

## Thermodynamics of thallium alkanoates

### III. Heat capacity and thermodynamic functions of thallium(I) *n*-tetradecanoate from 7 to 450 K<sup>a</sup>

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The heat capacity of thallium(I) *n*-tetradecanoate was measured by adiabatic calorimetry to 350 K and by d.s.c. from 235 through 460 K. Good agreement between the methods was obtained within the common temperature range. Several phases were observed in the sample. Two solid-to-solid transitions were found, a very sharp one at 318.5 K ( $C_{p,m}/R$  for the maximum is about  $10^4$ ; enthalpy ( $\Delta_{\text{trs}}H_m/R$ ) and entropy ( $\Delta_{\text{trs}}S_m/R$ ) increments are 1913.5 K and 6.00, respectively) and the other at 378.0 K:  $\Delta_{\text{trs}}H_m/R = 346$  K,  $\Delta_{\text{trs}}S_m/R = 0.92$ . Between these transitions there is a broad diffuse hump whose maximum is at about 360 K. The sample melts into a liquid-crystal phase at 396.3 K:  $\Delta_{\text{trs}}H_m/R = 754$  K,  $\Delta_{\text{trs}}S_m/R = 1.9$ . Finally, "clearing" occurs at 460.7 K:  $\Delta_{\text{trs}}H_m/R = 201$  K,  $\Delta_{\text{trs}}S_m/R = 0.44$ . Smoothed thermophysical properties are tabulated through "clearing".

## 1. Introduction

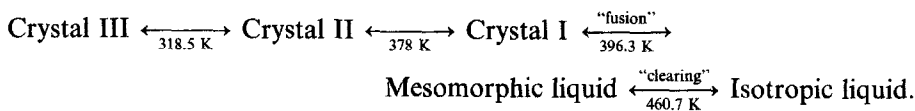
The thermophysical properties of thallium(I) *n*-hexanoate and thallium(I) *n*-heptanoate have been measured earlier<sup>(1,2)</sup> and properties of these salts were established. Below ambient temperatures thallium(I) *n*-hexanoate, showed two solid-to-solid transitions (203.5 and 280.3 K) while thallium(I) *n*-heptanoate showed up to five transitions, one of which, however, is presumably due to the formation of a (salt + acid) complex.

This paper deals with the study of thallium *n*-tetradecanoate. Two techniques were used: d.s.c. from 235 to 450 K and sub-ambient adiabatic calorimetry from 7

<sup>a</sup> The previous papers in this series are references 1 and 2.

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to 350 K to delineate the morphology of the heat capacity from 7 K through melting to "clearing" and hence provide the energetic spectrum of the material. Several phases were found including a mesomorphic liquid crystal. The phase transitions can be summarized as:



## 2. Experimental

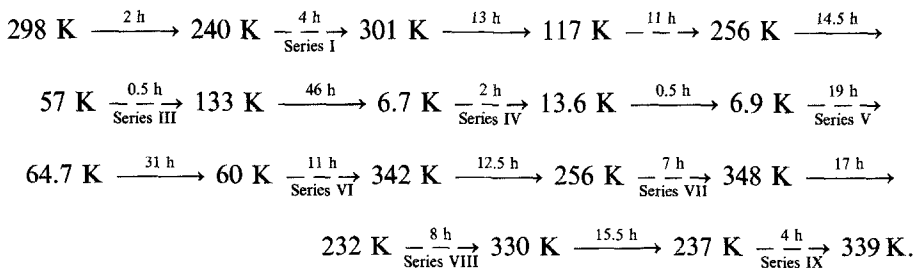
The sample was prepared by reaction of *n*-tetradecanoic acid with thallium carbonate in dry methanol, according to the procedure of Meisel *et al.*<sup>(3)</sup> A d.s.c. purity determination using fractional-fusion techniques indicated 99.85 moles per cent of liquid-soluble solid-insoluble purity.

*Adiabatic calorimetry.* The programming, data logging, and calorimetry were done by computerization described elsewhere.<sup>(4,5)</sup> Measurement of mass, time, resistance, and weight corrections were referred to calibrations of the National Bureau of Standards.

