

# Thermophysics of metal alkanoates

## I. Heat capacities and thermodynamic properties of sodium methanoate and ethanoate<sup>a</sup>

P. FRANZOSINI,<sup>b</sup> W. A. PLAUTZ, and  
EDGAR F. WESTRUM, JR.

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

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The heat capacities of two sodium alkanoates have been studied by adiabatic calorimetry. Earlier measurements from this laboratory on sodium methanoate between 5 and 350 K are supplemented from 300 K to melting. Sodium ethanoate is measured from 7 through 350 K; the results differ markedly from those reported by Strelkov in that we find the 21 K transition peak is much larger and the higher temperature values are 15 to 20 per cent higher and in good accord with reported d.s.c. studies at still higher temperatures. We estimate  $\Delta_{\text{tr}}S_m^\circ/R$  of the 21 K peak to be about 1.5 although no isostructural lattice contribution is available. Even with adjuvant X-ray diffraction results by Hsu and Nordman the mechanism of the transition has not been identified. The 298.15 K values of  $C_{p,m}/R$ ,  $S_m^\circ/R$ ,  $\{H_m^\circ - H_m^\circ(0)\}/R$  and  $\{G_m^\circ - H_m^\circ(0)\}/RT$  are 12.127, 16.610, 2308.1 K, and  $-8.868$  for form II  $\text{CH}_3\text{COONa}$ .

### 1. Introduction

Systematic d.s.c. analysis by one of us (P.F.) on about 100 linear and branched alkanoates to deduce an extensive and homogeneous overview of the phase relations in the alkali alkanoates has been succinctly reviewed together with relevant information available from other sources through 1979.<sup>(1)</sup> More results on long-chain homologs ( $13 \leq n_c \leq 20$ ;  $n_c$ : number of carbon atoms) have been discussed elsewhere.<sup>(2-4)</sup> Complete understanding of the thermophysics of alkali alkanoates, however, is still precluded by the serious lack of quantitative equilibrium adiabatic heat-capacities. Westrum *et al.* had determined the molar heat capacity of sodium methanoate between 5 and 350 K in 1960 by adiabatic calorimetry,<sup>(5)</sup> while Strelkov<sup>(6)</sup> had performed an analogous investigation on sodium ethanoate between 13 and 291 K. In the superambient region only semi-quantitative (*i.e.* accurate within  $\pm 3$  per cent) measurements taken by one of us with the d.s.c. baseline-displacement technique were available for sodium methanoate, ethanoate,

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<sup>b</sup> Present address: Dipartimento di Chimica-Fisica, University of Pavia, Pavia, Italy.

propanoate, and *n*-butanoate.<sup>(7,8)</sup> Such results do not appear to exist either for homologs where  $n_C > 4$  in the sodium family, or for alkanoates whose cation is different from sodium. Although the equilibrium results for the methanoate<sup>(5)</sup> are in good accord with the d.s.c. values at super-ambient temperatures,<sup>(8)</sup> a serious discrepancy exists between Strelkov's<sup>(6)</sup> low-temperature and super-ambient d.s.c.<sup>(8)</sup> ethanoate values. Moreover the former ethanoate values<sup>(6)</sup> intersect the low-temperature methanoate<sup>(5)</sup> values.

A further desideratum was to ascertain whether methanoate does exist—as claimed<sup>(9)</sup> in 1969 on the basis of d.s.c. evidence—over a rather restricted temperature range below fusion, as a stable polymorph different from that stable at 300 K. This report has apparently escaped the attention of most investigators.

The present contribution to the thermophysics of alkali alkanoates thus endeavors to resolve these uncertainties in the literature and deals with the behavior of sodium methanoate in the super-ambient region and that of sodium ethanoate at low temperatures.

## 2. Experimental

### SAMPLE PROVENANCE

The HCOONa sample (reagent-grade sodium methanoate recrystallized twice from distilled water at a temperature above 303 K to prevent the formation of hydrate, then baked in an oven at 400 K, and finally dried in high vacuum) was a portion of that employed in 1960 by Westrum *et al.*<sup>(5)</sup> which had been kept since then under helium in a sealed Pyrex ampoule; before use it was heated at about 400 K under vacuum for a few d. The CH<sub>3</sub>COONa sample was an anhydrous ultrapure material manufactured by Ventron's Alfa Division, Danvers, Massachusetts. Before the calorimeter was sealed, this sample was heated at 335 K for 1 d under vacuum so as to eliminate any contaminating traces of atmospheric moisture. A heating curve recorded, thereafter, above 300 K was completely smooth and in particular showed no anomaly near the decomposition temperature (331 K) of the trihydrate.

