Thermophysics of thallium alkanoates

IV. Heat capacity and thermodynamic functions of thallium(I) *n*-dodecanoate from 7 to 470 K [a]

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The thermal behavior of thallium(I) *n*-dodecanoate was studied by adiabatic calorimetry from 6 to 350 K and by d.s.c. from 230 through 470 K. The agreement between the results (temperature and thermal functions of transitions and heat capacity) from both methods was within the experimental error over the common temperature range. Several phases were observed in the sample. Four of the five solid-to-solid transitions appeared in the common temperature range of both techniques. The two lowest-temperature transitions appear as a bifurcated pair (at 282.65 and 284.8 K) with $(C_{p,m}/R) \approx 250$ and 450, respectively. The third and fourth occur at 293.1 and 312.1 K with $(C_{p,m}/R) \approx 250$ and 14000. Above 350 K three more transitions were measured by d.s.c.: solid-to-solid, solid-to-mesophase, and mesophase-to-isotropic-liquid transformations at 356.6, 400.1, and 471.5 K. The corresponding values of $\Delta_{trs} S_m^\circ/R$ for the seven transitions were 0.91_0, 1.11_1, 0.71_0, 2.07_5, 0.6_9, 1.6_4, and 0.50. Smoothed thermodynamic values are tabulated at selected temperatures through the "clearing" point.
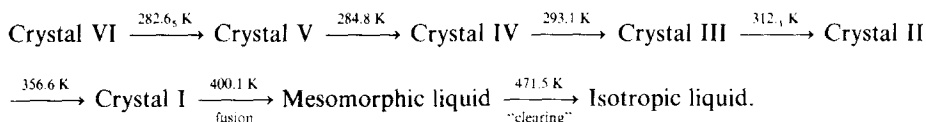
1. Introduction

The previous papers in this series[1-3] describe the thermophysical properties of thallium(I) *n*-hexanoate, *n*-heptanoate, and *n*-tetradecanoate. For each, several solid-to-solid phase transitions were observed and their temperatures, enthalpies, and entropies were measured. The complete morphology of the heat-capacity curve from 5 K to about 450 K for the three substances was obtained as well.

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This paper concerns another long-chain member of the series: thallium(I) *n*-dodecanoate. Previous studies[4-7] identify mainly transition temperatures and, seldom, enthalpies and entropies of transitions occurring above 300 K, by using microscopic observations, d.s.c., d.t.a., and hot-stage polarizing microscopy. We have measured the heat capacity of the sample combining sub-ambient adiabatic equilibrium calorimetry from 6 to 350 K with d.s.c. above 230 K.

Five solid-to-solid transitions were found in addition to fusion (solid to mesomorphic phase) and to "clearing" (mesomorphic phase to isotropic liquid). In summary:
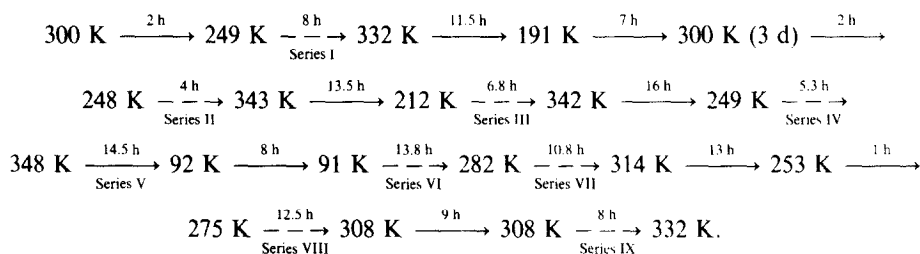
$$\text{Crystal VI} \xrightarrow{282.6\,\text{K}} \text{Crystal V} \xrightarrow{284.8\,\text{K}} \text{Crystal IV} \xrightarrow{293.1\,\text{K}} \text{Crystal III} \xrightarrow{312.1\,\text{K}} \text{Crystal II}$$

$$\xrightarrow{356.6\,\text{K}} \text{Crystal I} \xrightarrow[\text{fusion}]{400.1\,\text{K}} \text{Mesomorphic liquid} \xrightarrow[\text{"clearing"}]{471.5\,\text{K}} \text{Isotropic liquid.}$$

2. Experimental

Thallium(I) *n*-dodecanoate was prepared by reacting Fluka puriss (> 99.5 moles per cent pure by g.c. at the origin) *n*-dodecanoic acid dissolved in anhydrous methanol with a slight excess (≈5 per cent) of Fluka puriss Tl_2CO_3 (> 99 moles per cent pure) suspended in the same solvent. After refluxing under stirring (for about 3 h) and separating some unreacted carbonate by filtration, the solution was concentrated until incipient crystallization, which was completed by precipitation with dry diethyl ether. The recovered solid salt was further purified by repeated recrystallization with absolute ethanol and finally dried to constant mass at about 300 K under vacuum. Infrared spectroscopic determinations showed no traces of water or free acid. Moreover, several d.s.c. purity determinations by fractional-fusion techniques indicated a mean value of (99.83 ± 0.05) moles per cent of liquid–soluble solid–insoluble purity.