The sample was loaded into the gold-plated copper calorimeter designated W-62. After evacuation, dry helium gas was added at a pressure of 0.3 kPa to facilitate thermal equilibrium during data acquisition. The sealed calorimeter was then placed in the Mark X cryostat and assembled for data acquisition. The sample mass was 26.844 g ( $\hat{=} 0.062176$  mol).

Buoyancy corrections were calculated using a density of  $2.2 \text{ g} \cdot \text{cm}^{-3}$ , a quantity evaluated from the densities of the earlier members studied.<sup>(6)</sup> Crystallographic information on the density of none of the neighboring members is available; thallium acetate has a density of  $3.6 \text{ g} \cdot \text{cm}^{-3}$ .

The thermal history of the thallium *n*-tetradecanoate sample is shown below, where solid arrows indicate cooling and dashed arrows indicate data acquisition ranges for various series.



*Differential scanning calorimetry.* A Perkin-Elmer DSC-2 provided with an Intracooler II device was used. Its temperature display was calibrated at the melting temperatures of several high-purity ( $> 99.9$  moles per cent) substances (*n*-undecane, *n*-tridecane, *n*-pentadecane, gallium, stearic acid, benzoic acid, indium, and tin). The

enthalpies of transitions were determined with high-purity indium (>99.999 moles per cent pure) as reference. For the heat-capacity determination synthetic sapphire was used as an external standard.

### 3. Results and discussion

The experimental heat capacities are given in table 1 for adiabatic calorimetry and in table 2 for d.s.c. and are plotted together in figure 1 for the whole temperature region studied. An expanded-range plot is shown in figure 2 to enhance the features of the 318.5 K transition. The value of 318.5 K for the transition obtained by d.s.c. is in good agreement with the value obtained by adiabatic calorimetry. The standard deviations in the adiabatic-calorimetry heat capacities begin at 5 per cent at 7 K and decrease to 0.3 per cent at 20 K and to less than 0.1 per cent above 50 K. The standard deviations for the d.s.c. heat capacities are about 3 per cent.

The heat capacities were fitted to a series of orthogonal polynomials in regions of normal heat capacity. Integration of the polynomials yielded the thermodynamic

TABLE 1. Molar heat capacities of thallium(I) *n*-tetradecanoate C<sub>13</sub>H<sub>27</sub>CO<sub>2</sub>Tl  
( $R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

