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A Simple Differential Thermal Analysis Technique for Determining the Pressure Dependence of Solid–Liquid and Solid–Solid Transition Temperatures

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A simple differential thermal analysis technique for determining solid–liquid and solid–solid transition temperatures as functions of pressure is described. The important feature of the technique is the use of a thin-walled ptfe tube both to contain the sample and to transmit pressure to it. The method has been tested at temperatures in the range 200–310 K at pressures of up to 350 MPa. Transition temperatures as functions of pressure are reported for benzene, carbon tetrachloride, and acetonitrile and compared with literature data.

KEY WORDS: acetonitrile; benzene; carbon tetrachloride; differential thermal analysis; high pressure; phase transition.

1. INTRODUCTION

As an integral part of the interpretation of the density and temperature dependence of diffusion coefficients for pure liquids in terms of a hard-spheres model, we have needed values for liquid densities on solid–liquid coexistence curves, in order to estimate equivalent hard-sphere diameters. High-precision P, V, T data have been obtained using a bellows volumometer. A complementary experimental study has been the development of a technique for determining solid–liquid coexistence curves. The method utilizes differential thermal analysis (DTA), by means of which solid–liquid transition temperatures are directly determined with high precision and accuracy as a function of applied pressure.

Determination of solid–liquid equilibrium (coexistence) curves has been done, for the most part, by the method (or variations of it) used by

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Bridgman, viz., indirect measurement of density or specific volume as a function of pressure at constant temperature. Typically, the position of a piston which transmits pressure to the sample has been sensed, and piston displacement versus pressure curves for the solid and liquid phases have been extrapolated to evaluate the pressure at which the discontinuity in displacement and hence the solid–liquid transition occurs. The method is clearly applicable to the detection of any phase transition which is accompanied by a volume change sufficiently large to be detectable and has been applied to numerous solid–solid as well as solid–liquid transitions at elevated pressure.

The principal advantage of this method is that it provides a measure of the volume changes accompanying phase transitions. The disadvantage is that the accuracy of determination of transition pressures is usually not high unless measurements are made at small pressure intervals in the transition region. This difficulty is exemplified by the recent work of Landau and Würflinger [1] on acetonitrile, which gives solid–liquid and solid–solid transition pressures with a uncertainty (at most temperatures) of ±5 MPa, since displacement measurements were done mostly at 10-MPa pressure steps. From a practical point of view, the method is inherently slow and there are problems associated with maintaining, over a wide temperature range, a piston–cylinder fit which is at the same time sufficiently frictionless and pressure-tight that the applied pressure is transmitted wholly to the sample. Hysteresis effects which affect the accuracy of transition-pressure determination have been observed and attributed to friction, for example, in the work of Osugi and co-workers on benzene, chlorobenzene, and toluene [2].

Visual detection of crystallization or critical opalescence (in the case of liquid–liquid transition), as exemplified by the work of Schneider on the water + acetonitrile system [3], is advantageous where the objective is primarily the determination of the transition temperature or pressure rather than volume changes. There are obvious practical difficulties associated with this kind of method at very high pressures and low temperatures, and the method is inherently slow. Moreover, it may be very difficult to detect solid–solid transitions using such methods.

Most of the existing high-pressure DTA techniques which have been described in the literature (as reviewed by Takamizawa [4]) have been designed to operate at temperatures above 300 K. Recently, a DTA technique reported to be quantitative and operable from 250 K has been developed by Takamizawa and co-workers [4, 5].

The principal features of the present technique are its simplicity and the wide temperature range (to date, it has been used between 200 and 310 K, but those temperatures are not necessarily the upper and lower limits) in which it can be used. Although our objective was primarily the accurate determination of solid–liquid transition temperatures, the method is also applicable to solid–solid transitions.