The calorimetric measurements at Ann Arbor between 6 and 350 K were made in the Mark X cryostat described previously.[8] The intermittent-heating adiabatic equilibrium method was utilized. The programming, data logging, and calorimetry were done by automated computerization as described elsewhere.[9]

The sample loaded into a gold-plated copper calorimeter (designation W–62) had a mass of 40.200 g corresponding to an amount of substance of 0.099579 mol with a molar mass 403.70 $g \cdot mol^{-1}$ (on the basis of the 1978 IUPAC relative atomic masses). The buoyancy corrections were calculated assuming a density of 2.4 $g \cdot cm^{-3}$. (No crystallographic information on density is available for thallium(I) *n*-dodecanoate or adjacent members of the homologous series. Thallium acetate has a density of 3.6 $g \cdot cm^{-3}$). Following evacuation, 3.47 kPa of purified helium was added to the calorimeter to promote thermal equilibration. The calorimeter was then sealed within a chamber with a small pressure of purified helium gas by a remotely turned wrench operating a hexagonal cap which pressed a gold gasket against the circular knife edge of the vessel.

The thermal history outlined below shows the detail of the thermal cycles to which the sample was subjected; the solid arrows show cooling periods while dashed arrows show data-acquisition intervals:

300 K $\xrightarrow{\text{2 h}}$ 249 K $\underset{\text{Series I}}{\xrightarrow{\text{8 h}}}$ 332 K $\xrightarrow{\text{11.5 h}}$ 191 K $\xrightarrow{\text{7 h}}$ 300 K (3 d) $\xrightarrow{\text{2 h}}$

248 K $\underset{\text{Series II}}{\xrightarrow{\text{4 h}}}$ 343 K $\xrightarrow{\text{13.5 h}}$ 212 K $\underset{\text{Series III}}{\xrightarrow{\text{6.8 h}}}$ 342 K $\xrightarrow{\text{16 h}}$ 249 K $\underset{\text{Series IV}}{\xrightarrow{\text{5.3 h}}}$

348 K $\underset{\text{Series V}}{\xrightarrow{\text{14.5 h}}}$ 92 K $\xrightarrow{\text{8 h}}$ 91 K $\underset{\text{Series VI}}{\xrightarrow{\text{13.8 h}}}$ 282 K $\underset{\text{Series VII}}{\xrightarrow{\text{10.8 h}}}$ 314 K $\xrightarrow{\text{13 h}}$ 253 K $\xrightarrow{\text{1 h}}$

275 K $\underset{\text{Series VIII}}{\xrightarrow{\text{12.5 h}}}$ 308 K $\xrightarrow{\text{9 h}}$ 308 K $\underset{\text{Series IX}}{\xrightarrow{\text{8 h}}}$ 332 K.

A Perkin–Elmer DSC–2C at Madrid provided with the Intracooler–2 unit for sub-ambient temperatures was used between 230 and 480 K. Its temperature scale for the region of interest was calibrated by the melting temperatures of the usual high-purity standards: n-undecane, n-tridecane, n-pentadecane, gallium, indium, tin, stearic (octadecanoic) acid, and benzoic acid. The enthalpies of transitions were determined on several samples (about 15 mg) using high-purity indium (>99.999 moles per cent) as standard material for the calibration of power. For the heat-capacity determinations, synthetic sapphire disks of different masses were used as external standards.[10] The samples were weighed with a precision of ±2 mg. Special care was exercised to place the radiation lids over the panholders in a reproducible orientation so as to reduce as far as possible the changes in the heat-loss patterns in different scans. The results obtained by d.s.c. were the mean values from at least four different samples, ranging between 10 and 20 mg.

3. Results and discussion

Approximately 190 heat-capacity determinations were made in 9 series of measurements by adiabatic calorimetry. The experimental results at the mean temperature of each measurement are listed in table 1 in chronological sequence by series, so that the temperature increment of a determination may be inferred from the mean temperatures of adjacent determinations. The standard deviations of the heat capacities by adiabatic calorimetry are 3 per cent at 6 K, 0.4 per cent at 20 K, and <0.1 per cent above 50 K.

The heat capacity of the sample represented about 90 per cent of the total (sample + helium + calorimeter) at 10 K and was always higher than 60 per cent of the total (the minimum value being reached at about 200 K).

The d.s.c. results are listed in table 2. No d.s.c. measurements of the heat capacity were made at temperatures above 470 K because decomposition of the sample starts within about 10 K of this limit.

