

Thermophysics of metal alkanoates II. Heat capacities and thermodynamic properties of sodium propanoate^a

P. FRANZOSINI,^b EDGAR F. WESTRUM, JR.,
and W. A. PLAUTZ

*Department of Chemistry,
University of Michigan,
Ann Arbor, Michigan 48109, U.S.A.*

(Received 4 January 1983)

The heat capacity of sodium propanoate has been measured from 9 to 580 K by adiabatic calorimetry and considerable metastability noted between 60 and 215 K. Values at 298.15 K of $C_{p,m}/R$, S_m°/R , $\{H_m^\circ - H_m^\circ(0)\}/R$, and $\{G_m^\circ - H_m^\circ(0)\}/RT$ are 16.16, 18.29, 2809.1 K, and -8.872 . Comparisons with d.s.c. results and other reported phase behavior are provided.

1. Introduction

The first paper of this series⁽¹⁾ dealt with the thermal behavior of sodium methanoate and ethanoate. Here we report on the next higher homolog of this alkanoate family, sodium propanoate ($\text{CH}_3\text{CH}_2\text{CO}_2\text{Na}$), hereafter designated as Na3C. The investigation of the thermophysics of this salt in the temperature range between 9 K and the melt region was regarded to be of special significance for the following reasons: (i) the available literature gave conflicting information about the number, temperature ranges of stability, and nature of the phases existing above 300 K, particularly whether or not Na3C exists in a mesomorphic liquid state, *i.e.* as a liquid crystal within a temperature range interposed between those pertinent to the “true” crystalline and the “true” liquid states; (ii) the few available enthalpy increments associated with the transitions exhibited rather large discrepancies; (iii) adiabatic equilibrium heat capacities were completely missing, although above 300 K a few semi-quantitative measurements had been taken by one of us⁽²⁾ in 1975 on the solid and on the melt by d.s.c. employing the ordinate displacement method.

^a This research was supported in part by the Structural Chemistry and Chemical Thermodynamics Program of the Chemistry Section of the National Science Foundation under Grant CHE-8007977. The preceding paper in this series is reference 1.

^b Present address: Dipartimento di Chimica-Fisica, University of Pavia, Pavia, Italy.

For a better understanding of the first two points listed above, a few more details (arranged in chronological order) are given. Sokolov, using a visual-polythermal technique, found⁽³⁾ a fusion temperature T_{fus} of 571 K and⁽⁴⁾ non-specified solid-to-solid transitions (NST's), *i.e.* transitions for which neither structural nor phenomenological information is given for the phases concerned, at 560, 490, 468, and 350 K. Baum *et al.*⁽⁵⁾ obtained $T_{\text{fus}} = 563$ K by hot-stage polarizing microscopy. Ubbelohde *et al.*⁽⁶⁾ reported "a fugitive mesophase extending only 1 K above the melting point" ($T_{\text{fus}} = 566$ K, and $\Delta_{\text{fus}}H_m = 8.8 \text{ kJ} \cdot \text{mol}^{-1}$; both of them "provisional" values by d.s.c.), but did not mention it in a subsequent paper⁽⁷⁾ where a fusion temperature of (561 ± 1) K is given and the occurrence of two (instead of Sokolov's four) NST's is claimed by d.t.a. at (498 ± 1) and (475 ± 1) K. Storonkin *et al.*⁽⁸⁾ obtained, again by d.t.a., $T_{\text{fus}} = 563$ K and—on the basis of a cooling curve— $(12.6 \pm 2.1) \text{ kJ} \cdot \text{mol}^{-1}$ as the relevant enthalpy change: no mention is made of mesophases. Ferloni *et al.*⁽²⁾ measured by d.s.c. $T_{\text{fus}} = 562.4$ K and $\Delta_{\text{fus}}H_m = 13.4 \text{ kJ} \cdot \text{mol}^{-1}$, and found—in agreement with the British authors quoted above—two NST's (at 494 and 470 K); for the latter, due to some difficulties in evaluating separately the peak areas, they preferred to consider the "transition group" as a whole, for which the overall enthalpy increment was $7.4 \text{ kJ} \cdot \text{mol}^{-1}$. The number and (approximate) temperatures of solid-state transitions as given in Ferloni *et al.*⁽²⁾ was supported further by a subsequent⁽⁹⁾ polythermal X-ray diffractometric (130 to 540 K) and conductometric (420 to 540 K) investigation in the same laboratory. Feloni *et al.* also did not find evidence for a mesomorphic phase. Roth *et al.*,⁽¹⁰⁾ however, on the basis of simultaneous d.t.a. and electric-conductivity measurements claimed that the salt melted at 545 K having undergone a single NST at 478 K, and that it existed in a liquid-crystalline state between 545 and 561 K. The situation is summarized in figure 1.