### ADIABATIC CALORIMETERS

The acquisition of data from both calorimeters described was computer-assisted. The computer recorded (i) drift readings of the calorimeter temperature (as well as of its first and second derivatives) over a suitable period before and after each energy input, and (ii) during each energy input, the current and potential readings and the heating time. Information on the initial, final, and mean temperatures, on the energy input and resistance of the heater, and on the heat capacity of the system including the calorimetric vessel, heater, thermometer, and sample, was also recorded.

*Cryogenic calorimetry.* A gold-plated copper calorimeter (laboratory designation W-62) was loaded with 49.2035 g of CH<sub>3</sub>COONa, *i.e.* 0.59979 mol on the basis of the IUPAC 1973 relative atomic masses. After loading, the air was evacuated and

replaced with 2.8 kPa (at 300 K) of helium within the calorimeter, which was finally sealed by means of an annealed gold gasket tightly pressed on to the stainless-steel knife edge of the calorimeter top using a screw-type closure. The helium gas facilitated thermal conduction throughout the finely subdivided salt sample. Buoyancy corrections were calculated on the basis of the X-ray crystallographic density ( $1.534 \text{ g}\cdot\text{cm}^{-3}$ ) of the salt.<sup>(10)</sup> The Mark-X cryostat employed is an improved (by addition of a guard shield surrounding the adiabatic shield) version of the Mark-II cryostat previously described<sup>(11)</sup> together with the relevant operating techniques.

*Super-ambient calorimetry.* The silver calorimeter W-60 and its super-ambient Mark-IX thermostat are similar to items described elsewhere.<sup>(12,13)</sup> A HCOONa sample of mass 43.5603 g (0.64052 mol) was used. An X-ray crystallographic density<sup>(14)</sup> of  $1.955 \text{ g}\cdot\text{cm}^{-3}$  was employed to calculate the buoyancy corrections, and 3.1 kPa (at 300 K) of helium was introduced into the calorimeter before it was sealed.

### 3. Results and discussion

#### HEAT CAPACITIES AND RELATED FUNCTIONS

The experimental molar heat capacities (corrected for curvature when appropriate) are listed in table 1 for the methanoate and in table 2 for the ethanoate, in chronological order. This allows one to deduce the thermal history of each sample (from the sequence of the series of measurements), as well as the approximate temperature increment for most points (from the differences in the mean temperatures of their neighbors). The probable errors are estimated to decrease from a few per cent at 7 K to about 1 per cent around 15 K and to 0.15 per cent at higher temperatures (except for phase I of HCOONa).

The smoothed  $C_{p,m}/R$ 's listed in tables 3 and 4 for a set of selected temperatures, and the corresponding standard thermodynamic functions were obtained respectively by fitting (with the least-squares method) the appropriate polynomials to the experimental results, and by integrating the resulting functions. For methanoate the low-temperature results by Westrum *et al.*<sup>(5)</sup> were employed when needed to supplement the present super-ambient results in the calculations.

The experimental values of tables 1 and 2 are (in part) displayed as plots of  $C_{p,m}/R$  against  $T$  in figure 1 and in figures 2 and 3, respectively.

#### SODIUM METHANOATE—HEAT CAPACITY, TRANSITION, AND MELTING

During the last 60 y no less than 11 authors (or groups of authors) carried out high-temperature thermodynamic investigations on sodium methanoate or on mixtures including sodium methanoate. Melting temperatures  $T_{\text{fus}}$  spreading between 524 and  $526^{(15)}$  and  $545 \text{ K}^{(16)}$  were reported, along with the three following enthalpies of melting  $\Delta_{\text{fus}}H_m/R \text{ K}$ : ( $2000 \pm 500$ ), estimated by Schwab *et al.*<sup>(17)</sup> in 1951; ( $2040 \pm 50$ ) calculated by Leonesi *et al.*<sup>(18)</sup> on the basis of cryometric measurements; and 2060, measured by d.s.c.<sup>(9)</sup> along with a melting temperature of 530.7 K.