Heat-capacity results from both adiabatic and d.s.c. measurements are shown in figure 1. Good agreement between both sets was obtained over the common temperature range. The standard deviations in the d.s.c. measurements are generally about 1 to 2 per cent. Figure 2 presents an expanded plot of the region between 250 and 340 K the better to reveal the features of the transitions.

Between the solid III-to-II and solid II-to-I transitions, a broad and diffused hump with a maximum at about 345 K is observed in the $C_{p,m}/R$ against T curve. A similar behavior has been described already for the equivalent phase (the penultimate solid phase before the mesophase in thallium(I) n-tetradeconoate)[3]

TABLE 1. Experimental molar heat capacities of thallium(I) n-dodecanoate:
$R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

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		281.01	69.35	20.11	3.315	118.32	22.37	292.08	62.67	285.62	73.54
253.53	38.01	300.06	58.19	21.24	3.627	123.39	22.97	293.06	204.1	286.78	54.92
260.52	39.51	316.54	85.96	22.50	3.980	128.46	23.54	293.49	149.5	289.44	54.86
266.63	40.63	334.48	73.36	23.91	4.370	133.54	24.03	294.84	55.14	291.76	59.25
272.71	42.43	340.18	76.51	25.32	4.753	138.64	24.55	296.68	56.68	292.49	87.17
278.56	49.05	Series IV		26.73	5.158	143.74	25.02	298.51	57.59	292.92	120.4
282.40	123.80	256.98	38.73	28.15	5.555	149.34	25.64	301.21	57.75	293.10	183.8
285.07	151.39	262.43	39.78	29.81	6.020	155.45	26.21	304.78	59.35	293.20	172.3
290.15	85.99	280.99	71.51	31.69	6.561	161.57	26.81	307.94	62.62	293.59	69.03
296.15	56.94	298.14	57.43	33.58	7.093	167.69	27.49	310.15	66.78	294.44	55.42
301.96	58.11	300.57	57.31	35.77	7.845	173.82	28.04	311.49	107.9	301.46	58.47
307.87	63.47	312.53	92.49	38.16	8.355	179.96	28.64	312.08	1452	Series IX	
314.75	141.74	326.33	70.54	40.54	8.964	186.09	29.34	312.12	3931	308.45	63.10
325.50	70.82	332.41	72.46	42.92	9.576	192.23	29.88	312.15	2298	309.56	65.49
Series II		338.47	76.07	45.21	10.175	198.37	30.62	312.68	117.9	310.38	67.49
250.89	37.85	344.49	78.55	47.76	10.814	204.50	31.29	313.88	82.2	311.16	71.73
255.55	38.66	Series V		50.64	11.437	210.64	31.97	Series VIII		311.78	126.6
260.19	39.48	7.20	0.37	53.53	12.170	217.04	32.69	277.07	48.33	312.07	823
280.47	68.74	7.86	0.50	56.91	12.911	233.67	33.66	280.21	50.84	312.10	2896
299.55	57.67	7.93	0.56	60.76	13.751	230.31	34.46	281.63	61.13	312.108	5640
316.06	85.66	8.83	0.63	64.61	14.575	251.99	37.84	282.22	122.0	312.114	13639
334.32	73.25	9.69	0.81	68.50	15.316	Series VII		282.43	204.8	312.13	2586
340.23	77.08	10.52	0.993	72.43	16.02	272.38	42.11	282.58	224.3	312.21	354.4
Series III		11.39	1.137	76.59	16.65	276.43	47.24	282.70	228.5	312.32	192.7
218.30	32.76	12.28	1.352	81.00	17.47	280.32	58.40	283.02	107.2	312.75	94.0
223.36	33.43	13.18	1.513	85.44	18.25	282.31	193.1	283.73	58.36	313.39	85.1
229.50	34.26	14.09	1.760	89.91	18.90	283.19	96.3	284.39	88.19	314.07	80.9
235.62	35.19	14.99	2.008	Series VI		284.23	135.5	284.68	311.6	315.13	76.8
241.76	36.03	15.91	2.209	93.30	19.53	284.79	447	284.76	416.7	317.74	73.05
247.88	37.02	16.84	2.474	98.14	20.05	285.30	183.6	284.84	361.5	321.52	70.00
254.00	38.02	17.86	2.738	103.18	20.76	286.55	56.03	284.93	342.8	325.45	70.57
260.10	39.26	18.98	3.010	108.21	21.20	288.42	53.73	285.04	355.2	329.59	71.34
				113.27	21.79	290.30	55.54	285.17	346.2		

TABLE 2. Molar heat capacity of thallium(I) n-dodecanoate by d.s.c. (230 to 460 K);
$R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

