

# Thermodynamics of thallium alkanoates

## V. Heat capacity and thermodynamic functions of thallium(I) *n*-decanoate from 6 to 480 K<sup>a</sup>

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The heat capacity of thallium(I) *n*-decanoate was measured by adiabatic calorimetry from 6 to 350 K and by d.s.c. from 200 through 480 K. Excellent overlap occurs over the common temperature range of both techniques. Four solid-to-solid transitions were found; at 232.9 K, at 288.3 K, and two more at 305.6 K (very sharp with a for the maximum of about 1700R), and at 327.6 K. The corresponding values of  $\Delta_{\text{irs}}H_m^\circ$  are 352R · K, 83.8R · K, and 1026R · K (for the set of two transitions), respectively, and of  $\Delta_{\text{irs}}S_m^\circ$  are 1.46<sub>1</sub>R, 0.28<sub>3</sub>R, and 3.19R (for the set of two), respectively. The compound melts to a liquid-crystal phase at 405.0 K:  $\Delta_{\text{irs}}H_m^\circ = 682R \cdot K$ ,  $\Delta_{\text{irs}}S_m^\circ = 1.68R$ . Finally, "clearing" occurs at 484.0 K:  $\Delta_{\text{irs}}H_m^\circ = 307R \cdot K$ ,  $\Delta_{\text{irs}}S_m^\circ = 0.63R$ . Smoothed thermophysical functions are tabulated through "clearing" at selected temperatures.

### 1. Introduction

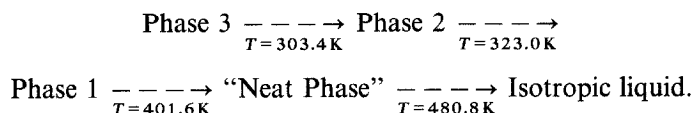
Molar heat capacities and relevant thermodynamic functions of thallium(I) *n*-hexanoate, *n*-heptanoate, *n*-dodecanoate, and *n*-tetradecanoate (obtained by equilibrium adiabatic calorimetry and d.s.c.) have been provided in papers I to IV of this series.<sup>(1-4)</sup> A similar detailed study of the several crystal and liquid-crystal-like

<sup>a</sup> Previous papers in this series are those of references 1 to 4.

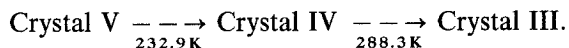
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phases of thallium(I) *n*-decanoate (denoted hereafter by Tl10C) has been carried out and this paper reports on that study. Theoretical calculations have been made on disordering in decane systems<sup>(5-7)</sup> as this chain length is of particular interest.

Previous studies on the thermal and phase behavior of Tl10C in the superambient region have been reported by several authors. We summarize here their main results for better understanding of ours. Pelzl and Sackmann<sup>(8)</sup> measured the refractive indices of several thallium(I) *n*-alkanoates in their "neat" (smectic A-like) phases; for Tl10C, they determined microscopically the temperatures of transition into the "neat" phase (404.0 K) and the "clearing" point (482.5 K). Polarizing microscopy and d.s.c. determinations above room temperature allowed Lindau *et al.*<sup>(9)</sup> to claim for Tl10C the phase transformations in the superambient region:



Our results agree qualitatively with this scheme above 300 K with some noteworthy changes in the temperatures of the phase transitions. However, the phase behavior below 300 K has not been investigated previously. In this paper, besides the complete morphology of the heat-capacity curve, we report the existence of two new solid-to-solid phase transitions:



As we have accurate thermodynamic functions and heat capacities for several members of the thallium(I) *n*-alkanoates series, we present also an overview of those for such compounds.

## 2. Experimental

The calorimetric sample of Tl10C was prepared by reacting Fluka puriss ( $\geq 99$  moles per cent; tested at the origin by g.c.) *n*-decanoic acid with a slight excess of Fluka puriss  $\text{Tl}_2\text{CO}_3$  in anhydrous methanol, following the procedure explained in detail in references 4 and 5. The white powder obtained was purified by repeated recrystallization from absolute ethanol. After drying under vacuum at 295 K (a temperature intermediate between  $T_{\text{IV} \rightarrow \text{III}}$  and  $T_{\text{III} \rightarrow \text{II}}$ ) the sample was submitted to d.s.c. purity analysis using fractional-fusion techniques; a mean value of  $(99.90 \pm 0.10)$  moles per cent (average of four determination with different samples from the bulk of the synthesized sample) of liquid-soluble solid-insoluble purity was obtained.

