CHEMISTRY LETTERS, pp. 1347-1350, 1985.

SOLID-SOLID TRANSITION IN HEXAMETHYLBENZENE THAT DEPENDS ON THERMAL HISTORY[1)]

Yoshikazu YOSHIMOTO,[††] Takahiro FUJIWARA,
Tooru ATAKE,[†] and Hideaki CHIHARA*
Chemical Thermodynamics Laboratory and Department of Chemistry,
Faculty of Science, Osaka University, Toyonaka, Osaka 560
[†]Research Laboratory of Engineering Materials, Tokyo Institute of
Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 227

New results about the II-III phase transition in hexamethylbenzene have been obtained, which show large hysteresis. From the adiabatic calorimetry in the cooling direction, combined with those in the heating direction, the true transition point was determined to be 115.5 ± 0.3 K with the entropy of transition, 9.55 ± 0.08 J$\cdot$K$^{-1}\cdot$mol^{-1}. Under certain conditions, the anomalous heat capacity curve can be made to consist of two separate peaks. It is a manifestation of "memory effect" of the first-order transition.

The transition temperatures of solid-to-solid phase transitions have been considered to be the most accurate if they are the ones determined by the adiabatic calorimetry. In the case of the first-order phase transitions, however, inherent hysteresis effect is almost unavoidable and makes it difficult to interprete the "equilibrium" calorimetric properties at and in the vicinity of the transition point.2) The present letter provides new results about the transition in hexamethylbenzene at about 117 K, which give clear evidence that the adiabatic calorimetric measurements do not represent the "equilibrium" properties in the case of first-order transitions if measured only in the heating direction. The results obtained by combining the adiabatic calorimetric measurements both in the heating and the cooling directions showed that not only the transition temperature but also the shape of the heat capacity anomaly is strongly dependent on the thermal history of the specimen, a manifestation of "memory effect" of the first-order transition.

We have recently developed a novel type of adiabatic calorimeter which works in the cooling direction.3) Use of the calorimeter in combination with the ordinary adiabatic calorimeter (in the heating direction) made it possible to campare the "equilibrium" properties in the heating and cooling directions with the comparable precision. Not only were the properties different in an interesting way but there was strong dependence of those properties on the temperature to which the specimen had been heated or cooled before the heat capacity measurements were commenced, i.e. an effect which might be called the memory effect.

[††] Present address: Central Research Laboratory, Sharp Corporation, Tenri, Nara 632.

Our previous studies on hexamethylbenzene revealed that its phase transition between Phase III and Phase II was not of the second-order as had been considered but actually it was of the first-order with a very broad anomaly of heat capacity superimposed on top it.[4)] What puzzled us was the fact that the transition temperature we obtained (117.5 K) was very different from the previous determinations (108 K[5)] and 116.48 K[6)]) by the usual standards of adiabatic calorimetry. The purity of the specimen did not seem to be the problem.

The present experiments were carried out by using the same specimen as in the previous paper, that has a purity of 99.99%. We remeasured the heat capacity only in the transition region in question after various heat treatments. Figure 1 shows the typical results in the heating direction. In this series of measurements, the pulverized crystals were first heated to 180 K and cooled down to T_r below the transition region, where the measurements were begun upwards.

Although no special allowance was made to anneal the specimen at T_r, apparent equilibrium condition that there is no spontaneous heat evolution was noted at T_r before heat was input for the measurements. If we take the point of maximum slope of Fig. 1 as the transition temperature T_t, T_t becomes higher and the enthalpy of transition ΔH_t becomes larger as T_r is chosen to be lower. The relationship between T_t and T_r is shown in Fig. 2. When T_r is chosen at 78 K, the transition temperature was the same (highest T_t) as when the specimen was cooled to a much lower temperature (T_r < 15 K) and the enthalpy of transition was also the largest (1103 ± 5 J•mol^{-1}).