<i>T</i> /K	<i>C</i> <sub><i>p,m</i></sub> / <i>R</i>	<i>T</i> /K	<i>C</i> <sub><i>p,m</i></sub> / <i>R</i>	<i>T</i> /K	<i>C</i> <sub><i>p,m</i></sub> / <i>R</i>	<i>T</i> /K	<i>C</i> <sub><i>p,m</i></sub> / <i>R</i>	<i>T</i> /K	<i>C</i> <sub><i>p,m</i></sub> / <i>R</i>
Series I		221.31	37.017	11.40	1.339	40.26	9.991	Series VII	
244.15	40.205	227.66	37.832	12.29	1.497	43.42	10.927	$\Delta H_m$	Detn. H
251.12	41.576	234.01	38.813	13.19	1.737	46.58	11.856	$\Delta H_m$	Detn. I
257.88	42.604	240.36	39.676	Series V		50.22	12.884	303.92	55.679
264.64	43.812	246.71	40.755	Series V		54.32	13.925	308.92	57.650
271.38	45.257	253.05	41.826	7.36	0.45	58.45	14.997	315.07	284.07
278.11	46.761	Series III		8.07	0.63	62.64	15.996	328.09	89.862
284.83	48.415	Series III		8.87	0.77	Series VI		340.31	81.627
291.54	50.367	60.73	15.527	9.71	0.95	Series VI		345.63	84.316
298.23	52.644	65.51	16.657	10.57	1.126	73.27	18.211	Series VIII	
Series II		69.55	17.486	11.45	1.300	$\Delta H_m$	Detn. A	$\Delta H_m$	Detn. J
121.59	25.567	73.66	18.275	12.33	1.543	$\Delta H_m$	Detn. B	294.30	51.879
127.25	26.179	78.27	19.199	13.23	1.735	121.81	25.577	314.00	60.839
132.53	26.790	83.36	20.215	14.14	1.994	$\Delta H_m$	Detn. C	317.65	108.49
137.82	27.390	88.48	21.132	15.05	2.251	$\Delta H_m$	Detn. D	318.31	1086.08
143.12	27.938	93.63	21.909	15.97	2.500	$\Delta H_m$	Detn. E	318.42	1536.19
148.43	28.576	98.82	22.601	17.11	2.820	$\Delta H_m$	Detn. F	318.48	1827.35
153.74	29.119	104.03	23.344	18.47	3.213	294.21	51.280	318.50	8282.2
159.06	29.686	109.26	24.001	19.82	3.626	300.14	53.312	318.51	3047.6
164.39	30.273	114.50	24.694	21.19	4.049	$\Delta H_m$	Detn. G	318.56	1548.7
169.72	30.787	119.76	25.368	22.57	4.458	312.24	59.269	318.62	2361.8
175.05	31.368	125.02	26.002	23.96	4.893	317.03	139.403	318.62	2932.3
180.38	31.980	130.14	26.582	25.36	5.332	318.80	2549.48	319.54	292.23
185.71	32.568	Series IV		26.77	5.770	319.02	1723.33	323.01	79.360
191.05	33.227	7.24	0.45	28.50	6.315	319.94	309.73	328.15	78.431
196.39	33.844	8.05	0.62	30.53	6.961	323.24	80.917	Series IX	
202.24	34.544	8.86	0.75	32.57	7.611	328.34	78.579	310.78	58.816
208.60	35.340	9.67	0.94	34.62	8.244	333.49	79.034	324.47	161.47
214.95	36.098	10.53	1.104	36.26	8.781			336.83	79.957
				37.76	9.259				

TABLE 2. Heat capacity of thallium(I) *n*-tetradecanoate by d.s.c. ( $R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

<i>T</i> /K	$C_{p,m}/R$	<i>T</i> /K	$C_{p,m}/R$	<i>T</i> /K	$C_{p,m}/R$	<i>T</i> /K	$C_{p,m}/R$	<i>T</i> /K	$C_{p,m}/R$
235	38.5	280	47.7	Trs: (III)→(II)		Trs: (II)→(I)		420	82.3
240	39.4	285	49.2	330	77.3	380	62.9	425	82.5
245	40.7	290	50.6	335	79.2	385	64.6	430	82.7
250	41.6	295	52.2	340	81.0	390	67.6	435	82.9
255	42.5	300	54.3	345	83.4	Fusion: (I)→(M)		440	83.1
260	43.5	305	56.5	350	86.1			445	83.5
265	44.5	310	58.5	355	87.8	405	80.95	450	83.8
270	45.6			360	86.2	410	81.4		
275	46.3			365	82.6	415	81.9		
				370	80.0				

functions. In the region of transitions, excess enthalpies and entropies were obtained by drawing the appropriate lattice curves and assuming isothermal transition. One first-order transition was observed in the heat-capacity curve from the adiabatic calorimetry at 318.5 K. The reproducibility of the heat-capacity curve in this transitional region in our measurements was within the experimental error, as shown in table 3 for several determinations through this transition region. Moreover, enthalpy-type determinations in this normal heat-capacity region were compared with the values obtained from heat-capacity values and the results are shown in table 4.

In table 5 the transition properties obtained by d.s.c. measurements are summarized. The values of the enthalpy and entropy for the transition measured by both techniques are in good agreement.

At clearing an exothermic effect was observed attributable to the decomposition of the sample. For this reason, d.s.c. heat-capacity values could not be obtained in this region.

Lindau *et al.*<sup>(7)</sup> observed two transitions below 350 K, *viz.* 315.2 K and 309.7 K giving a total enthalpy of transition of  $1323.01R \cdot \text{K}$ . This value is considerably smaller than the  $1913.53R \cdot \text{K}$  value observed in this study. Lindau does not mention the transition at 309.7 K in a later publication<sup>(8)</sup> which makes his results in reference (7) above questionable. It is apparent from cooling curves that undercooling occurs in this sample and that the transition to a lower-temperature phase begins to take place only at about 315 K, 3 K below the observed transition temperature.