### ADIABATIC CALORIMETRY

The salt was loaded into a gold-plated OHFC copper calorimeter (laboratory designation W-62B); the determinations of the heat capacity from 6 to 350 K were made in the Mark X cryostat described elsewhere.<sup>(10)</sup> Data logging, calorimetry, and programming were computer assisted.<sup>(11)</sup>



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

<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	$C_{p,m}/R$	<i>T</i> /K	$C_{p,m}/R$
Series I		221.10	29.85	32.45	6.284	230.94	33.10	294.54	48.48	288.49	86.68
211.50	28.50	233.22	50.63	34.34	6.757	232.33	78.46	296.69	49.56	288.74	67.68
216.84	29.20	245.55	34.57	36.50	7.282	232.82	406.4	Series VII		289.09	58.25
221.96	30.06	251.84	35.90	38.90	7.856	232.91	454.4	$\Delta H_m$	Detn. D	294.92	49.51
227.07	30.66	258.14	37.15	41.29	8.394	233.15	194.3	283.06	43.89	301.83	55.44
231.24	63.25	264.44	38.54	43.68	8.928	234.28	37.28	284.23	44.30	303.67	63.28
236.27	64.30	282.05	46.03	46.08	9.477	236.48	33.22	285.15	44.98	304.70	85.9
242.68	34.22	297.86	50.08	48.50	9.989	238.74	33.54	286.07	45.29	305.31	288.6
248.56	35.22	300.55	51.78	50.85	10.475	241.00	33.77	286.98	45.77	305.53	740.1
254.67	36.43	Series III		53.46	11.027	243.23	34.38	287.72	82.7	305.59	1669.0
260.77	37.71	223.35	30.15	56.39	11.559	245.98	34.66	288.20	105.2	305.68	537.4
266.88	38.98	233.19	52.43	59.31	12.118	Series VI		288.84	52.23	305.84	269.2
272.96	40.61	243.07	34.23	62.73	12.776	224.18	30.33	289.69	47.85	306.43	84.57
279.02	42.60	Series IV		66.62	13.417	229.39	31.31	290.58	46.82	315.62	62.22
284.74	49.01	6.49	0.37	70.53	13.997	231.66	36.82	291.69	47.38	324.79	64.98
290.04	53.04	7.47	0.43	74.47	14.593	232.46	78.9	295.13	48.74	325.88	68.29
294.99	48.57	8.31	0.59	78.42	15.211	232.75	262.5	300.57	52.13	326.86	89.22
299.40	51.17	9.13	0.69	82.63	15.83	232.85	286.2	304.43	143.1	327.40	324.2
Series II		10.00	0.84	87.10	16.44	232.90	362.5	306.26	293.0	327.53	703.3
128.45	20.79	10.86	1.002	91.58	17.00	232.98	258.4	309.14	64.96	327.60	716.8
132.83	21.16	11.74	1.169	Series V		233.16	123.2	313.78	60.90	327.68	509.3
137.92	21.68	12.63	1.370	93.59	17.22	233.70	42.84	318.51	61.47	327.98	146.9
143.02	22.13	13.53	1.553	98.33	17.76	234.73	33.40	323.11	65.30	329.57	46.23
148.12	22.58	14.43	1.776	103.37	18.06	235.85	33.28	326.50	150.2	Series IX	
153.23	23.04	15.35	1.995	108.41	18.85	237.54	33.22	328.66	172.5	288.32	79.33
158.35	23.49	16.36	2.234	113.45	19.22	241.97	33.99	332.57	45.73	288.62	64.63
163.46	23.94	17.47	2.498	118.52	20.04	$\Delta H_m$	Detn. C	338.35	45.43	288.97	55.22
168.58	24.37	18.58	2.778	123.61	20.48	272.29	40.27	344.15	45.28	289.35	52.12
173.71	24.83	19.69	3.051	128.72	20.80	276.19	41.49	349.94	45.47	289.75	50.61
178.84	25.27	20.82	3.332	133.81	21.28	280.02	42.74	Series VIII		290.17	48.08
183.96	25.83	21.95	3.620	138.90	21.77	282.84	43.85	283.64	45.16	292.51	47.83
189.09	26.28	23.23	3.944	$\Delta H_m$	Detn. A	284.70	44.49	287.52	57.95	314.53	81.32
194.22	26.77	24.64	4.300	$\Delta H_m$	Detn. B	286.49	48.70	287.79	51.89	336.43	45.39
199.35	27.29	26.05	4.663	217.74	29.38	287.80	92.78	287.94	68.77	Series X	
204.48	27.79	27.47	5.020	222.81	30.15	289.24	46.86	288.08	73.95	300.85	55.55
209.61	28.35	28.90	5.378	226.50	30.72	291.02	47.11	288.21	65.20	316.00	100.5
215.17	28.99	30.56	5.798	228.86	30.97	292.79	47.65	288.36	66.88	331.34	47.38

transition regions (because of the nature of the method itself) nor at temperatures above the "clearing" temperature (484.0 K) because decomposition of the sample, starting at temperatures only slightly higher than 484 K.

