Thermodynamics of thallium alkanoates II. Heat capacity and thermodynamic functions of thallium(I) *n*-heptanoate [a]

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The sub-ambient heat capacity of thallium(I) *n*-heptanoate is characterized by two sets of transitions between 262 and 301 K. The lowest transition (at 262.8 K) has a maximum $C_{p,m}/R \approx 700$. Next, a bifurcated pair (at 267.8 and 271.7 K) has $(C_{p,m}/R)$'s ≈ 200, and the highest bifurcated pair (at 297.2 and 300.9 K) has maximum $(C_{p,m}/R)$'s ≈ 450 and ≈ 16000. The corresponding values of $\Delta_{trs}S_m^{\circ}/R$ for the two sets are about 1.93_5 and 2.21_5. The heat capacities are in fair accord with the d.s.c. values of Fernandez-Martin, Lopez de la Fuente, and Cheda over the common range of superambient values. At 298.15 K the values of $\{S_m^{\circ}(T) - S_m^{\circ}(0)\}/R$, $\{H_m^{\circ}(T) - H_m^{\circ}(0)\}/R$, and $-\{G_m^{\circ}(T) - H_m^{\circ}(0)\}/RT$ are 38.58, 5514.7 K, and 20.30. Smoothed thermodynamic values are tabulated at selected temperatures through melting.

1. Introduction

A recent paper describes heat-capacity measurements over the cryogenic region on thallium(I) *n*-hexanoate. The second thallium compound to be investigated is thallium(I) *n*-heptanoate (Tl7C). Studies by d.s.c. at higher temperatures have been published by Fernandez-Martin *et al.*,[2] and the thermophysical properties as measured previously have been summarized by Franzosini and Sanesi.[3] Relatively little else is known about the compound, but thermal methods[4, 5] and microscopic methods[5−7] have also been used in the superambient region. The phase behavior observed in the superambient region can be summarized as:

Crystal II = Crystal I = Mesomorphic liquid = Isotropic liquid

T_{trs}:   301.9 K   420.7 K   502.7 K

The subambient phase behavior has not been investigated previously and will be seen to be complex on the basis of our thermophysical studies. Only the highest of the five transitions has been reported previously.

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2. Experimental

The sample of Tl7C used is a portion from a batch prepared at the Universidad Complutense, Madrid, Spain and used for superambient d.s.c. studies.[2] The salt was obtained by reaction of purified n-heptanoic acid with thallium carbonate in methanol according to the procedure of Meisel *et al.*[4] The salt was recrystallized several times from (ethanol + ether): infrared spectroscopic determinations failed to reveal any traces of water or free acid. In addition, the sample was analyzed by Spang Microanalytical Laboratory for all four elements and the reported values are H, 4.03 mass per cent, theoretical: 3.93 mass per cent; C, 25.37 mass per cent, theoretical: 25.21 mass per cent; O, 9.75 mass per cent, theoretical: 9.59 mass per cent; and Tl, 60.94 mass per cent, theoretical: 61.27 mass per cent. Moreover, a d.s.c. purity determination using fractional-fusion techniques indicated a value of 99.89 moles per cent of liquid-soluble solid-insoluble purity.

The calorimetric measurements were made in the Mark X cryostat described previously.[8] This calorimeter uses intermittent-heating adiabatic equilibrium methods. The programming, data logging, and calorimetry were done by automated computerization described elsewhere.[9] All measurements of mass, time, resistance, *etc.*, were referred to calibrations of the National Bureau of Standards. The sample loaded into the gold-plated OFHC copper calorimeter W-62 had a mass of 65.615 g, which corresponds to an amount-of-substance factor of 5.083, on the basis of the 1978 IUPAC relative atomic masses. The buoyancy corrections are calculated on the assumed density of $2.85 \text{ g} \cdot \text{cm}^{-3}$. 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 acetate which has a density of $3.6 \text{ g} \cdot \text{cm}^{-3}$. Following evacuation, 2.4 kPa of purified helium was added to the calorimeter to enhance thermal equilibration; the calorimeter was then sealed *via* a screw cap which pressed a gold gasket against the circular knife edge on the stainless-steel neck of the calorimeter. The calorimeter was sealed by a remotely operating hexagonal wrench within the vacuum chamber.