On the other hand, the d.s.c. cooling thermograms of the (Crystal II-to-Crystal III) transition show three peaks that change depending on the thermal treatment of the sample; however, during heating a single peak was always observed.

The smoothed table of thermophysical properties obtained in this work is summarized in table 6 at selected round temperatures. A summary of the observed transition temperatures and literature values for comparison is shown in table 7.

Utilizing the approach already developed<sup>(9-11)</sup> for estimating the lattice heat capacity by incrementation with  $\text{CH}_2$ -units for the tetradecanoate referred to

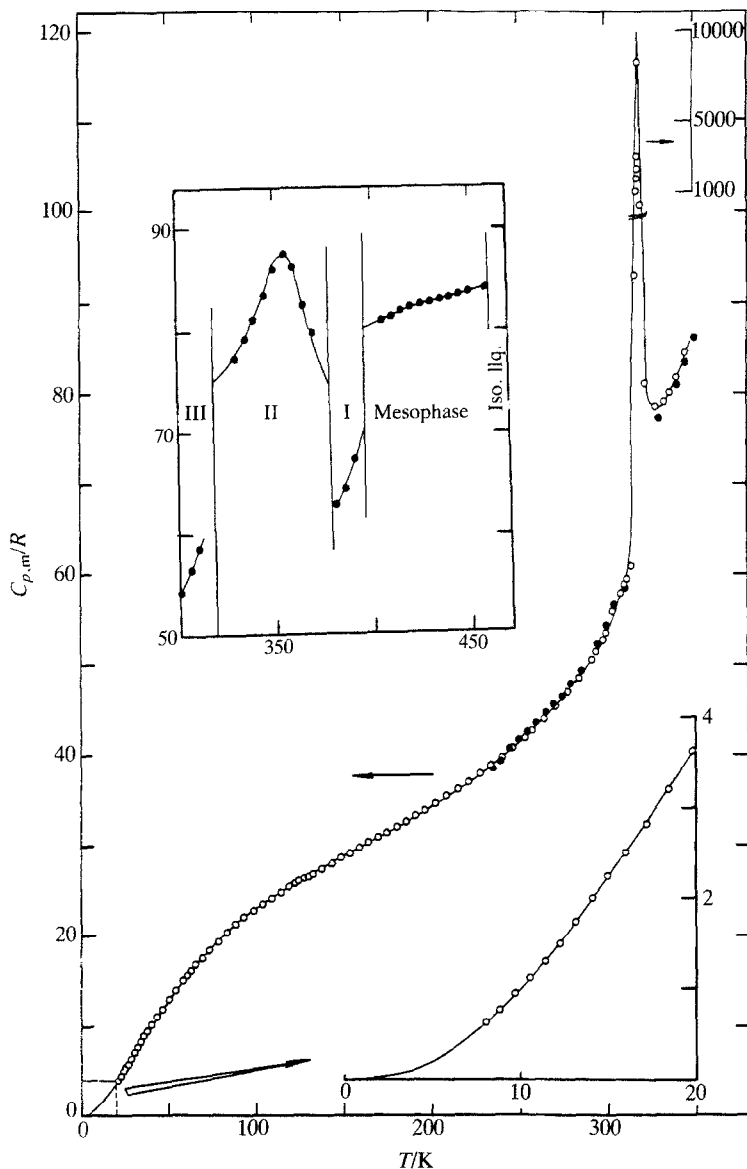


FIGURE 1. Heat-capacity curve for thallium(I) *n*-tetradecanoate.  $\circ$ , Adiabatic calorimetric determinations;  $\bullet$ , d.s.c. determinations.

thallium heptanoate<sup>(1)</sup> we found that the estimated lattice heat capacity fits within 5 per cent to 230 K at which temperature a transition in the reference compound commences. Over the region extending up to the first transition in the thallium hexanoate<sup>(2)</sup> this alternative reference compound provides almost as good a fit even