The purposes of this communication are to describe the technique, which has some novel features, particularly with respect to the manner in which pressure is transmitted to the sample under study, and to illustrate the attainable precision and accuracy by comparison of solid–liquid (p, T) data for benzene, carbon tetrachloride, and acetonitrile with literature data. In addition, data on the pressure dependence of solid–solid transition temperatures for carbon tetrachloride and acetonitrile are presented. The p, T data for acetonitrile are used in conjunction with volume-change data [1] to evaluate transition enthalpies as a function of temperature.

2. EXPERIMENTAL

The principal features of the high-pressure part of the system are shown (not to scale) in Fig. 1. Most of the metal components (pressure vessel, closures, closure nuts, sealing rings, and 0-ring nuts) are beryllium–copper; the sample tube nut is brass.

The essential and novel part of the system is the sample tube (J), which contains the (initially liquid) sample and transmits the pressure. The sample tube is 20 mm long and 3 mm in external diameter, and the volume of sample used is about 80 mm^3. The tube is machined from ptfe rod to a wall thickness of 0.1 mm and is similar in design to the sample tube (for diffusion coefficient measurements at high pressure by nuclear magnetic resonance) described by us previously [6]. The wall thickness of the sample tube is fairly critical, and pinholes can appear if the thickness is much less than 0.1 mm. However, since the tubes can be machined in quantity and pretested for leaks through the wall, it is relatively simple to determine the minimum thickness which can be utilized.

As was our experience with the nmr sample tubes, no failures have been encountered with tubes which have been subjected to repeated pressurization to about 350 MPa and depressurization, at temperatures between about 200 and 310 K. The sample tube is sealed against ingress of hydraulic fluid (Aero-Shell Fluid 4) by compression of 0-ring G between the upper closure (B) and the upper end of the sample tube, by tightening nut F.

The thermocouples (supplied by Omega Engineering, Inc.) are copper–constantan. The wires are 0.254 mm in diameter, sheathed with 1.5-mm-o.d. stainless steel which is silver soldered to the closures. Pressure seals at the pressurized open ends of the thermocouple sheaths are made with epoxy resin. In preliminary tests some liquid samples were apparently

