A Dilatometric Study of the Transition in Methyl Alcohol.

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Advantage has been taken of the small solubility of methyl alcohol in *iso*pentane at low temperatures to investigate the volume changes which occur on the solidification of the alcohol and also at what has hitherto been considered as the single λ-point transition which this substance appeared to possess. It has been found, however, that there are two transitions, separated by only 3°. The upper transition is no doubt what has previously been regarded as the single transition, but it seems that this sets in much more abruptly than has been supposed, and it is probably more of the nature of a first-order phase change than a λ-point. It is the lower transition which is probably gradual in character, and its discovery is briefly discussed in the light of other information about solid methyl alcohol, and in particular in relation to recent crystallographic work.

The contraction in volume on solidification is 2·75 c.c./mole. On cooling, there is a further contraction of 0·49 c.c./mole at the upper transition at 159° K, and another contraction of ~0·14 c.c./mole at the lower transition.

The transition in methyl alcohol has been the subject of several recent papers. This transition occurs at ~159° K, *i.e.*, about 16° below the m. p. Cooke and Drain (*Proc. Phys. Soc.*, 1952, **65**, 894) examined the change in the proton magnetic resonance line width which accompanies it. Tauer and Lipscomb (*Acta Cryst.*, 1952, **5**, 606) carried out careful *X*-ray diffraction studies of the high- and the low-temperature form, and proposed structures for them. These authors consider that the transformation from the high- to the low-temperature form involves only a puckering of the infinite chains of hydrogen bonds to give more compact packing, these displacements being confined to planes normal to the direction of the chains. While this work rules out any possibility that the transition is in any way connected with the loss or gain of intermolecular rotation (or of intramolecular rotation of hydroxyl groups), Tauer and Lipscomb have nevertheless been able to account for the dielectric-constant changes associated with this transition (Smyth and McNeight, *J. Amer. Chem. Soc.*, 1936, **58**, 1597), and have also pointed out that their proposed structure for the low-temperature form is consistent with Weltner and Pitzer's conclusion (*ibid.*, 1951, **73**, 2606) that solid methanol probably has no residual entropy at the absolute zero.

A different structure for the high-temperature form, based on *X*-ray powder photographs, has been proposed by Dreyfus-Alain and Viallard (*Compt. rend.*, 1952, **235**, 536).

In reporting the results of a comparison of the thermodynamic properties of methyl alcohol and methyl deuteroxide, which included information about the transitions in the two solids, Staveley and Gupta (*Trans. Faraday Soc.*, 1949, **45**, 50) commented on the tendency of solid methyl alcohol, after being rapidly frozen in liquid air and then warmed in a glass container, to shatter the vessel. They suggested that this might be because the transformation of the high-temperature into the low-temperature form may be accompanied by a volume increase, since on very rapid cooling in liquid air the high-temperature form tends to be preserved in a metastable state, but changes spontaneously to the more stable form on warming. The experiments to be described were carried out with the object of testing this suggestion about the direction of the volume change. The guess proved to be wrong. The high-temperature form passes into the low-temperature form with a volume decrease. The interesting discovery was made, however, that solid methyl alcohol has *two* transitions, only about 3° apart. The lower of these is associated with only a very small volume change. The higher is no doubt what has hitherto been regarded as the single transition, and our work shows that this sets in much more abruptly than had been supposed, so that it may be a first-order phase change rather than a λ-point.

Experimental

The choice of a suitable dilatometric fluid presented some difficulty. The requirements were that it should remain liquid down to at least 140° K (without becoming too viscous), and that the mutual miscibility with methyl alcohol should be as low as possible. After preliminary experiments, it was decided to use *iso*pentane. The m. p. of methyl alcohol in the presence of *iso*pentane was found to be about 1° less than that of the pure alcohol. This means that a saturated solution of *iso*pentane in methyl alcohol contains about 1·3 moles % of the hydrocarbon at 175° K. The solubility of the alcohol in the *iso*pentane seemed to be not more than one-fifth of this. Since the mutual miscibility of the liquids at the m. p. of the alcohol is so small, and in view of the dissimilarity in the shapes of the two molecules, it seems very unlikely that *solid* methyl alcohol dissolves appreciable quantities of *iso*pentane.

The dilatometer used was that described by Mandleberg and Staveley (*J.*, 1950, 2736). In the first experiment, however, the bulb of the dilatometer shattered when being warmed with solid methyl alcohol in it, so for all later experiments the dilatometer was slightly modified by enclosing within it a loose inner tube into which the capillary of the dilatometer projected, as shown in Fig. 1. Even after the inner tube was shattered it was still possible to continue making measurements on the solid alcohol, but it was obviously undesirable to allow the alcohol to melt and to re-freeze it once the inner tube was broken. Accordingly, after the dilatometer had been filled, the alcohol was frozen and all experiments on the solid were carried out before any of the alcohol was allowed to melt; then, finally, the alcohol was melted to determine the volume change on melting. Two separate series of experiments were carried out in this way.