T/K ⁽³⁾	4	5	6	7	8	2	10	This
580			clr					work
560	fus		fus	fus	fus	fus	clr	fus
540	trs	fus					fus	
500				trs		trs		
480	trs						trs	trs
460	trs			trs		trs		trs
350								
340	trs							

FIGURE 1. Schematic representations of phase transitions in $\text{CH}_3\text{CH}_2\text{CO}_2\text{Na}$. (clr, clearing; fus, fusion; trs, transition).

2. Experimental

SAMPLE PROVENANCE

Na3C was prepared by adding to a suspension of Merck "Suprapur" sodium carbonate in anhydrous methanol a slight excess (5 mass per cent) of Fluka puriss p.a. propanoic acid (≥ 99.5 moles per cent; tested by g.c. at the origin). After refluxing for 45 min the solvent and excess acid were evaporated under a reduced pressure in a Rotavapor device at about 330 K; the last traces of them were removed by further drying under vacuum at the same temperature. The solid recovered (about 200 g) was purified by recrystallization from (methanol + ethanol) (volume ratio: 1); only the portion precipitated at room temperature (about 57 g), after drying at 400 K for a few days, was employed for the preparation of the samples. The melting interval was less than 0.1 K (see figure 5), and d.s.c. analysis gave traces fully agreeing with those reported in reference 2.

CALORIMETERS, ADIABATIC ASSEMBLIES, AND COMPUTER ASSISTANCE

These have been previously described.⁽¹⁾ The gold-plated copper calorimeter employed between the liquid-helium region and 320 K with the Mark X cryostat, and the silver calorimeter employed between 300 and 580 K with the Mark IX thermostat were loaded with 25.719 and 28.928 g of Na3C; the corresponding amounts of substance were taken as (1/3.73499) and (1/3.32073) mol on the basis of the IUPAC 1973 relative atomic masses. After loading, the air within the calorimeters was removed and replaced with a few kPa (at 300 K) of helium; tight sealing was obtained by means of annealed gold gaskets pressed on to the knife-edges of the calorimeter sealing ports. Buoyancy corrections were calculated using the average of the densities obtained by X-ray crystallography and by pycnometry at 298 K {1.506 and (1.49 ± 0.03) g · cm⁻³, respectively}.⁽¹¹⁾

3. Results

HEAT CAPACITIES AND RELATED FUNCTIONS

The molar heat capacity obtained in the Mark X cryostat and the Mark IX thermostat are listed in chronological order in table 1 and plotted in figures 2, 3, and 4.

The probable errors in the different temperature regions are the same as those specified elsewhere,⁽¹⁾ except for Crystal II (see below). The overlapping of the upper end of the low-temperature curve pertinent to Crystal III with the lower end of the high-temperature curve was fully satisfactory.

For the latter phase, the smoothed ($C_{p,m}/R$)s calculated as described⁽¹⁾ at selected temperatures are listed in table 2 along with the corresponding derived standard thermodynamic functions.

TABLE 1. Experimental molar heat capacity of sodium propanoate ($\text{CH}_3\text{CH}_2\text{CO}_2\text{Na}$). ($R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