The occurrence of a transition not far below melting was first mentioned by Sokolov in 1956<sup>(19)</sup> ( $T_{\text{trs}} = 515$  K; visual polythermal method), but later clearly supported only by the quoted (1969) d.s.c. investigation<sup>(9)</sup> which gave  $T_{\text{trs}} \approx 502$  K and  $\Delta_{\text{trs}}H_m/R$  K = 141, although, for the sake of completeness, it must be added that in 1974 Storonkin *et al.*<sup>(20)</sup> reported (on the basis of a d.t.a. cooling curve) ( $2110 \pm 250$ ) as the cumulative  $\Delta H_m/R$  K associated with the crystallization (at 528 K) and a polymorphic transformation occurring at an unspecified temperature.

TABLE I. Super-ambient-temperature heat capacity for HCOONa. ( $R = 8.3143$  J · K<sup>-1</sup> · mol<sup>-1</sup>.) Results taken in Mark IX thermostat

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Phase II							
Series I		347.18	10.572	398.65	11.239	448.74	11.900
298.80	9.928 <sup>a</sup>	357.47	10.704	408.86	11.370	458.48	12.033
306.00	10.053	367.77	10.832	418.97	11.507	468.13	12.161
316.30	10.178	378.07	10.981	429.00	11.603	477.68	12.301
326.59	10.315	388.36	11.096	438.92	11.805	≈ 486	— <sup>b</sup>
336.89	10.444						
Phase II (incompletely converted) <sup>c</sup>							
Series II		Series IV		467.03	12.050	$\Delta_{\text{trs}}H$	Detn. E
372.73	10.932	302.78	9.934	481.81	12.242		
382.64	10.999	313.05	10.065	$\Delta_{\text{trs}}H$	Detn. C	Series IX	
392.97	11.117	349.25	10.531	Series VI		338.67	10.370
403.25	11.236	389.12	11.005	451.52	11.739	353.88	10.583
412.97	11.353	409.02	11.274	471.77	11.961	374.68	10.854
422.12	11.467	429.07	11.529	$\Delta_{\text{trs}}H$	Detn. D	395.26	10.980
Series III		469.65	11.022	Series VII		415.73	11.292
389.63	11.089	482.80	12.204	472.58	11.964	436.08	11.612
446.78	11.775	$\Delta_{\text{trs}}H$	Detn. B	477.84	12.059	456.46	11.843
$\Delta_{\text{trs}}H$	Detn. A	Series V		483.02	12.107	475.14	12.068
		446.77	11.703			$\Delta_{\text{trs}}H$	Detn. F
Phase I							
Series III'		Series V'		Series VII'		507.54	12.388
498.07	12.301	500.89	12.334	504.43	12.344	513.16	12.456
503.58	12.119 <sup>a</sup>	506.53	12.398	510.06	12.417	Series IX'	
508.73	12.656 <sup>a</sup>	511.71	12.454	Series VIII		497.97	12.285
513.89	12.514	Series VI'		467.29	11.859	503.64	12.235 <sup>a</sup>
519.09	12.620	499.20	12.290	472.56	11.938	508.81	12.640 <sup>a</sup>
Series IV'		504.85	12.355	477.74	11.991	513.97	12.499
499.01	12.306			482.92	12.048	519.18	12.566
				495.00	12.234	524.33	12.785

<sup>a</sup> Not included in curve fit because of deviation from smooth curve.

<sup>b</sup> Determination aborted after energy input sufficient to reach the transition region and to convert about 10 per cent of the sample into Phase I.

<sup>c</sup> Thermal histories: Series II after cooling to  $\approx 365$  K from  $\approx 491$  K; III,  $\approx 360$  K from  $\approx 426$  K; IV,  $\approx 296$  K from  $\approx 522$  K; V,  $\approx 435$  K from  $\approx 502$  K; VI,  $\approx 440$  K from  $\approx 514$  K; VII,  $\approx 460$  K from  $\approx 507$  K; VIII,  $\approx 465$  K from  $\approx 512$  K (undercooling of phase I); IX,  $\approx 330$  K from  $\approx 515$  K.

We note the following from our adiabatic calorimetric results.