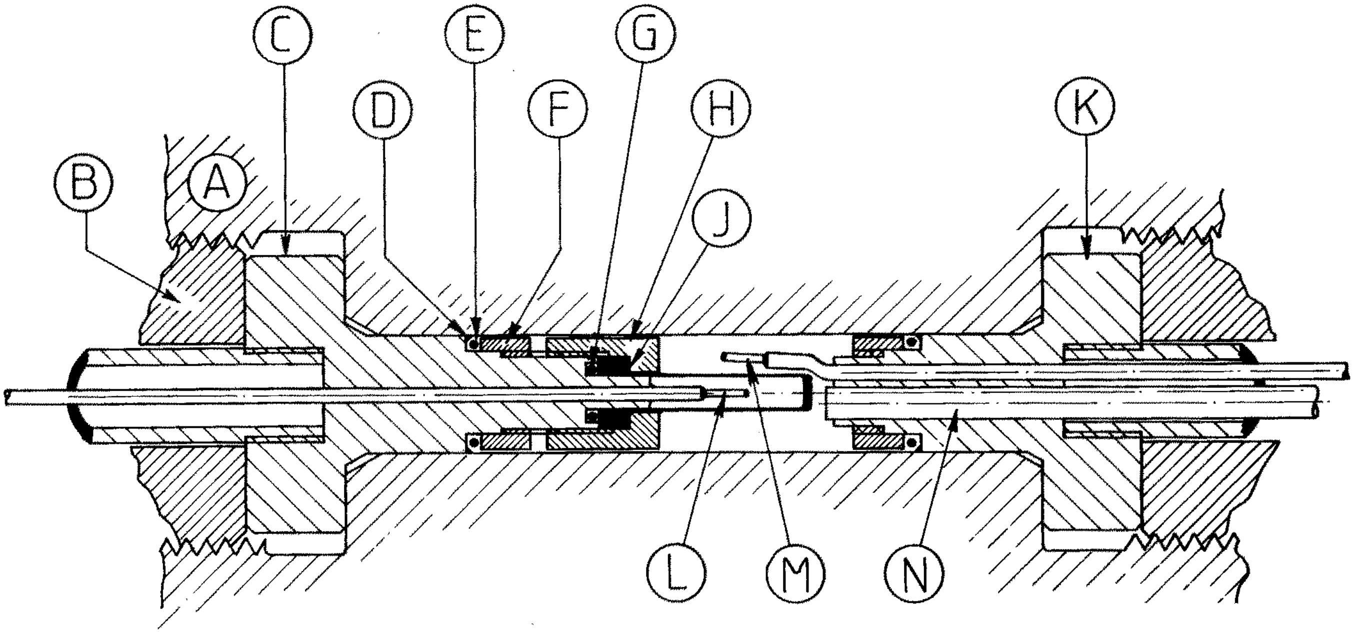

Fig. 1. High-pressure DTA apparatus. A, pressure vessel; B, closure nut; C, closure (sample end); D, sealing ring; E, 0-ring; F, 0-ring nut; G, 0-ring; H, sample-tube nut; J, sample tube; K, closure (pressure end); L, sample thermocouple; M, reference thermocouple; N, pressure line.

contaminated by the epoxy resin, and a formamide sample was contaminated as a result of chemical attack (presumably due to traces of water in the formamide) on the thermocouple wires. These problems were overcome by sheathing the exposed sample thermocouple wires and epoxy resin seal with polyvinylidene fluoride heat-shrink sleeving (with a wall thickness of 0.25 m).

The sample thermocouple measures both the sample temperature relative to the temperature of the adjacent pressurizing fluid and the actual sample temperature by the use of an Omega-CJ cold-junction compensator. The sample thermocouple + compensator was calibrated in the temperature range 200 to 313 K against a platinum resistance element which had been calibrated with an accuracy of ±10 mK at the National Measurement Laboratory, Sydney. The effect of pressure on the thermocouple was investigated, and at 298 K and pressures up to 380 MPa the thermocouple emf was invariant within experimental uncertainty.

The pressure vessel is immersed in a sealed bath of about 1.5-dm^3 capacity through which methylcyclohexane is pumped by a Lauda UK-80-DW Ultra Kryostat. The accessible temperature range of the cryostat is about 190–320 K. Pressures are generated with a 400-MPa screw press and measured with a 0- to 400-MPa Heise bourdon-tube gauge calibrated against deadweight testers. The uncertainty in pressure measurement is within ±0.1 MPa. At present, the pressure limit of our measurements is 350 MPa, which is the highest pressure at which we are currently able to calibrate pressure gauges.

The sample thermocouple emf and the differential emf are simultaneously measured with a two-channel potentiometric recorder during continuous heating and cooling experiments. The sample thermocouple emf is also measured with a digital multimeter to allow constant monitoring of the accuracy of recording the sample thermocouple emf. At present, the heating and cooling rates (typically of the order $2\ \text{K} \cdot \text{min}^{-1}$) are not controlled. The results we have obtained to date indicate, however, that the uncertainty in estimation of transition temperatures, arising from slightly nonlinear differential thermal-emf trace baselines is not larger than about ±0.05 K. The overall uncertainty in transition-temperature measurements is believed to be ±0.1–0.2 K.

For the liquids for which p, T data are reported below, supercooling was invariably observed. For benzene and acetonitrile, freezing points were nonetheless reproducible within experimental uncertainty and were systematically higher (by up to about 1 K) than melting points determined by the usual extrapolation methods from the differential thermal-emf traces of the melting transition. In these cases the freezing points were taken to represent the solid–liquid equilibrium temperatures. In the case of carbon tetrachloride, excessive supercooling led to irreproducibility in freezing-point measurements and the melting temperatures were recorded. Solid–solid transition temperatures were recorded in continuous-heating experiments since transition temperatures obtained in continuous-cooling experiments were not reproducible within the uncertainty of determination.