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	$C_{p,m}/R$
Results taken in Mark X cryostat											
Crystal III											
Series I	31.03	1.409	Series II	263.80	14.927	83.24	6.641	137.01	9.972		
9.80	0.062 ^a	33.94	1.701	252.96	14.547	269.99	15.149	87.69	7.011	143.10	10.269
10.67	0.077 ^a	37.14	2.034	268.72	15.103	276.72	15.383	92.60	7.360	149.19	10.549
11.52	0.096	40.72	2.413			290.18	15.850	97.38	7.687	155.28	10.821
12.38	0.117	43.08	2.668	Series IV ^b	296.20	16.058	101.97	7.976	161.39	11.088	
13.27	0.145	45.11	2.882	220.05	13.361	302.80	16.306	105.01	8.170	167.50	11.326
14.24	0.181	47.27	3.117	226.21	13.586	309.34	16.523	106.58	8.244	173.62	11.596
15.29	0.226	49.53	3.368	232.38	13.866	315.20	16.731	108.13	8.388	183.64	11.979
16.43	0.279	51.90	3.623					109.67	8.460	189.63	12.240
17.70	0.346	54.40	3.889	Series V		Series VI		111.19	8.543	196.27	12.472
19.12	0.430	57.02	4.167	223.99	13.504	70.66	5.539	112.69	8.654	202.42	12.703
20.73	0.517 ^a	59.78	4.460	230.19	13.711	72.41	5.681	114.18	8.725	208.57	12.933
22.48	0.656	62.68	4.762	235.39	13.933	74.11	5.836	115.66	8.834	214.73	13.159
24.39	0.811	65.73	5.074	238.60	14.002	75.76	5.994	119.19	8.823 ^a	220.89	13.379
26.23	0.965	68.94	5.373	240.79	14.106	77.38	6.127	124.94	9.453	227.05	13.618
28.36	1.155	72.32	5.670	245.13	14.261	78.95	6.256	130.93	9.781		
				251.45	14.496	80.49	6.400				
				257.62	14.712						
Crystal III'											
Series IV'	128.33	8.710 ^a	152.46	10.022	176.98	11.286	201.58	12.408			
110.23	7.657	134.36	8.920	158.52	10.336	183.16	11.559	207.80	12.727		
116.33	7.920	140.39	9.292	164.65	10.652	189.25	11.861	213.92	13.126		
122.35	8.184	146.41	9.687	170.81	10.974	195.37	12.130				
Crystal III''											
Series III	74.57	5.611	84.93	6.505	Series IV	79.84	6.061	94.35	7.203		
64.77	4.733	78.13	5.182 ^a	86.83	6.634	73.46	5.540	82.61	6.372	98.78	7.449
67.74	4.999	80.98	6.170	89.18	6.818	75.79	6.014 ^a	86.40	6.641	104.17	7.815
71.16	5.309	82.98	6.346	93.07	7.092	77.80	5.887	90.37	6.914		
Results taken in Mark IX thermostat											
Crystal III											
Series I	383.75	19.202	Series II		Series IV	331.20	17.262	433.57	21.299		
301.42	16.240	394.00	19.585	397.20	19.661	357.26	18.215	341.60	17.646	454.84	22.876 ^a
312.07	16.619	404.25	19.966	406.00	20.030	367.47	18.610	351.83	18.029	461.05	22.887
322.30	17.026	414.47	20.398	430.48	21.118			362.06	18.427		$\Delta H_{\text{III} \rightarrow \text{II}}$ detn.D
332.54	17.360	424.70	20.848	440.77	21.635			382.53	19.144		
342.79	17.716	434.92	21.353	450.95	22.223			392.78	19.538		Series VIII
353.03	18.065	445.21	21.874	461.06	23.212 ^a			403.02	19.933		ΔH run C
363.27	18.431	455.41	22.760 ^a					413.25	20.329	444.50	21.832 ^b
373.51	18.813	$\Delta H_{\text{III} \rightarrow \text{II}}$	detn.A	Series III		Series VI		423.48	20.765	454.48	22.417 ^b
				$\Delta H_{\text{III} \rightarrow \text{II}}$	detn.B	310.31	16.556			$\Delta H_{\text{III} \rightarrow \text{II}}$	detn.E
Crystal II											
Series II'		Series IV'		Series V	479.48	28.568	484.31	23.727	481.29	28.960	
473.86	23.875	479.77	26.793	477.50	23.207	483.52	29.626	489.48	31.513		
478.27	26.755	484.39	31.434	483.75	24.188	487.52	29.883				
482.96	29.814	488.49	32.217	488.99	29.635			Series VIII'			
$\Delta H_{\text{II} \rightarrow \text{I}}$	detn.A	$\Delta H_{\text{II} \rightarrow \text{I}}$	detn.B	Series VII				473.16	27.778		
				Series VI'	478.51	23.319	477.27	28.881			