The thermal history of the thallium heptanoate sample is shown by the linear array: (solid arrows indicate cooling and dashed arrows indicate data acquisition ranges for various series).
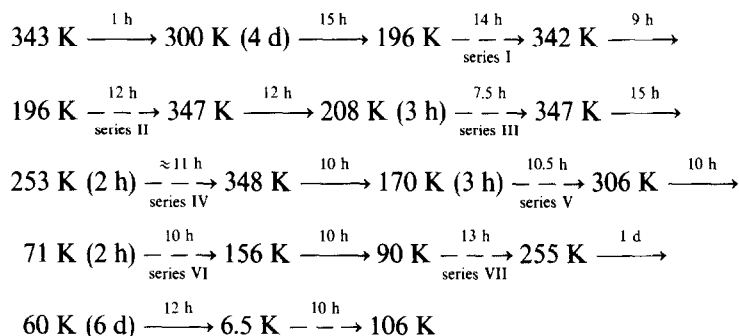
$$343 \text{ K} \xrightarrow{1 \text{ h}} 300 \text{ K (4 d)} \xrightarrow{15 \text{ h}} 196 \text{ K} \underset{\text{series I}}{\xrightarrow{14 \text{ h}}} 342 \text{ K} \xrightarrow{9 \text{ h}}$$

$$196 \text{ K} \underset{\text{series II}}{\xrightarrow{12 \text{ h}}} 347 \text{ K} \xrightarrow{12 \text{ h}} 208 \text{ K (3 h)} \underset{\text{series III}}{\xrightarrow{7.5 \text{ h}}} 347 \text{ K} \xrightarrow{15 \text{ h}}$$

$$253 \text{ K (2 h)} \underset{\text{series IV}}{\xrightarrow{\approx 11 \text{ h}}} 348 \text{ K} \xrightarrow{10 \text{ h}} 170 \text{ K (3 h)} \underset{\text{series V}}{\xrightarrow{10.5 \text{ h}}} 306 \text{ K} \xrightarrow{10 \text{ h}}$$

$$71 \text{ K (2 h)} \underset{\text{series VI}}{\xrightarrow{10 \text{ h}}} 156 \text{ K} \xrightarrow{10 \text{ h}} 90 \text{ K} \underset{\text{series VII}}{\xrightarrow{13 \text{ h}}} 255 \text{ K} \xrightarrow{1 \text{ d}}$$

$$60 \text{ K (6 d)} \xrightarrow{12 \text{ h}} 6.5 \text{ K} \xrightarrow{10 \text{ h}} 106 \text{ K}$$

