

Thermodynamics of the thallium alkanoates

VIII. Heat capacity and derived thermophysical properties of thallium(I) propanoate and pentanoate at temperatures from 6 K to 490 K ^a

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Heat-capacity measurements by adiabatic calorimetry at temperature $T = 5$ K to 350 K were supplemented by differential-scanning calorimetry (d.s.c.) into the liquid region on thallium(I) propanoate and pentanoate. Apparent phase transitions were noted for the propanoate for the crystal III-to-crystal II transition with $\Delta_{\text{trans}}S_m^\circ = (1.473 \pm 0.001)R$ at $T = (277.7 \pm 0.1)$ K adiabatic calorimetry and for the crystal II-to-crystal I transition at $(0.10 \pm 0.01)R$ at $T = (268.4 \pm 0.4)$ K by d.s.c. and for the crystal I-to-liquid transition with $\Delta_{\text{trs}}S_m^\circ = (2.70 \pm 0.09)R$ at $T = (468.0 \pm 0.4)$ K. For the VI-to-V and V-to-IV transitions of the pentanoate by adiabatic calorimetry the corresponding values are $(0.359 \pm 0.002)R$ and (235.1 ± 0.1) K, $(1.511 \pm 0.003)R$ and (219.3 ± 1) K. For the IV-to-III, III-to-II, II-to-I, plus crystal I-to-mesophase and mesophase-to-isotropic liquid for the same compound the pairs of values by d.s.c. (only) are: $(0.26 \pm 0.02)R$ and (234.6 ± 0.4) K; $(1.00 \pm 0.04)R$ and (284.5 ± 0.4) K; $(0.72 \pm 0.03)R$ and (353.0 ± 0.4) K; $(1.50 \pm 0.05)R$ and (455.0 ± 0.5) K; and $(0.75 \pm 0.04)R$ and (488.0 ± 0.8) K. Like thallium(I) butanoate, the propanoate does not show a mesotropic liquid phase.

1. Introduction

Important gaps in our survey of the properties of the thallium(I) alkanoates include the odd-numbered propanoate and pentanoate, Tl3C and Tl5C hereafter, (Chemical

^aThe first paper in this series is reference 1; the last is reference 2. Supported in part by the National Science Foundation. Address correspondence to Edgar F. Westrum, Jr.

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Abstracts registry numbers [63424-48-6] and [34244-89-8]) and the intermediate even-numbered butanoate [63424-49-7]. The first two are studied in this work, the other has been reported separately.⁽²⁾ Previous studies on such metallic cations associated with organic anions have demonstrated not only that they often reveal the typical mesophase properties of liquid crystals, but in addition reveal a progression of other type of mesomorphic transformations, as plastic crystalline and the more recently identified "condis" phase,⁽³⁾ (prior to the liquid-crystal phase) as the liquid state is approached. This concentration of enthalpies of transition over a limited temperature region provides an opportunity for technological thermal-energy storage. From the physicochemical aspects, these metal organic salts provide much of interest and of novelty. The recently recognized formation of molecular compounds ("acid soaps")⁽⁴⁾ between equal amounts of a thallium organic salt and the corresponding acid is also being addressed.⁽⁵⁾

Unfortunately, the structural study of these interesting salts has lagged behind the thermophysical work. The rather fragile crystals, typically laminar structures, twin readily, and with other complexities tend to complicate the X-ray determination on polycrystalline powders—less so on single crystals. However, two recent papers summarize the thermodynamic properties through the studied series members⁽⁶⁾ as well as the revealing contributions from spectroscopy⁽⁷⁾—both f.t.i.r. and Raman—including "chain-melting" and ionic-melting phenomena.

Foremost among the groups of alkanooate salts on which we have focused our systematic thermophysical endeavors has been the thallium(I) salts⁽⁸⁾ in supplement to a parallel series on those of the alkali metals.⁽⁹⁾ The pioneering work of Luzzati *et al.*⁽¹⁰⁾ in the sixties, of Ubbelohde *et al.*⁽¹¹⁾ in the seventies, and of Franzosini and his collaborators⁽¹²⁾ in the seventies and early eighties opened the frontier to enable the understanding of the process of gradual "chain melting"; of vitreous and mesomorphic phases; as well as of the relevance of chain length in homologous series on the structural states, molecular freedom, and thermophysical properties.

TABLE I. Thermal history diagrams

Thallium(I) propanoate										
$T = 300 \text{ K}$	$\xrightarrow{t = 28 \text{ h}}$	5 K	$\xrightarrow{25 \text{ h}}$	352 K	$\xrightarrow{8 \text{ h}}$	224 K	$\xrightarrow{9 \text{ h}}$	291 K		
			Series I				Series II			
	$\xrightarrow{5 \text{ h}}$	266 K	$\xrightarrow{11 \text{ h}}$	298 K	$\xrightarrow{2.5 \text{ h}}$	247 K	$\xrightarrow{15 \text{ h}}$	295 K		
			Series III				Series IV			
Thallium(I) pentanoate										
$T = 300 \text{ K}$	$\xrightarrow{t = 30 \text{ h}}$	5 K	$\xrightarrow{28 \text{ h}}$	347 K	$\xrightarrow{18 \text{ h}}$	194 K	$\xrightarrow{19 \text{ h}}$	341 K	$\xrightarrow{14 \text{ h}}$	166 K
			Series I				Series II			
	$\xrightarrow{15 \text{ h}}$	300 K	$\xrightarrow{11 \text{ h}}$	193 K	$\xrightarrow{4 \text{ h}}$	310 K	$\xrightarrow{6 \text{ h}}$	188 K	$\xrightarrow{5 \text{ h}}$	309 K
		Series III			Series IV			Series V		

TABLE 2. Experimental values for the molar heat capacity at constant pressure ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