The standard deviations for the d.s.c. heat-capacity results are 2 per cent in the "normal" heat-capacity regions and about 4 per cent in the pre-transitional regions.

Both heat-capacity sets are plotted together in figure 1; good overlap exists. An expanded section which highlights the features of the curve of  $C_{p,m}/R$  against  $T$  between 200 and 350 K is depicted in figure 2. The overall d.s.c. with both heating and cooling thermograms showing all the observed peaks is plotted in figure 3.

Four presumably first-order phase transitions were observed both by adiabatic calorimetry and by d.s.c. between 200 and 340 K in addition to the fusion and "clearing" transitions observed only by d.s.c. at temperatures above the upper limit

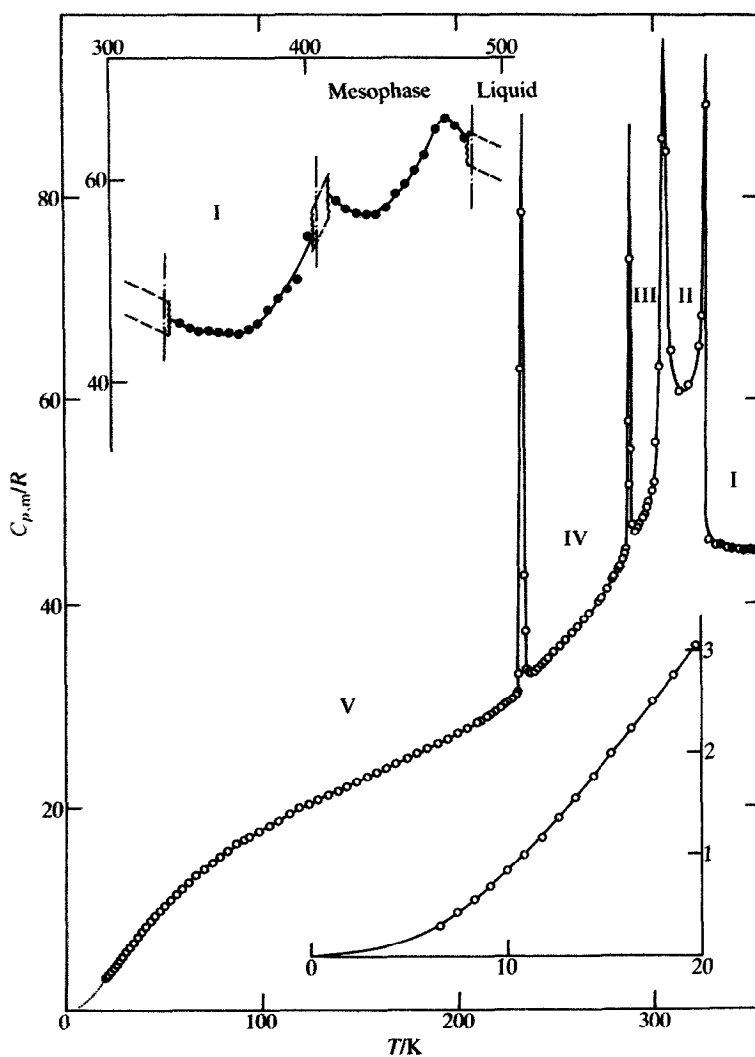


FIGURE 1. Experimental heat capacities of thallium(I) *n*-decanoate. O, Adiabatic-calorimetry determinations; ●, d.s.c. determinations.

TABLE 2. Heat capacity of thallium(I) *n*-decanoate determined by d.s.c. in the temperature range 330 to 480 K ( $R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

$T/\text{K}$	$C_{p,m}/R$	$T/\text{K}$	$C_{p,m}/R$	$T/\text{K}$	$C_{p,m}/R$	$T/\text{K}$	$C_{p,m}/R$	$T/\text{K}$	$C_{p,m}/R$
330	62.4	360	45.0	390	49.3	425	56.7	455	61.0
335	45.9	365	44.8	395	50.1	430	56.6	460	62.5
340	45.4	370	45.3	400	54.6	435	56.5	465	65.1
345	45.1	375	45.8	trs: (I)→mesophase		440	57.4	470	66.4
350	45.3	380	47.2	415	58.0	445	58.7	475	65.4
355	45.0	385	48.3	420	57.2	450	59.7	480	64.1