(i) The values taken on the unheated salt present in a phase here designated as Solid II (see table 1, Series I) satisfactorily overlapped (at 300 to 350 K) with the upper end of the low-temperature curve by Westrum *et al.*<sup>(5)</sup> Moreover they substantially confirm the trend of the heat capacities outlined by d.s.c.<sup>(8)</sup> from 340 K

TABLE 2. Experimental heat capacity of sodium ethanoate ( $\text{CH}_3\text{COONa}$ ). ( $R = 8.3143 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .)  
Results taken in Mark X cryostat

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Phase V							
Series I		17.04	0.861	19.01	1.187	20.19	1.529
7.50	0.064	18.47	1.082	19.79	1.375	20.65	1.776
8.11	0.086 <sup>a</sup>	20.20	1.663	20.46	1.657	20.79	1.951
8.94	0.120			20.96	2.582	20.91	2.393
9.87	0.172	Series II				20.99	3.628
10.99	0.243	15.98	0.719	Series III			
12.86	0.385	17.11	0.870	18.57	1.105	Series IV	
14.05	0.497	18.10	1.021	19.42	1.277	$\Delta_{\text{trs}}H$	Detn. A <sup>b</sup>
15.69	0.683						
Phase IV							
Series I'		42.96	3.186	187.74	9.691	335.32	12.903
22.22	1.864	46.41	3.482	200.11	9.969	341.63	13.013
24.97	1.680	50.24	3.805	206.28	10.118	347.83	13.143
27.90	1.884	54.29	4.134	212.44	10.269		
		58.35	4.454	218.61	10.400	Series VI <sup>c</sup>	
Series II'		62.45	4.770			65.49	4.969
21.39	2.175	66.53	5.063	Series V		69.69	5.287
21.91	1.725	70.84	5.342	217.85	10.373	73.81	5.539
22.51	1.627	75.45	5.604	224.01	10.524	76.34	5.686
23.11	1.609	80.07	5.943 <sup>a</sup>	230.18	10.657	77.25	5.744
23.72	1.618	84.70	6.188	236.36	10.790	78.15	5.778
24.32	1.643	89.38	6.437	242.53	10.925	79.04	5.852
		94.08	6.662	248.71	11.068	80.36	5.923
Series III'		95.52	6.722	254.89	11.198	82.09	6.046
21.07	3.804	100.93	6.959	261.07	11.352		
21.24	2.521	106.16	7.170	267.25	11.459	Series VII <sup>c</sup>	
21.35	2.209	111.39	7.392	273.44	11.599	77.62	5.763
21.47	2.008	116.64	7.598	279.63	11.731	78.31	5.802
		127.20	7.984	285.81	11.859	79.02	5.847
Series IV'		132.71	8.167	291.99	12.005	79.72	5.874
24.54	1.654	138.81	8.365	298.18	12.126	80.39	5.940
26.97	1.811	151.09	8.732	304.41	12.250	81.09	5.967
30.16	2.070	157.09	8.903	310.63	12.381	81.79	6.010
33.30	2.342	163.22	9.073	316.82	12.521	82.47	6.059
36.48	2.625	169.36	9.231	322.97	12.644	83.12	6.095
39.70	2.905	181.65	9.536	329.12	12.789	83.78	6.142

<sup>a</sup> Not included in curve fit because of deviation from smooth curve.

<sup>b</sup> The enthalpy Detn. A (Series IV) from 15.57 through 23.74 K has a  $\Delta_{\text{trs}}H_m/R$  of 11.324 K, in good accord with the last three determinations of Series I and the first determination of Series I' adjusted to cover the temperature range above ( $\Delta_{\text{trs}}H_m/R = 11.295 \text{ K}$ ).

<sup>c</sup> Series of points of typically smaller temperature increment in search of transition; not included in curve fit.

up to the transition: thus, *e.g.* at 340, 400, and 460 K the smoothed adiabatic-calorimetric  $C_{p,m}/R$  results were 10.48, 11.25, and 12.06 ( $\pm 0.016$ ) to be compared with those ( $10.6 \pm 0.2$ ), ( $11.2 \pm 0.1$ ), and ( $11.8 \pm 0.1$ ) obtained by d.s.c.

