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Thermophysics of metal alkanoates

IV. Heat capacities and thermodynamic properties of potassium 2-methylpropanoate [a]

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The molar heat capacity of potassium 2-methylpropanoate, $(CH_3)_2CHCO_2K$, has been measured between 8 and 350 K by adiabatic calorimetry, and found to be normal. The corresponding thermodynamic functions have been calculated. The values found at 298.15 K for $C_{p,m}(T)/R$, $\{S^\circ_m(T)-S^\circ_m(0)\}/R$, $\{H^\circ_m(T)-H^\circ_m(0)\}/R$, and $\{G^\circ_m(T)-H^\circ_m(0)\}/RT$ are 20.08, 23.14, 3457.3 K, and −11.546, respectively.

1. Introduction

In the latest paper of this series[3] it was shown *inter alia* that for potassium propanoate $CH_3CH_2CO_2K$ the phase stable in the lowest temperature range (crystal III) goes to an isotropic liquid through the steps:

$$\text{crystal III} \overset{T_{trs}=255\text{ K}}{\underset{\Delta_{trs}S_m/R=0.24}{=}} \text{crystal II} \overset{T_{trs}=352.5\text{ K}}{\underset{\Delta_{trs}S_m/R=0.59}{=}} \text{crystal I} \overset{T_{fus}=638.3\text{ K}}{\underset{\Delta_{fus}S_m/R=3.79}{=}} \text{liquid,}$$

with $\Sigma\Delta S_m/R \approx 4.6$.

Previous d.s.c. records taken by one of us[4] from the melt region down to about 100 K proved that the next higher linear homolog: potassium butanoate, $CH_3CH_2CH_2CO_2K$, undergoes a much more complicated "stepwise melting process" implying the phase relations:

$$\text{crystal IV} \overset{\langle T_{trs}\rangle=133\text{ K}}{\underset{\Delta_{trs}S_m/R=0.60}{=}} \text{crystal III} \overset{\langle T_{trs}\rangle=464.3\text{ K}}{\underset{\Delta_{trs}S_m/R\approx 0.30}{=}} \text{crystal II} \overset{\langle T_{trs}\rangle=551.6\text{ K}}{\underset{\Delta_{trs}S_m/R=0.97}{=}} \text{crystal I,}$$

$$\text{crystal I} \overset{T_{fus}=626.1\text{ K}}{\underset{\Delta_{fus}S_m/R=2.08}{=}} \text{liquid crystal} \overset{T_{clr}=677.3\text{ K}}{\underset{\Delta_{clr}S_m/R=0.89}{=}} \text{liquid,}$$

with clr, clearing; $\Sigma\Delta S_m/R \approx 4.8$. Crystal IV is probably the lowest stable solid

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phase, and the intercrystalline transition temperatures are indicated as $\langle T_{trs} \rangle$'s since each transformation gave rise to twin peaks in the d.s.c. records {at 123 and 143 K ($\langle T_{trs} \rangle$ = 133 K), 461.4 and 467.2 K ($\langle T_{trs} \rangle$ = 464.3 K), and 541 and 562.2 K ($\langle T_{trs} \rangle$ = 551.6 K), respectively}.

Further, d.s.c. analysis, restricted, however, to the superambient region, provided evidence[5] for the following transformations in the isomeric salt, potassium 2-methylpropanoate, $(CH_3)_2CHCO_2K$:

$$\text{crystal II} \overset{T_{trs} = 424\ \text{K}}{\underset{\Delta_{trs}S_m/R = 2.32}{=}} \text{crystal I} \overset{T_{fus} = 553.9\ \text{K}}{\underset{\Delta_{fus}S_m/R = 1.91}{=}} \text{liquid crystal} \overset{T_{clr} = 625.6\ \text{K}}{\underset{\Delta_{clr}S_m/R = 0.87}{=}} \text{liquid},$$

with: $\Sigma\Delta S_m/R \approx 5.1$. It is noteworthy that branching apparently causes the 2-methylpropanoate clearing and fusion temperatures to be depressed to the level of butanoate fusion and II → I transition temperatures, respectively.

The peculiarities made evident by d.s.c. suggested that a more detailed investigation of the thermophysics of the isomeric butanoates of potassium was advisable, in order (i) to get information (so far completely missing) on the behavior of 2-methylpropanoate in the sub-ambient region, and (ii) to provide adiabatic equilibrium heat capacities as complete as possible for both butanoate and 2-methylpropanoate.

The present paper reports on point (i).

2. Experimental

The potassium 2-methylpropanoate was prepared by reacting Fluka puriss ($\geqslant 99$ moles per cent) potassium carbonate and 2-methylpropanoic acid (the latter present in slight excess) in anhydrous methanol. The solvent and excess acid were removed under a reduced pressure by evaporation in a Rotavapor device, and further by subsequent drying at about 330 K. Further purification was obtained by recrystallization from propan-2-ol. The solid recovered was completely dried by heating at about 400 K under vacuum for a few days, and then handled in a glove-box due to its remarkable hygroscopicity: d.s.c. analysis gave values fully agreeing with those in reference 5.

The calorimeter and computer-operated adiabatic assembly have been previously described.[1] The gold-plated copper calorimeter employed with the Mark X cryostat was loaded with 38.839 g of potassium 2-methylpropanoate, which corresponds to 0.30777 mol of $(CH_3)_2CHCO_2K$ on the basis of the IUPAC 1973 relative atomic masses. Within the calorimeter, air was replaced with a few kPa (at 300 K) of helium, and tight sealing was obtained, as usual, by means of an annealed gold gasket. Buoyancy corrections were calculated using an (estimated) density of 1.40 $g \cdot cm^{-3}$.