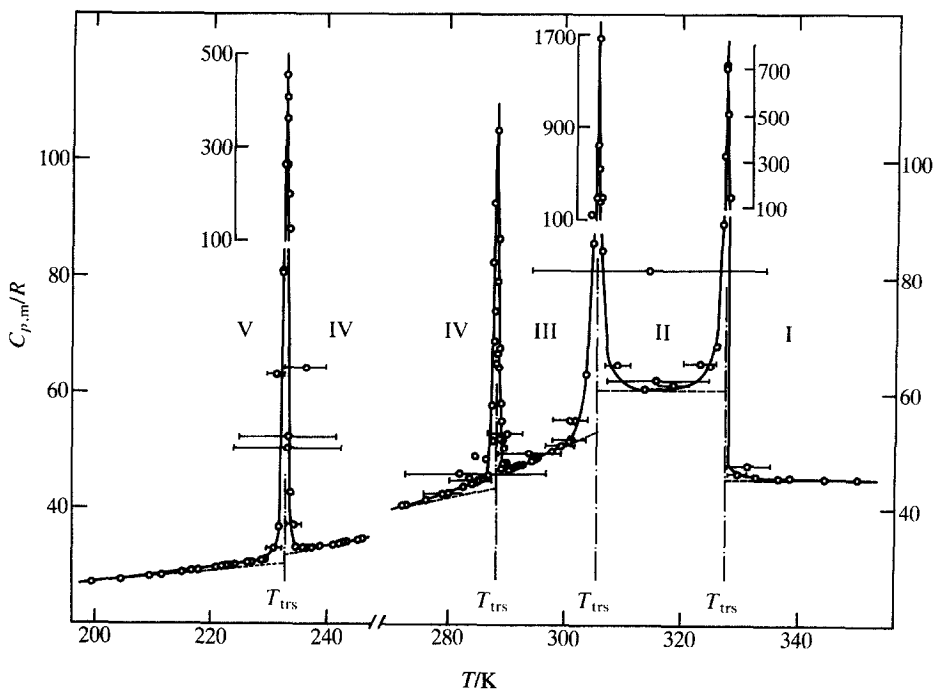


FIGURE 2. Expanded plot of experimental adiabatic-calorimetry heat capacities of thallium(I) *n*-decanoate through the V→I transition region showing the transitions ( $T_{trs}(V\rightarrow IV) = 232.9$  K,  $T_{trs}(IV\rightarrow III) = 288.3$  K,  $T_{trs}(III\rightarrow II) = 305.6$  K,  $T_{trs}(II\rightarrow I) = 327.6$  K), and the arbitrary lattice lines used for transition thermal-function determinations. Horizontal bars indicate the extent of the enthalpy-type measurements.

of equilibrium calorimetry. The enthalpies and entropies of transition in the transformation regions were obtained as the difference of the appropriate integrations of the  $C_{p,m}/R$  curve and the estimated lattice heat-capacity curve. Tables 3, 4, and 5 give these values for the different transitional regions and

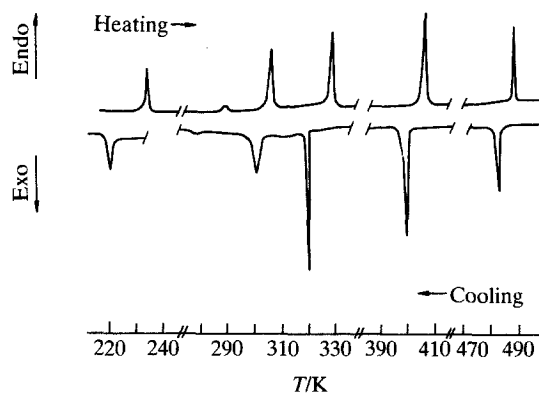


FIGURE 3. Heating and cooling d.s.c. thermograms showing all the observed peaks.

TABLE 3. Enthalpy and entropy of 232.9 K (V to IV) transition in thallium(I) *n*-decanoate ( $R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

Designation	No. of detns	$\frac{T_1}{\text{K}}$	$\frac{T_2}{\text{K}}$	$\frac{\Delta T_1 H_m^\circ}{R \cdot \text{K}}$	$\frac{\Delta_{200\text{K}}^{245\text{K}} H_m^\circ}{R \cdot \text{K}}$	$\frac{\Delta_{200\text{K}}^{245\text{K}} S_m^\circ}{R}$
Series I	7	208.71	245.50	1479.5	1704	
Series II	6	201.91	248.70	1784.3	1708	
Series III	3	221.84	244.61	1070.6	1707	
Series V	14	215.19	244.34	1250.0	1699	
Series VI	13	227.64	245.28	903.9	1693	
Graphical integration:					1700 <sup>a</sup>	7.52 <sub>3</sub>
Mean value:					1702 ± 3	
Lattice contribution (estimated):					1350	6.06 <sub>2</sub>
				$\Delta_{\text{trs}} H_m^\circ / (R \cdot \text{K}) =$	352	
$T_{\text{trs}} = 232.9 \text{ K}$				$\Delta_{\text{trs}} S_m^\circ / R =$		1.46 <sub>1</sub>

<sup>a</sup> Not included in the mean.

different series, showing the reproducibility of the measurements.

