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**Publication Date**
1970-08-01

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Journal to be decided later

UCRL-19673
Preprint

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August 1970

AEC Contract No. W-7405-eng-48

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UCRL-19673

# HEAT CAPACITY OF LIQUID BISMUTH

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# 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.

# INTRODUCTION

A detailed knowledge of the heat capacity of liquid bismuth is of interest from an engineering as well as a scientific point of view. Liquid bismuth has been suggested as a possible reactor coolant either in elemental form or in a eutectic with lead[1]; it also has been suggested as an alloy with uranium to produce a liquid metal fuel[2]. Scientifically, heat capacity offers a sensitive measure of change of liquid metal structures; bismuth is of particular interest because of its non close-packed structure in the solid state and its decrease of volume on melting.

Previous measurements of the heat capacity of liquid bismuth differ considerably (see Fig. 1). Carpenter and Harle[3] (1932) found the Cp decreased steadily to 644°K; Forster and Tschentke[4] (1940) obtained results about 8% higher with Cp decreasing to 690°K, then increasing above that temperature. Person[5] (1848) very early found an intermediate value, Cp = 7.59, constant with T. Enthalpy measurements of Umino[6] (1926) led to a constant Cp = 7.80; while those of Wüst, Meuthen, and Durrer[7] (1918) indicated Cp increased with T, from 71 to 8.76 at 1273°K.

For most liquid metals Cp is tabulated as constant with temperature[8]. The reason for this is that most measurements are of enthalpy contents and are not accurate enough to show a trend of Cp with temperature. In the relatively few cases where precise

measurements exist, Cp has been found to decrease with temperature. For mercury, potassium, and sodium, the decrease continues to a minimum value at a temperature somewhat higher than twice the melting point; above this temperature, the heat capacities increase. For most metals the measurements have not been made at sufficiently high temperatures to indicate if this behavior is generally found.

## EXPERIMENTAL

### Materials

The bismuth was obtained from Consolidated Mining and Smelting Company and was reported to be 99.9999% pure. Spectrographic showed only a single impurity; a trace of iron.

### Methods

The liquid tin solution calorimeter, described elsewhere[9], as modified by Heffan[10], was used for the measurements. Into a large quantity of liquid bismuth is dropped a small amount of solid bismuth; the temperature drop is measured. From the heat required to melt the solid, and raise it to the temperature of the liquid, the Cp of bismuth and the container is determined.

The crucible was made of 36.66 g of sheet molybdenum, and contained tantalum baffles weighing 7.07 g and a copper-constantan thermocouple. The baffles were arranged to protect the thermocouple from stray currents of liquid metal which had been cooled by the

pellets. About 600 g of bismuth were melted into the crucible under an inert argon atmosphere. The crucible and contents were supported on three sharp refractory points in the calorimeter, surrounded by a large copper block. The atmosphere was evacuated and the crucible and block were raised to the measurement temperature, T. The temperature of the block was maintained constant closer than 0.001°K by a resistance thermometer-Wheatstone bridge arrangement. After 24 hours, when temperature stability was achieved, a pellet of solid bismuth weighing about 300 mg was dropped from room temperature into the liquid. Temperature difference between crucible and block were read to 0.001°K at intervals of 15 seconds to 1 minute, and a temperature-time curve constructed.

In less than a minute the sample reached a minimum temperature, a fraction of a degree lower than T. After this, the sample returned to the original temperature, following Newton' s law for the rate of exchange of energy between two radiating surfaces at nearly the same temperature. From the heat exchange constant, determined from this stage, the temperature drop may be corrected for heat received from the copper block druing the fall in temperature. The heat capacity of crucible and contents is, of course, the heat required to heat the pellet divided by the corrected drop of temperature.

From the heat capacity so determined were subtracted the heat capacities of the molybdenum, tantalum, and the thermocouple

materials, (about 10% of the total measured) to give the heat capacity of the liquid bismuth sample. The results are shown in Table 1. From smoothing these values, the values of Table 2 were calculated. The enthalpy content of bismuth at the melting point (4200 cal/g-atom) and the heat capacities of the crucible materials were taken from the literature.[11]

TABLE 1

Experimentally Determined Heat Capacity Data for Liquid Bismuth

| Run No. | T, °K | Cp cal/deg. g-atom | Run No. | T, °K | Cp cal/deg. g-atom |
|---|---|---|---|---|---|
| 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 |

TABLE 2

Selected Data for Liquid Bismuth

| T, °K | Cp cal/deg. g-atom | $H_T - H_{298}$ cal/g-atom |
|---|---|---|
| 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 |

Results from this and previous measurements are shown in Figure 1.

## DISCUSSION OF RESULTS

The data show a smooth decrease in the Cp of liquid Bi, agreeing fairly well with those of Carpenter and Harle[3] and extending them to higher temperatures. Other workers found much higher values.

According to a popular theory of the liquid state [12, 13], the liquid near the melting point consists of aggregates of atoms which are joined together in each aggregate to form a lattice similar to that in the solid. As the temperature is increased, these aggregates are gradually broken up, absorbing heat and leading to anomalously high Cp values. This anomaly should grow less important as the temperature rises, finally disappearing altogether so the Cp should first decrease, then

resume a normally increasing value with temperature.