3. Results

The experimental molar heat capacities are presented in table 1 in chronological sequence (so that the temperature increments usually can be inferred from the mean

TABLE 1. Molar heat capacities of potassium 2-methylpropanoate, $(CH_3)_2CHCO_2K$ ($R = 8.3144$ $J \cdot K^{-1} \cdot mol^{-1}$)

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	$C_{p,m}/R$
Series I		325.64	21.364	195.74	14.995	10.31	0.138	41.99	3.778	107.22	10.222
247.63	17.469	332.42	21.668	201.87	15.262	11.51	0.189	46.27	4.360	113.02	10.621
253.48	17.788	339.32	21.942	208.02	15.559	12.92	0.264	50.75	4.946	118.84	10.986
259.84	18.110	346.10	22.191	214.17	15.840	14.53	0.369	55.26	5.505	124.95	11.360
266.20	18.452	Series II		220.31	16.149	16.52	0.525	59.90	6.059	131.17	11.721
272.57	18.772			226.46	16.435	18.80	0.733	64.54	6.592	137.24	12.068
278.93	19.105	150.96	12.780	232.60	16.736	21.39	1.004	69.48	7.097	143.32	12.408
285.27	19.429	155.60	13.016	238.85	17.078	21.09	0.970	74.76	7.616	149.41	12.728
291.81	19.761	161.22	13.310	245.20	17.414	23.86	1.292	80.08	8.127	155.51	13.045
298.57	20.085	166.84	13.594	251.68	17.753	26.97	1.686	85.43	8.614		
305.34	20.445	172.46	13.863			30.46	2.156	90.63	9.031		
312.22	20.754	178.09	14.142	Series III		34.19	2.682	95.66	9.405		
318.99	21.087	183.71	14.396	8.32	0.074	38.03	3.229	101.44	9.824		
		189.60	14.652	9.31	0.103						

temperatures) and are plotted in figure 1. The smoothed $C_{p,m}/R$'s at selected temperatures, and the corresponding molar thermodynamic functions listed in table 2, are calculated as described, and are affected by the same precision indices specified, in reference 1.

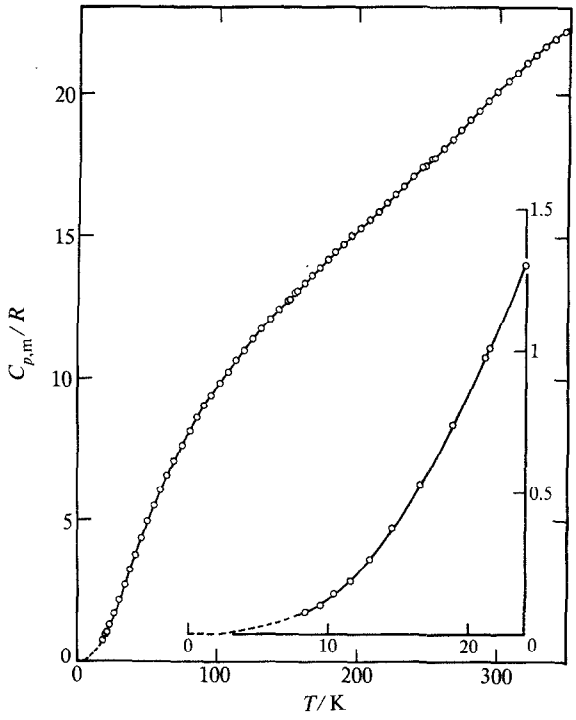

FIGURE 1. Molar heat capacity of potassium 2-methylpropanoate, $(CH_3)_2CHCO_2K$, between 8 and 350 K. The region below 24 K is enlarged in the lower right-hand corner.

TABLE 2. Thermodynamic functions for potassium 2-methylpropanoate, $(CH_3)_2CHCO_2K$ ($R = 8.3144$ $J \cdot K^{-1} \cdot mol^{-1}$)

$\frac{T}{K}$	$\frac{C_{p,m}}{R}$	$\frac{S^\circ_m(T)-S_m(0)}{R}$	$\frac{H^\circ_m(T)-H^\circ_m(0)}{R\,K}$	$-\frac{G^\circ_m(T)-H^\circ_m(0)}{RT}$
0	0	0	0	0
10	0.126	0.042	0.316	0.010
15	0.403	0.139	1.559	0.035
20	0.854	0.313	4.639	0.081
25	1.432	0.564	10.311	0.152
30	2.094	0.883	19.101	0.246
40	3.503	1.678	47.087	0.501
50	4.850	2.606	88.93	0.828
60	6.073	3.601	143.66	1.206
70	7.155	4.620	209.92	1.621
80	8.110	5.639	286.34	2.060
90	8.958	6.644	371.76	2.513
100	9.722	7.628	465.22	2.976
120	11.060	9.522	673.4	3.910
140	12.218	11.316	906.4	4.841
160	13.254	13.016	1161.3	5.758
180	14.222	14.633	1436.1	6.655
200	15.17	16.18	1730.1	7.531
220	16.13	17.67	2043.1	8.385
240	17.13	19.12	2375.6	9.220
260	18.14	20.53	2728.2	10.036
280	19.16	21.91	3101.2	10.835
298.15	20.08	23.14	3457.3	11.546
300	20.17	23.27	3494.5	11.618
320	21.12	24.60	3907.6	12.388
350	22.34	26.55	4560.2	13.519

In the sub-ambient region, no evidence was found for any phase transformation: the curve $C_{p,m}/R$ against T is completely smooth, as expected from the already mentioned large value (5.1) of the sum $(\Delta_{trs}S_m + \Delta_{fus}S_m + \Delta_{clr}S_m)/R$ obtained for the transformations occurring in the super-ambient region, as evidenced by d.s.c. records.[5]

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