In table 6 the transition properties obtained by d.s.c. are summarized. The values of temperatures, enthalpies, and entropies for the transitions measured by both techniques are in excellent agreement.

A test of the accuracy of the overall calorimetric procedure upon comparing the results provided by the  $C_p$ -type runs with several  $\Delta H$ -type determinations (table 7) shows that excellent agreement obtains.

Apart from the transition regions, the numerical results have been fitted to appropriate orthogonal polynomials, on the basis of which the relevant thermodynamic functions (as well as smoothed  $C_{p,m}/R$  values) were calculated for both the total and the lattice curves at selected temperatures (table 8).

TABLE 4. Enthalpy and entropy of the 288.3 K (IV to III) transition in thallium(I) *n*-decanoate ( $R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

Designation	No. of detns	$\frac{T_1}{\text{K}}$	$\frac{T_2}{\text{K}}$	$\frac{\Delta T_1 H_m^\circ}{R \cdot \text{K}}$	$\frac{\Delta_{265\text{K}}^{295\text{K}} H_m^\circ}{R \cdot \text{K}}$	$\frac{\Delta_{265\text{K}}^{295\text{K}} S_m^\circ}{R}$
Series I	6	263.82	297.24	1512.2	1356.8	
Series II	2	267.59	299.22	1466.9	1357.5	
Series VI	11	270.32	295.41	1167.6	1355.5	
Series VII	10	282.37	297.92	789.8	1355.0	
Series VIII	12	287.34	300.56	700.8	1354.0	
Graphical integration:					1354.6 <sup>a</sup>	4.82 <sub>1</sub>
Mean value:					1355.8 ± 0.9	
Lattice contribution:					1272.0	4.53 <sub>8</sub>
				$\Delta_{\text{trs}} H_m^\circ / (R \cdot \text{K}) =$	83.8	
$T_{\text{trs}} = 288.3 \text{ K}$				$\Delta_{\text{trs}} S_m^\circ / R =$		0.28 <sub>3</sub>

<sup>a</sup> Not included in the mean.

TABLE 5. Enthalpy and entropy of the higher transition set: III to II (305.6 K) and II to I (327.6 K) in thallium(I) *n*-decanoate ( $R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

Designation	No. of detns	$\frac{T_1}{\text{K}}$	$\frac{T_2}{\text{K}}$	$\frac{\Delta_{T_1}^T H_m^\circ}{R \cdot \text{K}}$	$\frac{\Delta_{295\text{K}}^{345\text{K}} H_m^\circ}{R \cdot \text{K}}$	$\frac{\Delta_{295\text{K}}^{345\text{K}} S_m^\circ}{R}$
Series VII	12	297.92	347.05	3645.4	3697	
Series	19	300.56	330.90	2762.2	3682	
Series IX	2	294.65	338.46	3416.8	3696	
Series X	3	297.69	334.86	3093.9	3686	
Graphical integration:					3690 <sup>a</sup>	11.55
Mean value:					3690 ± 2	
Lattice contribution:					2664	8.36
$\Delta_{\text{trs}} H_m^\circ(\text{III to II, II to I})/(R \cdot \text{K})$ :					1026	
$\Delta_{\text{trs}} S_m^\circ(\text{III to II, II to I})/R$ :						3.19
$T_{\text{trs}}(\text{III to II}) = 305.6 \text{ K}$				$\frac{\Delta_{\text{III}}^{\text{II}} H_m^\circ}{(R \cdot \text{K})} = 530$		$\frac{\Delta_{\text{III}}^{\text{II}} S_m^\circ}{R} = 1.71$
$T_{\text{trs}}(\text{II to I}) = 327.6 \text{ K}$				$\frac{\Delta_{\text{II}}^{\text{I}} H_m^\circ}{(R \cdot \text{K})} = 496$		$\frac{\Delta_{\text{II}}^{\text{I}} S_m^\circ}{R} = 1.48$

<sup>a</sup> Not included in the mean.TABLE 6. Transition properties of thallium(I) *n*-decanoate as obtained by d.s.c. (mean values of six determinations with standard deviations)