The materials used were "AnalaR" grade, used as received except for treatment with molecular sieve for at least several weeks before use.

3. RESULTS AND DISCUSSION

In Eqs. (1) through (10) given in this section, p denotes pressure in MPa and T denotes temperature in K.

Solid–liquid transition temperatures for benzene are compared with Deffet's data [7] in Fig. 2. With the exception that Deffet's freezing pressure at 288.15 K appears to be low, the two sets of data agree within 0.2 K. The present data fit the relationship

$$T_{\mathrm{ls}} = 278.4882 + 0.2792\,p - 1.1629 \times 10^{-4}\,p^2 \qquad (1)$$

with the rms deviation (of the experimental points from the calculated curve) 0.11 K. The freezing point at 0.1 MPa from Eq. (1) is 278.52 K, in

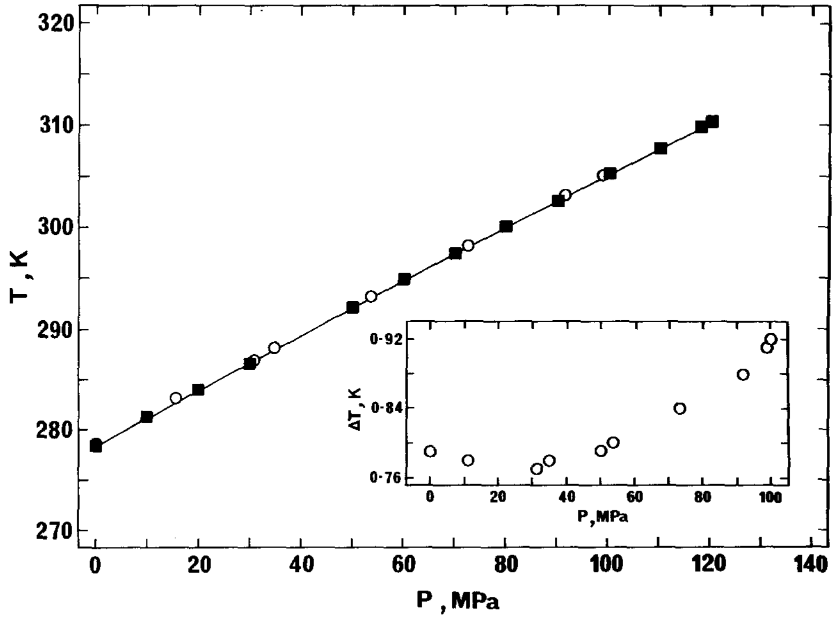

Fig. 2. Solid–liquid transition temperatures for benzene. (■) This work; (○) data from Ref. 7. Inset: the difference between observed freezing points and observed melting points.

good agreement with the literature value [8] (278.683 K). The inset in Fig. 2 shows the difference between observed freezing and observed melting temperatures for benzene. The origin of the discrepancy is not known. Interpolation of Eq. (1) at several pressures leads to the following expression for the freezing pressure as a function of temperature:

$$P_{\mathrm{ls}} = -523.5435 + 0.1857\,T + 6.0838 \times 10^{-3}\,T^2 \qquad (2)$$

Solid–liquid and solid–solid transition temperatures for carbon tetrachloride are shown in Fig. 3, in which the solid–liquid transition temperatures are again compared with Deffet's data [7]. As for benzene, the agreement is within experimental uncertainty except at 50–65 kPa, where our values of T are up to 0.3 K higher than those of Deffet. The solid–liquid and solid–solid transition temperatures can be represented by Eqs. (3) and (4):

$$T_{\mathrm{ls}} = 250.0897 + 0.3736\,p - 1.4691 \times 10^{-4}\,p^2 \qquad (3)$$