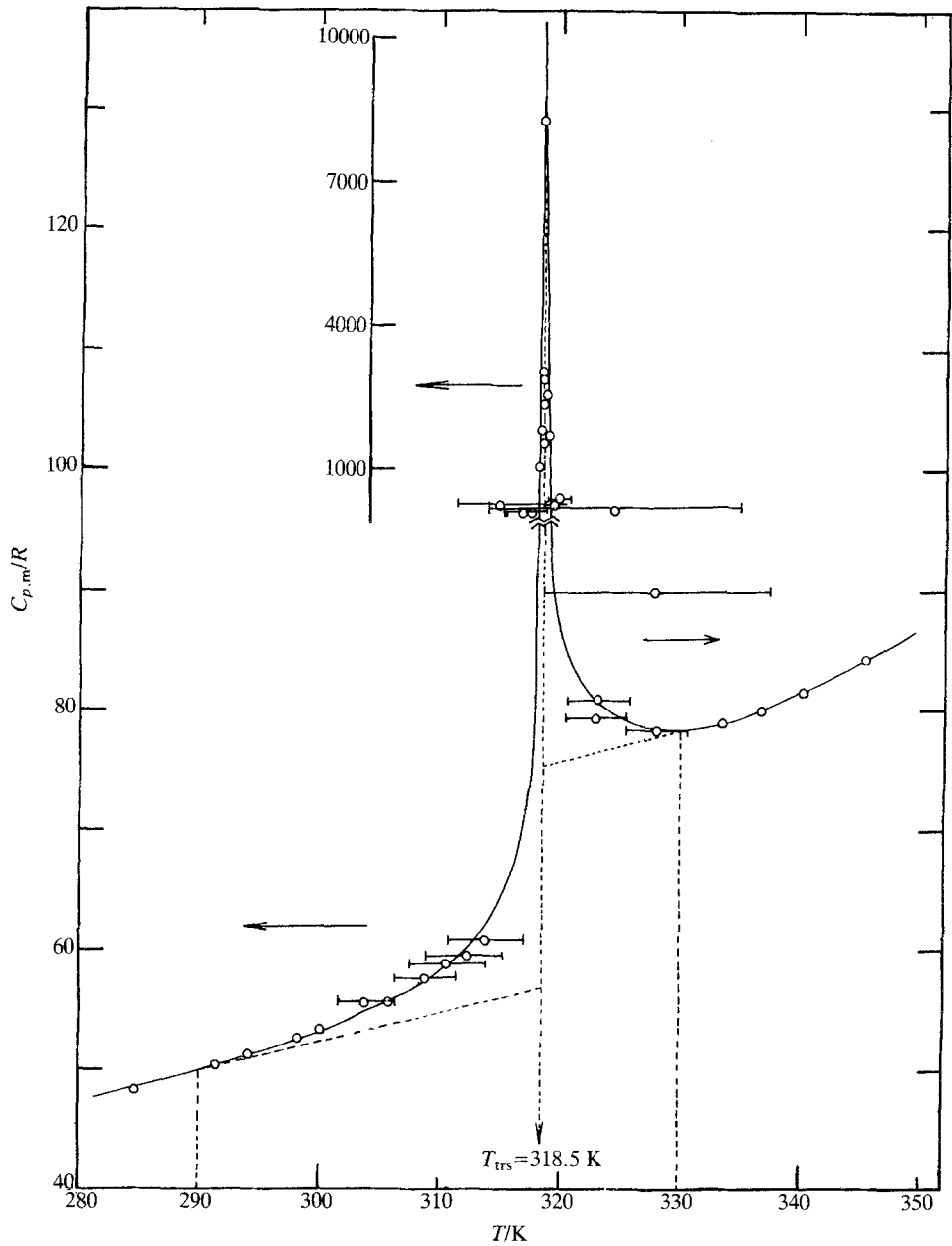
FIGURE 2. Expanded heat-capacity curve of thallium(I) *n*-tetradecanoate in the transition region.

