# Thermodynamics of the thallium alkanoates VII. Heat capacity and thermophysics of thallium(I) butanoate at temperatures from 6 K to 480 K [a]

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The heat capacity of thallium(I) butanoate has been determined by adiabatic calorimetry from temperatures $T$ of 5 K to 350 K and by differential-scanning calorimetry (d.s.c.) from 320 K to 480 K. A transition at $T = (154.2 \pm 0.5)$ K, two very closely spaced crystalline-phase transitions at $T = 285.3_6$ K and $289.8_6$ K as well as a crystal I-to-isotropic liquid transition at $T = 456.7$ K have been studied repeatedly by adiabatic calorimetry and/or d.s.c. The standard molar entropies of the several transitions are IV-to-III, $1.278 \cdot R$; III-to-II, $1.235 \cdot R$; II-to-I, $0.624 \cdot R$, and I-to-isotropic l, $2.02 \cdot R$, respectively. Unlike higher members in this series, no mesomorphic phase occurs between crystalline phase I and the isotropic liquid phase.

## 1. Introduction

This paper aims to provide thermophysical quantities on a new member of the thallium(I) alkanoate system leading to an overview of the significant complexity of the phase relations in the portion of the series studied to date.[1] Heat-capacity measurements on thallium(I) butanoate, hereafter "Tl4C" (Chemical Abstracts registry number [63424-49-7]) were made by adiabatic calorimetry from temperature $T = 5$ K to 350 K and by differential-scanning calorimetry (d.s.c.) from 320 K to 480 K. The rich variety of transitions seen in the crystalline polymorphs and mesomorphic liquid phase in higher members of the series differs by the absence of a

mesomorphic phase. The technological uses may involve energy storage, use as lubricants, or as anisotropic vitreous matrix for various spectroscopic purposes, *etc.*, and the results provide an appreciation of the less complex organic-anion salts of materials-science and biological-process concerns. The ease of variation of the cation together with the aspect of homologous series permits a comparative basis for study that shows unusual gradation of property values.

The use of both d.s.c. and cryogenic adiabatic equilibrium calorimetry permits determination of the phase behavior over an important range of temperature and provides useful thermophysical quantities. In the general absence of diffractional results to elucidate structures and molecular freedom we have been aided by polarized-light microscopy as well as by some X-ray diffraction as a function of temperature in characterizing these phases. Such studies are, however, being described elsewhere.[2]

## 2. Experimental

The sample of TL4C used for this calorimetric study was prepared by the general method described elsewhere,[1] except that the method described earlier[3] was adjusted by adding the base in excess instead of the acid to avoid the coprecipitation of salt and acid as a molecular complex or acid soap. $CH_3(CH_2)_2CO_2H$ (Fluka, puriss grade, >99.5 moles per cent) tested by gas chromatography at the origin and $Tl_2CO_3$ (Fluka, puriss grade, >99 moles per cent purity) were both dissolved in dry methanol as a reacting medium. The salt was purified twice by recrystallization from ethanol and vacuum dried at room temperature. Purity control was followed quantitatively by d.s.c. using fractional-fusion techniques.[4]