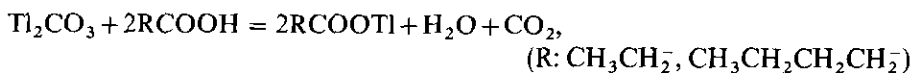
T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Thallium(I) propanoate											
Series I	39.48	4.993	103.66	10.321	211.71	14.871	295.68	18.35			
5.37	0.198	41.59	5.256	107.47	10.540	216.98	14.946	300.82	18.43	Series IV	
6.18	0.276	43.72	5.532	111.31	10.801	222.11	15.087	305.98	18.51	253.01	16.15
7.14	0.357	45.87	5.769	115.20	11.062	227.27	15.304	310.88	18.70	256.72	17.07
8.22	0.424	48.01	6.000	119.04	11.187	232.43	15.330	316.16	18.92	258.83	16.47
9.39	0.579	50.39	6.326	123.30	11.410	237.58	15.632	321.34	19.08	260.39	16.62
10.61	0.760	52.96	6.58	127.74	11.604	242.70	15.928	326.47	19.17	262.45	16.60
11.83	0.901	55.52	6.889	132.24	11.912	247.84	16.08	331.62	19.25	265.01	16.76
13.13	1.116	58.09	7.097	136.75	12.061	252.96	16.42	335.77	19.35	267.32	16.88
14.64	1.335	60.67	7.373	141.25	12.350	258.10	16.53	339.73	19.45	269.56	17.09
16.10	1.570	63.26	7.563	145.77	12.503	262.95	16.69	347.20	19.65	271.78	17.33
17.60	1.815	65.86	7.767	150.56	12.711	266.60	16.66			273.35	17.50
19.14	2.070	68.45	8.010	155.67	12.930	269.56	17.05	Series II		274.92	17.86
20.68	2.310	71.05	8.735	160.78	13.331	272.62	17.36	269.77	17.06	276.42	19.78
22.33	2.577	73.66	8.460	165.89	13.427	275.64	18.68	272.73	17.14	277.37	91.3
24.07	2.800	76.70	8.617	171.04	13.593	277.47	126	278.81	59	282.46	48.2
25.86	3.080	80.06	8.869	176.23	13.755	277.72	8100	285.92	17.93	290.17	18.10
27.66	3.330	83.28	9.104	181.37	13.794	277.91	886	291.08	18.21	295.32	18.23
29.43	3.160	86.50	9.342	186.47	14.001	278.08	243				
31.23	3.877	89.73	9.510	191.59	14.452	278.98	44.02	Series III		Series V	
33.18	4.146	92.97	9.686	196.71	14.652	281.33	18.16	268.19	17.00	290.17	18.10
35.27	4.360	96.23	9.890	201.81	14.739	285.43	1798	271.09	17.10	295.32	18.40
37.36	4.718	99.78	10.120	206.62	14.801	290.57	18.15	277.09	60		
Thallium(I) pentanoate											
Series I	69.06	9.723	234.49	38.17	238.16	21.67	312.31	26.72	252.30	22.77	
6.15	0.214	72.75	10.065	239.99	22.02	239.81	21.66	317.61	26.64	273.16	26.57
7.19	0.315	76.80	10.502	246.32	22.19	240.94	21.73	323.12	26.69	283.62	31.83
8.39	0.474	80.78	10.899	251.46	22.70	242.07	21.76	328.38	26.67	284.58	49.67
9.61	0.631	84.78	11.170	256.58	23.30	244.38	21.97	333.75	26.79	285.05	44.2
10.85	0.840	88.77	11.545	261.47	24.04	247.87	22.16	339.14	27.00	285.15	500
12.18	1.024	93.03	11.891	266.83	24.81	251.34	22.48	344.50	27.35	285.19	980
13.58	1.256	97.55	12.232	271.92	25.85	254.76	22.87			286.63	28.87
15.01	1.535	102.07	12.51	276.96	27.38	258.13	23.30	Series III		289.34	29.11
16.48	1.768	106.62	12.919	281.91	30.30	261.47	24.13	195.77	19.38	295.43	27.30
17.99	2.053	111.17	13.236	284.58	229	264.78	24.45	200.72	19.82	298.45	26.51
19.50	2.316	115.72	13.618	287.16	40.24	268.03	25.05	204.42	19.90		
21.04	2.633	120.60	13.902	291.77	26.96	270.64	25.20	206.12	21.29	Series IV	
22.69	2.912	125.77	14.265	301.44	26.70	272.61	26.12	207.04	24.86	195.62	19.51
24.44	3.204	130.94	14.668	315.46	26.85	274.57	26.28	207.44	1640	206.17	24.59
26.18	3.557	136.12	15.00			276.50	26.78	207.61	97.1	221.44	21.28
27.94	3.886	141.29	15.40	Series II		278.37	28.33	207.92	154	236.36	25.40
29.72	4.204	146.55	15.827	204.60	19.85	280.23	28.60	209.89	20.54	254.80	23.01
31.52	4.524	151.78	16.20	209.28	19.96	282.01	30.65	212.18	20.33	269.51	25.35
33.46	4.885	156.98	16.65	211.60	20.34	283.74	32.27	214.44	20.43	279.61	47.8
35.54	5.245	162.22	17.00	213.92	20.35	284.73	39.8	216.72	20.78	295.14	27.02
37.64	5.591	167.45	17.40	216.24	20.65	284.97	105	218.93	22.94	307.35	26.80
39.75	5.910	172.67	17.69	218.47	21.40	285.07	221	221.10	22.03		
41.87	6.245	177.81	18.17	220.66	21.94	285.12	482	223.34	21.10	Series V	
43.99	6.592	182.92	18.51	222.89	20.78	285.14	714	225.60	21.17	184.38	18.45
46.14	6.904	188.00	18.90	225.12	21.16	285.20	129	227.84	21.46	189.56	19.00
48.29	7.149	193.06	19.20	227.41	21.35	285.14	334	230.09	21.48	194.60	19.25

TABLE 2—*continued*

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	$C_{p,m}/R$
50.63	7.502	198.15	19.50	229.63	21.58	285.15	1630	232.31	21.51	205.11	24.70
53.17	7.828	203.31	19.74	231.84	21.78	285.16	670	234.14	41.90	220.38	21.28
55.71	8.216	207.57	39.55	233.90	27.67	285.17	810	235.14	48.47	235.27	25.48
58.27	8.453	213.20	20.60	234.97	74.21	285.16	1780	236.14	22.72	253.78	22.96
60.84	8.828	219.64	22.00	235.49	40.54	285.23	270	237.71	21.79	268.53	24.95
63.49	9.132	224.78	21.20	236.43	22.26	285.27	68.7	239.81	21.66	278.95	45.18
66.15	9.429	230.10	21.52	237.55	21.76	285.21	163	240.63	21.75	294.29	27.47
						306.18	26.66			306.11	26.81

2. Experimental

Two basic procedures yield the (anhydrous) thallium(I) alkanooates. In one of them, thallium carbonate reacts with the corresponding acid,⁽¹³⁾ the other assumes the neutralization of the hydroxide of thallium with the stoichiometric amount of acid.⁽¹⁴⁾ We have now amply tested from experience acquired in the course of this work the synthesis method that yields definitive results and provides substances of characteristically high purity.⁽⁸⁾ Using reactants of very high purity, the salts of thallium have been prepared following the general scheme of the reaction:



The corresponding acid (RCOOH) is slowly dissolved in dry methanol, with a quantity of thallium(I) carbonate slightly in excess of stoichiometry, dispersed in the same solvent. The mixture is slowly refluxed under agitation, and warmed gradually for 1 h to 3 h. After separating the excess of thallium(I) carbonate by filtration, the

TABLE 3. D.s.c. determined heat capacities ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T/K	$C_{p,m}/R$ ^a	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Thallium(I) propanoate											
Crystal II		335	19.3	Crystal I	390	19.8	410	20.3	430	21.4	
320	19.0	340	19.4	375	19.6	395	19.8	415	20.7	435	21.6
325	19.1	345	19.6	380	19.7	400	19.9	420	20.9	440	21.7
330	19.2	350	19.7	385	19.7	405	20.1	425	21.2		Isotropic liquid
Thallium(I) pentanoate											
Crystal II		340	27.1	375	26.3	400	27.4	425	29.2	Mesophase	
320	26.0	345	27.4	380	26.4	405	27.7	430	29.6	470	35.0
325	26.2	Crystal I		385	26.6	410	28.2	435	30.0	475	35.9
330	26.5	365	26.0	390	26.7	415	28.6	440	30.3	480	36.7
335	26.7	370	26.2	395	27.0	420	28.9				Isotropic liquid

^aThe temperatures have a standard deviation of $\pm 0.5 \text{ K}$.

^bThe standard deviation of the heat capacity is ± 2 per cent and $\Delta_{\text{trs}}H$ is about ± 2 to ± 8 per cent depending on the magnitude of $\Delta_{\text{trs}}H$.

TABLE 4. Experimental molar transition-enthalpy determinations for thallium(I) propanoate ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

For III-to-II transition by adiabatic calorimetry						
N^a	n^b	$\frac{T_i}{\text{K}}$	$\frac{T_f}{\text{K}}$	$\frac{T_{\text{trs}}}{\text{K}}$	$\frac{\Delta_{270\text{K}}^{285\text{K}} H_m^\circ}{R \cdot \text{K}}^c$	$\frac{\Delta_{\text{trs}} H_m^\circ}{R \cdot \text{K}}^d$
I	11	267.99	293.15	277.7 ± 0.1	665.10	406.8
II	4	268.27	288.52		665.14	406.8
III	5	266.71	291.12		665.17	406.9
IV	7	268.55	287.59		665.15	406.8
V	2	270.01	285.11		665.14	406.8
Means:					665.14 ± 0.08	406.8 ± 0.2
Graphical:					666	409
$\Delta_{\text{trs}} S_m^\circ / R = 1.473 \pm 0.001$						
Transitions by differential scanning calorimetry ^e						
Transition designation		$\frac{T_{\text{trs}}}{\text{K}}$		$\frac{\Delta_{\text{trs}} H_m^\circ}{R \cdot \text{K}}^d$		$\frac{\Delta_{\text{trs}} S_m^\circ}{R}$
III-to-II		277.7 ± 0.4		372 ± 10		1.34 ± 0.04
II-to-I ^f		364.8 ± 0.4		38 ± 5		0.10 ± 0.01
I-to-isotropic liquid (l) ^f		468.0 ± 0.4		1260 ± 40		2.70 ± 0.09
Transitions as reported in the literature						
Transition designation	$\frac{T_{\text{trs}}}{\text{K}}$	$\frac{\Delta_{\text{trs}} H_m^\circ}{R \cdot \text{K}}$	Method	Year	Reference	
Thallium(I) propanoate						
Solid to solid	365	48	d.t.a.	1976	14	
Fusion	461		micr	1926	19	
Fusion	459		micr	1970	1	
Fusion	468	1107	d.t.a.	1976	14	

^a Adiabatic series designation.^b Number of heating increments.^c $\Delta_{T_i}^{T_f} H_m^\circ$ is the molar energy input from the selected initial temperature T_i to the selected final temperature T_f adjusted to span the rounded temperature interval from T_i to T_f and for quasi-adiabatic drift.^d $\Delta_{\text{trs}} H_m^\circ$ is the net molar enthalpy increment of transition relative to the selected lattice curve (compare table 6).^e Mean values from six determinations.^f F. Fernández-Martín, F. Lopez de la Fuente, and J. A. R. Cheda.⁽¹⁶⁾

solution is concentrated until the crystallization of the corresponding thallium alkanoate is imminent. The precipitation is completed by addition of diethyl ether. A white finely divided solid obtained is subsequently rinsed with diethyl ether and with propanone and is crystallized many times from ethanol for members of the series of the long chains or (ethanol + ether) for the short-chain member. Finally, the pure solid, generally in the form of powder or platelets, is dried under vacuum until constant mass is achieved near $T = 300 \text{ K}$. To ensure the content of water and/or of

acid in the salts, they are systematically analyzed by infrared spectroscopy. Moreover, the purity of the salts has been determined quantitatively by d.s.c. We have used a Perkin-Elmer d.s.c.: DSC 2C, with the data acquisition station TADS 3700. When necessary, liquid nitrogen as a refrigerant (controlled cooling accessory B012-8743) was also utilized. The purge gas was dry helium at a flow rate of $0.5 \text{ cm}^3 \cdot \text{s}^{-1}$ in this instance. Dry nitrogen gas was sometimes used.

Another useful criteria to ascertain the purity of the product is the temperature T_c of "clearing" and the form of the corresponding "peak" for that transition in the d.s.c. thermograms. High purity corresponds to higher values of T_c and greater ratios between the height and width of the sharp clearing peak.