TABLE 1. Experimental values of heat capacity of thallium(I) n-heptanoate ($R = 8.3144$ 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	$C_{p,m}/R$
Series I		330.72	39.53	262.68	344	Series VI		Series VIII	
264.83	74.40	338.13	39.17	262.79	546	78.36	12.766	6.63	0.33
271.40	68.87	344.41	38.92	263.13	112.5	92.75	14.262	7.30	0.34
280.67	34.74			264.13	37.620	96.55	14.574	8.14	0.45
290.93	50.24	Series IV		265.62	35.506	100.24	14.927	9.05	0.59
298.04	87.10	ΔH_{trs} Det'n B		266.97	48.26	104.04	15.262	9.91	0.719
300.82	1528	285.18	36.075	267.83	126.0	107.92	15.541	10.78	0.859
307.41	40.20	288.19	37.690	269.69	55.57	111.78	15.784	11.65	1.011
312.79	39.71	289.75	39.380	271.54	128.4	115.60	16.225	12.62	1.194
318.18	39.79	291.72	43.682	272.12	96.8	119.29	16.679	13.68	1.391
323.57	39.91	293.52	56.330	272.74	105.8	122.90	16.723	14.75	1.613
328.98	39.63	294.93	109.6	273.76	38.162	126.80	17.025	15.84	1.832
334.41	39.37	296.31	144.3	275.28	34.237	130.95	17.317	16.94	2.057
339.85	39.07	299.02	72.14	276.87	33.932	135.02	17.605	18.07	2.175
		300.927	193.7	278.07	33.985	139.02	17.898	19.19	2.534
Series II		302.25	69.5	278.86	34.088	142.97	18.186	20.296	2.766
197.41	22.124	305.65	40.39	279.65	34.315	146.84	18.436	21.36	2.998
201.88	22.552	309.67	39.89	280.43	34.443	150.65	18.707	22.38	3.2197
208.05	23.123	312.13	39.89	281.22	34.584	154.41	18.972	23.46	3.452
214.19	23.676	313.17	39.86	282.00	34.785			24.59	3.700
220.31	24.352	314.73	39.72	283.16	35.236	Series VII		25.78	3.952
226.42	25.063	316.81	39.78	284.69	35.720	94.96	14.451	27.02	4.221
232.52	25.902	318.89	39.81	286.21	36.401	103.40	15.164	28.49	4.538
238.61	26.773	322.90	39.90	287.70	37.221	111.42	15.878	30.096	4.884
244.68	27.900	326.94	39.74	289.16	38.446	119.05	16.625	31.58	5.199
250.79	28.976	333.22	39.36	290.58	40.482	126.37	17.002	32.96	5.497
257.15	30.489	339.49	39.05	292.94	52.31	133.49	17.524	34.73	5.874
261.63	108.9	345.76	38.82	294.93	109.6	140.42	18.011	36.93	6.329
266.71	57.9			295.44	159.6	147.19	18.489	39.13	6.757
275.05	50.34	Series V		295.75	267.7	153.80	18.951	41.35	7.186
285.12	36.35	195.72	21.996	295.98	344	160.28	19.394	43.81	7.648
293.07	60.4	206.38	22.949	296.39	92.1	166.64	19.839	46.51	8.144
298.03	88.2	216.67	23.973	297.17	42.849	172.88	20.285	49.22	8.620
303.82	76.2	226.60	25.113	298.05	44.139	179.01	20.714	51.97	9.095
312.12	39.81	236.21	26.357	298.90	45.88	185.01	21.173	55.11	9.605
322.57	39.77	243.68	27.579	299.73	48.40	190.88	21.615	58.61	10.134
331.43	39.54	249.15	28.555	300.47	58.13	195.51	22.003	62.11	10.678
338.21	39.13	252.73	29.145	300.88	450	198.95	22.304	65.62	11.171
344.48	38.90	254.48	29.564	300.92	2368	202.36	22.590	69.16	11.611
		256.21	30.079	300.93	1727	205.72	22.903	72.72	12.053
Series III		257.92	30.443	300.95	1289	210.63	23.423	76.42	12.508
221.59	24.481	259.19	30.867	301.27	82.2	218.44	24.132	84.33	13.452
ΔH_{trs} Det'n A		260.02	31.375	302.12	42.7	227.06	25.203	92.37	14.227
263.80	42.99	260.84	32.406	303.22	41.8	235.12	26.251	96.52	14.636
267.01	59.74	261.59	38.761	304.34	40.82	243.20	27.522	100.60	14.974
272.45	59.95	262.14	80.5	305.47	40.43	251.24	29.564	104.65	15.277
281.39	34.95	262.44	168.9						
306.85	54.45	262.59	283.6						

The obligatory rejection of the lower transition set for series IV is seen to have been occasioned by our only having cooled to 253 K—even though it was done very slowly.

The values of C_p measured have a standard deviation varying from 2 per cent at 6 K to 0.5 per cent at 10 K and 0.08 per cent above this temperature to 350 K. The d.s.c. data[2] are less accurate. The values of the smoothed integrated thermophysical properties are more reliable and have a standard deviation of 0.06 per cent above 100 K.