A Perkin-Elmer DSC-2C connected to a Model 3600 Data Station and when necessary liquid nitrogen as refrigerant (in accessory B012.-8743) for subambient temperatures was used at temperatures from 240 K to 470 K. The temperature scale for this region was established by measuring the melting temperature of usual high-purity standard materials (*e.g.* undecane, tridecane, pentadecane, indium, and tin, as well as lauric, stearic, and benzoic acids). The energy scale was calibrated with high-purity In (>99.999 moles per cent) as standard material. The purity of the alkanoate was determined on three samples of mass between 3 mg and 6 mg weighed with a Mettler SM-3 balance with a precision of $\pm 0.002$ mg at low heating rates and high sensitivity. The purity taken as the average of three determinations was >99.85 moles per cent of $TlO_2C(CH_2)_2CH_3$ (*i.e.* 0.15 mole per cent of liquid-soluble solid-insoluble impurities). For the enthalpy-of-transition determinations, three to four samples of mass 5 mg to 15 mg were generally determined at a heating rate of $0.17 \text{ K} \cdot \text{s}^{-1}$. The thermogram for thallium(I) butanoate is shown in figure 1. In the temperature region up to 400 K regular solid-substance pans were used to encapsulate the sample and hermetically sealed pans for volatile substance were used at higher temperatures to reduce decomposition of the sample. The estimated standard deviations are 0.5 K and about 2 per cent for transition temperatures and enthalpies, respectively. For the heat-capacity measurements, four to six samples of mass between 10 mg and 20 mg were scanned at $T$ between 300 K and 400 K at a
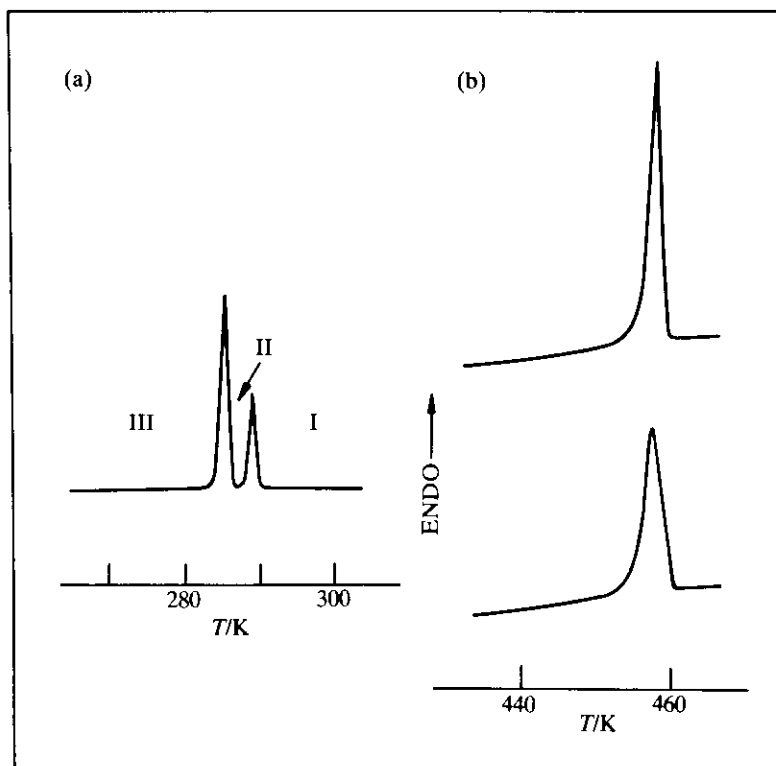
FIGURE 1. Thermogram for thallium(I) butanoate. (a), Peaks corresponding to transitions between crystalline phases; (b), crystal I-to-isotropic liquid {on first pass (above)}, on second and subsequent passes after cooling from the isotropic liquid.

heating rate of $0.17\ K \cdot s^{-1}$. Each scan involved approximately $\Delta T = 30\ K$ increments overlapping each other to reduce base-line uncertainties. The estimated standard deviations were about 3 per cent.

The calorimetric measurements were made in the Mark XIII cryostat described previously.[5] This calorimeter uses intermittent-heating adiabatic equilibrium methods. The programming, logging of results, and calorimetry were done by automated computerization described elsewhere.[6] All measurements of mass, time, resistance, *etc.*, were referred to calibrations of the National Bureau of Standards (formerly NBS, currently NIST). The sample loaded into the gold-plated OFHC copper calorimeter W-62 had a mass of 23.3670 g $\doteq$ 12.4726 $mol^{-1}$, for a molar mass of the TlC4 of 291.4761 $g \cdot mol^{-1}$ on the basis of the 1992 IUPAC relative atomic masses.[7] The buoyancy corrections were calculated on the assumed density of $3.50\ g \cdot cm^{-3}$. No crystallographic information is available for this compound nor for adjacent members of the homologous series. The closest member of the series for which the density is available is that of thallium ethanoate which has a density of $3.6\ g \cdot cm^{-3}$. Following evacuation, 3.7 kPa of purified helium was added to the calorimeter to enhance thermal equilibration; the calorimeter was then sealed *via* a

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TABLE 1. Molar experimental values for the heat capacity at constant pressure for thallium(I) butanoate
($R = 8.31451$ J·K$^{-1}$·mol$^{-1}$)