(rms deviation, 0.16 K) and

$$T_{\mathrm{ss}} = 226.8652 + 0.2121\,p - 2.4484 \times 10^{-5}\,p^2 \qquad (4)$$

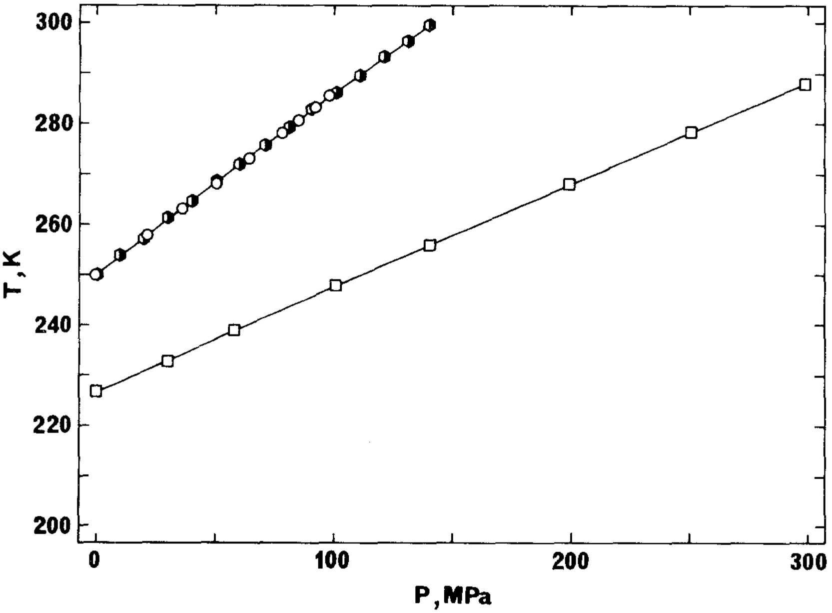

Fig. 3. Solid–solid (□) and solid–liquid transition temperatures for carbon tetrachloride. (◑) This work; (○) data from Ref. 7.

(rms deviation, 0.06 K). From Eq. (3), the melting point at 0.1 MPa is 250.13 K, in good agreement with the literature value [8] (250.20 K). From Eqs. (3) and (4) the transition pressures are expressed as functions of transition temperature by Eqs. (5) and (6):

$$P_{\mathrm{ls}} = -455.1313 + 0.9751\,T + 3.3785 \times 10^{-3}\,T^2 \tag{5}$$

$$P_{\mathrm{ss}} = -921.4366 + 3.4144\,T + 2.8531 \times 10^{-3}\,T^2 \tag{6}$$

A comparison of solid–solid transition temperatures[2] obtained in this work with values from Bridgman [9] and Deffet [7] is given in Table I.

Solid–liquid and solid–solid transition temperatures for acetonitrile are compared with literature data in Fig. 4. The agreement with the data of Schneider [3] and Timmermans and Kasanin [10] (whose data extend to three pressures above 400 MPa) is good overall. The present data lie, for the most part, between the other two sets of data. The measured transition temperatures for acetonitrile are represented by the expressions

$$T_{\mathrm{ls}} = 229.0757 + 0.2051\,p - 7.2309 \times 10^{-5}\,p^2 \tag{7}$$

(rms deviation, 0.15 K) and

$$T_{\mathrm{ss}} = 219.5750 + 0.2002\,p - 1.3699 \times 10^{-5}\,p^2 \tag{8}$$

(rms deviation, 0.15 K). From Eq. (7) the freezing point at 0.1 MPa is 229.10 K, compared with the literature value 229.315 K [8]. Equating the right-hand sides of Eqs. (7) and (8) gives 446.4 MPa, 306.23 K as the

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[2] Bridgman [9] reported, in addition, a higher-pressure solid phase of carbon tetrachloride, occurring in a p, T region which is at present inaccessible to us.