T/K	$C'_{p,m}/R$ [a]	$C_{p,m}/R$ [b]	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
235	34.8	34.9	Trs: VI to V to		350	77.0	390	58.1	435	71.3
240	36.0	37.0	IV to III to II						440	71.7
245	36.5	38.6	320	69.3	Trs: II to I		Trs: I to Meso		445	72.2
250	37.3	39.6	325	70.1	365	54.5	410	68.0	450	72.5
255	38.4	41.2	330	71.4	370	54.3	415	68.8	455	72.9
260	39.4	42.6	335	74.0	375	54.7	420	69.5	460	73.1
265	40.6	43.6	340	76.7	380	55.4	425	70.1		
270	42.2	45.7	345	78.0	385	56.1	430	70.8		

[a] Crystal V' heat capacity (dotted line in figures 1 and 3).
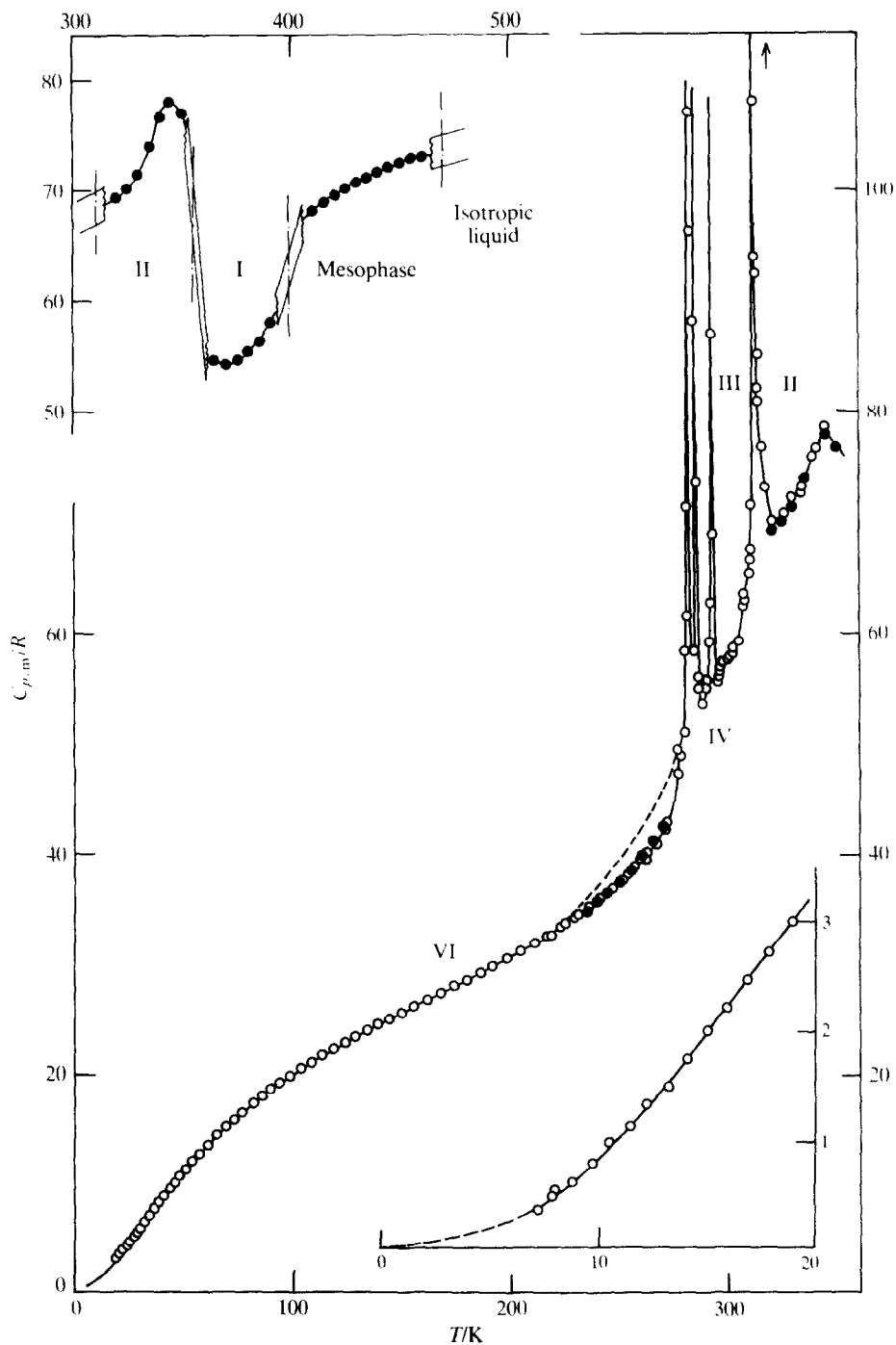[b] Crystal VI heat capacity (continuous line in figures 1 and 3).

FIGURE 1. Heat-capacity curve for thallium(I) *n*-dodecanoate. ◯, Adiabatic calorimetric determinations; ●, d.s.c. determinations; — — —, d.s.c. determinations when Crystal V' is present.