The heat capacity of the sample decreased from 95 per cent of the total (sample + calorimeter + helium) at 6 K to 66 per cent at 131 K and then increased gradually to 76 per cent at 350 K, except, of course, in transition regions.

3. Results and discussion

Experimental heat capacities given in tables 1 and 2 are plotted in figure 1. These results are given in chronological order. Within a series the temperature interval of
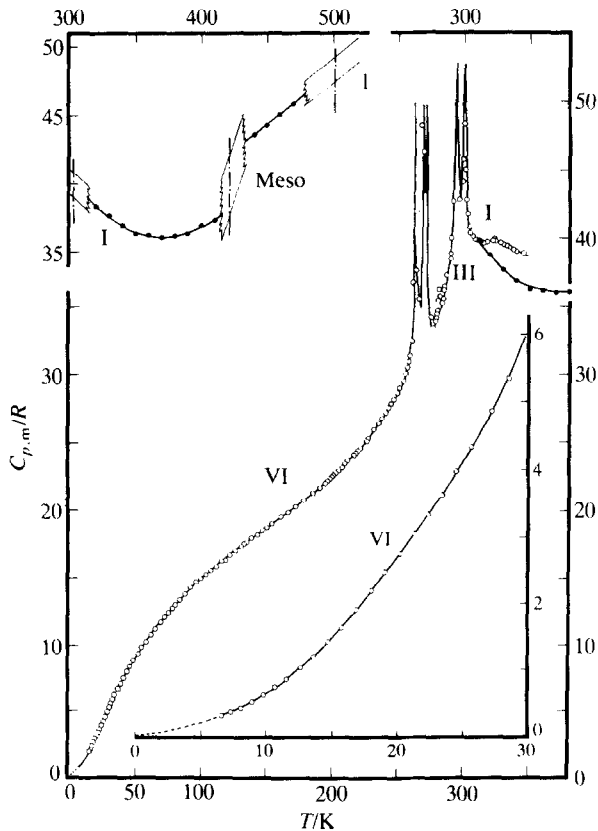

FIGURE 1. Heat capacity of thallium(I) *n*-heptanoate with phase designations. ○, This work; ●, reference 2 by d.s.c.

each measurement may usually be ascertained from the difference between adjacent mean temperatures. These results have been fitted to a series of orthogonal polynomials in the region of normal heat capacity. Integration of these polynomials yields the thermodynamic functions. Tabulation of the smooth $C_{p,m}/R$ values are given for selected temperatures in table 3. The heat-capacity values within transition regions given in this table are those both for the measured-compound heat capacity and for the estimated lattice contributions obtained by the procedure followed in previous papers of a related series.[10-13]

It is interesting that both sets of results show the heat capacity to diminish for some tens of kelvins above the II-to-I transition. There is a significant discrepancy in the pattern of this decrease. Our results are highly reproducible over four separate and independent determinations made in this region. Above 310 K our $C_{p,m}/R$ values show a deviation from the d.s.c. values of reference 2 in the form of a broad

TABLE 2. Summary of transition sets for thallium(I) n-heptanoate ($R = 8.3144$ J·K^{-1}·mol^{-1})

Series	No. of detns	$\dfrac{T_1}{K}$	$\dfrac{T_2}{K}$	$\dfrac{H_m^\circ(T_2)-H_m^\circ(T_1)}{R\,K}$	$\dfrac{H_m^\circ(280\,K)-H_m^\circ(250\,K)}{R\,K}$	$\dfrac{S_m^\circ(280\,K)-S_m^\circ(250\,K)}{R}$
Transition set VI-to-V, V-to-IV, and IV-to-III						
I	3	261.65	286.54	1355.9	1478.9	
II	4	253.82	279.45	1355.6	1485.6	
III	4 + Detn A	229.34	287.23	2302.9	1487.1	
IV	$\Delta_{trs}H_m^\circ$ Detn B	253.72	282.72	1344.8	1358.9[a]	
V	27	255.35	280.82	1355.5	1482.6	5.59_1
Graphical integration					1484	5.59_1
Mean:					1484^a	
Lattice contribution:					965.7	3.65_2
$\Delta_{trs}H_m^\circ$(VI-to-V-to-IV-to-III)/R K:					518.3	
$\Delta_{trs}S_m^\circ$(VI-to-V-to-IV-to-III)/R:						1.93_9