| $T/K$ | $C_{p,m}/R$ | $T/K$ | $C_{p,m}/R$ | $T/K$ | $C_{p,m}/R$ | $T/K$ | $C_{p,m}/R$ | $T/K$ | $C_{p,m}/R$ | $T/K$ | $C_{p,m}/R$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Series I | | 57.67 | 7.542 | 196.80 | 17.53 | 332.03 | 21.70 | 299.36 | 21.45 | 347.95 | 22.00 |
| 5.81 | 0.174 | 60.24 | 7.808 | 202.10 | 17.71 | 334.76 | 21.17 | 304.42 | 21.26 | | |
| 6.62 | 0.230 | 62.82 | 8.096 | 207.38 | 18.04 | | | 309.53 | 21.20 | Series VI | |
| 7.43 | 0.307 | 65.42 | 8.296 | 212.77 | 18.28 | Series II | | | | 126.95 | 12.22 |
| 8.62 | 0.447 | 68.02 | 8.595 | 218.14 | 18.52 | 272.94 | 21.27 | Series IV | | 131.36 | 12.65 |
| 9.91 | 0.610 | 70.63 | 8.863 | 223.45 | 18.58 | 278.20 | 21.52 | 272.62 | 21.07 | 135.69 | 12.94 |
| 11.20 | 0.803 | 73.27 | 9.032 | 228.76 | 18.85 | 282.17 | 22.20 | 277.85 | 21.25 | 139.92 | 13.16 |
| 12.53 | 1.015 | 75.91 | 9.300 | 234.04 | 18.99 | 284.47 | 43.5 | 284.78 | 67.2 | 144.08 | 13.57 |
| 13.95 | 1.282 | 78.81 | 9.452 | 239.31 | 19.10 | 285.33 | 2830 | 289.23 | 247.2 | 146.97 | 14.60 |
| 15.48 | 1.535 | 82.42 | 9.676 | 244.60 | 19.24 | 285.46 | 2470 | 292.83 | 22.00 | 148.80 | 16.20 |
| 17.07 | 1.878 | 86.42 | 10.040 | 249.77 | 19.49 | 285.53 | 551 | 298.94 | 21.61 | 150.52 | 18.47 |
| 18.65 | 2.070 | 90.43 | 10.32 | 255.00 | 19.85 | 286.48 | 37.0 | 304.03 | 21.44 | 151.98 | 21.50 |
| 20.29 | 2.292 | 94.47 | 10.61 | 260.26 | 20.13 | 288.36 | 42.9 | | | 152.99 | 54.60 |
| 21.92 | 2.599 | 98.84 | 10.79 | 265.51 | 20.52 | 289.36 | 372 | Series V | | 153.63 | 211 |
| 23.62 | 2.875 | 103.51 | 11.10 | 270.76 | 20.94 | 290.70 | 26.36 | 272.79 | 21.12 | 153.67 | 190 |
| 25.38 | 3.173 | 108.16 | 11.33 | 275.35 | 21.36 | 293.35 | 22.00 | 277.99 | 21.50 | 154.48 | 159 |
| 27.15 | 3.458 | 112.81 | 11.581 | 280.75 | 22.00 | 297.33 | 21.88 | 284.25 | 71.7 | 154.85 | 80 |
| 28.95 | 3.722 | 117.49 | 11.801 | 284.18 | 68.8 | 302.44 | 21.47 | 288.58 | 43.9 | 155.85 | 40.7 |
| 30.75 | 3.998 | 128.90 | 12.471 | 285.40 | 1868 | | | 291.63 | 44.1 | 158.45 | 20.75 |
| 32.56 | 4.285 | 129.92 | 12.57 | 286.31 | 81.7 | Series III | | 296.58 | 21.67 | 162.13 | 19.40 |
| 34.52 | 4.584 | 140.14 | 13.208 | 288.30 | 59.8 | 272.73 | 21.15 | 301.72 | 21.49 | 165.83 | 18.10 |
| 36.63 | 4.904 | 144.85 | 13.764 | 290.93 | 37.2 | 277.94 | 21.26 | 306.76 | 21.35 | 169.45 | 17.17 |
| 38.72 | 5.23 | 149.73 | 17.34 | 295.03 | 21.90 | 283.90 | 75.6 | 311.87 | 21.18 | | |
| 40.85 | 5.503 | 152.97 | 67.8 | 299.88 | 21.56 | 287.92 | 26.68 | 316.89 | 21.17 | Series VII | |
| 42.98 | 5.810 | 160.63 | 20.00 | 304.67 | 21.40 | 288.91 | 52.7 | 321.93 | 21.20 | 131.46 | 12.70 |
| 45.13 | 6.055 | 170.31 | 17.03 | 309.72 | 21.29 | 289.26 | 260.3 | 326.92 | 21.20 | 144.50 | 14.00 |
| 47.47 | 6.360 | 175.86 | 16.91 | 314.94 | 21.03 | 289.37 | 373 | 331.90 | 21.29 | 157.51 | 29.00 |
| 50.01 | 6.681 | 181.09 | 16.88 | 320.19 | 21.20 | 289.86 | 23.66 | 336.85 | 21.68 | 167.87 | 17.61 |
| 52.55 | 6.982 | 186.35 | 17.04 | 325.43 | 21.40 | 291.00 | 23.10 | 341.77 | 21.80 | | |
| 55.11 | 7.224 | 191.58 | 17.29 | 329.40 | 21.40 | 294.25 | 21.80 | 345.47 | 22.15 | Series VIII | |
| | | | | | | | | | | 144.50 | 27.5 |
| | | | | | | | | | | 164.72 | 18.74 |

screw cap which pressed a gold gasket against the circular knife edge on the stainless-steel neck of the calorimeter. The calorimeter was sealed within the vacuum chamber by a remotely operating hexagonal wrench.

