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On the pressure dependence of the heat of fusion and melting temperature of indium

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Abstract

The pressure dependence of the fusion temperature and the fusion volume change of indium has been investigated with the aid of a high-pressure piston-cylinder-type dilatometer up to 400 MPa. From these results, the pressure dependence of the enthalpy of fusion can be calculated via the Clausius–Clapeyron equation. From our results, together with those of other authors, a best value approximation of the pressure dependence of both quantities has been performed, which we would like to suggest as the basis for calibration of high-pressure thermal analysis devices, especially for DTA and DSC apparatus.

Keywords: Calibration; DSC; Enthalpy of fusion; High pressure; Indium

1. Introduction

Indium is widely used for temperature and heat calibration in thermal analysis. For this reason, numerous publications on the phase transition behavior exist, but most of them deal with the thermodynamic data at normal pressure only. Recently, interest in high-pressure measurements has grown and an increasing number of appropriate devices have been described in the literature. Consequently there is a demand for calibration substances with well-known pressure dependences of thermodynamic data. Unfortunately, there are only few publications on the change of fusion temperature and heat with pressure for substances that are used for calibration of the instruments of differential thermal analysis (DTA) and differential scanning calorimetry (DSC). In addition, the results do not correspond very well. This is also true for the standard calibration substance, indium (see Fig. 5, below) [1–6]. For this reason we have measured the volume change and temperature of fusion of indium at different pressures

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with the aid of a high-pressure dilatometer [7]. From the volume change, the enthalpy of fusion has been calculated via the Clausius–Clapeyron equation. The results have been compared with those measured directly in our power-compensated high-pressure DSC [8,9]. Together with known measurements from the literature, we then arrived at a best value estimation which may be used for calibration purposes.

2. Experimental

2.1. The high pressure dilatometer

The dilatometer (Fig. 1) is a piston-cylinder-type device with two cylinders inside one another (1, 2) made of hardened steel and shrink-fitted to sustain a maximum pressure

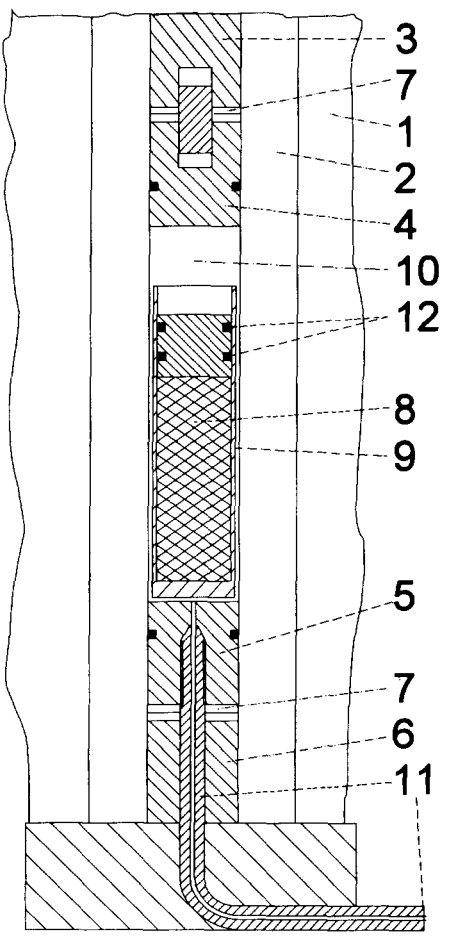

Fig. 1. Drawing of the piston-cylinder-type dilatometer. For explanation, see text (Section 2).

of 1 GPa. The pistons (3–6) are sealed against the inner cylinder by Bridgman-type unsupported area seals (7). The indium sample (8) was enclosed in a steel cylinder (9) by an o-ring (12) packing, in order to prevent any reaction with the silicon oil (10) used as the pressure medium to guarantee hydrostatic pressure on the sample. The pressure is generated (and controlled) by force onto the pistons from a hydraulic press. It is measured with a strain gauge pressure probe (of 700 MPa full scale) via a capillary (11) connected to the lower piston (5). The uncertainty of the measured pressure is about 0.5%. The volume change of the sample is determined from the displacement (measured with an inductive transducer) of the upper piston in relation to the lower one. Calibration was done with the aid of a steel cylinder with a well-known compressibility in order to correct the influence of pressure and temperature on the size of the pistons and seals. In the same way, the pressure effect on the oil used was determined. With these corrections, the specific volume of the sample can be determined with an uncertainty of $\pm 0.15\%$, in the case of our indium sample this is $\pm 2 \times 10^{-4}\,cm^3\,g^{-1}$.

