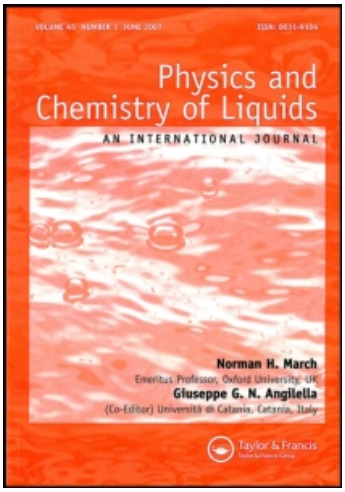

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The heat capacity of lead from 300 to 850°k: conversion of c_p to c_v for liquid lead

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The Heat Capacity of Lead from 300 to 850°k: Conversion of C_p to C_v for Liquid Lead

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Recent measurements of the heat capacity at constant pressure C_p for lead from 300 to 850°K have shown that C_p for liquid lead decreases continuously from the melting point to 850°K. Using data in the literature of density and velocity of sound, the dilation correction has been applied to C_p to obtain the heat capacity at constant volume C_v for liquid lead. Application of the dilation correction to solid lead gives a C_v curve which uncreases only about one joule/gm-atom-°K from 300 to 600°K, whereas the C_v curve for liquid lead decreases almost 5 joules/gm-atom-°K from 600 to 850°K. A careful assessment of the uncertainty in the quantities used in the dilation correction leads to an uncertainty in C_v of ± 2.5% (about one joule/gm-atom-°K), and thus the decrease in C_v for liquid lead is quite real.

1. INTRODUCTION

There are several metals for which the heat capacity at constant pressure C_p of the liquid shows a decrease with increasing temperature above the melting point, and in some cases C_p attains a minimum and then increases. Figure 1 presents selected data[1-7] for several metals. This behavior is of considerable interest in the theory of liquids, but it is also important to examine the temperature dependence of the heat capacity at constant volume, C_v. Although only measurements of C_p are available, C_v can be calculated from the expression

$$C_v = C_p - \frac{\alpha^2 v}{K} T \qquad (1)$$

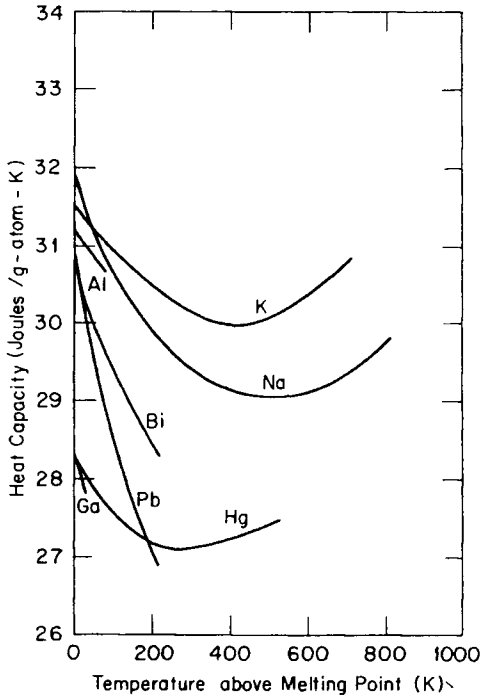

FIGURE 1 The heat capacity at constant pressure C_p for several metals as a function of the temperature above the melting point. Pb[1], Ga[2], Bi[3], Na[4], Hg[5], K[6], Al[7].

where K is the isothermal volume compressibility, α is the coefficient of volume thermal expansion, v is the specific volume and T is the absolute temperature. The purpose of this paper is to apply Equation (1) for liquid lead using literature data for K, v and C_p. An analysis has been made of uncertainties in each of these terms in order to assess the uncertainty in the calculated C_v.

2. C_p FOR LIQUID LEAD

The heat capacity of liquid metals must be carefully measured in order to observe a temperature dependence such as that shown in Figure 1. Drop calorimetry measurements are not always sufficiently sensitive to show a non-linear temperature dependence of the enthalpy. Generally, it is better to utilize a direct measurement of the heat capacity by such means as continuous adiabatic calorimetry.

In a previous paper[1], we reported values of C_p of lead from 300 to 850°K obtained by adiabatic calorimetry. The details of the measurements and an

analysis of errors are given there. It was concluded that C_p has an uncertainty of ± 1%. The polynomial fitted to the data is shown in Figure 2, along with data from other sources[8–16]. All the other data of the liquid are derived from enthalpy measurements.

For purposes of assessing the uncertainty in C_v, an uncertainty in C_p is taken to be ± 1%.

3. α AND v FOR LIQUID LEAD

There are several sets of measurements of v of lead over the temperature range of interest here.[17–20] The values of v used were those of Strauss *et al.*,[17] from which values of $(\alpha^2 v)$ were derived. Both quantities are plotted in Figure 3; the curves for solid lead are from reference[21]. From an examination of the reported uncertainties in v, and a comparison of v and dv/dT from the various measurements, I have assigned to v the uncertainty listed in Table 1.