TABLE 1.—*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	$C_{p,m}/R$
Crystal I											
Series II''		538.44	26.335	515.72	25.423	546.62	26.740	542.41	26.475		
508.01	25.156			523.10	25.676	555.05	27.230	549.04	26.861		
517.91	25.579 ^a	Series IV''		530.44	25.924	$\Delta_{fus}H_m$	detn.A	555.60	27.213		
528.18	25.864	502.19	25.080 ^a	538.22	26.286			$\Delta_{fus}H_m$	detn.B		
		508.29	25.171			Series V'					
Liquid											
Series IV''		569.38	26.350	579.19	26.493	567.99	26.287				
564.46	26.274	574.29	26.444			572.08	26.382				
				Series V''							

^a Not included in curve fit because of deviation from smooth curve.

^b Not employed for curve fit.

METASTABILITY PHENOMENA BELOW 300K

The sample in the cryostat underwent the following thermal cycles:

(1), 300 K → liquid helium region → 300 K (measurements taken between 9 and 75 K; Series I in table 1; Mark X cryostat);

(2), 300 K → about 240 K → 273 K (250 to 271 K; Series II);

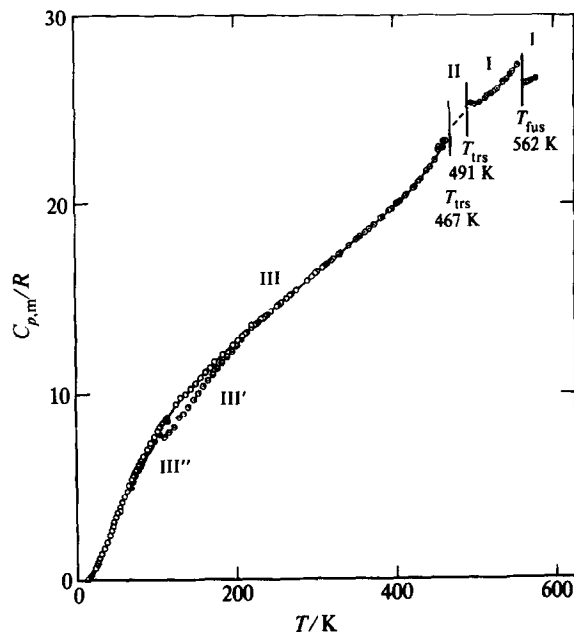


FIGURE 2. Molar heat capacity of $\text{CH}_3\text{CH}_2\text{CO}_2\text{Na}$. \circ , \bullet , \ominus , Results taken in the Mark X calorimetric cryostat; \odot , results taken in the Mark IX calorimetric thermostat.

TABLE 2. Standard molar thermodynamic properties of sodium propanoate $\text{CH}_3\text{CH}_2\text{CO}_2\text{Na}$.
($R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T K	$C_{p,m}$ R	S_m° R	$H_m^\circ - H_m(0)$ R K	$G_m - H_m(0)$ RT	T K	$C_{p,m}$ R	S_m° R	$H_m - H_m(0)$ R K	$G_m - H_m(0)$ RT
Crystal III									
10	0.076	0.025	0.191	0.006	160	11.016	9.957	922.4	4.191
15	0.212	0.076	0.842	0.020	180	11.852	11.303	1151.2	4.907
20	0.485	0.172	2.538	0.045	200	12.626	12.592	1396.1	5.612
25	0.860	0.319	5.864	0.085	220	13.357	13.830	1656.0	6.303
30	1.310	0.515	11.263	0.139	240	14.071	15.02	1930.3	6.980
40	2.335	1.029	29.392	0.294	260	14.789	16.18	2218.9	7.643
50	3.418	1.666	58.15	0.503	280	15.51	17.30	2521.9	8.293
60	4.479	2.384	97.68	0.756	298.15	16.16	18.29	2809.1	8.872
70	5.466	3.150	147.47	1.043	300	16.23	18.39	2839.1	8.930
80	6.358	3.939	206.67	1.356	320	16.94	19.46	3170.9	9.555
90	7.153	4.735	274.31	1.687	350	18.01	21.03	3695.2	10.472
100	7.861	5.526	349.44	2.031	400	19.85	23.55	4641.1	11.951
120	9.073	7.070	519.2	2.743	450	22.22	26.02	5688	13.377
140	10.100	8.547	711.1	3.467	467.00 ^a	(23.35)	(26.86)	(6075)	(13.852)
Crystal II									
467.00 ^a	(18.5)	(27.68)	(6460)	(13.852)	491.00 ^a	(30.5)	(28.91)	(7048)	(14.556)
480	25.00	28.28	6743	14.235					
Crystal I									
491.00 ^a	(24.73)	(30.00)	(7582)	(14.556)	550	26.95	32.91	9098	16.37
500	24.98	30.45	7806	14.838	561.88 ^a	(27.70)	(33.49)	(9423)	(16.73)
Liquid									
561.88 ^a	(26.35)	(36.33)	(11020)	(16.73)	580	(26.53)	(37.18)	(11499)	(17.35)