We no longer employ methods previously used for the preparation and purification of the thallium(I) alkanooates. Initially, the procedure differed in some details that subsequently were revealed to be of crucial importance for obtaining high-purity compounds. The earliest syntheses following the recommendations of Duruz *et al.*⁽¹¹⁾ referred particularly to the sodium *n*-alkanoates; the rates of decomposition of these compounds were high enough to ensure that a slight excess of the corresponding acid formed during the reaction. The addition of this excess of acid beyond the stoichiometric amount suppresses the action of the free hydrogen

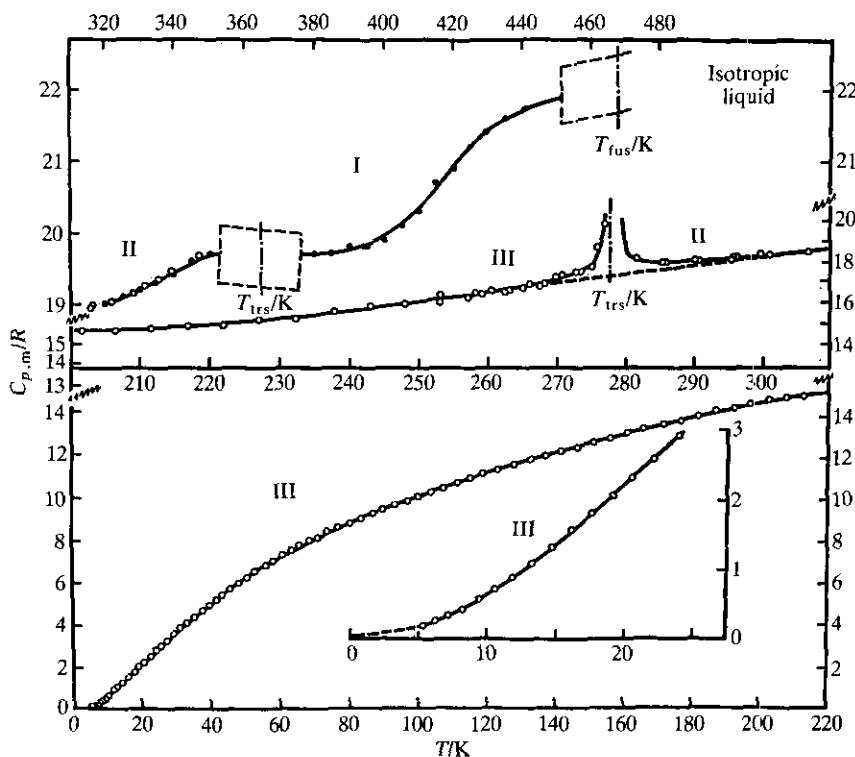


FIGURE 1. The heat capacity of thallium(I) propanoate by \circ , adiabatic calorimetry; \bullet , d.s.c. The low-temperature region is shown on an enlarged scale in the lower right corner.

ions, considered, in this class of salts, as the principal cause of instability. The explanation mentioned above is not valid exclusively for syntheses that are made in aqueous media. It is true for sodium alkanooates. However, the excess of acid reactant has been added systematically in preparation processes of alkaline salts of carboxylic acids even for reactions in anhydrous methanol.⁽¹⁵⁾

In the course of our work, we have proved, however, that such excesses of acid can provoke the contamination of the salt, leading to the formation in carefully documented examples of molecular complexes (or acid soaps) of various compositions.^(4, 5)

To guarantee with certainty the absence of molecular complexes or (associated acid + salt), in our work the synthesis of the thallium(I) *n*-alkanoates was done with only slight excess beyond the stoichiometric amount of thallium(I) carbonate, without having observed an increase of instability when prepared following this procedure. However, the substances prepared have been guarded in vessels protected from light (which clearly affects their decomposition) and were cooled as soon as possible after their preparation. Likewise, they have been manipulated under inert atmospheres, avoiding hygroscopicity, especially noticeable in the even members of the series with short aliphatic chains.

In particular, both compounds were prepared from >99 moles per cent Fluka Tl_2CO_3 *pro analysis* and the >99 moles per cent Fluka *puriss* $\text{CH}_3\text{CH}_2\text{COOH}$ or

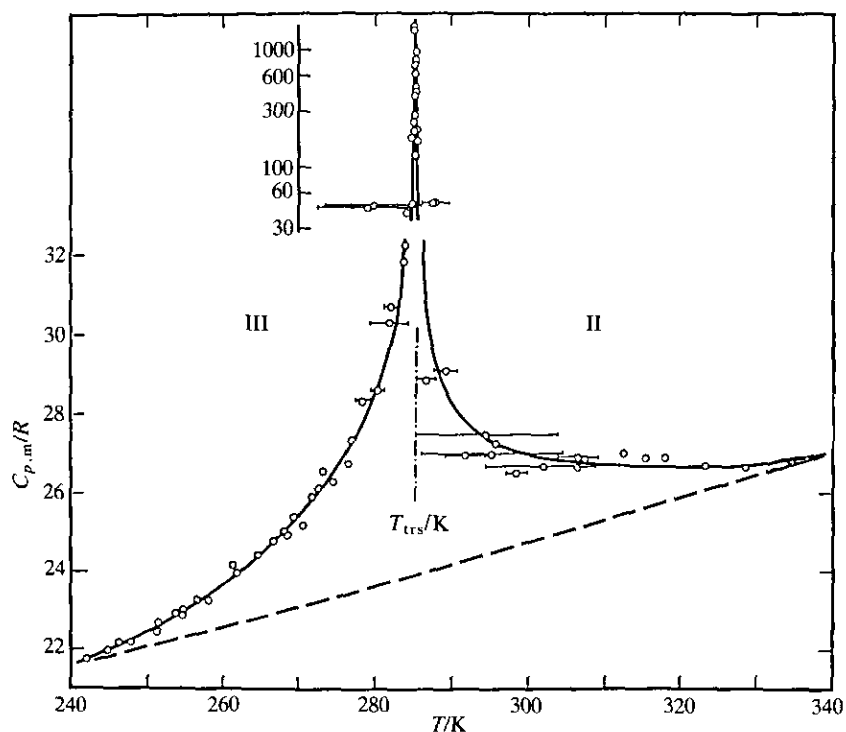


FIGURE 2. The III-to-II transition in thallium(I) propanoate.