The dilatometer can be heated from outside the cylinders by electrical heating. The temperature is measured by 4 platinum resistors inside the steel cylinders with an accuracy of ± 0.5 K. As the sample temperature is somewhat different, because of the heat leak through the pistons to the press which is at ambient temperature, the measured temperature must be corrected. This correction has been determined in dependence on the temperature of the dilatometer by direct measurement with a platinum resistance thermometer inside a dummy sample at normal pressure. However, this method is not very precise, so the overall uncertainty of the sample temperature may be ± 1–2 K. Nevertheless, the accuracy of measurements of the transition temperature *change* with pressure is much higher, because the sources of error do not alter very much within this rather narrow temperature range.

2.2. Results

The volume of an indium sample (mass, 100 g; purity, 99.9%) was measured in the high-pressure dilatometer both in dependence on temperature at constant pressure, and in dependence on pressure at constant temperature. From the raw data, collected with a computer-controlled data acquisition system, the corrected values of the volume change and transition temperature (or the transition pressure) were calculated via the corresponding calibration (Table 1). As usual, the transition temperature (or pressure) was determined from the extrapolated onset of the phase transition (Fig. 2). The volume change was likewise read at that temperature (or pressure).

The results are represented in Figs. 3 and 4. From these values the following regression curves have been calculated

$$T_{fus} = T_0 + (0.04929 \pm 0.0008)p - (3.9 \pm 2)10^{-6}p^2 \quad (1)$$

$$\Delta_{fus}V = \Delta_{fus}V_0 - (6.6 \pm 1.7)10^{-7}p + (5.3 \pm 3.8)10^{-10}p^2 \quad (2)$$

where p is the pressure in MPa, $T_0 = 429.75$ K (from ITS-90 [10]) and $\Delta V_0 = 3.28 \times 10^{-3}\,cm^3\,g^{-1}$ (from $\Delta_{fus}H_0 = 28.62\,J\,g^{-1}$ via the Clausius–Clapeyron equation) are chosen so as to fit to the well-known best values of this calibration substance at

Table 1
Results for the dilatometric high-pressure measurements of fusion data of indium

p/MPa	T/K	$\Delta V_{spec.} \times 10^3$/cm^3 g^{-1}	$\Delta_{fus}H$/J g^{-1}(calc.)
50[a]	433.0 ± 0.15	3.32 ± 0.03	29.7 ± 0.5
100[a]	435.4 ± 0.15	3.31 ± 0.05	29.4 ± 0.5
200[a]	440.3 ± 0.15	3.25 ± 0.01	30.1 ± 0.5
300[a]	444.9 ± 0.15	3.21 ± 0.015	30.4 ± 0.5
400[a]	449.6 ± 0.15	3.19 ± 0.02	31.2 ± 0.5
141.0[b]	441 ± 0.5	3.2 ± 0.1	
217.6[b]	437 ± 0.5	3.2 ± 0.1	

[a] Isobaric mode.
[b] Isothermal mode.

