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CALORIMETRIC STUDY OF THE PHASE CHANGES IN SOLID ETHANE

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The heat capacity of solid and liquid ethane was measured between 50 and 100 K. The transition occurs at 89.813 K with the heat of transition 2282 $Jmol^{-1}$. The triple point is 90.341 K and the heat of fusion is 583 $Jmol^{-1}$. The entropy of fusion is as small as 6.46 $JK^{-1} mol^{-1}$, indicating that the high temperature phase is a plastic crystal. The volume changes associated with the transition and fusion were derived as 1.05 cm^3mol^{-1} and 4.1 cm^3mol^{-1}, respectively. Molecular motion in the plastic phase is discussed.

1. Introduction

Recent discovery(1,2) of a phase transition in solid ethane below its melting point has prompted us to re-determine the heat capacity in the temperature range where the anomalies could be expected to occur.

Of a series of diatomic and pseudo-diatomic molecules of the first row elements, N_2, O_2, CO, F_2 and C_2H_2 are known to exhibit at least one phase transition, whereas H_2NNH_2, HOOH and H_2CCH_2 do not. There are reasons for the absence of transitions in the latter group: The molecules form hydrogen bonds or have a strong π-electron interaction. Molecules of the first group all possess cylindrical symmetry and form what are called plastic crystals below the melting point. Therefore it is predicted that the high-temperature form of ethane would also be plastic.

Earlier investigations(3-6) overlooked existence of the phase transition probably because it occurred at a close vicinity of the triple point; in fact, the transition point is only 0.53 K lower than the triple point as we shall show. Thus, Witt and Kemp(4) reported measurements of the heat capacity in 1937 and stated that the triple point was 89.87 ± 0.1 K, which actually was the transition point.

This Letter describes the results of precision measurements of the heat capacities of solid and liquid ethane between 50 and 100 K with particular attention to the transition and the melting regions.

2. Experimental

Commercial sample of high purity (better than 99.7 mol per cent) ethane was further purified by repeating fractional distillation to the final purity of 99.999 mol per cent as determined by the intermittent melting procedure. The quantity of the sample used for calorimetry was 0.2171 ± 0.0001 mol, which was the average of two independent determinations from P-V-T measurements before and after the calorimetric experiment. The corrections for non-ideality of the gas were made by using published values of the second virial coefficient(7).

The experimental set-up for calorimetry has been described in detail elsewhere(8). The temperature was measured with a Leeds & Northrup platinum resistance thermometer (model 8164) calibrated according to IPTS-68. No helium gas was introduced into the calorimeter vessel for heat exchange.

Thermal equilibrium within the calorimeter was generally attained in 15 min after the calorimeter heater was turned off except near the transition point. However, only between about 87 K and the transition point, the equilibration required as long as an hour.

The sample contributed more than 50 per cent to the total heat capacity at all temperatures studied. The vapor pressure of ethane was nowhere higher than 10 Pa so that the corrections arising from the heat of vaporization, the vapor heat capacity, the heat of compression, etc. were negligibly small.

3. Results and Discussion

The measured and the smoothed heat capacity values are given in Appendices 1 and 2 at the end of this Letter. Figure 1 compares those results with the results of Witt

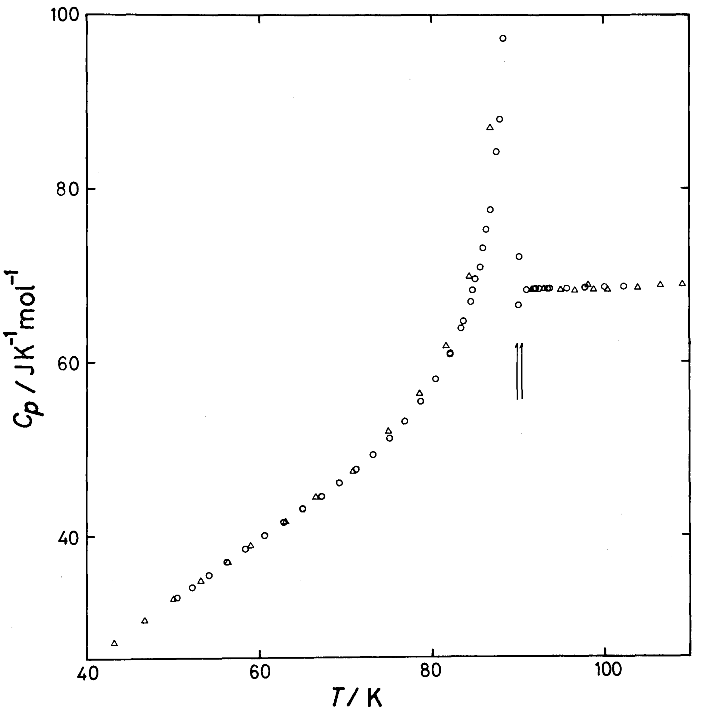

Fig. 1. Molar heat capacity of ethane. ○ This research, △ Witt and Kemp. (Two arrows indicate the positions of the transition and triple points).

and Kemp(4), where two vertical arrows indicate the positions of the transition and the triple points. Agreement of the two results is excellent except in the transition region.