Transition	$T/\text{K}$	$\Delta_{\text{trs}} H_m^\circ/(R \cdot \text{K})$	$\Delta_{\text{trs}} S_m^\circ/R$
Crystal V → Crystal IV	232.4 ± 0.5	290 ± 10	1.25 ± 0.05
Crystal IV → Crystal III	288.6 ± 0.4	72 ± 10	0.25 ± 0.03
Crystal III → Crystal II	306.8 ± 0.8	510 ± 20	1.67 ± 0.07
Crystal II → Crystal I	327.4 ± 0.5	478 ± 40	1.46 ± 0.12
Crystal I → mesophase	405.0 ± 0.5	682 ± 25	1.68 ± 0.06
mesophase → isotropic liquid	484.0 ± 0.8	307 ± 20	0.63 ± 0.05

TABLE 7. Comparison of thallium(I) *n*-decanoate enthalpy-type determinations with integrated smoothed heat-capacity curves ( $R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

Designation	$\frac{T_1}{\text{K}}$	$\frac{T_2}{\text{K}}$	$\frac{\Delta H_m}{R \cdot \text{K}}$	$\frac{\int C_{p,m} dT}{R \cdot \text{K}}$	Percentage deviation
A	141.45	180.27	919.98	918.33	0.18
B	180.25	215.19	948.76	947.65	0.12
C	245.28	270.32	929.83	928.12	0.18
D	244.69	282.36	1450.28	1450.62	0.02

THE HEAT CAPACITY OF A CH<sub>2</sub> GROUP

Because several members of the thallium(I) *n*-alkanoates have been studied, we have used a method similar to those of White<sup>(13)</sup> and of Ngeyi *et al.*<sup>(14)</sup> to determine the heat capacity of the CH<sub>2</sub> increment in this series of compounds and, hence, obtain "lattice curves" for their heat capacity. That is, the range of the heat capacity of a CH<sub>2</sub> unit as a function of temperature has been calculated from

$$C_{p,m}(\text{CH}_2) = \{C_{p,m}(\text{TlnC}) - C_{p,m}(\text{TlkC})\}/(n - k),$$



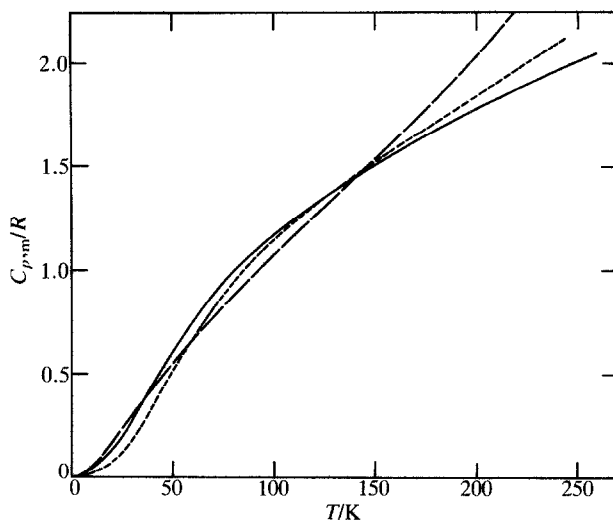


FIGURE 4. Comparison of the  $C_{p,m}$  values of the  $\text{CH}_2$  group; —, values obtained from our series of thallium compounds; ···, Broadhurst<sup>(15)</sup> for *n*-alkanes; - - -, White<sup>(13)</sup> for layered compounds (for formula, see the text).

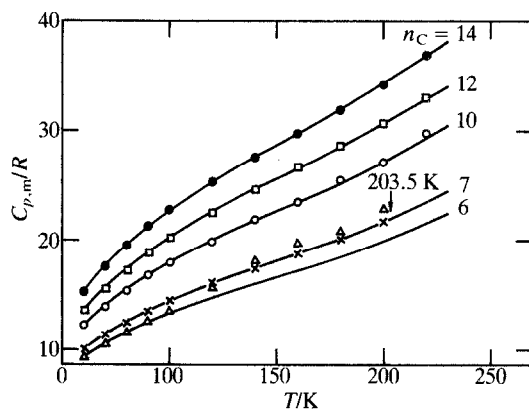


FIGURE 5. Estimated "lattice" heat capacity for thallium(I) normal alkanates of specified number of carbons ( $n = 6, 7, 10, 12,$  and  $14$ ) calculated by using increments in the heat-capacity values (symbols represent the experimental values). Thallium(I) *n*-hexanoate presents a broad and diffuse anomaly in the range 100 to 200 K.

for the 10 possible pairs of compounds for  $n, k = 6, 7, 10, 12$  and  $14$ .

The full line in figure 4 represents the values obtained for our series of compounds compared with those obtained by Broadhurst for the *n*-alkanes<sup>(15)</sup> (dotted line) and by White<sup>(13)</sup> for the layered compounds of general formula  $\{\text{C}_n\text{H}_{2n+1}\text{NH}_3\}_2\text{MX}_4$  (dashed line).