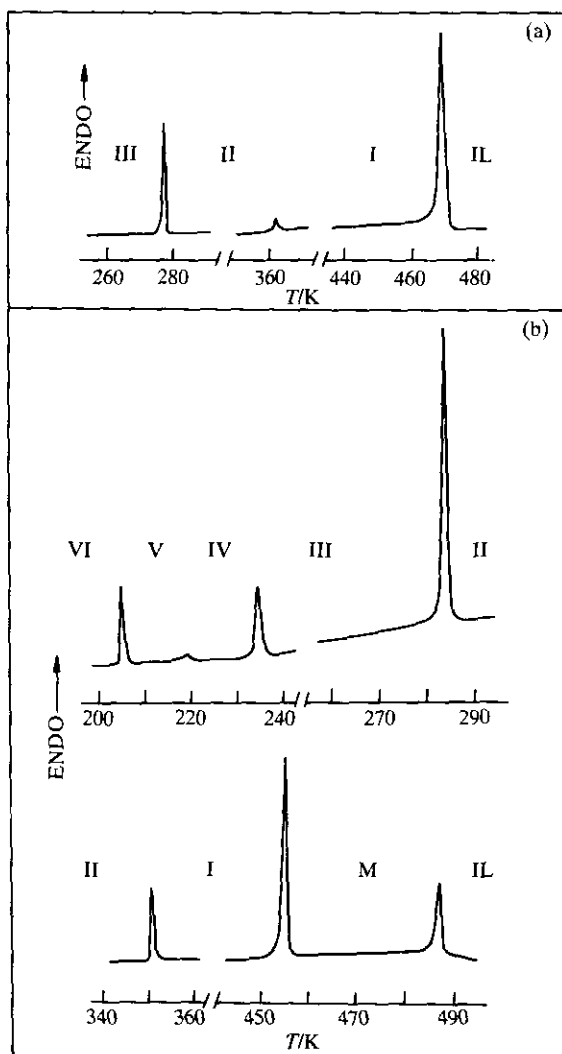


FIGURE 3. D.s.c. measurements for the higher-temperature transitions in 3(a), thallium(I) propanoate and in 3(b), thallium(I) pentanoate.

$\text{CH}_3(\text{CH}_2)_3\text{COOH}$. The average of three fractional-fusion determinations indicated the T13C to be >99.45 moles per cent and the T15C to be >99.86 moles per cent pure. D.s.c. thermograms are depicted elsewhere for the two salts.⁽¹⁶⁾

The intermittent-energy-addition equilibrium quasi-adiabatic calorimetry (AC) has been described in a previous paper.⁽¹⁷⁾ Calorimeters of laboratory designations W-139 and W-62 in the MARK XIII cryostat were employed. Samples of mass 23.909 g of propanoate and 41.366 g of pentanoate were used.

The programming, logging of results, and calorimetry were done by automated computerization described elsewhere.⁽¹⁷⁾ All measurements of mass, time, resistance,

TABLE 5. Experimental molar transition-enthalpy determinations for thallium(I) pentanoate ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

For VI-to-V transition by adiabatic calorimetry						
N^a	n^b	T_i K	T_f K	T_{trs} K	$\frac{\Delta_{200\text{K}}^{285\text{K}} H_m^\circ}{R \cdot \text{K}}^c$	$\frac{\Delta_{\text{trs}} H_m^\circ}{R \cdot \text{K}}^d$
I	3	200.720	217.142	207.5 ± 0.1	376.1 ± 0.2 ^e	76.3 ₄ ± 0.1
III	10	198.250	215.584		374.2	74.5
IV	1	198.128	214.211		372.7 ^e	73.0
V	1	197.083	213.129		374.8	75.0
					Means:	374. ₅ ± 1.7
				Graphical:	376	76
				$\Delta_{\text{trs}} S_m^\circ / R = 0.359 \pm 0.002$		
For transition V-to-IV by adiabatic calorimetry						
					$\frac{\Delta_{215\text{K}}^{225\text{K}} H_m^\circ}{R \cdot \text{K}}$	
I	4	217.580	227.410	219. ₃ ± 10	216.0	10.12
II	2	215.072	224.025		215.8	10.09
III	4	215.580	224.271		215.9	10.02
IV	1	214.172	228.709		215.8	10.09
V	1	213.107	227.651		216.0	10.12
				Means:	215.9 ± 0.8	10.1 ± 0.1
				Graphical:	217	10
				$\Delta_{\text{trs}} S_m^\circ / R = 0.046 \pm 0.0002$		
For transition IV-to-III by adiabatic calorimetry						
					$\frac{\Delta_{225\text{K}}^{245\text{K}} H_m^\circ}{R \cdot \text{K}}^c$	
I	5	222.145	248.899	235.1 ± 0.1	489.6	63.7
II	11	224.022	240.378		489.1	63.5
III	10	224.483	241.367		489.7	63.6
IV	1	228.723	243.998		489.5	63.6
V	1	227.645	242.896		489.9	63.9
				Means:	489.5 ± 0.2	63.7 ± 0.2
				Graphical:	490	64
				$\Delta_{\text{trs}} S_m^\circ / R = 0.2710 \pm 0.0007$		
For transition III-to-II by adiabatic calorimetry						
					$\frac{\Delta_{240\text{K}}^{310\text{K}} H_m^\circ}{R \cdot \text{K}}^c$	
I	5	243.733	308.511	285.2 ± 0.1	1897.2	413.4
II	19	240.373	309.628		1896.3	412.7
III	13	239.896	299.970		1880.0 ^e	409.0 ^e
IV	2	243.939	310.309		1897.0	413.1
V	2	242.901	308.929		1897.1	413.2
				Means:	1897. ₀ ± 1	413 ± 1
				Graphical:	1899	415
				$\Delta_{\text{trs}} S_m^\circ / R = 1.511 \pm 0.003$		

TABLE 5—*continued*

Transitions by differential scanning calorimetry ^a					
Transition designation	T_{trs} K	$\frac{\Delta_{\text{trs}} H_m^\circ}{R \cdot K}$	$\frac{\Delta_{\text{trs}} S_m^\circ}{R}$		
VI-to-V	206 ± 0.4	56 ± 5	0.27 ± 0.02		
V-to-IV	220 ± 0.4	10 ± 5	0.05 ± 0.02		
IV-to-III	234.6 ± 0.4	60 ± 5	0.26 ± 0.02		
III-to-II	284.5 ± 0.4	285 ± 10	1.00 ± 0.04		
II-to-I ^f	353.0 ± 0.4	253 ± 10	0.72 ± 0.03		
I-to-mesophase (fus) ^f	455.0 ± 0.5	686 ± 20	1.50 ± 0.05		
Mesophase-to-isotropic liquid (clr) ^f	488.0 ± 0.8	367 ± 20	0.75 ± 0.04		
Transitions as reported in the literature					
Transition designation	T_{trs} K	$\frac{\Delta_{\text{trs}} H_m^\circ}{R \cdot K}$	Method	Year	Reference
Solid II to solid I	351		micr. ^g	1926	18
Solid to solid	354.7	280	d.t.a. ^h	1976	13
Fusion	418 to 420			1924	20
Solid I to liquid crystal ⁱ	448		micr.	1926	18
Solid to neat	454		micr.	1970	19
Fusion	454.2		micro.	1971	21
Solid to mesophase ^j	455	650	d.t.a.	1976	13
Liq. crystal to isotrop. I ^f	485		micr.	1926	18
Mesophase to isotrop. I ^f	487	370	d.t.a. ^f	1976	13
Neat to isotropic	488		micr.	1970	19
Clearing	488.7		micr.	1971	21

^a Adiabatic series designation.