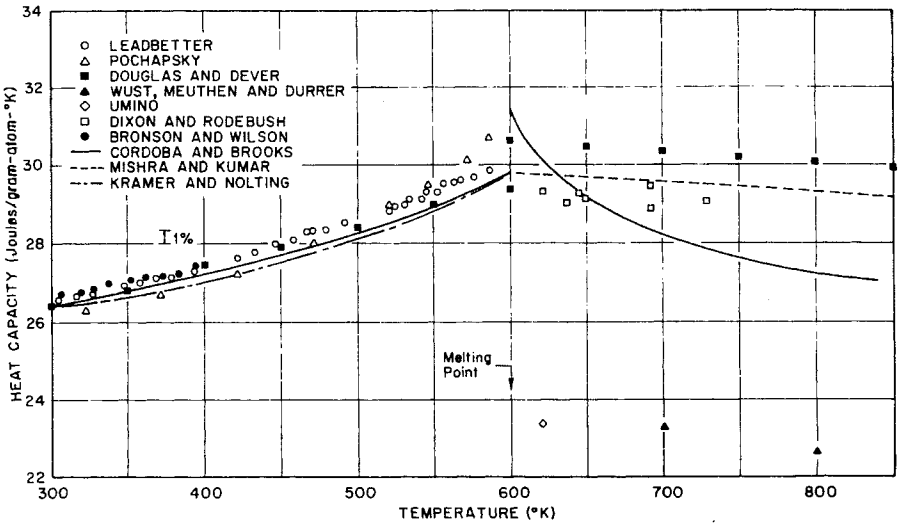

FIGURE 2 The heat capacity at constant pressure C_p for solid and liquid leads as obtained by several investigators.

TABLE 1

Uncertainty in quantities used to calculate Cv, and in Cv, at 800°K

Quantity	Uncertainty at 800°K (%)
$\alpha^2 v$	± 1.6%
C_p	± 1.0%
v	± 0.5%
u	± 1.7%
K_S	± 3.0%
K	± 5.0%
C_v	± 2.5%

4. K FOR LIQUID LEAD

The velocity of sound u has been measured in liquid lead by several investigators.[22-24] The adiabatic compressibility K_S is calculated from these measurements by the expression

$$K_S = v/u^2 \tag{2}$$

The values of u of Gitis and Mikhailov[24] were used to calculate K_S. Examination of all of the data of u lead to the uncertainty shown in Table 1, giving an uncertainty in K_S of ± 3%.

Equation (1) requires the isothermal compressibility K, which is obtained from K_S by the expression

$$K = K_S + \frac{(\alpha^2 v)}{C_p} T \tag{3}$$

The values of K used are plotted in Figure 4a; the curve for the solid is derived from reference[21]. Using the values of uncertainty in Table 1 leads to an uncertainty in K of ± 3.6% Because the number of independent measurements of u is limited, an arbitrary uncertainty in K of ± 5% (Table 1) is used in assessing the uncertainty in C_v.

5. C_v FOR LIQUID LEAD

The differences between data from the various sources were taken into account in assigning the uncertainties in Table 1. These values give an uncertainty in C_v of ± 2.5%.

C_v for liquid lead is shown in Figure 5; also shown is C_p. The curve for C_p for solid lead is from our previous paper[1] and the C_v for solid lead[21] was obtained

by a process similar to that being used here for liquid lead. The heavy bar at 580°K is the uncertainty in C_v for solid lead; the uncertainty in C_v for liquid lead is shown by the bar at the end of the liquid C_v curve.

6. DISCUSSION

The striking feature of the curves in Figure 5 is that the dilation correction for solid lead causes C_v to be approximately constant from 300 to 550°K, with a slight upturn as the melting point is approached, whereas C_v for liquid lead continues to decrease with a temperature dependence similar to that of C_p. Examination of the temperature dependence of K, v and α (Figures 3 and 4) for

