On the Phase Transition of Pentaerythritol

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Introduction

It is well kown that the crystal of pentaerythritol, $C(CH_2OH)_4$, shows a phase transition accompanying a change of the lattice form at about 180°. The crystal structures of low and high temperature modifications of this crystal have been determined by Nitta and Watanabe,(1) and others.(2) According to their reports the tetragonal form at room temperatures has a layer structure and in each layer molecules are bound by hydrogen bonds with each other, while in the cubic form at above 180° oxygen atoms in the molecule take statistical positions.

Since the nature of the phase transition of pentaerythritol and the accompanying changes in intermolecular and atomic binding will largely depend on the existence of hydrogen bond, it seems of interest to know the thermal behavior of this substance at the transitional range. We performed, therefore, specific heat measurements for this crystal. There are, however, some difficulties in the experimentation with this crystal. First, the complete purification of the specimen is very difficult, so that we can not expect to obtain accurate experimental data corresponding to that of the pure substance. Furthermore, the heat measurement is considerably disturbed by the fact that this crystal holds a very large transition energy and a high sublimation pressure. On account of these obstructions we could not obtain accurate data, but the obtained result as described below may be sufficient to show the general trend of the phenomenon.

Measurement of the Specific Heat, and Calculations of the Heat of Transition and of Fusion, and the Corresponding Entropy Change

We used the apparatus which has been reported by Takagi and one of the authors.(3) The sample for the specific heat measurement was put into a vessel made of pyrex (Fig. 1). The heat given to the specimen was generally in the range of $1/100 \sim 1.5/100$ cal./g.sec., and the velocity of temperature rise, at the range corresponding to the normal specific heat, was about $40 \sim 60$ sec./deg. The weight of specimens was in the order of 10 g.

Fig. 2 shows the "specific heat-temperature curve". The anomaly at about 180° corre-

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(1) I. Nitta and T. Watanabe, *Nature*, **140**, 365, (1937); This Bulletin, **63**, 28-35, (1938).

(2) F. J. Llewellyn, E. G. Cox and T. H. Goodwin, *J.Chem. Soc.*, **1937**, 883.

(3) S. Nagasaki and Y. Takagi, *J. Appl. Phys. Jap.*, **17**, No. 5, 104 (1948).

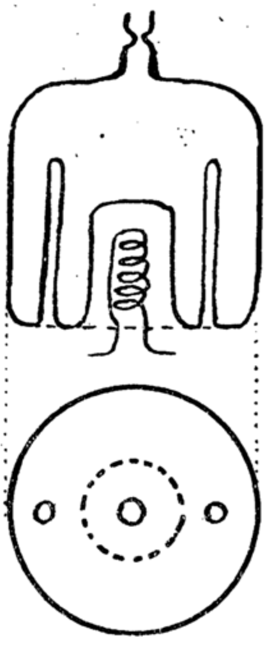

Fig. 1.— Glass vessel.

sponds to the transition of the crystal form from a tetragonal structure to a cubic one; and a peak at about 260° corresponds to melting. Above the melting temperature the curve rises again, owing to the vaporization of the substance. In order to avoid the influence of the sublimation of the specimen, we also performed the measurement with the sample sealed in the vessel. These results are shown in Figs. 3, 4. In these diagrams the dotted lines showing the cooling curves are indicated by an arbitrary scale. The broken lines are the reheating curves. In Fig. 4, it should be noted that in cooling and reheating processes there does not appear the latent heat of crystallization, or that of fusion. From these curves we calculated the heat of transition and of fusion, and the corresponding entropy changes, which are shown in Table 1.