$$\Delta_{VI}^{V}H_m^\circ/R\,K = 236._5 \qquad \Delta_{VI}^{V}S_m^\circ/R = 0.89_5$$
$$\Delta_{V}^{IV}H_m^\circ/R\,K = 140._3 \qquad \Delta_{V}^{IV}S_m^\circ/R = 0.52_4$$
$$\Delta_{IV}^{III}H_m^\circ/R\,K = 141._5 \qquad \Delta_{IV}^{III}S_m^\circ/R = 0.52_0$$

Series	No. of detns	$\dfrac{T_1}{K}$	$\dfrac{T_2}{K}$		$\dfrac{H_m^\circ(310\,K)-H_m^\circ(280\,K)}{R\,K}$	$\dfrac{S_m^\circ(310\,K)-S_m^\circ(280\,K)}{R}$
Transition set III-to-II, II-to-I						
I	4	274.80	300.86	1490.2	1748.0	
II	5	279.45	306.89	1654.5	1759.8	
III	2	275.56	326.47	2557.2	1749.8	
IV	12	282.72	311.61	1714.0	1751.1	
V	29	280.04	306.04	1585.9	1745.8	5.89_5
Graphical integration:					1750	5.89_5
Mean:					$1750._9$	5.89_6
Lattice contribution:					$1089._2$	3.69_1
$\Delta_{trs}H_m^\circ$(III-to-II, II-to-I)/R K:					$661._7$	
$\Delta_{trs}S_m^\circ$(III-to-II, II-to-I)/R:						2.20_5

$$\Delta_{III}^{II}H_m^\circ/R\,K = 355._5 \qquad \Delta_{III}^{II}S_m^\circ/R = 1.20_5$$
$$\Delta_{II}^{I}H_m^\circ/R\,K = 306._2 \qquad \Delta_{II}^{I}S_m^\circ/R = 1.01_0$$

^{a} The Series IV value and the graphical integration were not included in the mean.

diffuse transition with a $\Delta_{trs} H_m^{\circ}/R$ of about 56 K. It is also interesting to note that their $\Delta_{II}^l H_m^{\circ}/R$ is about 15 K higher than the area under our peak. Since the samples are from the same batch, it is difficult to account for the discrepancy. However, the decrease has been noted[2] as an odd-even effect in Tl3C, Tl5C, and more prominently in Tl7C. Moreover, it has been suggested[2] that in pure samples the heat capacity would be monotonic increasing.

In evaluating the superambient thermodynamic functions, we chose to use their heat-capacity curve which joins ours smoothly at 310 K and fits with the mesomorphic and isotropic liquid transitions. We have chosen to use the d.s.c. data in this region in preference to our own in evaluating thermodynamic functions at superambient temperatures with the reservation that since adiabatic equilibrium calorimetry may be more reliable than d.s.c., we shall need to revise this judgment when our measurements have been extended to higher temperatures.

Although it might be surmised that one or more of the transitions might be occasioned by impurities, this possibility is ruled out by the following arguments. The most likely impurities are heptanoic acid and water. The melting temperature of the former has been recorded as 265.83 K,[13] and that for ice is 273.15 K. Hence, either the transition at 267.8 K or that at 271.7 K might be suspect. The values for the microanalysis of the sample are within experimental reliability. However, if we utilize the reported carbon analysis and assume the sample is made up of a mixture of thallium heptanoate and heptanoic acid, we would calculate the presence of mole fraction 0.011 of the acid. The calculated values for hydrogen, oxygen, and thallium on the assumption of this mole fraction of impurity (4.05, 9.75, and 60.24 mass per cent) are consistent with the reported values. However, it would require a mole fraction of acid of about 0.08 to account for either of the above transitions—about eight times the amount indicated by (this interpretation of) the gravimetric analysis.