TABLE 3. Enthalpy and entropy of 318.15 K transition in thallium(I) *n*-tetradecanoate  
( $R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

Designation	No. of dctns.	$\frac{T_1}{\text{K}}$	$\frac{T_2}{\text{K}}$	$\frac{\Delta_{T_1}^T H_m^c}{R \cdot \text{K}}$	$\frac{\Delta_{290\text{K}}^{330\text{K}} H_m^c}{R \cdot \text{K}}$	$\frac{\Delta_{290\text{K}}^{330\text{K}} S_m^c}{R}$
Series VI	10	290.82	330.92	4341.6	4315.5	
Series VIII	14	277.66	330.74	4961.1	4318.6	
Series IX	2	307.65	335.03	3777.1	4316.9	
				mean:	4317.0	
Graphical integration					(4315)	13.72
Lattice contribution					2403	7.72
				Calculated $\Delta_{\text{trs}} H_m^c$ :	1914	
				Graphical $\Delta_{\text{trs}} H_m^c$ :	(1912)	
				$\Delta_{\text{trs}} S_m^c$ :		6.00

TABLE 4. Comparison of enthalpy-type determinations with integrated heat capacities over the same heat-capacity regions

Designation	$\frac{T_1}{\text{K}}$	$\frac{T_2}{\text{K}}$	$\frac{\Delta_{T_1}^T H_m}{R \cdot \text{K}}$	$\frac{\int C_{p,m} dT}{R \cdot \text{K}}$	$10^2 \frac{\Delta H_m - \int C_{p,m} dT}{\Delta H_m}$
A	75.05	109.12	728.04	731.65	0.12
B	109.11	120.80	289.35	289.22	0.05
C	122.81	165.65	1198.82	1200.43	0.03
D	165.62	206.96	1351.32	1355.22	0.07
E	206.95	249.21	1602.71	1607.60	0.07
F	249.20	290.82	1879.71	1881.75	0.03
G	302.68	309.14	360.29	361.60	0.09
H	253.82	272.53	820.33	816.09	0.12
I	272.53	301.53	1435.62	1432.39	0.06
J	236.10	277.67	1766.93	1770.63	0.05

TABLE 5. Transition properties of thallium(I) *n*-tetradecanoate by d.s.c. (mean values of four determinations)

Transition	$\frac{T}{\text{K}}$	$\frac{\Delta_{\text{trs}} H_m^c}{R \cdot \text{K}}$	$\frac{\Delta_{\text{trs}} S_m^c}{R}$
Crystal III → Crystal II	318.2	1816	5.7
Crystal II → Crystal I	378.0	346	0.92
Crystal I → Mesophase	396.3	754	1.9
Mesophase → Isotropic liquid	460.7	201	0.44

TABLE 6. Smooth thermodynamic values at selected temperatures for thallium(I) *n*-tetradecanoate  
 $\{R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}; \Phi_m^\circ(T, 0) \stackrel{\text{def}}{=} -\Delta_0^T H_m^\circ(T)/T + \Delta_0^T S_m^\circ(T)\}$