By using the increments we have calculated the estimated "lattice" heat capacities for thallium(I) normal alkanates with  $n = 6, 7, 10, 12,$  and  $14$ . Figure 5 shows the results as consistent and reasonable when compared with the corresponding

TABLE 8. Smooth thermodynamics values at selected temperatures for thallium(I) *n*-decanoate ( $R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

$\frac{T}{\text{K}}$	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot \text{K}}$	$\frac{\Phi_m^\circ}{R}$	$\frac{T}{\text{K}}$	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot \text{K}}$	$\frac{\Phi_m^\circ}{R}$
		Phase V					Phase III		
0	0	0	0	0	288.3 <sup>b</sup>	( $\approx 110$ )	(46.57)	(6696.0)	(23.35)
5	0.116	0.0388	0.146	0.0096		[45.56]	[44.82]	[6266.2]	[23.09]
10	0.843	0.310	2.317	0.0781	290	46.8	46.84	6774.1	23.48
15	1.907	0.842	9.055	0.238		[46.37]	[45.09]	[6344.3]	[23.21]
20	3.123	1.556	21.62	0.475	300	51.3	48.49	7261.4	24.29
25	4.392	2.390	40.41	0.773		[50.97]	[46.74]	[6831.6]	[23.97]
30	5.659	3.303	65.55	1.118	305.6 <sup>b</sup>	( $\approx 1700$ )	(49.46)	(7553.6)	(24.74)
35	6.918	4.270	97.00	1.498		[53.40]	[47.71]	[7123.8]	[24.40]
40	8.106	5.273	134.61	1.907					
45	9.230	6.292	177.93	2.338					
50	10.27	7.321	226.80	2.785	305.6 <sup>b</sup>	( $\approx 1700$ )	(51.17)	(8083.6)	(24.74)
60	12.28	9.373	339.70	3.712		[60.7]	[47.71]	[7123.8]	[24.40]
70	13.95	11.40	471.2	4.666	314 <sup>c</sup>	(60.7)	(52.82)	(8593.5)	(25.45)
80	15.40	13.36	618.0	5.630		[60.7]	[49.36]	[7633.7]	[25.05]
90	16.77	15.25	779.0	6.595	327.6 <sup>b</sup>	( $\approx 750$ )	(55.39)	(9419.0)	(26.63)
100	17.97	17.08	952.9	7.552		[60.7]	[51.93]	[8459.2]	[26.11]
120	19.93	20.53	1332.0	9.432					
140	21.94	23.76	1751.0	11.25					
160	23.52	26.79	2205.9	13.01	327.6 <sup>b</sup>	( $\approx 750$ )	(56.87)	(9915.0)	(26.63)
180	25.52	29.67	2695.5	14.70		[45.25]	[51.93]	[8459.2]	[26.11]
200 <sup>a</sup>	27.19	32.45	3223.5	16.34	340	45.35	58.55	10476.1	27.74
	[27.19]	[32.45]	[3223.5]	[16.34]		[45.25]	[53.61]	[9020.3]	[27.08]
210	28.37	33.80	3500.8	17.13	360	45.0	61.14	11381	29.53
	[28.21]	[33.80]	[3501.0]	[17.13]	380	47.2	63.60	12292	31.25
220	29.75	35.16	3791.8	17.92	400	54.6	66.13	13277	32.94
	[29.11]	[35.13]	[3787.6]	[17.91]		[51.3]	[61.19]	[11821]	[31.64]
230	32.01	36.51	4096.2	18.70	405.0 <sup>b</sup>	(—)	(66.77)	(13536)	(33.34)
	[30.02]	[36.45]	[4083.3]	[18.70]		[52.3]	[61.83]	(12080)	[32.01]
232.9 <sup>b</sup>	( $\approx 460$ )	(36.83)	(4170.7)	(18.92)					
	[30.28]	[36.83]	[4170.7]	[18.92]	405.0 <sup>b</sup>	(—)	(68.45)	(14218)	(33.34)
						[58.9]	[61.83]	[12080]	[32.01]
232.9 <sup>b</sup>	( $\approx 460$ )	(38.30)	(4516.7)	(18.92)	420	57.2	70.56	15089	34.63
	[32.00]	[36.83]	[4170.7]	[18.92]		[57.2]	[63.94]	[12951]	[33.10]
240	33.67	39.28	4749.0	19.49	440	57.4	73.20	16225	36.33
	[33.45]	[37.81]	[4403.0]	[19.46]	460	62.5	75.86	17422	37.98
250	35.51	40.68	5100.7	20.28	480	64.1	78.63	18723	39.62
260	37.51	42.12	5465.7	21.09	484.0 <sup>b</sup>	(—)	(79.29)	(19041)	(39.95)
270	29.80	43.57	5851.9	21.90		[63.1]	[72.67]	[16903]	[37.75]
	[39.64]	[42.10]	[5505.9]	[21.71]					
280	42.60	45.05	6258.7	22.70					
	[41.72]	[43.58]	[5912.7]	[22.46]	484.0 <sup>b</sup>	(—)	(79.92)	(19348)	(39.95)
288.3 <sup>b</sup>	( $\approx 110$ )	(46.29)	(6612.2)	(23.35)					
	[43.45]	[44.82]	[6266.2]	[23.09]					
							Isotropic liquid		

<sup>a</sup> Quantities in square brackets represent selected lattice heat capacities or the corresponding integrated thermodynamics function.