The thermal history of the thallium butanoate sample is shown by the linear array: (solid arrows indicate cooling and dashed arrows indicate acquisition-of-results

TABLE 2. D.s.c.-determined heat capacities of thallium(I) butanoate ($R = 8.31451$ J·K$^{-1}$·mol$^{-1}$)

| $T/K$ [a] | $C_{p,m}/R$ [a] | $T/K$ | $C_{p,m}/R$ | $T/K$ | $C_{p,m}/R$ | $T/K$ | $C_{p,m}/R$ | $T/K$ | $C_{p,m}/R$ | $T/K$ | $C_{p,m}/R$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Crystal I | | 340 | 21.7 | 360 | 22.4 | 380 | 23.1 | 400 | 23.7 | 420 | 24.3 |
| 320 | 21.1 | 345 | 21.8 | 365 | 22.6 | 385 | 23.2 | 405 | 23.8 | 425 | 24.4 |
| 325 | 21.2 | 350 | 22.1 | 370 | 22.7 | 390 | 23.4 | 410 | 24.0 | 430 | 24.5 |
| 330 | 21.4 | 355 | 22.2 | 375 | 22.9 | 395 | 23.5 | 415 | 24.2 | Isotropic liquid | |
| 335 | 21.6 | | | | | | | | | | |

[a] Standard deviations are typically $\pm 0.5$ in $T$ and $\pm 3$ per cent in the heat capacity.
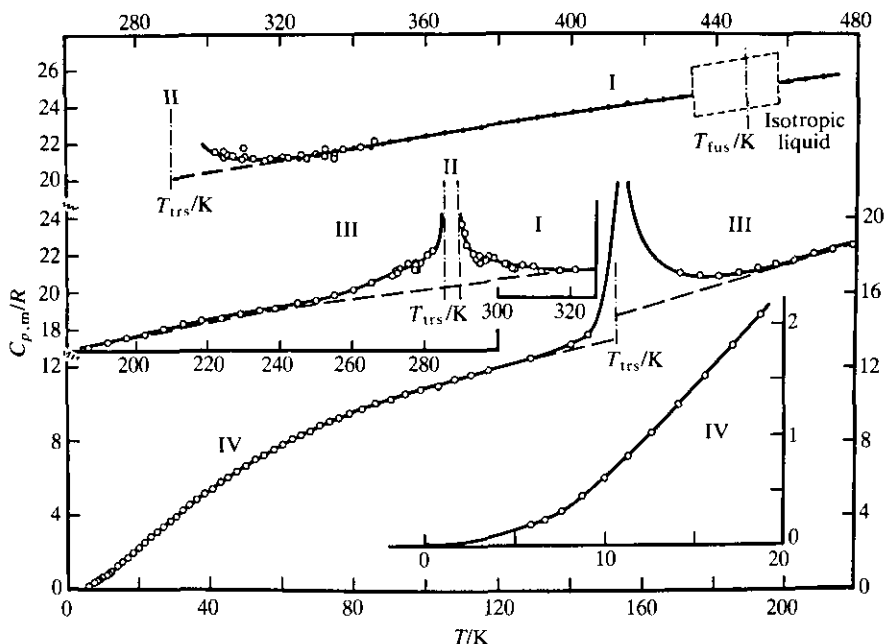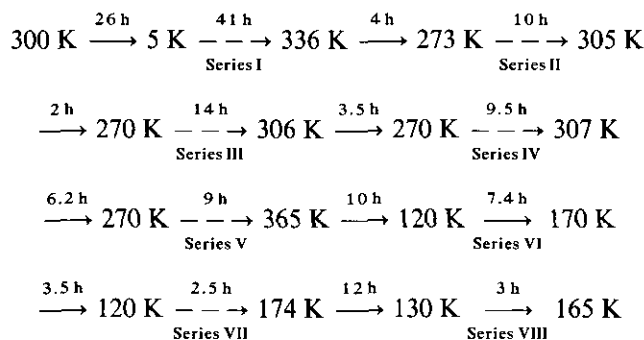
FIGURE 2. The overall heat capacity of thallium(I) butanoate. $\bigcirc$, Adiabatic calorimetric points; $\bullet$, d.s.c. points; $-\,-\,-$, lattice heat capacities.

ranges for various series).

$$300\ K \xrightarrow{26\,h} 5\ K \xdashrightarrow{41\,h} 336\ K \xrightarrow{4\,h} 273\ K \xdashrightarrow{10\,h} 305\ K$$
$$\underset{\text{Series I}}{\qquad\qquad} \underset{\text{Series II}}{\qquad\qquad}$$

$$\xrightarrow{2\,h} 270\ K \xdashrightarrow{14\,h} 306\ K \xrightarrow{3.5\,h} 270\ K \xdashrightarrow{9.5\,h} 307\ K$$
$$\underset{\text{Series III}}{\qquad\qquad} \underset{\text{Series IV}}{\qquad\qquad}$$

$$\xrightarrow{6.2\,h} 270\ K \xdashrightarrow{9\,h} 365\ K \xrightarrow{10\,h} 120\ K \xrightarrow{7.4\,h} 170\ K$$
$$\underset{\text{Series V}}{\qquad\qquad} \underset{\text{Series VI}}{\qquad\qquad}$$

$$\xrightarrow{3.5\,h} 120\ K \xdashrightarrow{2.5\,h} 174\ K \xrightarrow{12\,h} 130\ K \xrightarrow{3\,h} 165\ K$$
$$\underset{\text{Series VII}}{\qquad\qquad} \underset{\text{Series VIII}}{\qquad\qquad}$$

