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Note

Specific Heat Capacity of Solids under Pressure from Measurements of $(\partial T/\partial P)_S$

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A procedure is described for calculating specific heat capacity under pressure, $c_p(T, P)$, from data for $c_p(T, 0)$ and adiabatic $(\partial T/\partial P)_S$. The main advantage is that $(\partial T/\partial P)_S$ can be readily measured under high-pressure conditions.

KEY WORDS: adiabatic compression; calculational procedure; high pressure; specific heat capacity.

1. INTRODUCTION

Heat capacity under pressure is a difficult measurement, and there are so far relatively few results (see reviews by Bäckström [1] and Loriers-Susse [2]). On the other hand, there exist extensive results at effectively zero pressure for specific heat capacity at constant pressure as a function of temperature, $c_p(T, 0)$ (see the compilation by Touloukian and Buyco [3]). The purpose of the present note is to describe how the relatively simple measurement of $(\partial T/\partial P)_S$ under pressure enables data for $c_p(T, 0)$ to be extended to high-pressure conditions.

2. DESCRIPTION OF THE PROCEDURE

A method for measurement of the rate of change of temperature with pressure at constant entropy, $(\partial T/\partial P)_S$, has been described by Boehler et al.

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[4]. A solid specimen of the substance under investigation is arranged to have a thermocouple junction immersed in it at a central location. The specimen is then coated with an elastomer and placed in the pressure-transmitting medium in a pressure vessel. A sufficiently rapid change of pressure yields a T, P trajectory which is effectively adiabatic. The temperature is measured using the thermocouple located within the specimen and the pressure is measured using a manganin resistance gauge located in the pressure-transmitting medium.

Figure 1 shows a T, P projection which may be taken to refer to the central part of the specimen. It is assumed that $c_p(T, 0)$ is known from T_{min} to T_{max} and that the lines in Fig. 1 labeled $s_1, s_2, \ldots, s_n$ correspond to the results of adiabatic experiments of the type just described. It can be assumed that the specific entropy $s(T, 0)$ is also known, apart from a constant term, since

$$s(T, 0) = s(T_{\text{min}}, 0) + \int_{T_{\text{min}}}^{T} c_p(T', 0)\, d \ln T' \tag{1}$$

It follows that the entropies $s_1, s_2, \ldots, s_n$ of the adiabats are also known from the intercept of each adiabat with the axis $P = 0$. We now consider the

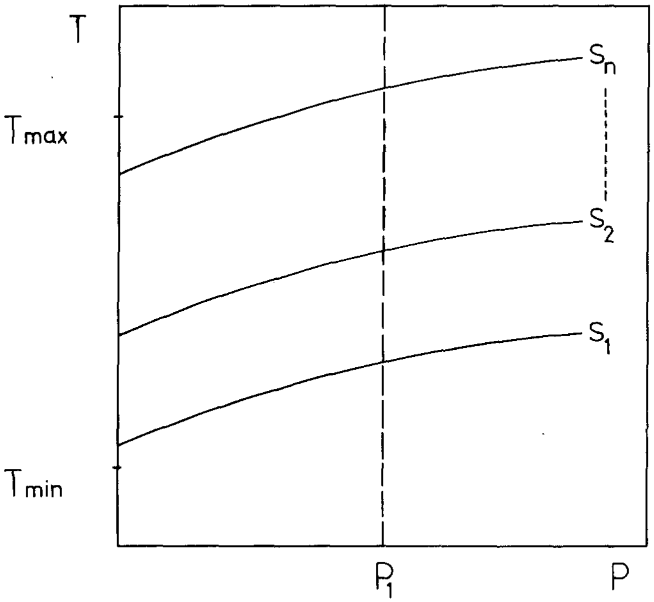

Fig. 1. T, P projection for substance under investigation. $c_p(T, 0)$ is assumed to be known over the temperature range T_{min} to T_{max}. Lines labeled $s_1, s_2, \ldots, s_n$ are from measurements of $(\partial T/\partial P)_S$. Dashed line indicates isobar at $P = P_1$.

intersections of some isobar at $P = P_1$ with the adiabats and, thereby, obtain a discrete set of data points which represents the function $s(T, P_1)$. Suitable differentiation then yields $c_p(T, P_1)$ and the calculation can be repeated for a number of different isobars to yield a data set for $c_p(T, P)$.

