59. *On the Phase Transition in Pentaerythritol (I).*

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(Comm. by S. NISHIKAWA, M.J.A., Nov. 13, 1950.)

It has been already known from the crystal structure determined independently by Watanabé and one of the present authors^{1a)} and by Cox and his co-workers^{1b)} that the molecules in this tetragonal crystal are linked together by hydrogen bonds in such a way that they constitute typical layer lattice. Recently two of the present authors and Suzuki have measured the vapor pressures of this tetragonal form at various temperatures and determined the lattice energy of this crystal. They have also calculated theoretically the lattice energy and by comparing these results they evaluated the energy of hydrogen bond in this crystal.²⁾ On the other hand, it has also been found by Ebert³⁾ in 1931 that this substance undergoes transformation at about 180°C. The crystal structure of the high temperature cubic form has been then determined by Watanabé and one of the present authors in 1938⁴⁾.

It will be now of some interest to elucidate the mechanism of this transition phenomenon from the knowledge of these crystal structures and thermal and other properties. For this purpose, we have measured the specific heats of this crystal at various temperatures and determined the heat effect accompanied with the transition, of which the experimental results will be given in the present paper.

Materials and Experimental Method

The sample used in the beginning was the product of Kahlbaum Company, recrystallized from distilled water, and finally dried over calcium chloride for about two months. As will be mentioned below, it was found that this sample showed a slight anomaly of specific heat at about 120°C. From our preliminary observation, it has already been known that the transparent single crystal of this substance became opaque at about 130°C when it was heated in a closed glass tube. It has been also found by x-ray investigation in our laboratory in 1939 that the thermal expansion coefficient along the *c*-axis went down slightly around this temperature⁵⁾. As these phenomena occur at nearly one and the same temperature, it may be supposed that they are correlated to each other.

It is generally known that crystalline alcohols occasionally form stable hydrates and on the other hand that sometimes it is very

difficult to remove trace of water from the crystals⁷⁾. Thus, in order to confirm whether the above-mentioned behavior may be of essential nature for this crystal or due to the trace of water involved in the specimen, we have tested by an oil manometer the evolution of water from the crystal on heating the sample under high vacuum. This experiment showed that the evolution of water became evident at about 130°C and then increased more markedly with the rise of temperature, reaching to a maximum at the transition temperature, after which it became negligible. Hence, in order to remove trace of water from the crystal, the sample should be heated above the transition temperature under high vacuum^{8,9)}. Thus for the subsequent use we have purified this crystal by fractional sublimation under high vacuum (below 10^{-4} mmHg) at about 200°C. The transition and melting points of the sample extremely purified in this way were, then, determined by the differential thermal analysis. The results are shown in Fig. 1 and Table II. It was found that these values are higher than any

Fig. 1. Curves of differential thermal analysis for the determination of the transition and the melting points of pentaerythritol.

previously reported⁹⁾. For the measurement of the specific heat we used a conduction calorimeter. By means of this, we could measure also the specific heat in the direction of descending temperature. The accuracy of using the apparatus has been already determined by our own measurement of the specific heats and heats of transitions of hexachloroethane⁷⁾. The details of the construction and operation of this calorimeter will be published later. We have measured always the specific heat at the heating rate

of about $0.1^{\circ}\text{C}/\text{min}$. It took about fifteen hours from the beginning of transition to its completion.

Experimental Results

All the obtained specific heat-temperature curves are illustrated in Fig. 2. The curve (a) is the one obtained using the sample which is merely recrystallized from water and not further purified by sublimation. However, after heating up to about 130°C and then cooling down to about 100°C , the same sample did not show such anomaly anymore on heating again up to about 145°C (curve (b)). Keeping the sample at a constant temperature of 145°C for about three hours, the specific heat for that temperature drops to a smaller value and then increases continuously with rising temperature as shown by the curve (c). The rapid increase of the curve with temperature begins at about 180°C , but it does not reach to the infinite value and the first peak is followed by a sharp drop down to the magnitude of about 650 cal/mole (the details of this behavior is shown in an enlarged scale by curve (d) in Fig. 2), the curve then rises to the infinite value at 187.7°C and finally falls down to the value of ordinary magnitude⁸⁾. The specific heats

Fig. 2. Specific heats of pentaerythritol as functions of ascending and descending temperature.