(ii) The existence of the transition is definitively confirmed, although occurring at a temperature  $T_{trs} = (491.5 \pm 1)$  K, *i.e.* some 10 K lower than that found by d.s.c.<sup>(9)</sup> This discrepancy, however, is not surprising if one takes into account on the one hand the basic difference between d.s.c. (which is a dynamic method) and adiabatic calorimetry (which is an equilibrium method), and on the other hand the sluggishness often exhibited by solid-state transitions in the lowest homologs of the alkali alkanoates. This sluggishness also causes Solid I (*i.e.* that stable between the transition and fusion temperatures) to offer marked hysteresis to conversion into Solid II on cooling. Indeed, the heat capacities taken within the field of stable existence of Solid II after the sample had been heated up to or above the transition temperature and subsequently cooled down to 460 K or less (see table 1, Series II to VII and IX under the heading "Phase II, incompletely converted") are lower than

TABLE 3. Standard molar thermodynamic functions for  $\text{CH}_3\text{COONa}^a$  ( $R = 8.3143 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

$T$ K	$C_{p,m}/R$		$S_m$ R	$H_m - H_m(0)$ R K	$- \{G_m - H_m(0)\}$ RT
	expt	latt.			
10	0.18	0.06	0.05	0.38	0.01
15	0.61	0.20	0.19	2.21	0.05
20	1.40	0.45	0.45	6.87	0.11
25	1.685	0.79	0.86	15.97	0.22
30	2.053	1.21	1.203	25.27	0.361
35	2.490	1.67	1.552	36.61	0.506
40	2.934	2.15	1.914	50.17	0.659
45	3.366	2.62	2.284	65.93	0.819
50	3.796	3.10	2.661	83.83	0.984
60	4.594	3.98	3.425	125.87	1.327
70	5.292	4.78	4.187	175.37	1.682
80	5.904	5.50	4.934	231.42	2.042
90	6.443	6.14	5.662	293.21	2.404
100	6.922	6.70	6.366	360.09	2.765
120	7.733	7.63	7.702	506.9	3.478
140	8.404	8.34	8.946	668.5	4.171
160	8.980	8.95	10.107	842.4	4.841
180	9.496	9.50	11.194	1027.3	5.488
200	9.974	9.97	12.220	1222.0	6.110
220	10.430	10.43	13.192	1426.1	6.710
240	10.873	10.87	14.119	1639.2	7.289
260	11.310	11.31	15.006	1861.0	7.849
280	11.741	11.74	15.860	2091.5	8.391
300	12.166	12.17	16.685	2330.6	8.916
320	12.585	12.59	17.483	2578.1	9.427
350	13.186	13.186	18.638	2964.8	10.167
273.15	11.594		15.571	2011.6	8.207
298.15	12.127		16.610	2308.1	8.868

<sup>a</sup> The third column indicates (tentative) lattice heat capacities as described in the text.

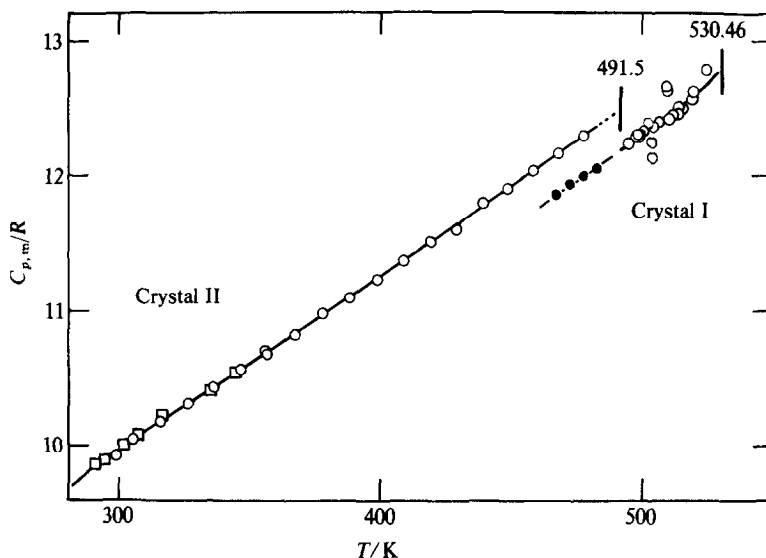


FIGURE 1. Experimental heat capacities of HCOONa in the super-ambient region.  $\square$ , Westrum *et al.*;<sup>(5)</sup>  $\circ$ , phase I and phase II, stable;  $\bullet$ , phase I, metastable.