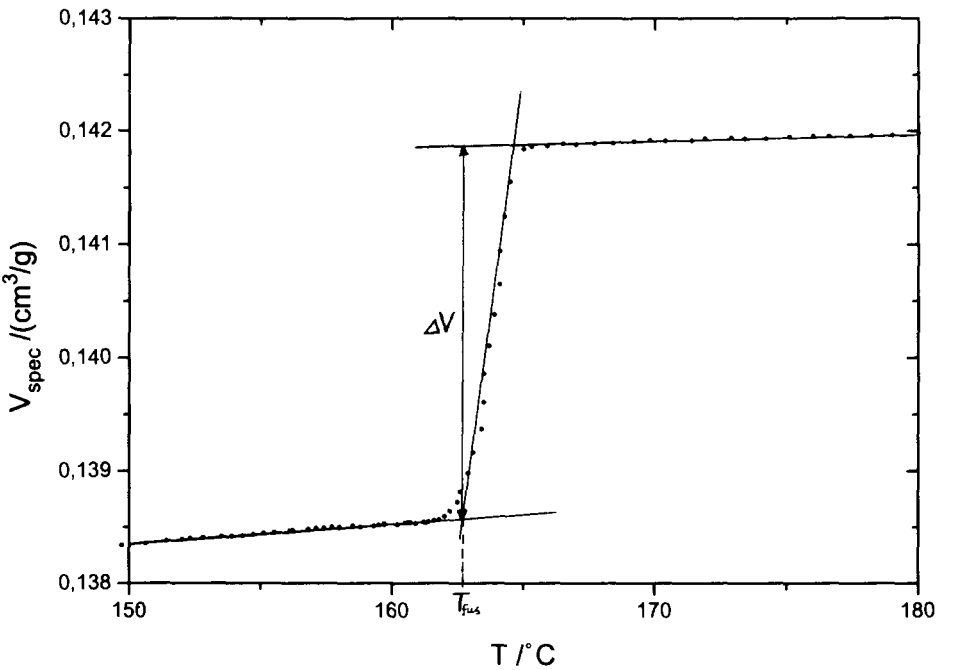

Fig. 2. Dilatometer measurement of indium melting at 100 MPa with definition of the evaluated quantities (mass, 100 g; heating rate, 5 K h^{-1}).

normal pressure [11–13]. From Eq. (1) we get

$$\frac{dT_{fus}}{dp} = (0.04929 \pm 0.0008) - (7.8 \pm 3.6)10^{-6}p \tag{3}$$

From the Clausius–Clapeyron equation

$$\frac{dT_{fus}}{dp} = \frac{\Delta V}{\Delta S} = \frac{T\Delta V}{\Delta H} \tag{4}$$

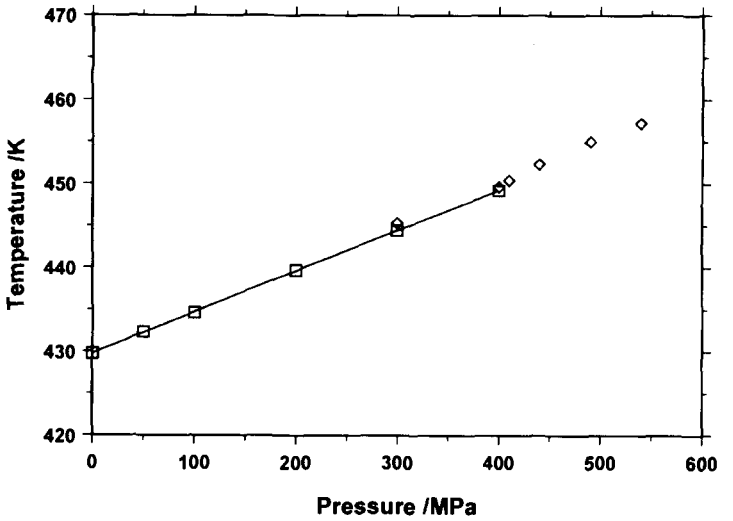

Fig. 3. Dependence of the fusion temperature of indium on pressure: □, results from dilatometric measurements together with the regression curve; ◇ results from high-pressure DSC measurements. (The data have been fitted to ITS-90 fixed point at normal pressure.)

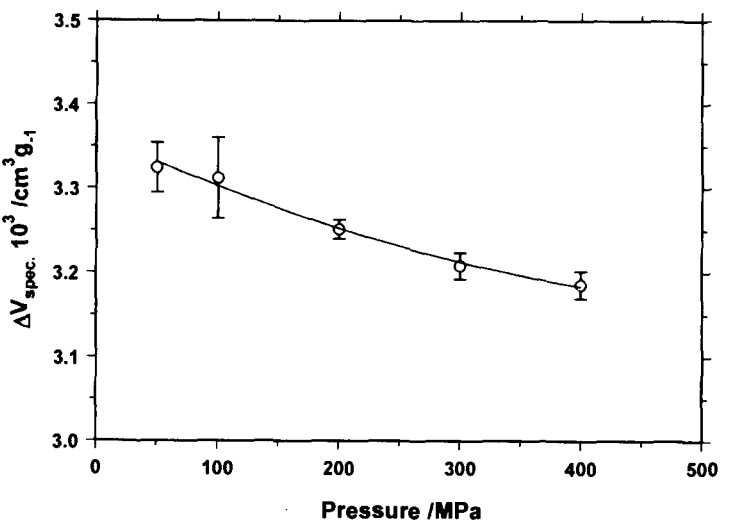

Fig. 4. Dependence of the change in the specific volume during fusion of indium on pressure (together with the regression curve).

together with Eqs. (2) and (3), we calculate the pressure dependence of the enthalpy and entropy of fusion of indium

$$\Delta_{fus}H = \Delta_{fus}H_0 + (0.0020 \pm 0.0016)p + (4 \pm 6)10^{-6}p^2 \quad (5)$$

$$\Delta_{fus}S = \Delta_{fus}S_0 - (2.9 \pm 2)10^{-6}p + (1 \pm 2)10^{-8}p^2 \quad (6)$$

with pressure p in MPa and $\Delta_{fus}S_0 = 28.62/429.76 = 0.0666\,J\,g^{-1}\,K^{-1}$ the entropy of fusion at normal pressure. The entropy of fusion does not change up to 400 MPa, as expected, whereas the heat of fusion increases somewhat with pressure. This increase has been calculated thermodynamically by Sandrock [4] (from other available data) to be about 1.2% per 100 MPa, a value well in accordance with the average value of our results. Nevertheless, an experimental check has, as far as we know, not been done before.