While the discussion just given illustrates the principles, a practical calculation could proceed as follows. We have

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\alpha T v}{c_p} = \frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_P \tag{2}$$

where α is thermal expansivity and v is specific volume. By setting $T^{-1}(\partial T/\partial P)_S = f(T, P)$ and $(\partial v/\partial T)_P = D(T, P)$, we obtain

$$fc_p = D(T, P) \tag{3}$$

the function f being measurable. Now

$$c_p(T, P) = c_p(T, 0) + \int_0^P \left(\frac{\partial c_p}{\partial P'}\right)_T dP' = c_p(T, 0) - T\int_0^P \left(\frac{\partial^2 v}{\partial T^2}\right)_{P'} dP' \tag{4}$$

Hence

$$fc_p(T, 0) - fT\int_0^P \left(\frac{\partial D}{\partial T}\right)_{P'} dP' = D$$

or

$$F_0 - F_1\int_0^P \left(\frac{\partial D}{\partial T}\right)_{P'} dP' = D \tag{5}$$

where

$$F_0 = fc_p(T, 0) = T^{-1}\left(\frac{\partial T}{\partial P}\right)_S c_p(T, 0)$$

and

$$F_1 = fT = \left(\frac{\partial T}{\partial P}\right)_S$$

F_0 and F_1 are known experimentally at discrete values of T, P so the problem reduces to solving Eq. (5) for $D(T, P)$. The desired result, $c_p(T, P)$, then follows from Eq. (3).

The quantity $D(T, P)$ may be represented by a polynomial in T and P. For purposes of illustration we neglect terms higher than quadratic and employ the relation

$$D(T,P) = D_{00} + D_{10}T + D_{01}P + D_{20}T^2 + D_{11}TP + D_{02}P^2 \tag{6}$$

Equation (5) then becomes

$$\begin{aligned} D_{00} &+ D_{10}(T + F_1 P) + D_{01}P + D_{20}(T^2 + 2F_1 TP) \\ &+ D_{11}(TP + F_1 P^2/2) + D_{02}P^2 = F_0 \end{aligned} \tag{7}$$

The six coefficients D_{ij} may be obtained by taking experimental data for six points in the T, P plane. The resulting system of equations is linear in the coefficients D_{ij} and will remain so whatever the order of the polynomial assumed for $D(T, P)$. In a realistic case there will be many more data points than coefficients to determine. Therefore the best procedure would probably be to minimize

$$\sum_k \left[F_0 - F_1 \int_0^P \left(\frac{\partial D}{\partial T}\right)_{P'} dP' - D\right]^2$$

with respect to the coefficients D_{ij}, the sum being taken over the experimental data points (k).

3. DISCUSSION

The main advantage of the procedure described here is that the quantity required under pressure, $(\partial T/\partial P)_S$, is relatively easy to measure with good accuracy. In the experiments of Boehler et al. [4] it appears [5] that the inaccuracy in this quantity was ±1% at pressures up to about 3 GPa at room temperature. Similar measurements have been described by Sandberg and Bäckström [6] and Dzhavadov and Krotov [7]. If $c_p(T, 0)$ should not be known for some substance of interest, then it is readily measurable by, say, differential scanning calorimetry, a technique which can employ commercially available equipment.

Although we are concerned here mainly with $c_p(T, P)$, we point out that if $v(T_0, P)$ along an isotherm (T_0) is also known for the substance under investigation, then values for $D(T, P)$ imply knowledge of the thermal expansivity $\alpha = v^{-1}(\partial v/\partial T)_P$ and $v(T, P)$ over the ranges of T and P for which measurements of $(\partial T/\partial P)_S$ have been made.

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REFERENCES

1. G. Bäckström, in *Proc. Seven. Symp. Thermophys. Prob.*, A. Cezairliyan, ed. (American Society of Mechanical Engineers, New York, 1977), pp. 169–180.
2. C. Loriers-Susse, *High Temp. High Press.* **12**:119 (1980).
3. Y. S. Touloukian and E. H. Buyco, *Thermophysical Properties of Matter, Vol. 5. Specific Heat, Nonmetallic Solids* (IFI/Plenum, New York, 1970).
4. R. Boehler, I. C. Getting, and G. C. Kennedy, *J. Phys. Chem. Solids* **38**:233 (1977).
5. R. Boehler and J. Ramakrishnan, *J. Geophys. Res.* **85**:6996 (1980).
6. O. Sandberg and G. Bäckström, *J. Appl. Phys.* **50**:4720 (1979).
7. L. N. Dzhavadov and Yu. I. Krotov, *Sov. Phys. Solid State* **22**:172 (1980).

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