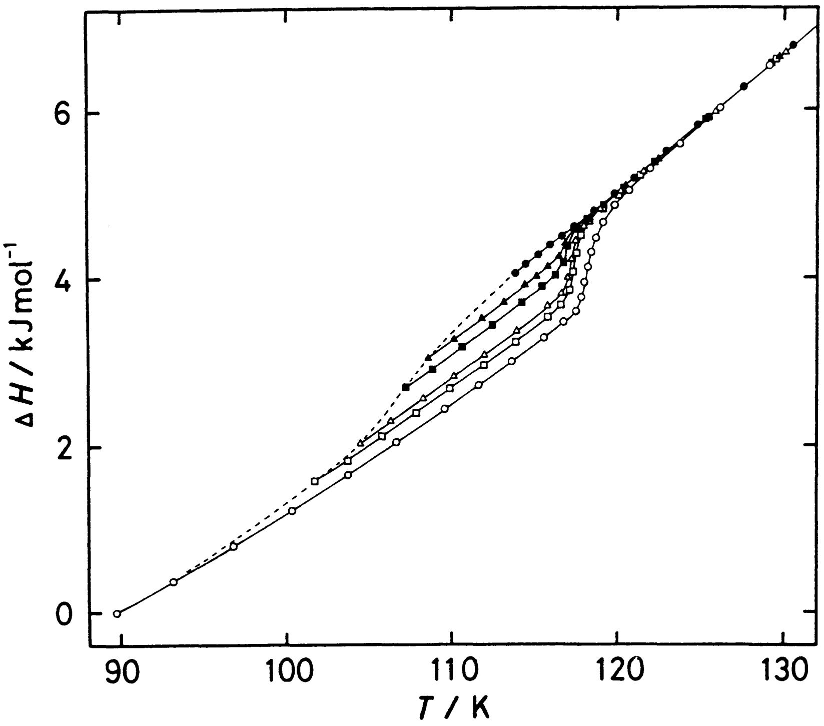

Fig. 1. Enthalpy of hexamethylbenzene measured in the heating direction. Each series of measurements is denoted by a different symbol: ●, T_r = 113.9 K; ▲, T_r = 108.6 K; ■, T_r = 107.3 K; △, T_r = 104.5 K; □, T_r = 101.7 K; ○, T_r = 78.0 K.

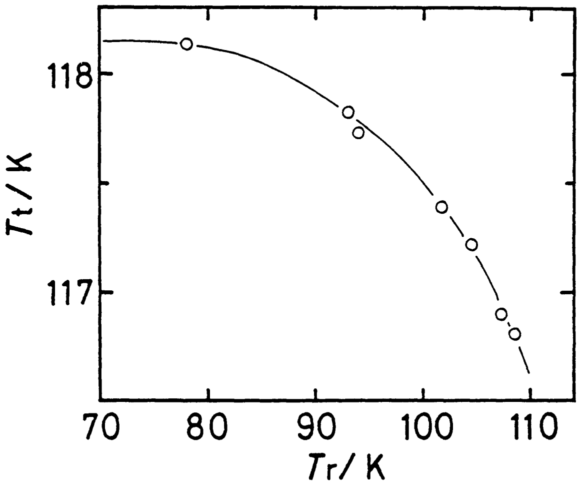

Fig. 2. Relationship between T_t (transition temperature) and T_r.

The other feature of Fig. 1 is that the transition becomes more diffuse as T_r is made closer to T_t: Apparent equilibrium was attained at each measured point by waiting long enough time (several hours) for the temperature of the specimen to reach a stationary value even in the transition region.

Measurements in the cooling direction led to the inverse results, i.e. the threshold value of T_r, below which the T_t and ΔH_t depended on T_r, was as high as 160 K and, only when T_r was higher than 160 K, ΔH_t was essentially the same as the maximum value of the enthalpy of transition in the heating direction.

The true or equilibrium temperature T_t* of transition must then lie between the highest T_t in the cooling experiments and the lowest T_t in the heating experiments, i.e. T_t* = 115.5 ± 0.3 K, in comparison with the literature values, 108 K,[5] 116.48 K,[6] and 117.5 K,[4] all determined from the heat capacity peak in the heating direction. The corresponding entropy of transition was 9.55 ± 0.08 $J\cdot K^{-1}\cdot mol^{-1}$; literature values are 9.68,[5] 10.08,[6] and 8.3[4] $J\cdot K^{-1}\cdot mol^{-1}$.

Such results as described above clearly show that the transition does not take place completely and the specimen is a certain mixture of Phase II and Phase III unless it has been cooled below 78 K (for pure Phase III) or heated above 160 K (for pure Phase II). There is no observable time effect; at each temperature the specimen stayed at a constant temperature under adiabatic conditions.