Our results concerning the pressure dependence of the fusion temperature of indium correspond to other results found in the literature [1, 3, 4, 14] (see Fig. 5).

2.3. *High pressure DSC*

The results have also been determined in the high-pressure cell of our power-compensated DSC [9] (which has been modified recently [15]). The function principle of this type of calorimeter, which uses platinum resistors as heater and thermometer, allows us to assume that every calibration-relevant change of the output signals must be caused by a change in the resistance of the platinum wires according to the pressure change. As this change is well known [4] and has been measured in our special case as well, we have the possibility to calculate the pressure dependence of both temperature and the heat calibration of the high-pressure DSC. Accordingly, we are able to determine the pressure dependence of the indium fusion heat and temperature directly in this type of calorimeter.

The results relative to the melting temperature are given in Fig. 3 (and Fig. 5). The heat of fusion has been found to be independent of pressure within the limits of accuracy (5%). Obviously the data are in accordance with the dilatometric measure-

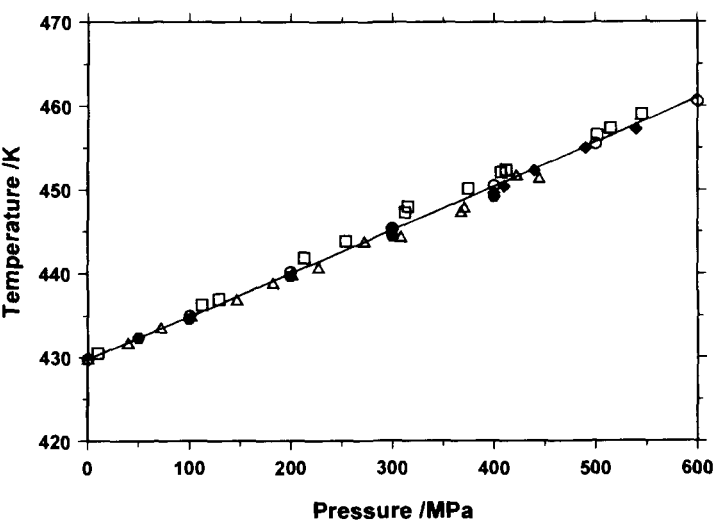

Fig. 5. Pressure dependence of indium fusion temperature, data points and average regression curve (best value recommendation): ○, Ref. [1]; △, Ref. [3]; □, Ref [4]; dilatometric results; ◆, DSC results.

ments. Nevertheless, these DSC results should not be overvalued, because of the experimentally unproved assumptions concerning the pressure dependence of the probe signals in question.

3. Conclusions

Our results, together with measurements from the literature, allow us to carry out a best-value estimation for the pressure dependence of the melting temperature and fusion heat of this widely used calibration substance. The mean value function (from all the results represented in Fig. 5) of the pressure dependence of the fusion temperature of indium reads

$$T_{fus} = T_0 + (0.0507 \pm 0.003)p \tag{7}$$

with $T_0 = 429.7485$ K, the fixed point of the ITS-90 for indium at normal pressure, and p the pressure in MPa. Eq. (7) is valid up to a pressure of 500 MPa. Within the limits of accuracy of this best-value estimation, this function is linear. As a result, the temperature calibration of any high-pressure thermal analysis device can be performed with the aid of indium with an uncertainty of a maximum of 1.5 K at 500 MPa. Of course, this statement is only valid for the indium melting temperature region.

A best value of the pressure dependence of the heat of fusion of indium, however, may be estimated from our results together with those from thermodynamical calculations (including the reasonable assumption of a pressure-independent entropy of fusion) as

$$\Delta_{fus}H = \Delta_{fus}H_0 + (3.3 \pm 2)10^{-3}p - (2.6 \pm 2)10^{-7}p^2 \tag{8}$$

with $\Delta_{fus}H_0 = 28.62 \pm 0.11\ J\,g^{-1}$ the best value [13] of the fusion heat at normal pressure and p in MPa.

With these results, indium is a suitable calibration substance not only at normal pressure but for successful calibration of high-pressure DTA and DSC as well.

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