Heats of Transition of Hexachloroethane

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It is known that the crystalline hexachloroethane has three modifications; triclinic, monoclinic and cubic. The transition points are 45°C (triclinic~monoclinic) and 72°C (monoclinic~cubic), respectively. X-ray investigations of these transition phenomena have been already undertaken by Finback[1] and West,[2] of whom the former concluded that in the cubic modification the molecules as a whole are in the rotational motion in a rough sense.

In connection with the structual investigations, Nitta and one of the authors[3] had several years ago measured the vapor pressures of this substance and found that the entropy change at 72°C is greater than that change at the melting point. This result suggests that the cubic modification of this substance may be a sort of the so-called plastic crystals.[4]

On the other hand, the transition point at 45°C was not found from our vapor pressure curves. Nelson[5] had already measured the vapor pressures below 72°C, but he could not

(1) C. Finback, *Tids. Kjmi. Bergwsen.*, **17**, No. 9 (1937)

(2) C. D. West, *Z. Krist.*, **88**, 195 (1934)

(3) I. Nitta, S. Seki, *J. Chem. Soc. Japan*, **62**, 581, (1941)

(4) According to the recent investigation by Aston and Pace, in the case of hexafluoroethane also the entropy change at transition point is greater than that at melting point. *J. Am. Chem. Soc.*, **70**, 566 (1948)

(5) Nelson, *Ind. Eng. Chem.*, **22**, 227 (1930)

also find the transition at this temperature.

Recently, Ivin and Dainton[6] have reported the measurement of vapor pressure of hexachloroethane without finding the lower transition point. From the accuracy of their apparatus they estimated that the enthalpy change at this transition point may be smaller than 700 cal./mol. Their data on vapor pressures are somewhat lower than our values, but much better agreement with ours than with that of Nelson when compared. It is also found from their results that the heat of transition at 72°C amounts to 1.9 ± 0.3 kcal./mol., which is in good agreement with our data, 2.07 kcal./mol.

It is now very desirable to determine the heat of transition at 45°C by the direct specific heat measurement. For this purpose and also as a part of our thermochemical investigation of plastic crystals, we have constructed a conduction calorimeter and measured the specific heats of this crystal. The details of experimental procedures may be described elsewhere. The obtained specific heat curves are represented in the accompaning figure and a part of the specific heats as well as heats of transition are indicated in Tables 1 and 2.

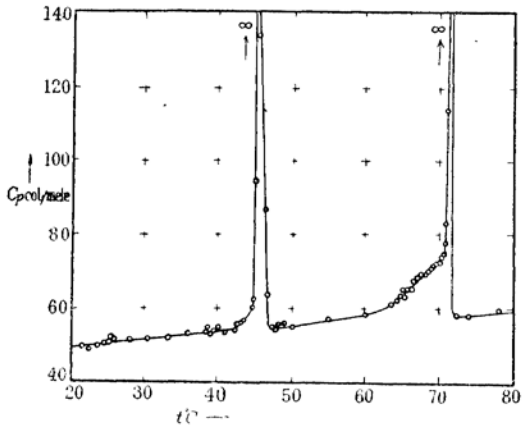

Fig. 1

Table 1
Specific heat of hexachloroethane

t°C	C_p cal./mol	t°C	C_p cal./mol	t°C	C_p cal./mol
22.25	48.9	45.80	110.7	67.47	68.8
23.45	49.7	43.05	95.9	68.18	68.6
24.55	51.5	46.55	86.5	68.48	69.3
25.35	52.1	46.75	63.0	68.85	69.1
35.95	52.9	47.45	54.8	69.09	70.9
37.85	53.4	47.70	54.2	69.45	71.0
38.51	54.8	47.95	55.3	69.90	71.7
39.35	53.3	48.55	55.9	70.14	73.3
41.12	53.0	48.95	55.0	70.50	74.2
42·90	55.7	50.00	54.7	70 63	77.2
43.25	56.4	55.05	55.7	70.85	82.6
44.58	59.9	60.0	57.7	transition	
44.75*	62.0	63.60	60.5		
45.40*	94.2	64.25	61.3	70.99	113.2
45.55*	328.7	64.65	63.0	71.02	175.3
transition		65.00	64.3	71.07	501.3
		65.35	62.0	71.50	307.9
45.00	253.9	65.70	64.4	72.70	57.1
45.15	213.8	66.05	64.4	73.80	57.3
45.25	173.8	66.40	66.9	78.00	58.7
45.40	133.5	67.10	67.7		

* superheating

Table 2

	t°C	ΔH cal./mol.	ΔS e. u.	ΔV cc./kg.
Transition	45.0	613[c]	1.93[c]	9.7
Transition	71.4	1965[c] {1900±300[a], 2070[b]}	5.70[c]	28.0
Melting	185	2330[d]	5.50[d]	—

a. K. J. Ivin, F. S. Dainton[6]
b. I. Nitta, S. Seki[3]
c. This research
d. Van der Lee

Since the transition at 45°C was found frequently to be superheated, we have measured the specific heat as slowly as possible (0.1°/minute) to avoid this. The observed magnitude of heat of transition at 45°C (613 cal./mol.) is in good agreement with that expected from the vapor pressure measurement by Ivin and Dainton and also by us. As shown in the figure, the upper transition is accompanied by the preceding gradual increase of specific heat. The heat of transition at 72°C (1.965 cal./mol) obtained by this direct method is also consistent with the data from the vapor pressure measurements.

In the table, the volume changes at transition points are also presented. We can see a very good parallelism between the entropy and the volume changes at these transition points.

For the theoretical treatment of the transition energies from the point of view of structual chemistry, it is necessary to determine the crystal structure more accurately. For this purpose, the X-ray analyses of these three modifications are now going on in this laboratory by other members and for the cubic form a model of molecular motions more precise than that of Hassel is gained. The discussion of the mechanism of the transitions may be postponed, to bring this investigation to completion.

In conclusion, the authors wish to express their sincere thanks to prof. Nitta for his kind guidance throughout this work. This study was helped by the Research Grant given by the Ministry of Education.

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(6) K. J. Ivin, F. S. Dainton, *Trans. Faraday Soc.*, **43**, 32 (1947)