^a These heat capacities represent the lattice contribution extrapolated to the transition temperature. The derived functions at these transition temperatures are predicted upon isothermal absorption of energy. The thermodynamic functions are taken to be zero at $T = 0$.

(3), 273 K \rightarrow 55 K \rightarrow about 95 K (63 to 95 K; Series III);

(4), about 95 K \rightarrow 56 K \rightarrow about 235 K (72 to 235 K; Series IV, IV', IV'');

(5), about 235 K \rightarrow about 220 K \rightarrow about 320 K (220 to 320 K; Series V);

(6), about 320 K \rightarrow 56 K \rightarrow 300 K (69 to 230 K; Series VI).

During the third cycle it was observed that the lower end of Series III did not overlap with the upper end of Series I. This peculiarity was found again in the fourth cycle. On the contrary, an overlap with Series I was obtained for the points belonging to Series VI. The above facts suggest that metastability exists in Na_3C at low temperatures, although the conditions for the occurrence of a metastable state during a given cooling are still not clearly understood. As shown in figure 3, the metastable $C_{p,m}$'s taken between the solid nitrogen region and about 215 K lie on two distinct curves with a marked discontinuity apparent at 105 to 110 K. This suggests further the existence of two metastable phases (designated as III' and III'', respectively, in table 1) with a phase transition at the temperature mentioned. No information on such phases was found in the literature.

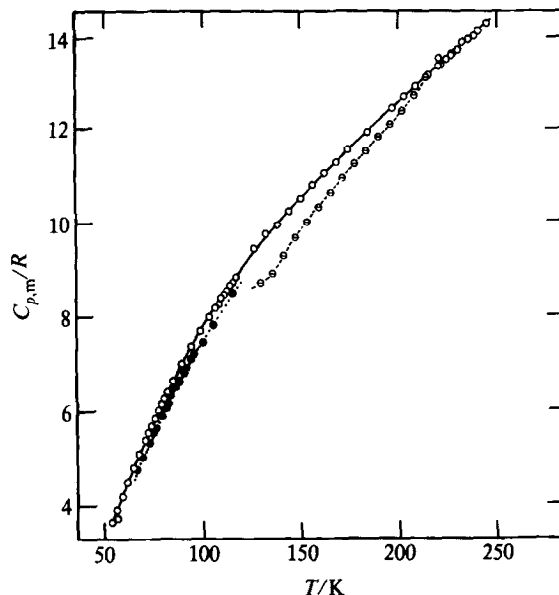


FIGURE 3. Detailed plot of molar heat capacities in the cryogenic region. ● and ⊖, Results for apparently metastable phases.

PHASE RELATIONS, HEAT CAPACITIES, AND TRANSITION ENTHALPIES IN THE SUPER-AMBIENT REGION

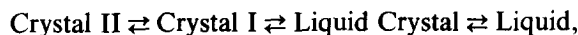
The present results (see last column of figure 1) provided unambiguous evidence for the phase relations:



in agreement with the findings of others^(2,7) (compare the same figure), whereas such schemes as



or



suggested by previous authors^(3,4,10) are seen to be inconsistent. In particular, no evidence was found for the occurrence of any mesomorphic phase intermediate between our Crystal I (crystalline, monoclinic)⁽⁹⁾ and the liquid.