TABLE 3. Smooth standard molar thermodynamic values at selected temperatures for thallium(I) n-dodecanoate; $R = 8.3144$ J$\cdot$K$^{-1}\cdot$mol^{-1}

$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{\Delta_0^T S_m^\circ(T)}{R}$	$\dfrac{\Delta_0^T H_m^\circ(T)}{R\cdot K}$	$\dfrac{\Phi_m^\circ(T,0)}{R}$	$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{\Delta_0^T S_m^\circ(T)}{R}$	$\dfrac{\Delta_0^T H_m^\circ(T)}{R\cdot K}$	$\dfrac{\Phi_m^\circ(T,0)}{R}$
				Phase VI					
0	0	0	0	0	120	22.58	22.69	1488.5	10.284
5	0.117	0.039	0.148	0.0094	140	24.68	26.33	1961.1	12.319
10	0.878	0.313	2.344	0.0786	160	26.69	29.75	2475.0	14.29
15	1.981	0.868	9.370	0.243	180	28.66	33.01	3028.3	16.19
20	3.305	1.616	22.54	0.489	200	30.78	36.14	3622.4	18.03
25	4.661	2.499	42.45	0.801	220	33.05	39.18	4260.5	19.81
30	6.081	3.473	69.25	1.164	240	35.88	42.17	4948.2	21.55
35	7.547	4.521	103.36	1.568	260 [a]	39.37	45.18	5700.8	23.25
40	8.842	5.616	144.41	2.005		[39.37]	[45.18]	[5700.8]	[23.25]
45	10.118	6.729	191.75	2.468	270	41.2	46.70	6103.8	24.09
50	11.32	7.859	245.44	2.951		[40.76]	[46.68]	[6101.1]	[24.08]
60	13.59	10.133	370.48	3.958	280	50.20	48.19	6518.5	24.91
70	15.56	12.379	516.4	5.001		[42.21]	[48.17]	[6515.8]	[24.90]
80	17.34	14.57	681.0	6.061	282.6_5 [b]	($\approx$250)	(48.60)	(6628.4)	(25.15)
90	18.93	16.71	862.6	7.127		[42.60]	[48.60]	[6628.4]	[25.15]
100	20.30	18.78	1059.0	8.189					
				Phase V					
282.6_5 [b]	($\approx$250)	(49.55)	(6898.4)	(25.15)	283.8 [c]	[50.0]	[48.80]	[6685.9]	[25.24]
	[50.0]	[48.60]	[6628.4]	[25.15]	284.8 [b]	($\approx$450)	(49.93)	(7005.9)	(25.33)
283.8 [c]	(58.0)	(49.75)	(6955.9)	(25.24)		[50.0]	[48.98]	[6735.9]	[25.33]
				Phase IV					
284.8 [b]	($\approx$450)	(51.04)	(7322.0)	(25.33)	288.5 [c]	[53.4]	[49.67]	[6933.5]	[25.64]
	[53.4]	[48.98]	[6735.9]	[25.33]	293.1 [b]	($\approx$210)	(52.57)	(7765.2)	(26.07)
288.5 [c]	(53.7)	(51.73)	(7519.6)	(25.67)		[53.4]	[50.51]	[7179.1]	[26.02]
				Phase III					
293.1 [b]	(210)	(53.30)	(7981.2)	(26.07)	310	66.4	56.52	8953.2	27.64
	[54.40]	[50.51]	[7179.1]	[26.02]		[59.64]	[53.73]	[8151.1]	[27.44]
298.15	(56.75)	(54.25)	(8261.1)	(26.54)	312.12 [b]				
	[56.53]	[51.46]	[7459.1]	[26.44]		($\approx$14000)	(56.93)	(9080.1)	(27.84)
300	57.70	54.60	8366.5	26.71		[60.05]	[54.14]	[8277.9]	[27.62]
				Phase II					
312.12 [b]					340	76.75	64.97	11675	30.63
	($\approx$14000)	(59.01)	(9730.4)	(27.84)	345	78.0	—	—	—
	[63.36]	[54.14]	[8177.9]	[27.62]	350	77.0	66.0_9	12060	31.6_2
320	(70.75)	(60.63)	(10243)	(28.62)	356.6 [b]	(—)	(67.5_1)	(12570)	32.2_7
	[66.86]	[55.76]	[8791]	[28.29]		[74.0]	$[62.6_4]$	[11110]	$[31.4_8]$
330	71.30	62.76	10935	29.62					
	[71.30]	[57.89]	[9482]	[29.16]					
				Phase I					
356.6 [b]	(—)	(68.2_0)	(12810)	(32.2_7)	390	58.1	73.0_8	14630	35.5_6
	[52.2]	$[62.6_4]$	[11110]	$[31.4_8]$		[57.1]	$[67.5_2]$	[12930]	$[34.3_6]$
370	54.3	70.1_6	13520	33.6_1	400.1 [b]	(—)	(74.5_5)	(15210)	(36.5_3)
	[54.0]	$[64.6_0]$	[11820]	[32.64]		[58.6]	$[68.9_9]$	[13510]	[35.22]
380	55.4	71.6_2	14070	34.5_9					