Fusion: The result of an intermittent melting experiment is shown in Table 1. By extrapolation, the triple point of our specimen was determined as 90.340 ± 0.002 K and that of pure ethane 90.341 ± 0.002 K. Liquid-soluble, solid-insoluble impurities amounted to less than 0.001 mol per cent. Determination of the heat of fusion was somewhat arbitrary because there were only few measured points between the transition and the fusion temperatures. It was estimated to be 583 ± 1 $\mathrm{Jmol^{-1}}$ and the corresponding entropy of fusion was 6.46 ± 0.01 $\mathrm{JK^{-1}mol^{-1}}$. The entropy value, which is smaller than 20 $\mathrm{JK^{-1}mol^{-1}}$(9), confirms our prediction that the high-temperature phase is a plastic crystal.

Table 1. The results of intermittent melting experiment.

Fraction melted	Temperature / K
0.243	90.3377
0.476	90.3396
0.664	90.3396
0.851	90.3400
(1.000)	(90.340 ± 0.002)

The triple point of pure ethane
90.341 ± 0.002 K.

Transition: The anomalous heat capacity associated with the transition has a long tail on the low-temperature side. However, the cooling curve through the transition region showed that the transition is easily undercooled. This suggests that the transition is of the first order. The transition point was determined to be 89.813 ± 0.005 K from the point of maximum slope in the enthalpy=temperature plot of Fig. 2.

To evaluate the heat of transition, the "normal" portion of the heat capacity was estimated by the formula

$$C_p(\mathrm{normal})/\mathrm{JK^{-1}mol^{-1}} = 0.69933T/\mathrm{K} - 2.385 \qquad (1)$$

which was derived by the least-squares fitting between 50 and 70 K. The excess over Eq. 1 was then used to derive the heat of transition 2282 ± 2 $\mathrm{Jmol^{-1}}$ and the entropy of transition 25.48 ± 0.02 $\mathrm{JK^{-1}mol^{-1}}$.

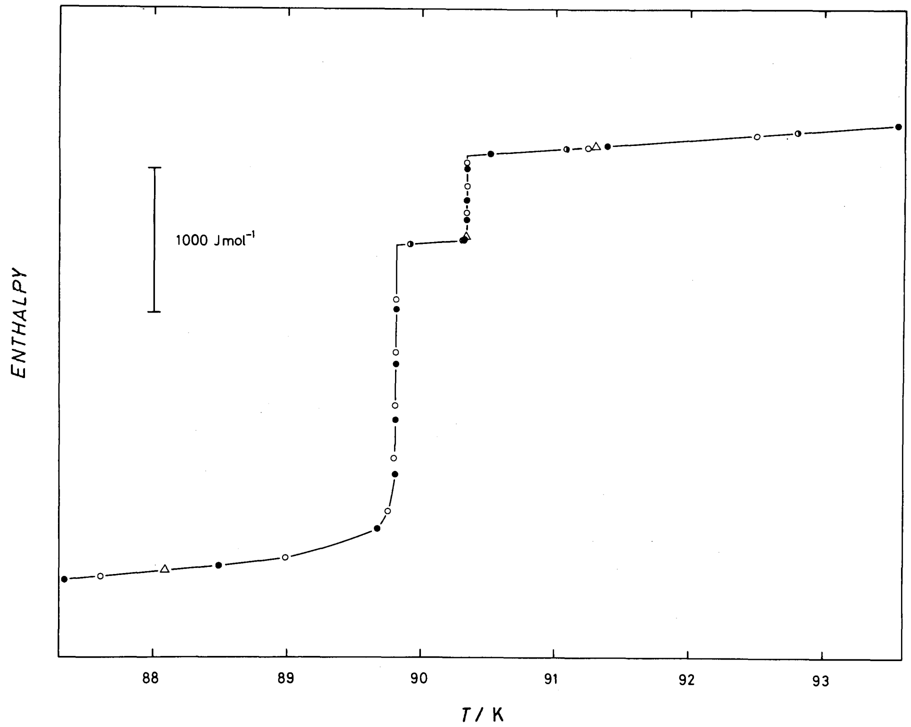

Fig. 2. The enthalpy change near the transition and triple points.
○ Series 1, △ Series 2, ● Series 3, ◑ Series 4.