The values of $C_p$ measured have a standard deviation varying from 5 per cent at $T = 6$ K to 0.6 per cent at 10 K and 0.13 per cent above this temperature to 350 K. The d.s.c. results have a standard deviation of about 0.5 K in $T$, 2 per cent in $C_p$, and 3 to 4 per cent in $\Delta_{trs}H$ determinations (depending on the magnitude of $\Delta_{trs}H$). The values of the smoothed integrated thermophysical properties are more reliable and have a standard deviation of 0.10 per cent at $T > 100$ K.

The heat capacity of the sample varied from 0.65 to 0.75 of the total (sample + calorimeter + heater/thermometer) over the measured range, except, of course, in transition regions.

TABLE 3. Experimental molar transition enthalpy determinations for thallium(I) butanoate
$(R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$

For IV-to-III transition by adiabatic calorimetry

| $N^a$ | $n^b$ | $\dfrac{T_i}{K}$ | $\dfrac{T_f}{K}$ | $\dfrac{T_{trs}}{K}$ | $\dfrac{\Delta_{120K}^{180K}H_m^{\circ\,c}}{R\cdot K}$ | $\dfrac{\Delta_{trs}H_m^{\circ\,d}}{R\cdot K}$ |
|---|---|---|---|---|---|---|
| I | 10 | 119.831 | 183.701 | 154.2±0.5 | 1123.30 | 185.80 |
| VI | 13 | 137.834 | 166.662 | | 1123.20 | 185.70 |
| VII | 2 | 133.653 | 166.060 | | 1123.33 | 185.83 |
| VIII | 2 | 134.087 | 166.538 | | 1123.37 | 185.87 |
| | | | Means: | | 1123.30±0.04 | 185.80±0.04 |
| | | | Graphical: | | 1124 | 187 |
| | | | $\Delta_{trs}S_m/R = 1.228 \pm 0.005$ | | | |

For transition III-to-II and II-to-I by adiabatic calorimetry

| | | | | | $\Delta_{280K}^{295K}H_m^{\circ}/(R \cdot K)$ | |
|---|---|---|---|---|---|---|
| I | 7 | 278.321 | 297.450 | $285.3_6 \pm 0.1$ | 838.2 | 533.9 |
| II | 11 | 208.759 | 299.851 | $289.8_6 \pm 0.1$ | 838.1 | 533.2 |
| III | 8 | 280.522 | 296.810 | | 838.1 | 533.3 |
| IV | 3 | 280.430 | 296.381 | | 838.2 | 533.5 |
| | | | Means: | | 838.2±0.4 | 533.5±0.5 |
| | | | Graphical: | | 840 | 536 |
| | | | $\Delta_{trs}S_m/R = 1.859 \pm 0.001$ | | | |

Division into separate transitions$^e$

Transition III/II
  $T_{trs} \approx 285._0$ K    $\Delta_{trs}H_m^{\circ}/(R \cdot K) = 352._5;$   $\Delta_{trs}S_m^{\circ}/R = 1.23_5$

Transition II/I
  $T_{trs} \approx 289._2$ K    $\Delta_{trs}H_m^{\circ}/(R \cdot K) = 181._0;$   $\Delta_{trs}S_m^{\circ}/R = 0.624$

Transitions by d.s.c. (mean values from 6 determinations of each)

| Transition designation | $\dfrac{T_{trs}}{K}$ | $\dfrac{\Delta_{trs}H_m^{\circ}}{R\cdot K}$ | $\dfrac{\Delta_{trs}S_m^{\circ}}{R}$ |
|---|---|---|---|
| III-to-II | 285.0±0.4 | 332±10 | 1.12±0.04 |
| II-to-I | 289.2±0.4 | 162±10 | 0.56±0.04 |
| I-to-isotropic liquid$^f$ | 456.7±0.05 | 925±30 | 2.03±0.07 |

Transitions as reported in the literature

| Transition designation | $\dfrac{T_{trs}}{K}$ | $\dfrac{\Delta_{trs}H_m^{\circ}}{R\cdot K}$ | Method | Year | Reference |
|---|---|---|---|---|---|
| Fusion | 455 | — | micr. | 1926 | 8 |
| Fusion | 450 | — | micr. | 1970 | 9 |
| Fusion | 451.9 | 866 | d.s.c | 1981 | 10 |
| Fusion | 459 | 806 | d.t.a. | 1984 | 11 |