TABLE 3—continued

$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{\Delta_0^T S_m^\circ(T)}{R}$	$\dfrac{\Delta_0^T H_m^\circ(T)}{R\cdot K}$	$\dfrac{\Phi_m^\circ(T,0)}{R}$	$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{\Delta_0^T S_m^\circ(T)}{R}$	$\dfrac{\Delta_0^T H_m^\circ(T)}{R\cdot K}$	$\dfrac{\Phi_m^\circ(T,0)}{R}$
				Mesophase					
400.1^b	(—)	(76.1_9)	(15870)	(36.5_3)	440	71.7	82.7_8	18640	40.4_2
	[66.5]	$[68.9_6]$	$[13510]$	$[35.2_2]$	460	73.1	86.0_0	20080	42.3_4
410	68.0	77.8_3	16530	37.5_1	471.5^b	(—)	87.8_1	20910	43.4_2
	[68.0]	$[70.6_3]$	$[14180]$	$[36.0_5]$		[73.5]	$[80.6_1]$	$[18570]$	$[41.2_2]$
420	69.5	79.4_9	17220	38.4_9					
				Isotropic liquid					
471.5^b	(—)	(88.3_1)	(21160)	(43.4_2)					

[a] Values in square brackets represent selected lattice heat capacities or the integrated thermodynamic functions of the selected lattice.

[b] Values in parentheses represent either estimated heat capacities or thermodynamic functions on the arbitrary assumption that the transitions are truly isothermal at the transition temperature indicated.

[c] Values at minimum points between bifurcated transitions.

with the maximum at about 360 K. Phases II of both compounds are reported to be structurally similar by studies on miscibilities by Lindau et al.[11]

The heat capacities have been fitted to a series of orthogonal polynomials in the region of normal heat capacities. Integration of these polynomials yields the thermodynamic functions. Table 3 summarizes the smoothed values of $C_{p,m}/R$ and derived functions at selected temperatures. The heat capacities within the transition region given in this table are those for both the measured heat capacity of the compound and the lattice contribution by extra regions of "normal" heat capacity.

Four presumably first-order transitions were observed in the heat-capacity curve

TABLE 4. Standard molar enthalpies and entropies of the lower-temperature (260 to 300 K) transitions in thallium(I) n-dodecanoate; $R = 8.3144$ J·K^{-1}·mol^{-1}

Designation	No. of detns.	$\dfrac{T_1}{K}$	$\dfrac{T_2}{K}$	$\dfrac{\Delta_{T_1}^{T_2} H_m^\circ}{R\cdot K}$	$\dfrac{\Delta_{260K}^{300K} H_m^\circ}{R\cdot K}$	$\dfrac{\Delta_{260K}^{300K} S_m^\circ}{R}$
Series I	7	263.57	299.00	$2465._2$	$2664._2$	
Series II	2	262.50	300.76	$2610._6$	$2665._6$	
Series III	3	257.05	301.27	$2855._8$	$2667._2$	
Series IV	3	259.88	299.36	$2630._5$	$2662._5$	
Series VII	17	270.35	299.41	$2217._1$	$2651._8$	
Series VIII	26	274.911	281.20	$1766._0$	$2667._5$	
Graphical integration:					$2666._5$	
Mean value:[a]					$2665._4 \pm 1$	9.41_8
Lattice contribution:					$1863._6$	6.63_1

$$\Delta_{trs} H_m^\circ(\text{VI to V, V to IV, IV to III})/(R\cdot K) = 802 \pm 2$$
$$\Delta_{trs} S_m^\circ(\text{VI to V, V to IV, IV to III})/R = 2.78_7$$

$T_{trs}(\text{VI to V}) = 282.6_5$ K;	$\Delta_{VI}^V H_m^\circ/(R\cdot K) = 270$	$\Delta_{VI}^V S_m^\circ/R = 0.95_0$
$T_{trs}(\text{V to IV}) = 284.8$ K;	$\Delta_V^{IV} H_m^\circ/(R\cdot K) = 316$	$\Delta_V^{IV} S_m^\circ/R = 1.11_1$
$T_{trs}(\text{IV to III}) = 293.1$ K;	$\Delta_{IV}^{III} H_m^\circ/(R\cdot K) = 217$	$\Delta_{IV}^{III} S_m^\circ/R = 0.72_6$