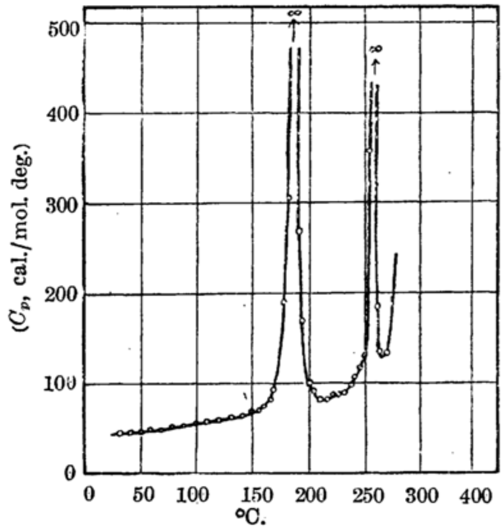

Fig. 2.— C_p-Temperature curve.

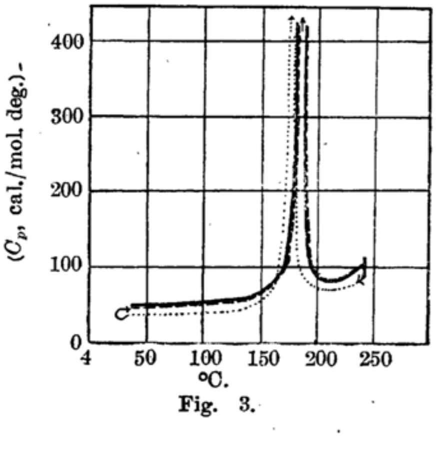

Fig. 3.

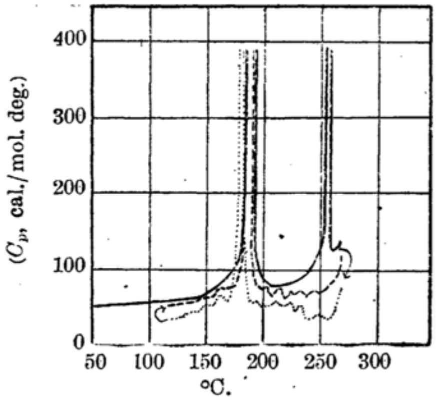

Fig. 4.

Table 1

	a	b
Transition point	184°C.	184°C.
$\Delta E_{\text{trans.}}$	8.4 kcal./mole	6.2 kcal./mole
$\Delta S_{\text{trans.}}$	8.5 R	6.5 R
Melting point	256°C.	——
$\Delta E_{\text{melt.}}$	1.3 kcal./mole	——
$\Delta S_{\text{melt.}}$	1.3 R	——

ΔE—energy change
ΔS—entropy change
a: data from the normal curve
b: from the anomalous reheating curve

Measurement of the Heat of Sublimation

In Fig. 2 we see that above the melting point the curve shows an anomalous rise. This phenomenon may be due to the vaporization of the sample. A direct measurement of the heat of vaporization is also possible by the method similar to the specific heat measurement, if we use a vessel of a copper block as indicated Fig. 5, and fill the upper cavity of the vessel with the sample. The vapor, evaporated from the sample at above 260°, is exhausted little by little by use of a vacuum pump. Obtained result is given in Fig. 6. In this figure the dotted line corresponds to the contribution due to the

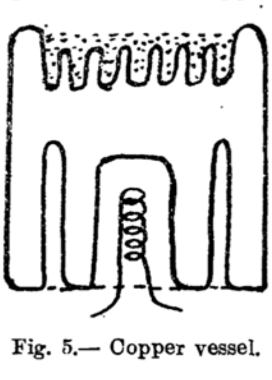

Fig. 5.— Copper vessel.

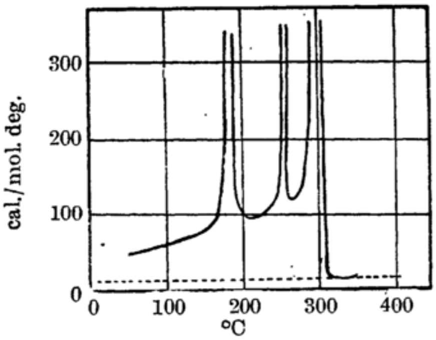

Fig. 6

copper vessel. The heat of vaporization can be estimated by the procedure of the calculation, just the same as that of the heat of transition. A mean value of the several measurements is about 22 kcal./mole. Using this value, the heat of transition and the heat of fusion, we can estimate the heat of sublimation of this crystal in the state of low or high temperature modification.