TABLE 4. Standard molar thermodynamic functions of sodium methanoate at super-ambient temperatures ( $R = 8.3143 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

$T/\text{K}$	$C_{p,m}/R$	$S_m^\circ/R$	$\{H_m^\circ - H_m^\circ(0)\}/R \text{ K}$	$-\{G_m^\circ - H_m^\circ(0)\}/RT$
Phase II, HCOONa				
298.15 <sup>a</sup>	9.944	12.480	1895.6	6.122
300	9.971	12.541	1914.0	6.161
320	10.229	13.193	2116.1	6.580
340	10.481	13.821	2323.2	6.988
360	10.736	14.427	2535.3	7.384
380	10.993	15.01	2752.6	7.771
400	11.254	15.58	2975.1	8.147
420	11.519	16.14	3202.8	8.515
440	11.786	16.68	3435.9	8.874
460	12.056	17.21	3674.3	9.225
480	12.329	17.73	3918.1	9.568
491.5	12.49 <sup>b</sup>	18.02	(4061)	(9.76)
Phase I, HCOONa				
491.5	(12.19) <sup>c</sup>	(18.31)	(4203)	9.76
500	12.29	18.52	4307	9.91
520	12.63	19.01	4556	10.25

<sup>a</sup> Values based on reference 5.

<sup>b</sup> Extrapolated lattice contribution, Phase II.

<sup>c</sup> Extrapolated lattice contribution, Phase I.

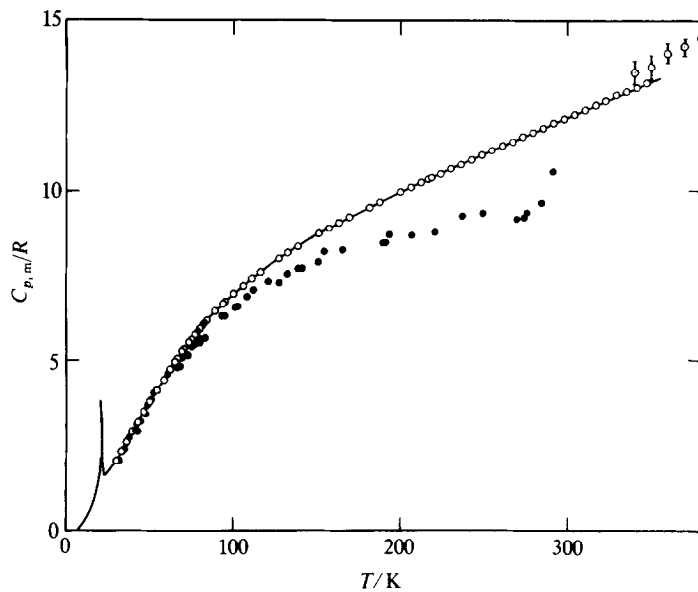


FIGURE 2. Experimental heat capacities of  $\text{CH}_3\text{COONa}$ .  $\circ$ —, The present research;  $\bullet$ — Strelkov;<sup>(6)</sup>  $\odot$ , d.s.c. determinations with the estimated uncertainties.

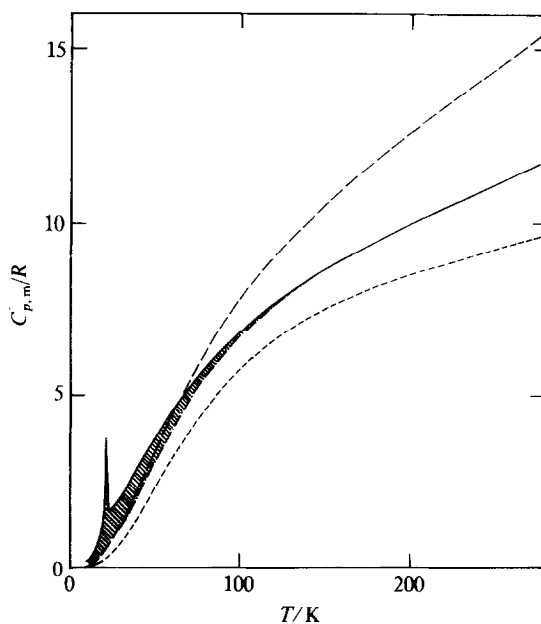


FIGURE 3. Heat capacities: —,  $\text{CH}_3\text{COONa}$ , this research; - - -,  $\text{CH}_3\text{CH}_2\text{COONa}$ ;<sup>(21)</sup> - - - - -  $\text{HCOONa}$ ;<sup>(5)</sup> - · - ·, estimated lattice heat capacities (see text) of  $\text{CH}_3\text{COONa}$ .