^b Number of heating increments.

^c $\Delta T_i H_m^\circ$ is the molar energy input from the initial temperature T_i to the final temperature T_f adjusted to span the rounded temperature interval T_1 to T_2 and for quasi-adiabatic drift.

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

^e Mean value from six determinations.

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^g Optical microscopy.

^h Differential thermal analysis.

ⁱ Actually "Fusion".

^j Actually "Clearing".

etc., were referred to calibrations of the U.S. National Bureau of Standards (presently designated National Institute of Science and Technology, NIST). The propanoate sample loaded into the gold-plated OFHC copper calorimeter W-139 had a mass of 13.127 g \pm 0.086177 mol on the basis of the 1992 IUPAC relative atomic masses. For the pentanoate sample calorimeter W-62 with a mass of 42.930 g was used. The molar mass M was 305.5086 g \cdot mol⁻¹ and the amount of substance n in the sample was 0.135400 mol, based on the IUPAC 1978 relative atomic masses. The buoyancy corrections are calculated on the assumed density of 2.85 g \cdot cm⁻³ and a molar mass of 277.4548 g \cdot mol⁻¹. No crystallographic information is available for this

TABLE 6. Smoothed values for the heat capacities and derived thermodynamic properties of thallium(I) propanoate
($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T/K	$C_{p,m}/R$	$\Delta_0^{\ddagger}S_m^{\circ}/R$	$\Delta_0^{\ddagger}H_m^{\circ}/(R \cdot \text{K})$	Φ_m°/R	T/K	$C_{p,m}/R$	$\Delta_0^{\ddagger}S_m^{\circ}/R$	$\Delta_0^{\ddagger}H_m^{\circ}/(R \cdot \text{K})$	Φ_m°/R
Crystal III									
0	(0)	(0)	(0)	(0)	110	10.701	11.576	671.1	5.474
					120	11.256	12.531	781.0	6.023
5	(0.141)	(0.050)	(0.187)	(0.013)	130	11.777	13.453	896.1	6.559
10	0.692	0.301	2.156	0.086	140	12.259	14.343	1016.4	7.084
15	1.367	0.706	7.263	0.222	150	12.709	15.20	1141.2	7.596
20	2.220	1.213	16.169	0.404					
25	2.949	1.792	29.216	0.624	160	13.137	16.04	1270.5	8.098
					170	13.545	16.85	1403.9	8.589
30	3.688	2.391	45.681	0.868	180	13.927	17.63	1541.3	9.070
35	4.351	3.015	65.99	1.130	190	14.268	18.39	1682.3	9.541
40	5.097	3.642	89.50	1.404	200	14.558	19.13	1826.5	10.002
45	5.685	4.275	116.39	1.688					
50	6.258	4.904	146.26	1.978	210	14.810	19.85	1973.3	10.454
					220	15.06	20.55	2122.7	10.897
60	7.285	6.138	214.11	2.569	230	15.36	21.22	2274.7	11.331
70	8.154	7.328	291.43	3.165	240	15.73	21.88	2430.1	11.757
80	8.882	8.466	376.71	3.757	250	16.17	22.53	2589.6	12.175
90	9.522	9.549	468.78	4.341					
100	10.122	10.584	567.0	4.914	260	16.60	23.18	2753.5	12.586
					270	16.96	23.81	2921.3	12.990
					277.72 ^a	(> 8100)	(24.29)	(3053.3)	(13.297)
Crystal II									
277.72 ^a	(> 8100)	(25.76)	(3461.6)	(13.297)	325	19.09	28.63	4326.2	15.32
280	17.44	25.90	3501.2	13.400	350 ^d	19.65	30.07	4811.1	16.32
290	17.88	26.52	3677.8	13.841					
298.15	18.21	27.02	3824.8	14.195	364.8	—	(30.89)	(5103)	(16.90)
300	18.28	27.14	3858.6	14.274					
Crystal I									
364.8	—	(30.99)	(5151)	(16.90)	425	21.10	34.05	6349	19.11
					450	21.89	35.28	6887	19.98
375	19.56	31.53	5341	17.29					
400	20.07	32.81	5835	18.22	468.00	—	(36.15)	(7284)	(20.58)
Isotropic liquid									
468.00	—	(38.84)	(8544)	(20.58)					
Assigned lattice thermophysical properties									
260	16.54	23.17	2752.8	12.586	380	19.57	30.22	4992.4	17.08
277.7	17.33	24.24	3053.9	13.400	400	20.07	31.23	5388	17.76
280	17.43	24.43	3092.4	13.388					
298.15	18.21	25.55	3416.0	14.094	420	20.89	32.23	5797	18.43
300	18.28	25.66	3449.7	14.165	440	21.63	33.22	6223	19.08
					460	22.08	34.19	6660	19.71
320	18.95	26.87	3822.3	14.922	480 ^e	(22.29)	(35.14)	(7104)	(20.33)
340	19.46	28.03	4206.7	15.66					
360 ^d	19.75	29.15	4599.4	16.38					

^aThe values in parentheses () refer to the presumed isothermal values of the derived functions at the transition temperature. The values at the nearest adjacent temperature may, therefore, be slightly lower than measured (compare figure 1). The heat capacities thus indicated are maximal values observed at the peak.

^bThe values of the heat capacity of the "lattice" curve to which the $\Delta_{\text{trs}}H_m^{\circ}$ and the $\Delta_{\text{trs}}S_m^{\circ}$ are arbitrarily referred is depicted in figure 2.

^cArbitrary (extrapolated) values to delineate selected lattice values.

^dFor $T > 350 \text{ K}$ all values are determined solely by d.s.c.