Now we will offer a discussion of the obtained results in the last section.

Discussion of the Results

By Fig. 2 and Table 1 *a*, we know the general nature of the specific heat curve and the values of the energy and entropy changes corresponding to the respective phase changes. We shall first discuss the heat of lattice transition and of fusion. Though the transition energy, owing to the change of crystal form, is large in value compared with that of many other substances, it is still too small to destroy all the hydrogen bonds existing in this crystal, because the bond energy of O—H···O is about 6.2 kcal./mole⁽⁴⁾ for methyl or ethyl alcohol, and pentaerythritol includes four hydrogen bonds in one molecule. This fact seems to mean that all of OH radicals in the high temperature cubic modification are not "rotating" freely. This conclusion has been confirmed by X-ray analysis.⁽¹⁾ It is also noted that the transition energy is several times greater than the heat of fusion, which is probably indicative of the fact that the crystal structure of the cubic form somewhat resembles the structure of the liquid state.

The great value of transition energy seems to mean that the phase transition of this crystal is related to the breaking of some hydrogen bonds. The observed value 8.4 kcal./mole agrees with the energy required to cut one hydrogen bond per molecule. We can expect, therefore, that pentaerythritol is containing some free OH radicals, not only in the liquid state but also in the high temperature crystal form. According to the result of the crystal analysis, the hydrogen bonds are arranged in two-dimentional layers in the structure of low temperature form. On the other hand, in the high temperature form, which is the cubic crystal, the three axial directions are equivalent to each other, so that the hydrogen bonds should form a three dimentional network. From the above consideration we can assume that in the high temperature cubic form there are only three hydrogen bonds per molecule, which are statistically arranged in a three dimentional way. We may also expect the behavior of the hydrogen bond in the liquid state to be similar to that in the cubic crystal form.

To ascertain the above conclusion, some experiments, such as the measurement of infrared absorption and observation of Raman effect, may be performed. Especially, the X-ray investigation of the diffuse scattering by using a single crystal of this substance may be important. However there are some difficulties in the experiment, since this crystal has a large thermal expansion coefficient, and therefore we can not easily obtain the single crystal of the high temperature form.

In the preceding section we stated that the heat of sublimation at room temperatures can be estimated as the total sum of the heat of transition, fusion and vaporization. The value obtained by this procedure is about 32 kcal./mole, and it is considered to contain the energy required to destroy all the hydrogen bonds. If we estimate this energy by using a value obtained from the other simple alcohol,⁽⁴⁾ it is about 25 kcal./mole. The difference of these values may be due to the contribution of the van der Waals energy of lattice. According to the latest publication⁽⁵⁾ the heat of sublimation of this crystal, determined by the method of vapor pressure measurement, is 31.4±0.2 kcal./mole at 120°, and it is in harmony with the result of our direct measurement.

We observed a fact difficult to explain well. Namely, when we cool the sample from above the melting temperature, the cooling curve (dotted line in Fig. 4) shows no clear latent heat of crystallization. The reheating curve (broken line) is also similar to this, and the transition energy calculated from the latter curve is exceedingly smaller than that from the normal curve (Table 1*b*). That is to say, the substance, which has once been heated above the melting temperature, does not completely return to the initial state when it cools. This peculiarity may be explained by the consideration that the sample polymerizes partly,

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(4) L. Pauling, "Nature of the Chemical Bond," p. 304.

(5) I. Nitta, S. Seki and K. Suzuki, unpublished yet, reported at the Meeting of the Chemical Society of Japan held at Osaka on 19th Nov. 1949.

or it becomes glassy. However, it is neccessary to make a deeper study, in order to give a conclusive explanation for this point.

In conclusion we wish to express our sincere thanks to Prof. I. Nitta, who kindly gave us the sample, and to M. Momodani for his valuable advice. This investigation was done throughout under the kind guidance of Prof. Y. Takagi, to whom the authors express also their best thanks. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the authors' thanks are due.

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