Table I. Solid–Solid Transition Temperatures for Carbon Tetrachloride

P (MPa)	T_{ss} (K)
0.1	226.89[a]; 227.15[b]
196.1	267.51[a]; 267.25[c]
294.2	287.13[a]; 286.95[c]
392.3	306.28[a,d]; 305.95[c]

[a] This work.
[b] Reference 7.
[c] Reference 9.
[d] By extrapolation of Eq. (4).

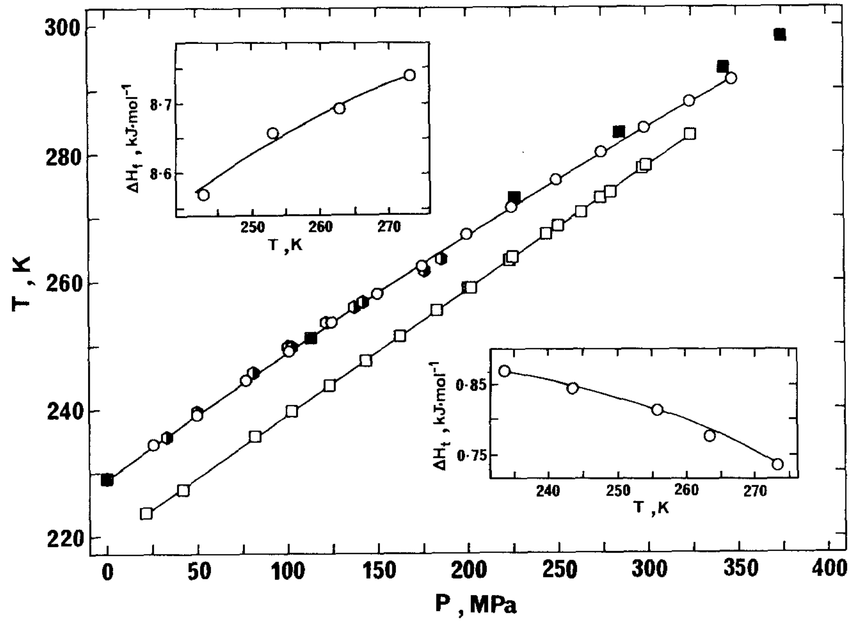

Fig. 4. Solid–solid (□) and solid–liquid transition temperatures for acetonitrile. (○) This work; (◐) data from Ref. 3; (■) data from Ref. 10. Insets: temperature variation of molar enthalpy changes. Upper curve, solid–liquid transition; lower curve, solid–solid transition.

solid I–solid II–liquid triple point for acetonitrile. Interpolation of Eqs. (7) and (8) leads to the following expressions for the transition pressure:

$$P_{\mathrm{ls}} = -1429.7111 + 10.5521\,T - 0.0318\,T^2 \qquad (9)$$

$$P_{\mathrm{ss}} = -1007.4356 + 4.1853\,T + 1.8349 \times 10^{-3}\,T^2 \qquad (10)$$

Use of Eqs. (9) and (10) to evaluate *dp*/*dt* at temperatures for which volume-change data were reported by Landau and Würflinger [1] and estimation of ΔV (change in molar volume) from their data at the pressures given by Eqs. (9) and (10) yields, from the Clapeyron equation, the values for enthalpies of transition shown in the insets in Fig. 4. It should be noted that the values of ΔV extracted from the literature data were somewhat scattered about smooth functions of temperature. Consequently the values of ΔH_{f} (solid–liquid) and ΔH_{t} (solid–solid) shown in Fig. 4 are based on smoothed values of ΔV. Extrapolation of the curve for ΔH_{f} to the freezing point at 0.1 MPa gives ΔH_{f} (0.1 MPa) = 8.43 kJ · mol^{-1}, which is about 2% higher than the literature [8] value. In view of the uncertainty in the estimation of ΔV and the extrapolation involved, the agreement appears to be satisfactory.

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