TABLE 7. Smoothed values for the heat capacities and derived thermodynamic properties of thallium(I) pentanoate ($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T/K	$C_{p,m}/R$	$\Delta_0^T S_m^\circ/R$	$\Delta_0^T H_m^\circ/(R \cdot \text{K})$	Φ_m°/R	T/K	$C_{p,m}/R$	$\Delta_0^T S_m^\circ/R$	$\Delta_0^T H_m^\circ/(R \cdot \text{K})$	Φ_m°/R
Crystal VI									
0	(0)	(0)	(0)	(0)	110	13.179	13.636	806.6	6.303
					120	13.892	14.813	942.0	6.963
5	(0.122)	(0.043)	(0.159)	(0.011)	130	14.608	15.95	1084.5	7.611
10	0.694	0.278	2.021	0.076	140	15.34 ₆	17.06	1234.2	8.247
15	1.515	0.711	7.501	0.211	150	16.07	18.15	1391.2	8.871
20	2.416	1.269	17.298	0.404					
25	3.340	1.908	31.701	0.640	160	16.79	19.21	1555.6	9.484
					170	17.50	20.25	1727.0	10.086
30	4.246	2.596	50.65	0.908	180	18.21	21.27	1905.6	10.679
35	5.162	3.321	74.21	1.201	190	18.94	22.27	2091.3	11.263
40	5.944	4.062	102.00	1.512	200	19.60	23.26	2284.2	11.838
45	6.746	4.809	133.76	1.837					
50	7.404	5.553	169.07	2.171	207.5 ^a	(> 1600)	(23.99)	(2432.7)	(12.264)
60	8.713	7.021	249.80	2.857					
70	9.824	8.450	342.64	3.555					
80	10.783	9.826	445.77	4.253					
90	11.647	11.146	558.0	4.946					
100	12.440	12.415	678.5	5.630					
Crystal V									
207.5 ^a	(> 1600)	(24.35)	(2507.2)	(12.264)	219.3	(> 23)	(25.47)	(2746.4)	(12.944)
210	20.10	24.59	2557.3	12.409					
Crystal IV									
219.3	(> 23)	(25.51)	(2756.5)	(12.944)	230	21.06	26.50	2979.1	13.552
220	20.59	25.58	2770.9	12.984	235.1	(> 74)	(26.97)	(3087.1)	(13.838)
Crystal III									
235.1	(> 74)	(27.24)	(3150.8)	(13.838)	270	23.15	30.31	3925.2	15.77
					280	23.72	31.16	4159.5	16.31
240	21.52	27.68	3255.7	14.116					
250	22.04	28.57	3473.4	14.677	285.2	(> 1800)	(31.60)	(4283.7)	(16.58)
260	22.58	29.45	3696.5	15.23					
Crystal II									
285.2	(> 1800)	(33.11)	(4714.7)	(16.58)	325	26.38	36.39	5716	18.81
					350 ^d	26.61	38.37	6383	20.13
290	24.26	33.51	4830.7	16.86					
298.15	24.67	34.19	5030	17.32	353.0	—	(38.60)	(6463)	(20.29)
300	24.78	34.35	5076	17.43					
Crystal I									
353.0	—	(39.32)	(6716)	(20.29)	425	29.18	44.33	8666	23.94
					450	31.77	46.07	9425	25.12
375	26.19	40.89	7290	21.45					
400	27.45	42.62	7959	22.72	455	—	(46.42)	(9586)	(25.36)
Mesophase									
455	—	47.93	(10272)	(25.36)	488	—	(50.40)	(11437)	(26.96)
475	35.88	49.40	10956	(26.34)					

TABLE 7—continued

T/K	$C_{p,m}/R$	$\Delta_0^T S_m^\circ/R$	$\Delta_0^T H_m^\circ/(R \cdot K)$	Φ_m°/R	T/K	$C_{p,m}/R$	$\Delta_0^T S_m^\circ/R$	$\Delta_0^T H_m^\circ/(R \cdot K)$	Φ_m°/R
Isotropic liquid									
488	—	(51.15)	(11804)	(26.96)					
Assigned lattice thermophysical properties									
190	18.93	22.27	2092.0	11.26	320	26.01	33.80	5006	18.16
200	19.54	23.26	2284.3	11.84	340	26.90	35.41	5536	19.13
207.5	19.96	24.00	2432.6	12.26	353 ^d	26.40	36.41	5884	19.74
210	20.09	24.23	2482.5	12.40	360	26.14	36.93	6068	20.07
219.3	20.56	25.10	2671.6	12.93	380	26.34	38.34	6591	21.00
220	20.60	25.17	2685.9	12.96	420	28.81	41.09	7690	22.78
230	21.08	26.10	2894.3	13.515	440	30.55	42.47	8282	23.64
235.1	21.32	26.57	3002.4	13.79	455	32.54	43.52	8755	24.28
240	21.56	27.01	3107.5	14.06	460	33.33	43.88	8919	24.49
250	22.05	27.90	3325.5	14.59	480	36.75	45.37	9620	25.33
					488	38.08	45.99	9920	25.67
260	22.58	28.77	3548.7	15.12					
270	23.13	291.63	3777.2	15.64	500 ^c	[40.21]	[46.94]	[10389]	[26.17]
280	23.71	30.49	4011.4	16.16					
285.2	24.01	30.93	4135.5	16.42					
290	24.29	31.33	4251.4	16.67					
300	24.87	32.16	4497.2	17.17					

^aThe values in parentheses () refer to the presumed isothermal values of the derived functions at the transition temperature. The values at the nearest adjacent temperature may, therefore, be slightly lower than measured (compare figure 1). The heat capacities thus indicated are maximal values observed at the peak.

^bThe values of the heat capacity of the "lattice" curve to which the $\Delta_{tr} H_m^\circ$ and the $\Delta_{tr} S_m^\circ$ are arbitrarily referred is depicted in figure 2.

^cArbitrary (extrapolated) values to delineate selected lattice values.

^dFor $T > 350$ K all values are determined solely by d.s.c.

compound nor for adjacent members of the homologous series. The closest member of the series for which a measured density is available is that of thallium ethanoate which has a density of $3.6 \text{ g} \cdot \text{cm}^{-3}$. Following evacuation, a pressure 2.7 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 within the vacuum chamber by a remotely operating hexagonal wrench.

The thermal-history diagrams for these two salts during the adiabatic calorimetry are presented in table 1 as a linear array; continuous-line arrows indicate cooling and dashed arrows indicate results acquisition ranges for various series.

The values of C_p measured on these two compounds have standard deviations varying from 5 per cent at $T = 6$ K to 1.2 per cent at $T = 10$ K, and 0.14 per cent above this temperature to 350 K. The values of the smoothed integrated thermophysical properties are more reliable and have a standard deviation of 0.10 per cent for $T > 100$ K.

The heat capacity of the Tl3C sample varied between 0.59 and 0.68 of the total (*i.e.* sample + calorimeter + heater + thermometer) over the range of adiabatic

calorimetric measurements—except, of course, in transition regions. The corresponding range for the Tl5C sample is between 0.77 and 0.87.