of this sample measured in the direction of descending temperature are indicated by curve (e). In this case, a considerable supercooling effect took place and, besides, there appeared also a small anomalous shoulder at about $183^{\circ}\text{C}^{\circ}$. We have here, like other higher order transition, a typical λ -type anomaly of specific heat. However, the repeated measurement using the sample extremely purified by fractional sublimation gave the results shown by curves (f) and (g) in Fig. 2. Of these curves (g) may probably be considered to be more reliable. In these curves we do not find any gradual pretransition rise and any fine structure as found in curves (c) and (d). Thus, we may conclude that these effects are ascribed to the intimately combined trace of water. The dilatometric investigation, which has been carried out in our laboratory with the extremely purified sample and of which a detailed account will be given later, has revealed that the above-mentioned anomalous effect of the thermal expansion coefficient is also due to the presence of minute amount of water. These results are also in accordance with the experiment of the evolution of water from the crystal. It will now be concluded that pentaerythritol, when extremely purified, shows rather sharp and narrow transition of the type of the first-order and not of the typical λ -type.

Table I.
Specific Heats of Pentaerythritol.

$t^{\circ}\text{C}$	C_p cal./mole	$t^{\circ}\text{C}$	C_p cal./mole	$t^{\circ}\text{C}$	C_p cal./mole
100.0	60.8	170.0	83.1	185.0	107.6
110.0	61.1	175.0	86.1	186.0	148.8
120.0	61.4	177.0	89.1	186.1	162.7
130.0	63.4	179.0	92.2	186.2	207.3
140.0	65.7	180.0	92.7	186.3	266.2
150.0	70.5	181.0	93.5	186.4	348.4
160.0	76.7	183.0	98.4	190.2	103.3
165.0	79.8	184.0	102.2	193.2	103.8

These data are interpolated from smooth curve (g) through the experimental observation.

Table II.
Enthalpies and Entropies of Transition and Fusion.

	$t^{\circ}\text{C}$	ΔH cal./mole	ΔS e.u.
Transition	187.7	10.5	22.8
Melting	265.5	1.7	3.2

Table I gives a part of specific heats measured at various temperatures, the data corresponding to curve (g). Table II shows

obtained enthalpy and entropy changes at the transition and the melting points***). The data at the melting points are estimated from the comparison of the heat of transition of the specific heat data with the results obtained from the differential thermal analysis. Their accuracy is thus less than those for the transition. So far we have obtained thermal data of the transition of pentaerythritol, of which the mechanism will be discussed later.

References

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- 2) I. Nitta, S. Seki, and K. Suzuki: *Bull. Chem. Soc. Japan*, (in press).
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- 4) I. Nitta and T. Watanabé: *Bull. Chem. Soc. Japan*, **13** (1938) 28.
- *) I. Nitta and T. Watanabé: (unpublished data).
- 5) For instance: Trapezorikov, *Acta Physicochim. U.R.S.S.* **XX**, 589 (1945); J.D. Hoffman and C.P. Smyth, *J. Am. Chem. Soc.*, **71** (1949) 431; F.E. Young and F.T. Jones, *J. Phys. and Colloid Chem.*, **53** (1948) 1320; J. M. Robertson and A.R. Ubbelohde, *Proc. Roy. Soc.*, **A167** (1938) 145.
- **) By this experiment it was found that the water involved in the crystals, which could not be removed at room temperature even under high vacuum, amounted to about 0.04 mole per one mole of pentaerythritol. Suzuki in our laboratory has also found similar circumstances in the case of sample which was recrystallized from methanol.
- 6) m.p.: Ebert, 260.5°C; Mark, 252.5°C; Seifert, 252°C; Schleede, 257°C; t.p.: Ebert, 179.5°C.
- 7) S. Seki and M. Momotani: *Bull. Chem. Soc. Japan*, **23** (1950), 30.
- 8) Similar fine structure in the specific heat curve is found for KD_3PO_4 : W. Bantle, *Helv. Phys. Acta.*, **15** (1942) 373.
- 9) Similar behavior is known for KNO_3 ; H. Miekko-Oja, *Ann. Acad. Sci. Fennicae, Ser. A1 Math.-Phys.*, **7** (1941).
- ***)) These results are somewhat different from the data of Mr. S. Hoshino, according to his private communication. We are indebted to him for the opportunity of seeing his results in advance of publication.