The degree of reversibility of the transitions was much more satisfactory than for the lower homologs (sodium methanoate and ethanoate).^(1,2) Indeed, fair agreement was obtained: (i) for Crystal I, between $C_{p,m}$'s taken before and after fusion (Series II" and IV", and Series V', in table 1; Mark IX thermostat), and (ii) for Crystal III, between $C_{p,m}$'s taken either on the fresh salt (Series I), or after the sample had undergone one or both solid-to-solid transitions (Series II and IV, respectively), or after the sample had been melted (Series VI). This agreement is reflected also in the strict coincidence between the enthalpy increments as measured

TABLE 3. Enthalpy determinations on Crystal III, $\text{CH}_3\text{CH}_2\text{CO}_2\text{Na}$. ($R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

Detn.	$\frac{T_{\text{initial}}}{\text{K}}$	$\frac{\Delta T}{\text{K}}$	$10^{-3}\Delta H_m/(R \text{ K})$	
			expt	calc.
A	372.57	44.95	0.8826	0.8812
B	417.51	44.16	0.9560	0.9556
C	409.21	30.42	0.6333	0.6344

in the three ΔH runs taken on Solid III (ΔH_{expt} , see table 3), and as calculated by graphical integration of the smoothed curve (ΔH_{calc}).

The situation, however, is far less favorable for Crystal II, *i.e.* in the 24 K wide interval between the two solid-to-solid transitions. The "sharpness" of the transitions seems to depend to some extent on the thermal history of the sample, which—*inter alia*—affects noticeably the shapes of the "tail" of Transition (III \rightarrow II), and of the "foot" of Transition (II \rightarrow I). This, in turn, affects the apparent heat capacities of the sample in the temperature interval pertinent to Crystal II (see table 1, under the heading "Crystal II," and figure 4). As an obvious consequence of the above facts, both the temperatures and the enthalpy increments relevant to the solid transitions were determined with less accuracy than that of those pertaining to fusion.

The thermodynamic functions obtained in this work for the Na3C phase transitions are summarized in table 4, where some selected literature values are also listed for the sake of comparison. It is to be stressed that both for T_{trs} 's and $\Delta_{\text{trs}}H_m$'s the closest agreement with the adiabatic calorimetric results is exhibited by those previously provided by one of us through d.s.c. analysis.⁽²⁾ In the same paper⁽²⁾ semi-quantitative d.s.c. heat capacities were reported in the temperature intervals

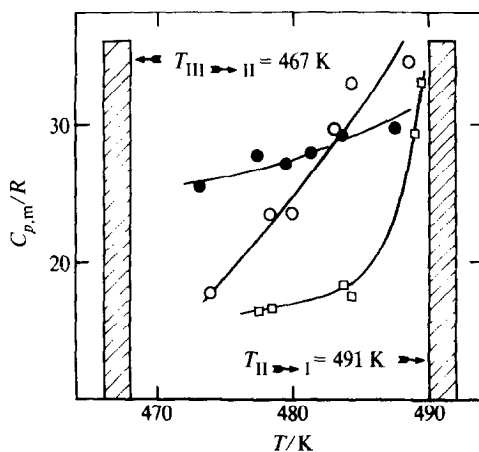


FIGURE 4. Heat capacities in the Crystal II region. The results relate to six separate series of determinations (see table 1, under the heading "Crystal II"): \circ , Series II' and IV'; \bullet , Series VI' and VIII'; \square , Series V and VII.

TABLE 4. Quantities relevant to phase transitions of $\text{CH}_3\text{CH}_2\text{CO}_2\text{Na}$. ($R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

Transition	T_{trs}/K	$10^{-3}\Delta_{\text{trs}}H_m/(R \text{ K})$	Method	Reference
III \rightarrow II	475 \pm 1	—	d.t.a.	7
	470.2	^a	d.s.c.	2
	467 \pm 1	0.386 \pm 0.008 ^b	ad. cal.	This work
II \rightarrow I	498 \pm 1	—	d.t.a.	7
	494	^a	d.s.c.	2
	491 \pm 1	0.524 \pm 0.017 ^c	ad. cal.	This work
I \rightarrow liquid (Fusion)	561 \pm 1	(1.05) ^d	d.t.a.	7
	563	1.50 \pm 0.25	d.t.a.	8
	562.4	1.61	d.s.c.	2
	561.88 \pm 0.03 ^e	1.5973 \pm 0.0006 ^f	ad. cal.	This work

^a Cumulative enthalpy increment for (III \rightarrow II) + (II \rightarrow I) from reference 2: (as $10^{-3}\Delta_{\text{trs}}H_m/R = 0.886 \text{ K}$; to be compared with the cumulative value of 0.910 K obtained in this work).