$^a$ Adiabatic series designation.
$^b$ Number of heating increments.
$^c$ $\Delta_{T_i}^{T_f}H_m^{\circ}$ is the molar energy input from the initial temperature $T_i$ to the final temperature $T_f$ adjusted to span the rounded temperature interval from $T_1$ to $T_2$ and for quasi-adiabatic drift.
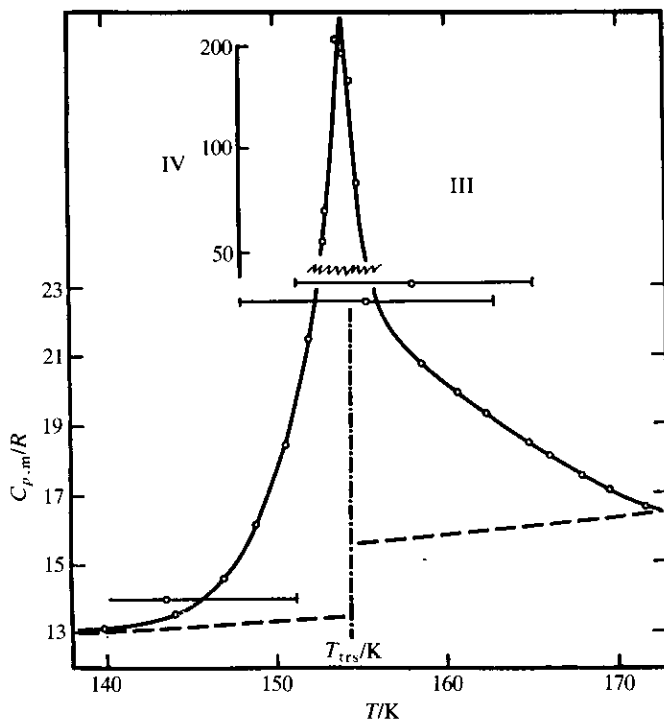
FIGURE 3. The IV-to-III transition in thallium(I) butanoate. Enthalpy runs are shown with a bar across the temperature increment; — — —, lattice heat capacity.

## 3. Results and discussion

The experimental adiabatic calorimetric heat capacities are given in table 1 and are plotted for the entire temperature range in composite figure 2. In regions of normal heat capacity the values were fitted to a series of orthogonal polynomials for smoothing, integration, etc. In table 1, the results are listed in chronological sequence; hence, the approximate temperature interval of each measurements may usually be inferred from the mean temperatures of adjacent determinations. Within transition regions other methods were invoked to evaluate (integrate) the total and excess enthalpy and the entropy increments. As may be seen in figure 2, four apparently first-order transitions occur over the experimental temperature range observed. The one at the lowest temperature (IV-to-III) was observed only by adiabatic calorimetry. The two at intermediate temperatures (III-to-II and II-to-I)

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$^d$ $\Delta_{trs} H_m^\circ$ is the net molar enthalpy increment of transition relative to the selected lattice curve (compare table 6).

$^e$ Division of this overlapping double peak is rather arbitrary. A vertical split was made at $T = 288.5$ K at the bottom of the valley. This does not affect the overall functions, only the division of the transitional increments—the sum of which is firmly ascertained by measurements.

$^f$ Reported by F. Fernández-Martín, F. L. López de la Fuente, and J. A. R. Cheda.[11]

TABLE 4. Smoothed values for the heat capacity with derived thermodynamic properties of thallium(I) butanoate ($R = 8.31451$ J·K$^{-1}$·mol$^{-1}$)