Moreover, an 8 moles per cent heptanoic acid contamination should be readily detectable by the infrared technique used, and fractional-fusion analysis indicates a maximum mole fraction of 0.001 of solid-insoluble liquid-soluble impurity. If it is assumed that the heptanoic acid (and ice) are immiscible in the solid sample, we can rule out the possibility that this peak results from heptanoic acid contamination. Were we to consider the possibility of water contamination, using the carbon content as a criterion, we would note that water could only contribute to a decrease in the apparent fraction of carbon—not to the increase observed. Disregarding the carbon and using observed oxygen mole fraction instead as a criterion, a mole fraction 0.031 of water might be expected. This is consistent with hydrogen and thallium mole fractions. However, the mole fraction of melting ice required to produce the thermal effect associated with the 271.7 K transition would be about 0.20. This is totally inconsistent with the gravimetric and infrared results and—if solubility of water in the solid sample is negligible—with the fractional-fusion determination by a factor of 20. In view of the careful drying of the sample at elevated temperatures, it is inconceivable that sufficient water could be present to produce such a peak. Solubilities of the salt are not available so that we might argue whether or not the melting-temperature depression needed to account for such a difference in the melting-temperature observed is possible. Moreover, it should be

TABLE 3. Thermodynamic properties of thallium(I) *n*-heptanoate ($R = 8.3144$ J·K^{-1}·mol^{-1})

$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{S_m^\circ}{R}$	$\dfrac{H_m^\circ(T)-H_m^\circ(0)}{R\,K}$	$\dfrac{-\{G_m^\circ(T)-H_m^\circ(0)\}}{RT}$
0	0	0	0	0
5	0.179	0.059	0.222	0.0146
10	0.738	0.334	2.36	0.0980
15	1.656	0.798	8.24	0.2491
20	2.710	1.418	19.14	0.4613
30	4.865	2.923	56.97	1.0238
40	6.928	4.611	116.14	1.707
50	8.758	6.357	194.7	2.462
60	10.348	8.098	290.4	3.257
70	11.740	9.800	401.1	4.070
80	12.941	11.448	524.6	4.890
90	13.982	13.034	659.3	5.708
100	14.903	14.555	803.8	6.517
120	16.51	17.42	1118.4	8.098
140	17.97	20.08	1463.5	9.622
160	19.37	22.57	1836.9	11.086
180	20.80	24.35	2238.4	12.494
200	22.38	27.20	2669.8	13.85
220	24.33	29.42	3136.0	15.166
240	26.99	31.64	3647.6	16.44
250 [a]	28.72	32.78	3925.9	17.08
	[28.72]	[32.78]	[3925.9]	[17.08]
260	31.36	33.95	4223.5	17.71
	[30.45]	[33.94]	[4221.6]	[17.70]
262.8 [b]	(≈700)	(34.27)	(4307.6)	(17.88)
	[30.95]	[34.27]	[4307.6]	[17.88]
		Phase V		
262.8 [b]	(≈700)	(35.17)	(4542.8)	(17.88)
	[33.95]	[34.27]	[4307.6]	[17.88]
265.6 [c]	(≈35.5)	(35.52)	(4639.2)	(18.06)
	[33.95]	[34.63]	[4402.7]	[18.05]
267.8 [b]	(≈200)	(35.82)	(4713.9)	(18.21)
	[33.95]	[34.92]	[4477.4]	[18.20]
		Phase IV		
267.8 [b]	(≈200)	(36.34)	(4854.1)	(18.21)
	[33.95]	[34.92]	[4477.4]	[18.20]
270 [c]	(≈43)	(36.62)	(4928.8)	(18.36)
	[33.95]	[35.20]	[4552.0]	[18.34]
271.7 [b]	(≈200)	(36.83)	(4986.6)	(18.48)
	[33.95]	[35.41]	[4609.7]	[18.45]
		Phase III		
271.7 [b]	(≈200)	(37.35)	(5127.8)	(18.48)
	[33.95]	[35.41]	[4609.7]	[18.45]
276.9 [c]	(33.95)	(37.99)	(5303.6)	(18.84)
	[33.95]	[36.05]	[4785.2]	[18.77]
280	34.35	38.37	5409.9	19.05
290	39.4	39.64	5772.2	19.74
296.2 [b]	(≈500)	(40.28)	(5959.8)	(20.16)
	[33.95]	[38.34]	[5441.5]	[19.97]