^b Average of the values 0.402, 0.381, 0.370, 0.386, 0.389 obtained in the $\Delta H_{\text{III} \rightarrow \text{II}}$ detns. A to E (A to C on the powdered sample; D, E on the previously melted sample) listed in table 1.

^c Average of the values 0.541, 0.508 obtained in the $\Delta H_{\text{II} \rightarrow \text{I}}$ detns. A, B listed in table 1.

^d "Provisional" d.s.c. value by the same authors given in a previous paper⁽⁶⁾ although not reported in reference 7.

^e The fusion temperature (561.88 \pm 0.03) K from the plot in figure 5 can be compared with the crystallization temperature (561.85 \pm 0.02) K determined during the cooling run after the first fusion.

^f Average of the values 1.5979 and 1.5968 obtained in the $\Delta_{\text{fus}}H_m$ detns. A, B listed in table 1.

340 to 460 K (Crystal III), 520 to 550 K (Crystal I), and 570 to 580 K (liquid): these also can be favorably compared with the present results, the mean difference being less than 3 per cent (compare table 5).

COMPARISON OF THE HEAT CAPACITIES OF THREE SODIUM ALKANOATES

From 300 K to the liquid-helium region, sodium methanoate (Na1C) Crystal II⁽¹²⁾ and Na3C Crystal III⁽¹¹⁾ are monoclinic, whereas Na2C Crystal IV⁽¹³⁾ is orthorhombic from 300 K to the transition peak at $T_{\text{trs}} = 21 \text{ K}$. Although the structure of Na2C is different, it seemed reasonable to expect $C_{p,m}/R$ values intermediate between those of the lower and higher homologs, except in the neighborhood of the transition peak. Actually, the heat capacity of Na2C remains

TABLE 5. Comparison between present and d.s.c. molar heat capacities of $\text{CH}_3\text{CH}_2\text{CO}_2\text{Na}$. ($R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T/K	this work	$C_{p,m}/R$		D^a	$\langle D \rangle$
			d.s.c. ⁽²⁾		
340	17.64		18.07	+2.4	+2.8
460	22.84		22.80	-0.2	
520	25.55		26.72	+4.4	
550	26.91		27.68	+2.8	
570	26.34		27.28	+3.4	
580	26.48		27.38	+3.3	

^a $D = 100(C_{p,d.s.c.} - C_{p,ad.cal.})/C_{p,d.s.c.}$

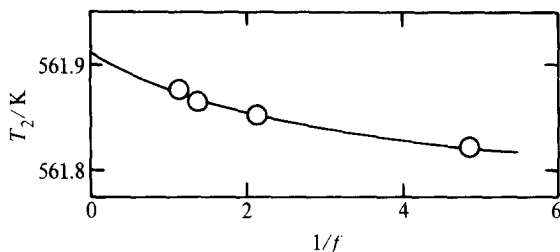


FIGURE 5. Fractional fusion plot from first enthalpy of fusion determination (T_2 represents the temperature reached after each energy input and f the fraction melted).

larger than that of Na₃C up to about 63 K, *i.e.* up to more than 40 K above the peak. This possibly means that the (so far unknown) intimate molecular process at the origin of the transition goes to completion only at a temperature significantly higher than T_{trs} . If such a view is accepted, the entropy increment, $\Delta_{trs}S_m$, of the above process is significantly enhanced by a large high-temperature "tail".

MELTING AND FRACTIONAL FUSION

Two separate enthalpy-type determinations (table 1) yielded $\Delta_{fus}H_m/R$ values of 1.5979 and 1.5968 K and a fractional-fusion determination (figure 5) indicated a melting temperature of (561.88 ± 0.03) K for the sample and (561.91 ± 0.03) K for the pure substance. The molality of liquid-soluble solid-insoluble impurity in our sample is seen to be $0.0016 \text{ mol} \cdot \text{kg}^{-1}$.

One of us (P.F.) gratefully acknowledges the financial support received by the National Science Foundation (U.S.A.) and by the Centro di Studio per la Termodinamica ed Elettrochimica dei Sistemi Salini Fusi e Solidi del CNR, Pavia (Italy).

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