**Left panel**

| $\frac{T}{K}$ | $\frac{C_{p,m}}{R}$ | $\frac{\Delta_0^T S_m^\circ}{R}$ | $\frac{\Delta_0^T H_m^\circ}{R \cdot K}$ | $\frac{\Phi_m^\circ}{R}$ |
|---|---|---|---|---|
| | | Crystal IV | | |
| 0 | (0) | (0) | (0) | (0) |
| 5 | (0.108) | (0.038) | (0.141) | (0.010) |
| 10 | 0.633 | 0.250 | 1.819 | 0.068 |
| 15 | 1.430 | 0.652 | 6.919 | 0.191 |
| 20 | 2.288 | 1.181 | 16.216 | 0.371 |
| 25 | 3.096 | 1.780 | 29.702 | 0.592 |
| 30 | 3.896 | 2.415 | 47.175 | 0.842 |
| 35 | 4.645 | 3.073 | 68.56 | 1.114 |
| 40 | 5.399 | 3.744 | 93.75 | 1.401 |
| 45 | 6.053 | 4.418 | 122.38 | 1.698 |
| 50 | 6.673 | 5.088 | 154.21 | 2.004 |
| 60 | 7.785 | 6.506 | 226.64 | 2.628 |
| 70 | 8.737 | 4.679 | 309.38 | 3.259 |
| 80 | 9.549 | 8.900 | 400.91 | 3.889 |
| 90 | 10.246 | 10.055 | 499.97 | 4.511 |
| 100 | 10.854 | 11.178 | 605.5 | 5.122 |
| 110 | 11.397 | 12.238 | 716.8 | 5.721 |
| 120 | 11.897 | 13.252 | 833.3 | 6.307 |
| 130 | 12.370 | 14.223 | 954.7 | 6.879 |
| 140 | 12.833 | 15.16 | 1080.7 | 7.982 |
| 150 | 13.300 | 16.06 | 1211.4 | 7.982 |
| 154.2[a] | (>220) | (16.43) | (1266.9) | (8.265) |
| | | Crystal III | | |
| 154.2[a] | (>220) | (17.65) | (1452.7) | (8.265) |
| 160 | 15.82 | 18.25 | 1547.6 | 8.573 |
| 170 | 16.38 | 19.22 | 1708.6 | 9.171 |
| 180 | 16.89 | 20.17 | 1874.9 | 9.756 |
| 190 | 17.35 | 21.10 | 2046.2 | 10.329 |
| 200 | 17.78 | 22.00 | 2221.9 | 10.890 |
| 210 | 18.15 | 22.88 | 2401.6 | 11.440 |
| 220 | 18.49 | 23.73 | 2584.8 | 11.979 |
| 230 | 18.79 | 24.56 | 2771.3 | 12.508 |
| 240 | 19.07 | 25.36 | 2960.6 | 13.027 |
| 250 | 19.33 | 26.15 | 3152.6 | 13.536 |
| 260 | 19.57 | 26.91 | 3347.1 | 14.036 |
| 270 | 19.83 | 27.65 | 3544.1 | 14.526 |
| 280 | 20.10 | 28.38 | 3743.7 | 15.01 |
| 285.3$_6$[a] | (>2830) | (28.66) | (3851.8) | (15.16) |
| | | Crystal II | | |
| 285.3$_6$[a] | (>2830) | (29.89) | (4204.3) | (15.16) |
| 289.8$_6$ | (>340) | (30.21) | (4295.7) | (15.39) |