TABLE 3—*continued*

$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{S_m^\circ}{R}$	$\dfrac{H_m^\circ(T)-H_m^\circ(0)}{R\,K}$	$\dfrac{-\{G_m^\circ(T)-H_m^\circ(0)\}}{RT}$
		Phase II		
296.2 [b]	(≈ 500)	(41.49)	(6316.9)	(20.16)
	[37.55]	[38.34]	[5441.5]	[19.97]
297.17 [c]	(42.00)	(41.60)	(6351.8)	(20.23)
	[37.55]	[38.46]	[5477.9]	[20.03]
298.15	(≈ 44.2)	41.74	6394.4	20.30
	[37.55]	[38.58]	[5514.7]	[20.08]
300	≈ 50.8	42.03	6481.6	20.43
300.9 [b]	(≈ 16000)	(42.08)	(6491.8)	(20.51)
	[37.55]	[38.94]	[5618.0]	[20.27]
		Phase I		
300.9 [b]	(≈ 16000)	(43.09)	(6795.8)	(20.51)
	[39.86]	[38.94]	[5618.0]	[20.27]
310.0	39.55	44.26	7160.7	21.16
	[39.86]	[40.13]	[5980.7]	[20.84]
320	38.3	45.50	7550.2	21.90
340	36.9	47.78	8300.5	23.37
360	36.2	49.87	9031	24.78
380	36.1	51.82	9753	26.15
400	37.0	53.69	10482	27.48
420.7 [b]	(——)	(55.55)	(11270)	(28.76)
	[39.10]	[51.40]	[10090]	[27.41]
		Mesophase		
420.7 [b]	(——)	(57.35)	(12048)	(28.76)
	[42.10]	[51.40]	[10090]	[27.41]
440	43.6	59.32	12876	30.05
460	45.1	61.29	13763	31.37
480	46.6	63.24	14681	32.66
500	48.2	65.18	15630	33.92
502.7 [b]	(——)	(65.44)	(15760)	(34.08)
	[48.4]	[59.45]	[13802]	[31.99]
		Isotropic liquid		
502.7 [b]	(——)	(66.22)	(16157)	(34.08)
	[——]	[59.45]	[13801]	[31.99]

[a] Quantities in square brackets represent estimated lattice heat capacities at indicated temperature.

[b] Quantities in parentheses represent estimated heat capacities or other thermodynamic functions estimated on the assumption that the transitions are truly isothermal at the transition temperatures indicated.