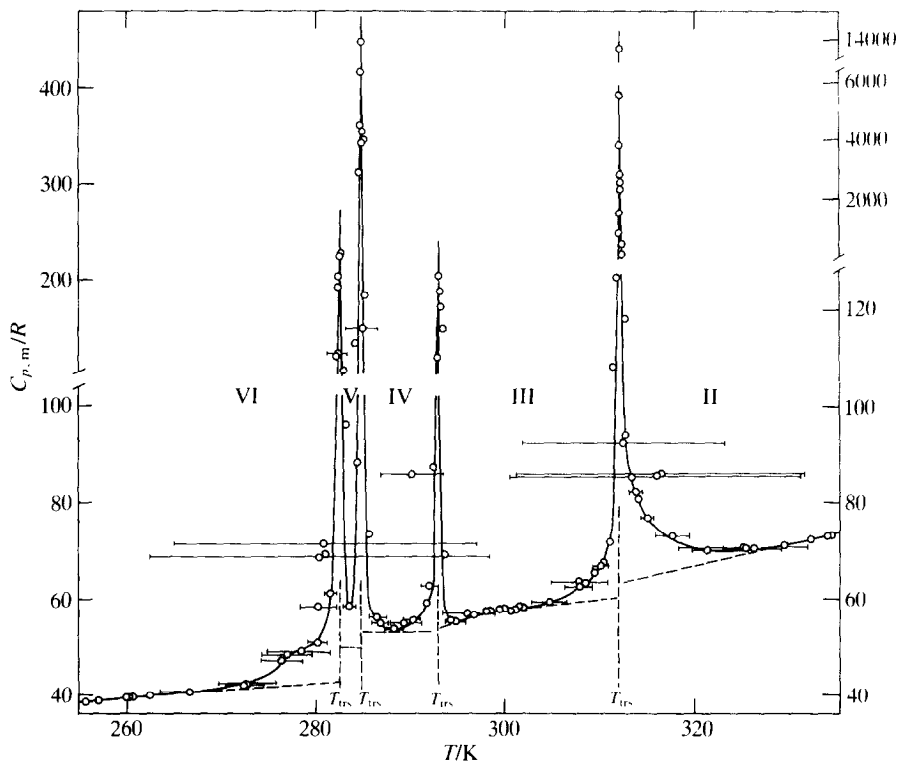[a] Average omitting Series VII and graphical integration values.

FIGURE 2. Expanded heat-capacity curve of thallium(I) *n*-dodecanoate showing the transition region below 350 K as determined by adiabatic calorimetry. Note adjuvant scales for peak values and phase designations. – – –, Estimated lattice heat-capacity contributions; ⊢——⊣, temperature increments of enthalpy-type determinations.

defined by our adiabatic calorimetric measurements (below 350 K). The total enthalpy increments through the transition regions for the various series of determinations are given in tables 4 and 5. Both tables show that the reproducibility

TABLE 5. Standard molar enthalpy and entropy of the 312.11 K transition (III-to-II transition) in thallium(I) *n*-dodecanoate; $R = 8.3144$ J·K^{-1}·mol^{-1}

| Designation	No. of detns.	$\dfrac{T_1}{K}$	$\dfrac{T_2}{K}$	$\dfrac{\Delta_{T_1}^{T_2} H_m^\circ}{R \cdot K}$	$\dfrac{\Delta_{300\,K}^{330\,K} H_m^\circ}{R \cdot K}$	$\dfrac{\Delta_{300\,K}^{330\,K} S_m^\circ}{R}$
Series I	4	298.98	332.34	2795.7	2568.8	
Series II	1	300.76	331.37	2622.2	2567.9	
Series III	1	301.28	331.80	2623.5	2568.4	
Series IV	3	299.36	329.36	2558.8	2567.1	
Series IX	20	307.75	331.65	2227.1	2566.6	
Graphical integration:					2567.5 [a]	8.15$_5$
Mean value:					2567.8 ± 0.8	
Lattice contribution:					1917.$_5$	6.08$_0$
T_{trs}(III to II) = 312.12 K				$\Delta_{trs} H_m^\circ/(R \cdot K) =$	650.3 ± 1	
				$\Delta_{trs} S_m^\circ/R =$		2.07$_5$