**Right panel**

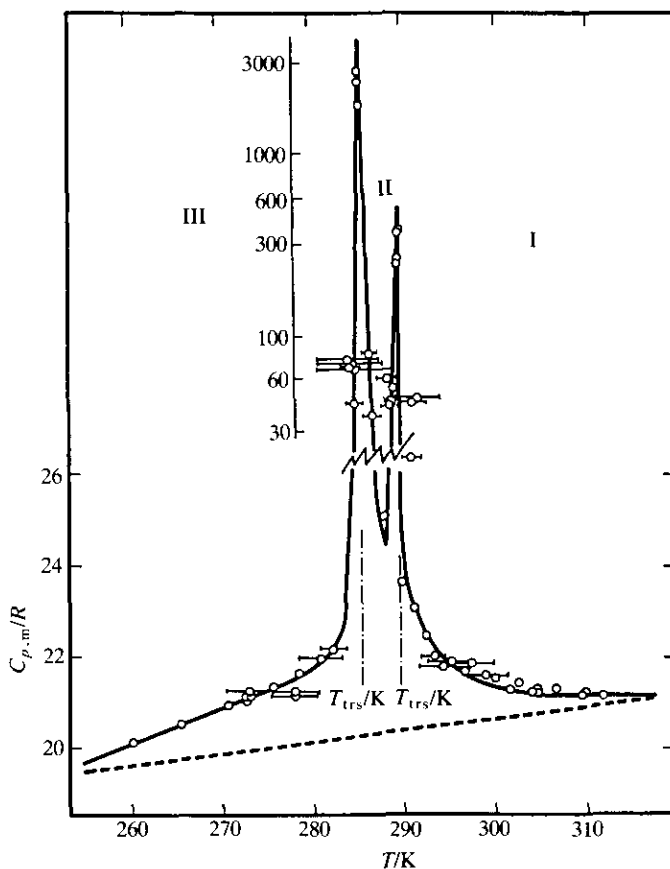| $\frac{T}{K}$ | $\frac{C_{p,m}}{R}$ | $\frac{\Delta_0^T S_m^\circ}{R}$ | $\frac{\Delta_0^T H_m^\circ}{R \cdot K}$ | $\frac{\Phi_m^\circ}{R}$ |
|---|---|---|---|---|
| | | Crystal I | | |
| 289.8$_6$ | (>340) | (30.83) | (4476.7) | (15.39) |
| 290 | 20.39 | 30.95 | 4479.7 | 15.50 |
| 298.15 | 20.53 | 31.52 | 4646.4 | 15.93 |
| 300 | 20.57 | 31.64 | 4684.4 | 16.03 |
| 325 | 21.25 | 33.31 | 5207 | 17.29 |
| 350 | 22.09 | 34.92 | 5748 | 18.50 |
| 375 | 22.93 | 36.47 | 6311 | 19.64 |
| 400 | 23.66 | 37.98 | 6894 | 20.74 |
| 425 | 24.22 | 39.43 | 7493 | 21.80 |
| 450 | 24.59 | 40.82 | 8103 | 22.82 |
| 456.7[a] | (—) | (41.19) | (8268) | (23.08) |
| | | Isotropic liquid | | |
| 456.7[a] | (—) | (43.21) | (9193) | (23.08) |
| 475 | (24.90) | (44.19) | (9646) | (23.88) |
| | | Assigned lattice thermophysical properties[b] | | |
| | | Crystal IV | | |
| 130 | 12.37 | 14.22 | 954.7 | 6.879 |
| 140 | 12.83 | 15.16 | 1080.7 | 7.437 |
| 150 | 13.30 | 16.06 | 1211.4 | 7.982 |
| 154.2[c] | 14.50 | 16.49 | 1279.8 | 8.236 |
| | | Crystal III | | |
| 154.2[c] | 15.60 | 16.49 | 1279.8 | 8.236 |
| 160 | 15.84 | 17.03 | 1361.7 | 8.516 |
| 180 | 16.92 | 18.96 | 1689.7 | 9.570 |
| 260 | 19.57 | 25.69 | 3160.5 | 13.533 |
| 280 | 20.09 | 27.16 | 3557.1 | 14.454 |
| 285.3$_6$[c] | 20.23 | 27.53 | 3666.2 | 14.694 |
| | | Crystal II | | |
| 285.3$_6$[c] | 20.23 | 27.53 | 3666.2 | 14.694 |
| 289.8$_6$[c] | 20.35 | 27.85 | 3757.8 | 14.895 |
| | | Crystal I | | |
| 289.8$_6$[c] | 20.35 | 27.85 | 3757.8 | 14.895 |
| 300 | 20.63 | 28.56 | 3964.3 | 15.35 |
| 320 | 21.19 | 29.91 | 4382.4 | 16.22 |
| 420 | 24.13 | 36.06 | 6652 | 20.23 |
| 440 | 24.53 | 37.20 | 7138 | 20.97 |
| 456.7 | 24.70 | 38.11 | 7549.7 | 21.58 |
| 456.7[c] | 24.71 | 38.11 | 7550 | 21.58 |
| | | Isotropic liquid | | |
| 456.7[c] | 24.71 | 38.11 | 7550 | 21.58 |
| 475 | 24.73 | 39.09 | 8003 | 22.24 |

FIGURE 4. The III-to-II, and II-to-I transitions in thallium(I) butanoate. Enthalpy runs are shown with a bar across the temperature increment; $- - -$, lattice heat capacity.

were studied both by d.s.c. and adiabatic calorimetry, and the highest temperature one (I-to-isotropic l) only by d.s.c. The results for the first three transitions are given in tables 2 and 3 and depicted graphically in figures 3 and 4. Where both techniques were employed on a transition, each is in good accord both in heat-capacity and transitional regions enhancing confidence that in those regions where only d.s.c. was performed the results can be presumed to be likewise reliable within the bounds imposed by the assigned standard deviations. However, the literature values are seen to be further afield.

[a] The values in parentheses refer to the presumedly isothermal values of the derived functions at the transition temperature. The values of the derived properties at the nearest adjacent temperature may, therefore, be slightly lower than measured (compare figure 1). The heat-capacity values thus indicated at the transition temperatures are maximal values observed at the peak or at the stated temperature.

[b] The values of the heat capacity of the "lattice" curve to which the $\Delta_{trs}H_m^o$ and the $\Delta_{trs}S_m^o$ are arbitrarily referred are depicted in figure 2.

[c] Arbitrary (extrapolated) values to delineate selected lattice values.

The butanoate transitional-entropy increments are relatively small because of the short chain length. The compound, however, has the longest chain length in the *n*-homologous series which does not have a mesomorphic liquid phase. Table 4 summarizes the smoothed values of the heat capacity at selected temperatures together with the derived thermodynamic properties. Resolution of the excess properties is achieved by the defined, albeit somewhat arbitrary, lattice heat-capacity curve and its corresponding thermodynamic properties. The selected curve has been carefully defined in the last section of table 4 recognizing that latter judgement may suggest a revision in its placement and adjustment in the excess contributions can be reliably made. It is emphasized that the placement of this curve does not influence the (observed) total heat capacity, but only the resolution in normal and excess portions.

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