such that nearest neighbors are distributed in the same manner as in the solid. As the temperature is increased, however, the structure changes to one of denser packing. This is just what would be expected if residual associations existed within a few degrees of 544.5°K. The idea of residual aggregates has frequently appeared in the literature to explain the anomalous properties of liquid bismuth within a few degrees of the melting point[15, 16, 17, 18]. These associations would also explain the fact that bismuth does not contract as much on melting as has been theoretically predicted by Saurevald and Teske[19].

Many models have been proposed that describe these residual aggregates as being pseudo-crystalline in the sense that they display a certain degree of local order, of the same type as that found in the solid. This is the case in the model proposed by Bartenev[20]. Other models of this nature include the crystallite model of Ookawa[21] and the cybotactic picture of Stewart and Benz[22]. The expressions derived from the models for the excess heat capacity near the melting point show only qualitative agreement with experiment, however,

Impurities would have a great effect on the nature of these aggregates and on the manner in which they change with temperature. In the present investigation, it is felt that the high purity of the sample excludes the chance of any error occurring from this source.

Whereas the breakup of associations will account for the sharp drop in Cp near the melting point, this explanation does not apply to the gradual decrease in Cp observed at higher temperatures, since the residual associations have essentially disappeared within a few degrees of the melting point. Eyring[23] in his treatment of liquid mercury attributes the decrease to a change in the potential function of the atoms in which turn affects the nature of the thermal motion of the atoms. At the lower temperatures the thermal motion consists chiefly of vibration, but increasing the temperature causes translational energy to become dominant. This results in a continual loss of degrees of freedom. Using this approach Eyring obtained a partition function for the liquid from which Cv could be obtained. His values of Cv start at a value of 3R at the melting point, in agreement with the law of Dulong and Petit, and decrease with increasing temperature. A minimum in Cp is to be expected because of the continually increasing value of (Cp-Cv). While this model will not account for the anomalously high values of Cp near the melting point, it shows good agreement with the high temperature values.

No minimum in the heat capacity was found, although the measurements extended to 800°K. If the trend that is followed by Hg, Na, and K is obeyed, however, a minimum value would be expected at a temperature about 2.3 times the melting temperature or 1250°K.

SUMMARY AND CONCLUSIONS

The true heat capacity of liquid bismuth was measured from 544.8°K to 801.8°K by a method of mixtures using a liquid bismuth solution calorimeter.

The following conclusions were reached:

1) The anomalously high heat capacity within a few degrees of the melting point can be accounted for by assuming the presence of residual aggregates resembling the solid which are broken up with rising temperature.

2) The heat capacity of liquid bismuth decreases with increasing temperatures over the range studied.

3) No minimum in Cp was observed although one may exist at a higher temperature.

APPENDIX

Sample Calculation Sheet

Run. No. 15

Tin Pellet

Weight = 0.28524 g.

Initial State

$$\begin{aligned}\text{Temperature} &= 982\,\mu\text{v}\\ &= 24.80^\circ\text{C}\\ -\text{Correction} &= \underline{-0.88}\\ &\ 23.92^\circ\text{C}\\ &\ \underline{273.15}\\ T_i &= 297.07^\circ\text{K}\end{aligned}$$

Final State

$$\begin{aligned}\text{Temperature} &= 13,308.55\,\mu\text{v}\\ -\Delta T_t &= \underline{-13.21}\\ &= 13,295.34\,\mu\text{v}\\ &= 272.73^\circ\text{C}\\ -\text{Correction} &= \underline{-1.17^\circ}\\ &\ 271.56^\circ\text{C}\\ T_f &= 544.71^\circ\text{K}\end{aligned}$$

$H_{T_i} - H_{298} = -6.7695$ cal/g-at.

$H_{T_f} - H_{298} = 4201.6270$ cal/g-at.

$$H_{T_f} - T_{T_i} = 4201.6270 + 6.7695 = 4208.3965 \text{ cal/g-at.}$$

$$\mathrm{Bi}_{(s,\,T_i)} \rightarrow \mathrm{Bi}_{(\ell,\,T_f)} \qquad \Delta H = \frac{0.28524}{209.00}\, 4208.3965 = 5.7436 \text{ cal.}$$

Correction to Cp

Material	Gram Atoms	Cp (cal/deg. g-at.)	cal/deg.
Ta	0.03906	6.24486	.2439
Mo	0.38210	6.20810	2.3721
Cu	0.00207	6.22704	.0129
Ni	0.00056	7.78009	.0044
Asbestos	0.109(gms.)	0.195(cal/deg. g.)	.0213
			2.6546

Temperature Change = 13.209 μv

Thermocouple Constant = 56.84 μv/deg.

Amount of Bismuth in Bath = 3.0051 g-atom

$$\frac{13.209}{56.84}(2.6546 + 3.0051\,\text{Cp}) = 5.7436$$

$$\text{Cp} = 7.34 \text{ cal/deg. g-at.}$$

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