Numerous X-ray and electron diffraction patterns have been interpreted on this basis, however, the results are not convincing[14]. It would seem, also, that if these aggregates exist, they should break up only a few degrees above the melting point, giving a much larger anomaly spreading over a limited number of degrees; not the gradual effect found.

More in accord with the Cp curve is the theory of Kincaid and Eyring[15], who consider the chemical bonding gradually changes to that in a monatomic gas; Cp trending toward 5R/2 at high temperatures. More recently Chapman[16] set forth a statistical mechanical theory leading to a similar result.

A few metals, notably, Na, K, and Hg, reach a minimum Cp at about $2.3T_m$; the present measurements on Bi have not been carried high enough to test this.

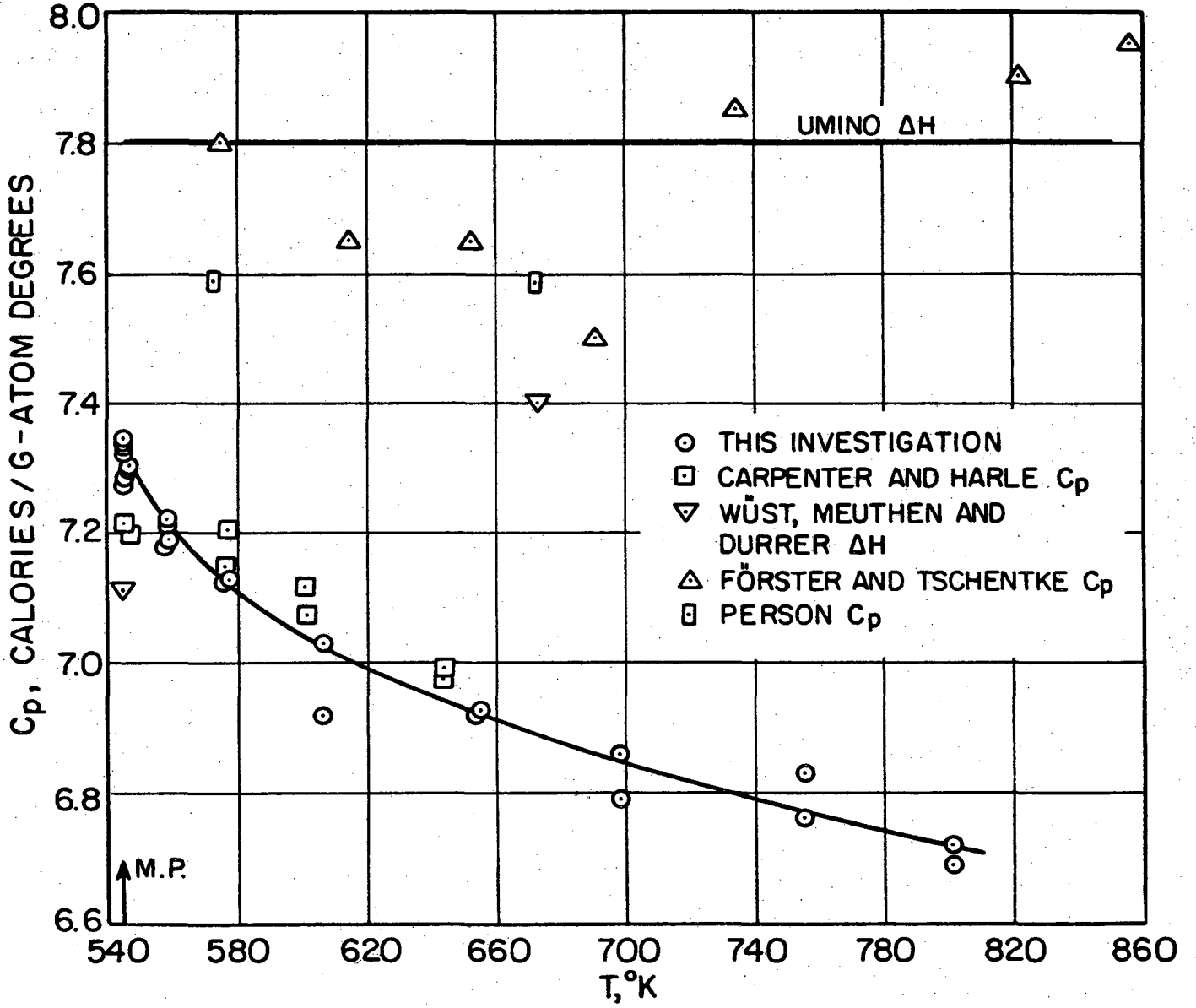
## SUMMARY AND CONCLUSIONS

(1) The Cp of liquid Bi steadily decreases for more than 250 °K above the melting point.

(2) The theory that liquids consist of fragments of the solid crystal which break up with increasing temperature does not explain this.

## ACKNOWLEDGMENT

The experimental work for this paper was supported by the Office of Ordnance Research, U.S. Army and by the U.S. Atomic Energy Commission.




HEAT CAPACITY OF LIQUID BISMUTH.

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