Molecular freedom of motion in the plastic phase: Let us consider the behavior of solid nitrogen as a typical diatomic molecular crystal. The X-ray diffraction studies showed that nitrogen molecules precess about the c-axis in the high-temperature plastic phase(10). Its entropy of fusion is 11.41 JK^{-1}mol^{-1}. Carbon monoxide is known to be isostructural with N_2 and its entropy of fusion (12.30 JK^{-1}mol^{-1}) is almost the same as that of N_2. Therefore CO molecules probably precess in a similar way, the molecular head and tail being distributed randomly. Now, in the case of ethane, its entropy of fusion determined by the present study is as small as 6.46 JK^{-1}mol^{-1}, even smaller than the entropy of fusion of inert gas solids (about 14 JK^{-1}mol^{-1}). This would indicate two things; i.e. one is that ethane molecules have a larger degree of freedom of motion in the plastic phase than N_2 or CO, probably undergoing spherical reorientation. The other is that there must be some short-range order persisting in the liquid state at least immediately above the melting point because the entropy of fusion is smaller than R, the communal entropy.

A similar conclusion may be drawn by examining the volume changes on melting. By using the phase diagram of ethane, one could derive the initial slope dp/dT of the equilibrium curve. This was then combined with the entropy change to compute the volume change on melting to be 1.05 cm^{3}mol^{-1} or only 2.2 % of the molar volume. In comparison with this value, the volume change for N_2 is 2.81 cm^{3}mol^{-1} or 8.1 % of the molar volume, thus showing that there is little change in the extension in the accessible configurational space in the case of ethane. The volume changes determined here agree well with the estimates from dilatometric study(1). Similarly the volume change at the transition point of ethane was found to be 4.1 cm^3mol^{-1}, compared with 4.56 cm^3mol^{-1} in the case of N_2.

The entropy that arises from excitation of internal rotation amounts to 0.57 $JK^{-1}mol^{-1}$ at 90 K if a value of 12.03 $kJmol^{-1}$ is assumed for the barrier hindering the rotation. The entropy of this magnitude cannot be a substantial portion of the entropy of fusion. Therefore, the ethane molecule not only reorient themselves but also undergo internal rotation in the plastic phase.

It is difficult to speculate about the structure in the low-temperature phase at the present stage but it is interesting to note that the transition point is much higher and the entropy of transition is much larger than those of N_2 in spite of the fact that the electric quadrupole moment of the molecule is much smaller⁽¹¹⁾. This suggests that the low-temperature structure of ethane is determined by a principle different from the case of N_2; the predominant interaction will probably be a repulsive one.

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Appendices

1. Measured Heat Capacities of Solid and Liquid Ethane.

IPTS-68

T / K	C_p / $JK^{-1}mol^{-1}$	T / K	C_p / $JK^{-1}mol^{-1}$	T / K	C_p / $JK^{-1}mol^{-1}$
(Run 1)		(Run 2)		93.548	68.444
82.098	60.754	88.298	97.372	(Run 3)	
83.402	63.865	(Transition and fusion)	Series 1	90.044	66.610*
84.675	68.311			(Fusion)	
85.913	73.210	91.875	68.441	91.832	68.436

Appendix 1. (continued)

(Run 4)	
50.522	32.933
52.243	34.120
54.166	35.522
56.245	36.978
58.420	38.484
60.640	40.052
62.852	41.550
65.042	43.071
(Run 5)	
67.179	44.519
69.241	46.109
71.248	47.656
73.204	49.337
75.095	51.200
76.930	53.141
78.714	55.425
80.441	58.005
82.119	61.032
83.638	64.672
84.985	69.572
86.273	75.265
87.489	84.305
(Transition and fusion)	Series 2
(Run 6)	
84.505	66.941
85.624	70.941
86.756	77.575
87.912	88.055
(Transition and fusion)	Series 3
90.953	68.334
92.470	68.433
(Run 7)	
90.112	72.219*
(Fusion)	Series 4
91.946	68.429
93.682	68.484
95.683	68.534
97.932	68.634
100.163	68.648
102.390	68.685

* plastic phase

2. Smoothed Heat Capacity Values of Ethane at Rounded Temperatures. IPTS-68

T/K	C_p/JK^{-1}mol^{-1}	T/K	C_p/JK^{-1}mol^{-1}	T/K	C_p/JK^{-1}mol^{-1}
50	32.54	70	46.66	87	79.50
55	36.10	75	51.06	91	68.38
60	39.59	80	57.32	95	68.52
65	43.03	85	68.68	100	68.66

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