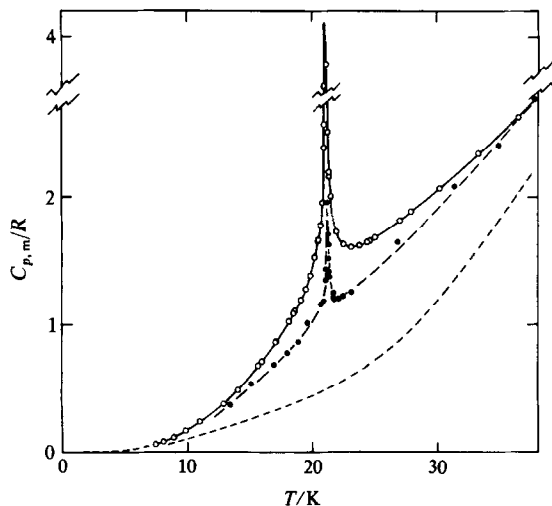


FIGURE 4. Transition-region heat capacities of  $\text{CH}_3\text{COONa}$ .  $-\circ-$ , The present research;  $-\bullet-$ , Strelkov;<sup>(6)</sup>  $---$ , the estimated lattice contribution.

those taken on the unheated sample by considerable amounts (at any rate, far larger than the experimental uncertainty in this temperature region). These values were not plotted in figure 1 so as to avoid confusion; if plotted, they would lie in a region whose upper boundary is represented by the curve of the points taken on the unheated salt (Solid II), and the lower one by the extension towards the lower temperatures of the curve for values taken on the sample after conversion to Solid I. This supports the idea that the results under discussion actually represent heat capacities of mixtures (in various ratios) of the two polymorphs.

(iii) Six enthalpy determinations, A through F (see table 1) were taken through the transition under the conditions and with the results listed below.

The last  $C_p$  determination of Series I was an "aborted" one, with an energy input sufficient to reach the transition region and to transform about 10 per cent of the sample into Solid I. The sample was then cooled to about 365 K, submitted on the next day to Series II measurements, cooled again to about 360 K and finally submitted on the following day to Series III measurements, which included the  $\Delta_{\text{trs}}H$  determination A. It can be reasonably assumed that at least 95 per cent of the sample was present as Solid II at the beginning of this enthalpy determination: a value  $\Delta_{\text{trs}}H_m(A)/R = 146$  K was obtained, which ought to represent, with an uncertainty (by default) not exceeding 5 per cent, the true enthalpy increment associated with the transition. This value is fully consistent with that (141 K) found by d.s.c.<sup>(9)</sup>

The results relevant to the other enthalpy determinations are summarized in table 5.

It is apparent that the value of  $T_C$  rather than the duration of the cooling and/or rest time is the determining factor in the completeness of transformation from

TABLE 5. Molar enthalpy of transition determinations on sodium methanoate  
( $R = 8.3143 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )

Designation	$T_{\max}/\text{K}^a$	$T_c/\text{K}^b$	(Cooling time + rest time) at $T_c$	Apparent $\Delta_{\text{II}}^{\text{I}} H_m/R \text{ K}$
B	521	296	4 d	140
F	515	330	2 d	126
C	502	435	9 h	119
D	514	440	1 d	77
E	507	460	7 h	49

<sup>a</sup>  $T_{\max}$  represents the highest temperature reached during the series of measurements preceding the designated enthalpy determination.

<sup>b</sup>  $T_c$  represents the minimum temperature to which the sample was cooled before the designated enthalpy determination.

Solid I to Solid II, at least as far as times not exceeding a few d are considered. Indeed, heat capacities taken on the sample after heating above 491.5 K and subsequent cooling to 465 K (see table 1, Series VIII) lie exactly on the extension towards the lower temperatures of Solid I curve: they are thus to be attributed to pure Solid I in a (metastable) undercooled state.

(iv) A single fractional-melting experiment led to evaluation of  $T_{\text{fus}} = (530.46 \pm 0.04) \text{ K}$  as the melting temperature of the sample (d.s.c.: 530.7 K),<sup>(9)</sup> and  $\Delta_{\text{fus}} H_m/R = 2130 \text{ K}$  as the relevant molar enthalpy change (d.s.c.: 2060 K).<sup>(9)</sup> Unfortunately, sodium methanoate caused the calorimeter to distort and crack during cooling after the first melting, presumably due to a volume increase on freezing. This prevented a further investigation of the melting process and of the molten state: on the basis of d.s.c. evidence,<sup>(8)</sup> however, it can be said that the heat capacity at the melting temperature increases by about 30 per cent on passing from Solid I to the liquid phase.