$T$ K	$C_{p,m}$ R	$\Delta_0^T S_m^\circ(T)$ R	$\Delta_0^T H_m^\circ(T)$ R · K	$\Phi_m^\circ(T, 0)$ R	$T$ K	$C_{p,m}$ R	$\Delta_0^T S_m^\circ(T)$ R	$\Delta_0^T H_m^\circ(T)$ R · K	$\Phi_m^\circ(T, 0)$ R
Phase III					325	78.70	68.11	11672.4	35.71
0	0	0	0	0		[76.90]	[62.11]	[9758.8]	[29.84]
10	0.998	0.333	2.496	0.083	330 <sup>a</sup>	78.2	69.45	12060.0	36.34
15	2.225	0.955	10.378	0.263		[78.2]	[63.45]	[10146.5]	[30.55]
20	3.678	1.792	25.102	0.537	340	81.5	71.81	12856.8	34.00
25	5.218	2.777	47.311	0.885			[65.81]	[10943.2]	[33.62]
30	6.788	3.867	77.32	1.290	350	86.1	74.24	13697	35.11
35	8.382	5.033	115.24	1.740			[68.24]	[11784]	[34.57]
40	9.921	6.254	161.05	2.228	360	86.2	76.72	14570	36.25
45	11.395	7.507	214.33	2.745			[70.72]	[12656]	[35.56]
50	12.809	8.782	274.89	3.285	370	80.0	79.00	15400	37.38
60	15.35	11.347	415.95	4.415			[73.00]	[13487]	[36.55]
70	17.60	13.886	580.9	5.587	378.0 <sup>b</sup>	(>400)	(80.65)	(16016)	(38.28)
80	19.57	16.37	767.0	6.780		74.23	[74.65]	[14102]	[37.34]
90	21.30	18.77	971.5	7.980			Phase I		
100	22.82	21.10	1192.3	9.176					
120	25.38	25.49	1675.1	11.534	378.0 <sup>b</sup>	(>400)	(81.57)	(16364)	(38.28)
140	27.63	29.58	2205.4	13.823		[63.1]	[74.65]	[14102]	[37.34]
160	29.79	33.41	2779.6	16.03	380	62.9	81.90	16486	38.51
180	31.94	37.04	3396.8	18.17		[62.5]	[74.98]	[14226]	[37.54]
200	34.25	40.52	4058.4	20.23	390	67.6	83.59	17136	39.65
220	36.82	43.91	4768.7	22.23		[67.4]	[76.67]	[14876]	[38.53]
240	39.68	47.23	5533	24.17	396.3 <sup>b</sup>	(>300)	(84.69)	(17570)	(40.36)
260	42.99	50.53	6359	26.07		[70.45]	[77.77]	[15310]	[39.14]
280	47.22	53.86	7259	27.94			Mesomorphic phase		
290 <sup>a</sup>	49.87	55.57	7744.0	28.86					
	[49.87]	[55.57]	[7744.0]	[28.86]	396.3 <sup>b</sup>	(>300)	(86.59)	(18321)	(40.36)
298.15	52.71	56.99	8161.0	29.62		[80.10]	[77.77]	[15310]	[39.14]
	[51.90]	[56.98]	[8158.4]	[29.62]	400	(>150)	(87.34)	(18621)	(40.79)
300	53.20	57.30	8254.7	29.78		[80.43]	[78.52]	[15607]	[39.50]
	[52.30]	[57.30]	[8254.7]	[29.78]	410		81.4	89.34	19430
310	58.00	59.06	8790.0	30.71		[81.4]	[80.52]	[16416]	[40.48]
	[54.76]	[59.06]	[8790.0]	[30.71]	420		82.3	91.31	20248
318.5 <sup>b</sup> ( $\approx 10500$ )	(56.84)	(60.57)	(9264.3)	(31.48)	430		82.7	93.25	21073
	[56.84]	[60.57]	[9264.3]	[31.48]	440		83.1	95.16	21902
					450		83.8	97.04	22737
					460.7 <sup>b</sup>	(>200)	(98.89)	(23580)	(47.71)
318.5 <sup>b</sup> ( $\approx 10500$ )	[56.84]	[60.57]	[9264.3]	[31.48]		[84.5]	[90.13]	[20595]	45.43
							Isotropic liquid		
					460.7 <sup>b</sup>	(>200)	(99.33)	(23781)	(47.71)

<sup>a</sup> Quantities in square brackets represent estimated lattice heat capacities at indicated temperature.

<sup>b</sup> 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.



TABLE 7. Summary of transition temperatures for thallium(I) *n*-tetradecanoate

Phases	$T_{trs}/K$			
	This work (adiabatic calorimetry)	This work (d.s.c.)	Lindau <i>et al.</i> <sup>(7,8)</sup> (d.s.c.)	Meisel <i>et al.</i> <sup>(9)</sup> (d.t.a.)
IV → III	—	—	309.7	—
III → II	318.5	318.2	315.2	313
II → I	—	378.0	368.0	371
I → Mesophase	—	396.3	392.1	393
Mesophase → Isotropic liquid	—	460.7	457.6	460

as low as 12 K. The odd–even effect noted previously with the lighter alkali metal does not obtain since it is overwhelmed by the massiveness of the thallium atoms.

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