[a] Not included in the mean.
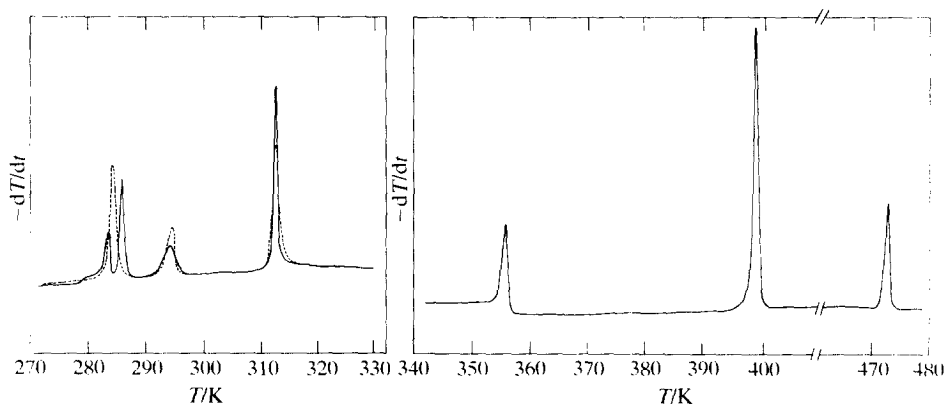
FIGURE 3. D.s.c. thermograms ("on heating") of thallium(I) n-dodecanoate. (a), — — —, The behavior when Crystal V′ is present. (b), Solid-to-solid, solid-to-mesophase, and mesophase-to-isotropic-liquid transitions above the upper limit of the adiabatic calorimetric measurements.

of the heat-capacity curve in the transitional regions in our measurements was within the experimental error. In addition to the four solid-to-solid transitions a small shoulder is observed below the VI-to-V transition. This is in agreement with the observations over successive heating thermograms taken by d.s.c.

In the region between 280 and 300 K, two different behaviors were found by d.s.c. (as summarized in figures 1 and 3 and in tables 2 and 6). In samples of very high purity (i.e. salt, >99.8 moles per cent), a simple transition at 284.6 K (Crystal V′) is first observed, but it transforms irreversibly into two at 283.0 (Crystal VI) and 285.2 K (Crystal V), with a small shoulder below them in successive scans (occasionally in the third, but mostly in the second scan). As can be seen in the figures and tables cited, the thermal functions of the V′-to-IV transition are lower than the sum of those of both VI-to-V and V-to-IV; but, correspondingly, the heat capacity of the V′ phase is higher than that of the VI phase. This $C_{p,m}$ variation approximately compensates for the difference. In less pure—but still high-purity samples—(i.e. salt, >99.5 moles per cent), the behavior directly affects phases VI and V′.

Above the upper limit of adiabatic calorimetric measurements, three more transitions were found by d.s.c.: a solid-to-solid one at 356.6 K; a

TABLE 6. Transition properties of thallium(I) n-dodecanoate by d.s.c. (mean values of five determinations)

Transition	T/K	$\Delta_{trs}H_m^\circ/(R \cdot K)$	$\Delta_{trs}S_m^\circ/R$
Crystal V′ → Crystal IV	284.6 ± 0.5	380 ± 40	1.34 ± 0.15
{ Crystal VI → Crystal V	283.0 ± 0.3	220 ± 10	0.78 ± 0.04
{ Crystal V → Crystal IV	285.2 ± 0.2	251 ± 17	0.88 ± 0.06
Crystal IV → Crystal III	293.6 ± 0.6	170 ± 17	0.58 ± 0.06
Crystal III → Crystal II	312.3 ± 0.4	540 ± 50	1.73 ± 0.15
Crystal II → Crystal I	356.6 ± 0.3	247 ± 18	0.69 ± 0.05
Crystal I → Mesophase	400.1 ± 0.2	656 ± 30	1.64 ± 0.07
Mesophase → Isotropic liquid	471.6 ± 0.3	237 ± 10	0.50 ± 0.02

TABLE 7. Summary of transition temperatures for thallium(I) n-dodecanoate(s)

Phase change	This work (adiabatic calorimetry)	This work (d.s.c.)	Lindau et al.[5] (d.s.c)	Meisel et al.[7] (d.t.a.)	Pelzl and Sackmann[6] (micr.)
VI → V	282.6₅	283.0	—	—	—
V → IV	284.8	285.2	—	—	—
IV → III	293.1	293.6	—	—	—
III → II	312.1₁	312.3	309.2	312	—
II → I	—	356.6	347.0	354	—
I → Mesophase	—	400.1	395.5	398	397.9
Mesophase → Isotropic liquid	—	471.6	470.0	471	470.0

solid-to-mesophase ("neat", similar to a smectic A phase) at 400.1 K; and the "clearing" or fusion of the neat phase into the isotropic liquid at 471.5 K.

In table 6 the transition properties obtained by d.s.c. are summarized. By comparison of the adiabatic calorimetric and d.s.c. results, the values of the d.s.c. enthalpy and entropy for the transitions are approximately 1.2 times lower than those obtained by adiabatic calorimetry. This is probably mainly due to differences in the base line chosen for resolution of the excess heat capacity. The agreement here is less satisfactory than for previous members of the series.[1-3]

Preliminary d.s.c. work showed clearly the presence of a very energetic transition at about 330 K for (thallium(I) n-dodecanoate + n-dodecanoic acid) similar to that observed for n-heptanoate.[2] This transition may also involve incongruent melting of the 1-1 (salt + acid) complex.

Finally, a summary of the observed transition temperatures and literature values for comparison is shown in table 7.

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