#### SODIUM ETHANOATE—HEAT CAPACITY AND 21 K TRANSITION

The reliability (within a few per cent) of the super-ambient d.s.c. heat capacities having been demonstrated for sodium methanoate, no explanation is available for the apparently large  $C_{p,m}$  jump existing in the case of ethanoate between the lower end of the d.s.c. curve<sup>(8)</sup> and the upper end of Strelkov's<sup>(6)</sup> curve except that systematic deviation caused the latter to be too low (by 15 to 20 per cent at  $\approx 290 \text{ K}$ ). This view was proved to be correct by the present results; indeed, the connection (at 340 to 350 K) between d.s.c.<sup>(8)</sup> and adiabatic-calorimetric results is again within the limits of uncertainty expected for the former, although less satisfactorily than for the methanoate. The  $C_{p,m}/R$  against  $T$  curve up to 350 K is a smooth one but for the presence of a sharp peak at 21.05 K, whose shape and easy reversibility suggest that it is due to the occurrence of a second-order transition. Strelkov<sup>(6)</sup> did observe at a practically identical temperature (21.1 K) a peak which, however, was much smaller. The intimate molecular process at the origin of this transition is not understood owing to a complete lack of structural information on the two phases

involved (which are designated in table 2 as Phase V and Phase IV, since d.s.c.<sup>(8)</sup> had provided evidence for three more solid-state transitions above 350 K). At any rate, it is believed that the transformation is actually complete only at a temperature far higher than that of the peak maximum, inasmuch as for several tens of kelvins the "tail" of the transition causes the overall heat capacity of the ethanoate to be larger than that of the propanoate.<sup>(21)</sup> A more detailed comparison among the low-temperature heat-capacity curves of the  $C_1$  to  $C_3$  homologs of the sodium family will be made in the next paper of the present series.

An attempt to evaluate the magnitude of  $\Delta_{\text{trs}}S_m^\circ/R$  for the 21 K transition—in the absence of a stand-in lattice contribution—was made on the basis of a rough corresponding-states extrapolation of  $C_{p,m}$ (sodium ethanoate) against  $C_{p,m}$ (sodium methanoate). This led to the conclusion that significant entropy-of-transition contributions were developed as high as 70 K and  $\Delta_{\text{trs}}S_m^\circ/R$  was estimated as  $(1.5 \pm 0.5)$  (about  $\ln 4$ ). The corresponding value from Strelkov's work is only 0.02 for  $\Delta_{\text{trs}}S_m^\circ/R$ . His 298.15 K entropy is inexplicably (although he acknowledges 1.5 to 3 per cent uncertainties in  $C_{p,m}$  values in various ranges) 11 per cent lower than ours.

To provide some insight into the mechanism of the transition at 21 K and to ascertain whether an isostructural alkali ethanoate existed we persuaded Hsu and Nordman<sup>(10)</sup> to study the crystal structure. Separate batches of anhydrous single crystals from aqueous solutions at  $(337 \pm 2)$  K—above the peritectic point ( $\approx 331$  K)—were found to be different orthorhombic forms designated I and II. Form I has alternating layers of  $\text{Na}^+$  ions and methyl–methyl contacts which account well for the good cleavage of this form. Of the 12 atoms per unit cell four are on 2-fold axes. Form II which has also been grown from methanol solution at 300 K (in a somewhat different habit), showed significant disorder in the oxygen positions and the same type of alternating layers. Variability of diffracted intensities between specimens indicates more than simple molecular disorder.

The calorimetric sample was identified as Form II both prior to and at the completion of measurements. This does imply, paradoxically, that Form II—rather than the less dense more ordered Form I—is the thermodynamically stable phase at low pressures to temperatures at least as high as 350 K. We cannot yet account for the thermodynamic situation of Form I. We detected no transition ourselves, and such d.s.c. transformations as have been reported in the vicinity of the crystallization temperature<sup>(1)</sup> are probably due to the trihydrate peritectic.

A meaningful structural interpretation of the 21 K transition is still precluded and the explanation of the great divergence of Strelkov's values unexplained. However, the crystallographic results do clearly show that it is not isostructural with the potassium analog and we may have to search further for a lattice heat capacity.

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