This can be interpreted in one of the two ways, i.e. (1) each crystallite of the specimen has a specific (and different) transition temperature and (2) the crystallites all have the same transition temperature but must be superheated or undercooled to a certain temperature characteristic to each crystallite in order for the transition to begin. The second interpretation would give the same results as the first in terms of heat capacity measurements and therefore we shall not distinguish between the two and take the first option in the following discussion.

There is one further interesting result which we believe is significant in reinforcing our model. It is shown in Fig. 3, which is the results of heating measurements with T_r at 108 K. Prior to this series of measurements, the specimen was cooled down to 90 K, then heated up to 118 K (the halt temperature), where the transition anomaly was partially complete, and cooled down to 108 K. There are two peaks in Fig. 3 with a minimum of the heat capacity at 118 K. According to the present model, there are crystallites (which we call A) which have T_t above 118 K and were not affected by the first heating to 118 K. Only such crystallites (called B) which have T_t below 118 K had been transformed to Phase II during the first heating. The low-temperature peak in Fig. 3 does not correspond to all B but represents transition of the portion of B that could be transformed back to Phase

III by cooling to 108 K. Because 108 K is higher than the threshold T_r (see Fig. 2), the specimen at 108 K when the upward measurements were begun consisted of three components, the portion A (Phase III) which will be transformed into Phase II only above 118 K, the portion of B (Phase III) which will have the heat capacity peak at 116.8 K (from Fig. 2) and the rest of B (Phase II) which failed to go back to Phase III because of insufficient cooling; the last portion remains indifferent during the measurements of Fig. 3.

Depending on the choice of the upper and the lower T_r's and of the halt temperature, we obtained heat capacity anomalies of various shapes both in the heating and the cooling directions, but they were completely reproducible. This effect may be called the memory effect of the transition.

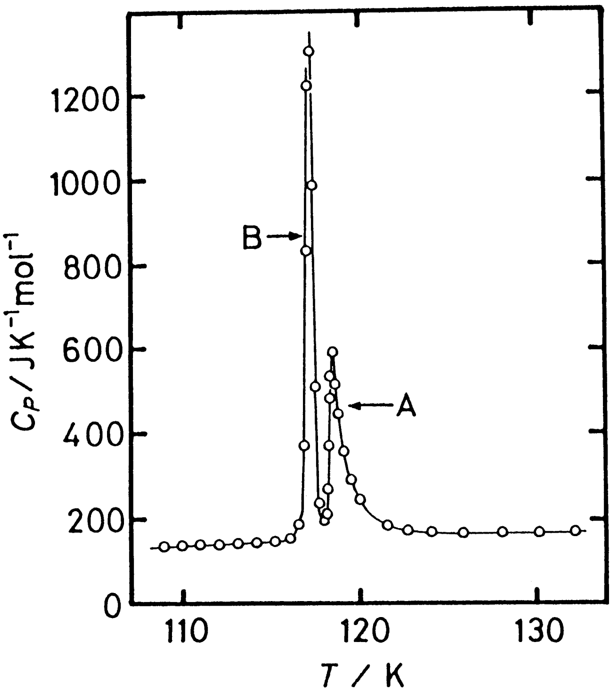

Fig. 3. Heat capacities of hexamethylbenzene showing two maxima (no curvature corrections made). For experimental conditions see in the text.

The present results are very significant in that they give evidence that the true transition temperature of a first-order transition can not be determined from the heating experiments alone and that there is a distribution in the temperature characteristic to the specimen at which various crystallites can begin the transformation. Expressed in terms of the transition temperature in the heating direction, such a distribution is a sharp one, main portion lying between 115 and 120 K, but its tails extend up to 160 K.

Further structural investigations will be necessary to elucidate what causes such a distribution of transition temperature and what causes the hysteresis effect after all.

References

1) Contribution No. 75 from Chemical Thermodynamics Laboratory, Faculty of Science, Osaka University.
2) Yu. V. Mnyukh, Mol. Cryst. Liq. Cryst., 52, 163 (1979).
3) Y. Yoshimoto, T. Atake, and H. Chihara, Netsu Sokutei, 9, 57 (1982).
4) T. Atake, H. Gyoten, and H. Chihara, J. Chem. Phys., 76, 5535 (1982).
5) H. M. Huffman, G. S. Parks, and A. C. Daniels, J. Am. Chem. Soc., 52, 1547 (1930).
6) M. Frankosky and J. G. Aston, J. Phys. Chem., 69, 3126 (1965).

(Received June 15, 1985)