<sup>b</sup> Quantities in parentheses represent either estimated heat capacities or the integrated thermodynamic functions on the assumption that the transitions are truly isothermal at the transition temperature indicated.

<sup>c</sup> Quantities at minimum points between bifurcated transitions.

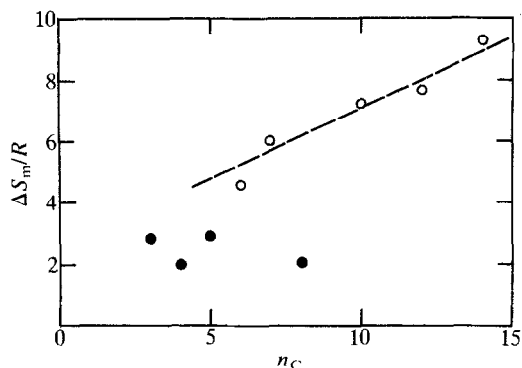


FIGURE 6. Overall entropy changes (solid-to-solid transitions, fusion, and "clearing") plotted against number  $n_c$  or carbons of the chain. For the  $n_c = 3, 4, 5,$  and  $8$  members of the series, transitions below 300 K are expected.

experimental values, except for thallium hexanoate. For this compound a broad and diffuse anomaly in the heat capacity curve is predicted in the range 100 to 200 K and was detected in the heat-capacity measurements by Boerio-Goates *et al.*<sup>(1)</sup> but the entropy change involved was not evaluated. The use of the heat-capacity increments for the  $\text{CH}_2$  group could lead to an estimation of this entropy change, especially if other compounds of the series (*e.g.* thallium pentanoate) were studied.

#### PHASE TRANSITIONS

Thallium(I) *n*-decanoate is found to exhibit five solid (crystalline) phases and a mesomorphic one of the smectic A ("neat") type. The overall molar-entropy change on going from crystal V (the lowest-temperature phase) to isotropic liquid is  $7.24R$  ( $=60.27 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ) which is only about 65 per cent of that observed for *n*-decanoic acid.<sup>(16)</sup> This suggests that a certain order persists in the liquid phase of the soap.

For thallium(I) *n*-hexanoate, *n*-heptanoate, *n*-dodecanoate, and *n*-tetradecanoate we have found<sup>(1-4)</sup> five, five, six, and four, solid crystalline phases, respectively, as well as a mesomorphic "neat" phase. The corresponding overall molar entropy changes (*i.e.*  $\Delta S_m = \Delta_{\text{fus}} S_m + \Delta_{\text{clearing}} S_m + \Sigma \Delta_{\text{trs}} S_m$ ) are plotted against the numbers of carbons of the hydrocarbon chain in figure 6. We represent there the values for the homologous series with  $n = 3, 4, 5,$  and  $8$ , compounds which have been studied only above 300 K<sup>(9,17)</sup> (filled circles in figure 6). It is apparent from figure 6 that these other compounds may be expected to have transitions below 300 K.

From the slope of the regression line  $\Delta S_m/R$  against  $n_c$  we obtain  $\Delta S_m \approx 0.5R$  for the entropy increment per  $\text{CH}_2$  group. This value can be compared with those for other long-chain series of compounds: *n*-alkanes (fusion):  $1.3R$ ; lead(II) *n*-alkanoates:<sup>(18)</sup>  $2.2R$  (two chains per molecule of soap); alkyl trimethylamine chlorides:  $0.72R$ . The thallium compounds—despite the incomplete information we have so far—exhibit smaller  $\Delta S_m$  values. Unsaturated fatty acids have, however, lower comparable values ( $0.45R$  to  $0.51R$  per  $\text{CH}_2$ ).<sup>(19)</sup> It seems important to clarify

the mechanism by which the conformational disorder of the hydrocarbon chains is controlled and how it is related to the structure of the polar or ionic groups to which the chains are linked. Structural (X-ray diffraction) and vibrational spectroscopic studies could help to illuminate the microscopic mechanism involved in the phase transitions occurring in this complex multistep process.

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