Fig. 1.

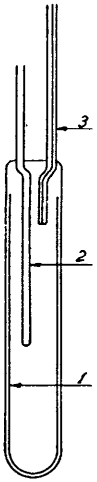

Fig. 2.

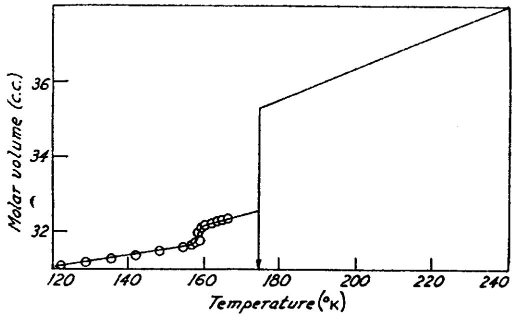

Fig. 1. *Dilatometer bulb, modified for experiments on methyl alcohol.* 1, *Loose inner tube*; 2, *re-entrant tube for thermocouple*; 3, *calibrated capillary tubing.*

Fig. 2. *Plot of the molar volume of solid and liquid methyl alcohol against temperature. The melting-point is indicated by the arrow.*

To fill the dilatometer, it was cooled in a bath of solid carbon dioxide and acetone, and a known weight of methyl alcohol (~15 g.) was sucked into the inner tube, sufficient almost to fill it. In order to de-gas the alcohol it was placed in a bath of melting carbon disulphide (m. p. —110° c), so that the alcohol froze but remained above the transition temperature. It was then pumped out, melted, and the process repeated. Finally, with the methyl alcohol solid, the remaining space in the dilatometer was filled by admitting de-gassed *iso*pentane.

The conversion of the high-temperature form (*i.e.*, that stable above 159° K) into the low-temperature form was attended by considerable supercooling. Even after being kept for 18 hr. below 159° K, a spontaneous evolution of heat about 30° below this temperature when the dilatometer was being warmed showed that some of the high-temperature form was still present. The procedure finally adopted was to cool the dilatometer to about 120° K, and then warm it very slowly to about 157° K, where it was kept for 1 hr. before being cooled again. After this, successive runs gave reproducible results.

The methyl alcohol used was a middle cut from a fractionation; it was freshly dried over lime and redistilled before use.

Results.—An overall picture of the volume relationships in methyl alcohol over a temperature range covering both the transitions and melting is given by Fig. 2, in which the molar volume is plotted against temperature. It will be seen that conversion of the low-temperature form into the high-temperature form at ~159° K is accompanied by a volume increase. This amounts to 0·49 c.c./mole, which is about 18% of the volume increase of 2·75 c.c./mole associated with melting. The only other value for the latter quantity is due to Korber (*Ann. Physik*, 1912, **37**, 1024), *viz.*, 2·4 c.c./mole.

In Fig. 2, the small transition which we have found to precede the main one is not apparent, but it is just discernible as a kink in the curve in Fig. 3, which is a plot, on a larger scale, of the observed volume increase of the contents of the dilatometer against temperature in the region of the transitions. To prove its existence beyond doubt, numerous measurements were made of the quantity $\Delta V/\Delta T$, where ΔV was the observed volume increase of the contents of the dilatometer when it was heated ΔT°. For some of these measurements ΔT was as small as 0·5°. In Fig. 4, which is a plot of $\Delta V/\Delta T$ against T, the two transitions appear very clearly.

FIG. 3.

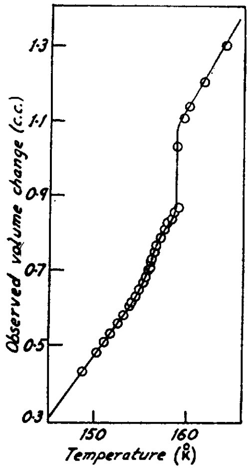

FIG. 4.