3. Results and discussion

The experimental results for both compounds obtained by adiabatic calorimetry (AC) measurements are summarized in table 2; those from d.s.c. in table 3. The experimental determination of transitional-enthalpy increments for the propanoate are listed in table 4 as determined and compared with available literature values. Only in one instance, the III-to-II transition, do we have both adiabatic calorimetric and d.s.c. results. The two values are in reasonably good accord. Literature values are also given here. The graphical presentation of the AC results on Tl3C is shown for the entire temperature range in figure 1, with details on the III-to-II transition in figure 2. The higher-temperature transitions from the d.s.c. measurements are shown in table 4 and depicted in the thermograms for figure 3(a).

A similar presentation of the entire region of transitional results for Tl5C is made in table 5. Finally, the smoothed heat-capacity values for each compound are

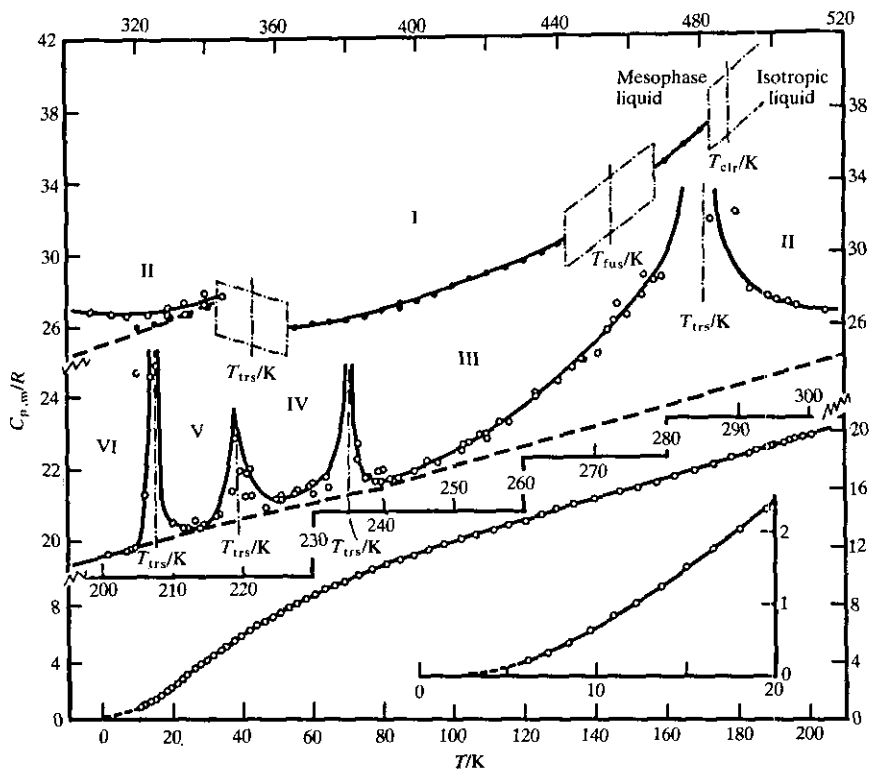


FIGURE 4. The heat capacity of thallium(I) pentanoate by \circ , adiabatic calorimetry; \bullet , d.s.c. The low-temperature region is shown on an enlarged scale in the lower right corner. The III-to-II transition with an explanation of the difference between the d.s.c. base line and the adiabatic calorimetric lattice (see text).

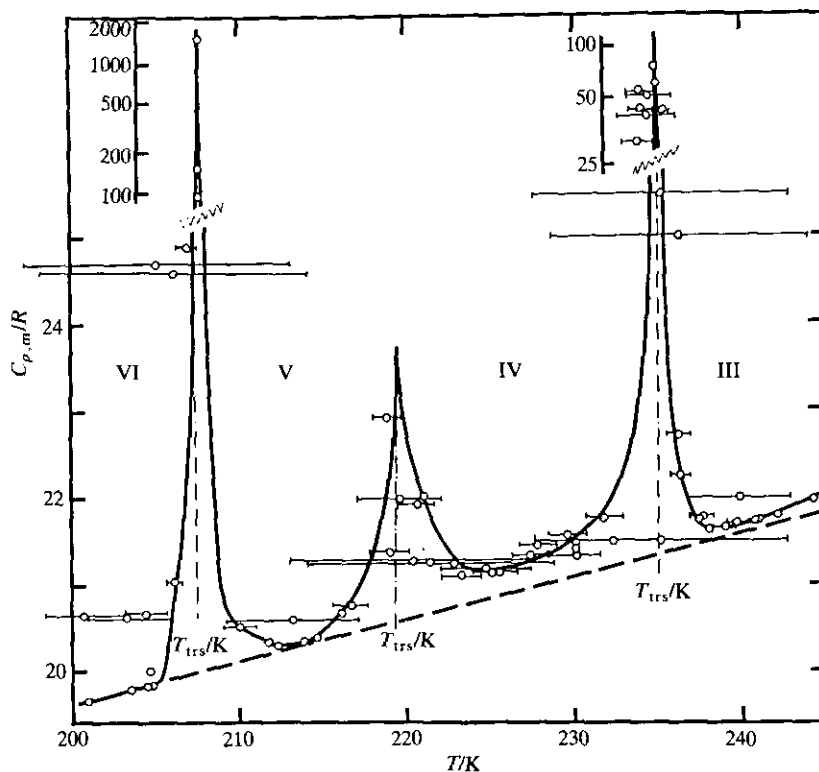


FIGURE 5. The VI-to-V, the V-to-IV, and the IV-to-III transitions in greater detail.

summarized in tables 6 and 7 at selected temperatures with the derived thermodynamic quantities presented at the same temperature.

The heat capacity of the Tl5C over the entire region is summarized in figure 4 with details of the four adiabatic calorimetrically measured transitions in figures 4 and 5.

For the pentanoate, the four lowest-temperature transitions were measured by both AC and d.s.c. techniques. The agreement of the thermal functions of the V-to-IV and IV-to-III transitions is very good; discrepancies were originally found for the other two. The reason for such discrepancies is fully explained in the next paper of this series⁽²²⁾ and a remedy discussed.

Adiabatic calorimetry is inherently more precise in designating lattice entropies and resolving enthalpies of transition like these with pre- and post-monitory effects taking place over a broad interval of temperature, because these effects are lost in the insensitivity of the d.s.c. base line at the scale used for transitional-enthalpy resolution. An overall correlation of these transitions with those of the other TlxC series members studied is in preparation.

The smoothed heat-capacity values for both substances have standard deviations of about 0.14 per cent at $T > 30$ K and the entropies slightly smaller standard percentage deviations.

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