[c] Quantities in parentheses are at minimum points between bifurcated transitions. Hence, values neither in parentheses nor brackets are real values at selected temperatures indicated.
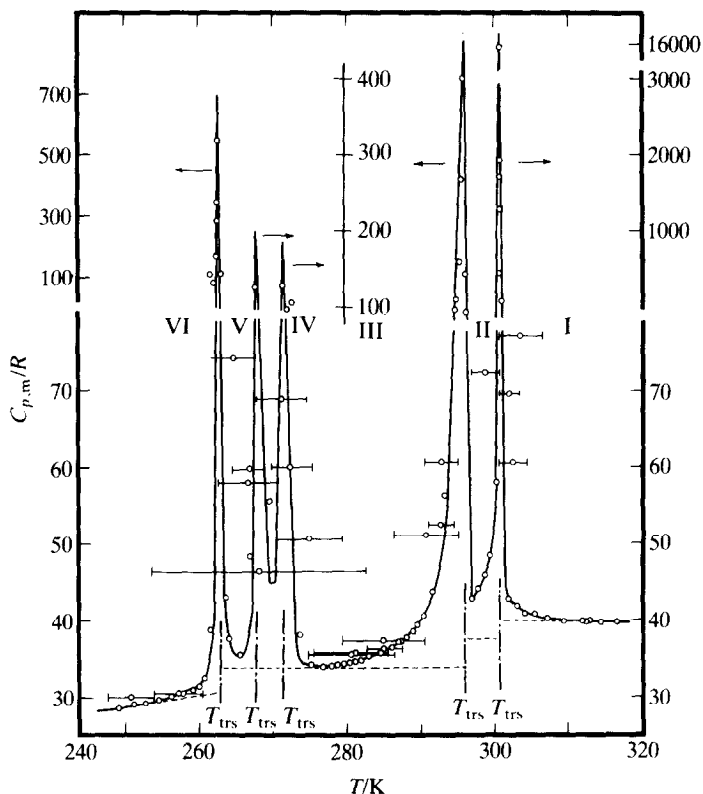
FIGURE 2. Sub-ambient transitions in thallium(I) *n*-heptanoate. Note adjuvant scales for peak values and phase designations. Horizontal bars indicate temperature increments of enthalpy-type determinations. Lattice heat-capacity contributions are indicated by dashed lines.

noted that water in the sample would be expected largely to hydrolyze the salt to acid and thallium hydroxide under the drying procedure used.

The smoothed values of the thermodynamic properties based on the information in the preceding two tables are summarized in table 3. For convenience in giving values in the transition regions and in indicating the current basis of estimating lattice heat-capacity contributions, the *entire* transition contribution (measured minus lattice) is attributed to an isothermal absorption of enthalpy. Heat capacities in parentheses ( ) are estimated; the other thermodynamic values in parentheses are predicted on the above attribution and are clearly more or less at variance with experiment—as may be noted in figure 2.

For completeness, table 3 includes also the superambient d.s.c. results of reference 2 (compare table 4), and our lattice contribution estimates are shown in square brackets [ ]. Phases in this table and the figures have been indicated in the usual fashion with Roman numbers increasing below the fusion to a mesomorphic phase.

TABLE 4. Summary of transition properties of thallium(I) *n*-heptanoate[a]

Transition	T_{trs}	$\Delta_{trs}H_m^\circ/R$ K	$\Delta_{trs}S_m^\circ/R$	Reference
VI-to-V	262.8	$236._5$	0.89_5	This work
V-to-IV	267.8	$140._3$	0.52_4	This work
IV-to-III	271.7	141.5	0.52_0	This work
III-to-II	296.2	$355._5$	1.20_5	This work
II-to-I	300.9	$306._2$	1.01_0	This work
	301.9	319	1.06	2
	299	332	1.11	4
I-to-Mesophase	420.7	758	1.80	2
	419	755	1.80	4
Mesophase-to-Isotropic liquid	502.0	397	0.79	2
	501	377	0.75	4

[a] Values from references 2 and 4 were determined by d.s.c.

The sum of the seven transitional entropies between 262 K and 502 K as $\Delta_{trs}S_m^\circ/R$ is 6.73, most of which occurs below 300 K and is, therefore, of little interest for conventional energy-storage purposes. It is, however, suggestive of the nature of these materials. All the transitions are relatively sharp and easily reproducible, but the high heat capacities of the II-to-I transition are especially noteworthy. The lack of structural information precludes interpretation of the transitions.

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Note added in proof

Subsequent to the submission of this paper, further d.s.c. measurements at Madrid on the sample used for cryogenic measurements indicated that it had undergone change tentatively ascribed to formation of some amount of a (salt + acid) complex, producing the transition at 297 K and the deviation about 323 K. Hence, thermodynamic properties at higher temperatures—other than the heat capacity— might need slight adjustment.