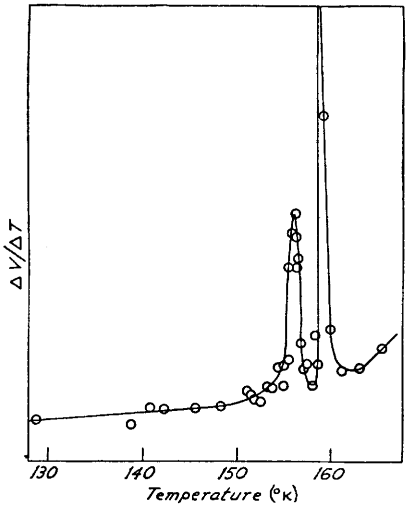

FIG. 3. *Showing the apparent change in volume of the contents of the dilatometer with temperature in the region of the two transitions.*

FIG. 4. *Plot of $\Delta V/\Delta T$ against temperature, where ΔV is the apparent increase in volume of the contents of the dilatometer for a temperature increase of ΔT. The highest observed value of $\Delta V/\Delta T$ for the upper transition was about six times the maximum value for the lower transition.*

DISCUSSION

From our value for the volume change on melting, we estimate that at —110° C the molar volume and density are respectively 32·25 c.c./mole and 0·993 g./c.c. From the unit-cell dimensions measured at this temperature, Tauer and Lipscomb (*loc. cit.*) gave 0·972 g./c.c. for the density. They interpret the diffraction pattern of the crystals at —160° C as indicating a monoclinic structure. Their unit-cell dimensions correspond to a density of 1·020 g./c.c. at this temperature. Our dilatometric work gives a value of 1·035 g./c.c.

Undoubtedly the main transition, corresponding to the single transition previously observed in calorimetric and other studies, is that which falls at the higher temperature, although there is not complete agreement between the value of the temperature at which the coefficient of expansion is a maximum (159° K), and that at which c_p is a maximum (157·8°, Staveley and Gupta, *loc. cit.*; 157·4°, Kelley, *J. Amer. Chem. Soc.*, 1929, **51**, 180). It would, seem, however, that the gradual rise in c_p which is noticeable several degrees before the maximum in c_p is reached must now be regarded as associated with the lower transition. Between the two transitions the coefficient of expansion falls to a low value which would seem to be almost normal. The major transition therefore sets in much more abruptly than had been supposed, and since it is clear from the crystallographic work that it involves a definite change in crystal structure, it should perhaps be regarded as a first-order phase change. The discovery of a second transition also throws light on some earlier observations made by Staveley and Gupta (*loc. cit.*) in their calorimetric investigation, namely, that equilibrium was reached only slowly in the neighbourhood of the maximum in c_p, and that here superheating was possible, while, in what were regarded as the early stages of the same transition, thermal equilibrium was rapidly attained without any appreciable superheating. This would have been difficult to understand if the transition had been like that in ammonium chloride, say, which is partly gradual and partly isothermal, where as far as we are aware it is not known for superheating to appear during the course of the transition. On the other hand, superheating is not infrequently associated with phase changes which appear to set in abruptly, such as that between rhombic and monoclinic sulphur. It is clearly the lower transition, which takes place gradually, in which equilibrium is rapidly attained.

The volume change at this lower transition cannot be estimated very accurately, but it is approximately 0·14 c.c./mole. A transition with a volume change about as small as this is that in solid deuterium sulphide at 108° K, for which the change is $\sim$0·18 c.c./mole (Clusius and Weigand, *Z. Elektrochem.*, 1938, **44**, 674). But the latter transition involves an entropy change of $\sim$4 cal./mole/degree, whereas the lower transition in methyl alcohol can only be associated with a very small entropy change, since the calorimetric work shows that up to 156° K c_p does not much exceed extrapolated "normal" values. The lower transition therefore only involves some very slight structural change. In this connection we may note that Tauer and Lipscomb (*loc. cit.*) proposed a monclinic unit cell containing two molecules for the low-temperature (α-form) of methyl alcohol, but that they remarked on the presence of some rather faint superlattice lines on the *X*-ray photographs, and suggested that these might be accounted for by a doubling of the unit cell due to a slight alternation in the position of the methyl groups (see Fig. 7 of their paper). It would be interesting to know whether these superlattice lines vanish at 156° K (the temperature at which the coefficient of expansion reaches a maximum for the first transition), *i.e.*, before the main transition at 159° K, and whether, therefore, the first transition is associated with the vanishing of the alternation in the position of the methyl groups just referred to, this being followed 3° later by the change into the orthorhombic modification. Finally, we may note that Cooke and Drain (*loc. cit.*) found that the proton magnetic resonance line width transition took the form " not of a steady decrease of the line width as the temperature was raised, but of a gradual replacement of the wide line by a narrow one." Since the narrow line first became detectable in their experiments at 145° K, it would seem that its appearance must be associated with the gradual onset of the lower transition, and it is interesting that the temperature recorded by Cooke and Drain as that at which the wide line was no longer detectable is 156° K, *i.e.*, that at which we find the coefficient of expansion for the *lower* transition to reach its maximum value.

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