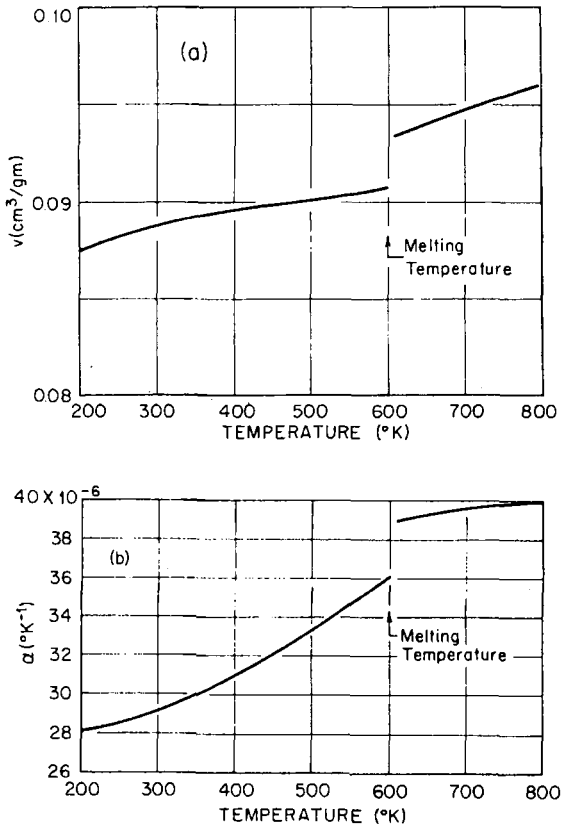

FIGURE 3 The specific volume v and $(\alpha^2 v)$ as a function of temperature for solid and liquid lead.

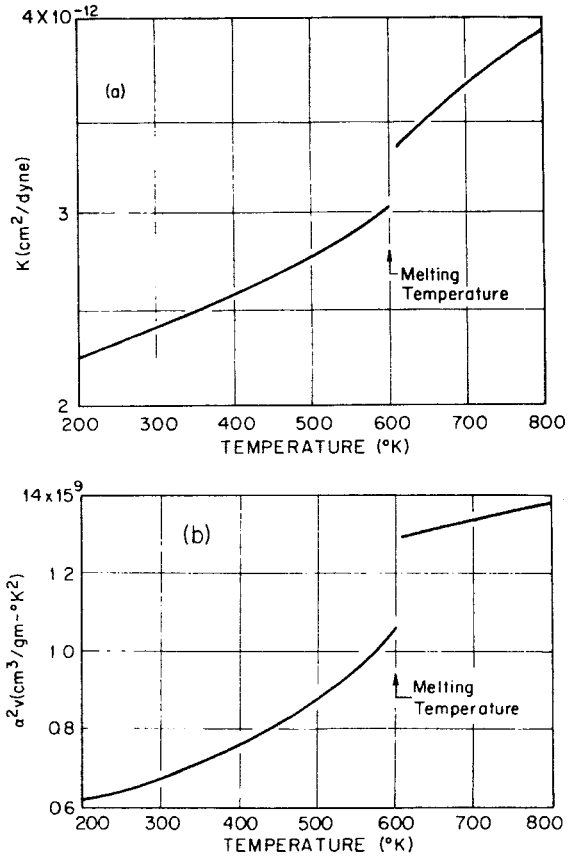

FIGURE 4 K and α as a function of temperature for solid and liquid lead.

both the solid and liquid phase at or near the melting point reveals that α is mainly responsible for the difference in the dilation correction for the solid and liquid phases.

Concepts of the stuctural configuration of liquid lead near the melting point have been discussed well recently by Pokorny and Astrom,[25] and will not be recounted here. The curves in Figure 5 clearly show that a considerable portion of the upturn in C_p of solid lead as the melting point is approached can be accounted for by the dilation correction, whereas the decrease in C_p with temperature for liquid lead cannot. The establishment here of the uncertainty in C_v clearly shows that these effects are quite real. (The contribution to the upturn in C_v and C_p for solid lead from the formation of lattice vacancies is quite small.[26]) The decrease of C_v for liquid lead could be due to the continued "solution" of rather ordered microregions referred to by Porkorny and Astrom.[25] Presumably

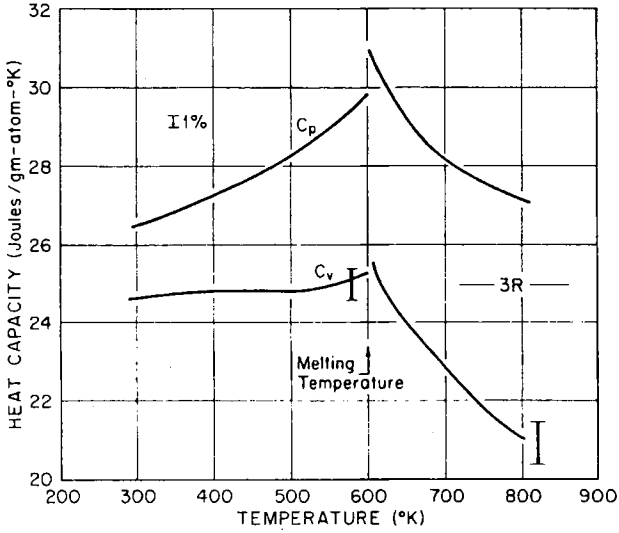

FIGURE 5 The heat capacity at constant pressure C_p and constant volume C_v for solid and liquid lead. The heavy bars give the uncertainty in the calculated C_v.

if data for C_p were available for sufficiently high temperatures, then a minimum would be observed corresponding to the complete "solution" of these regions.

Acknowledgements

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