Finding of the Glass-transition Phenomena of Methanol

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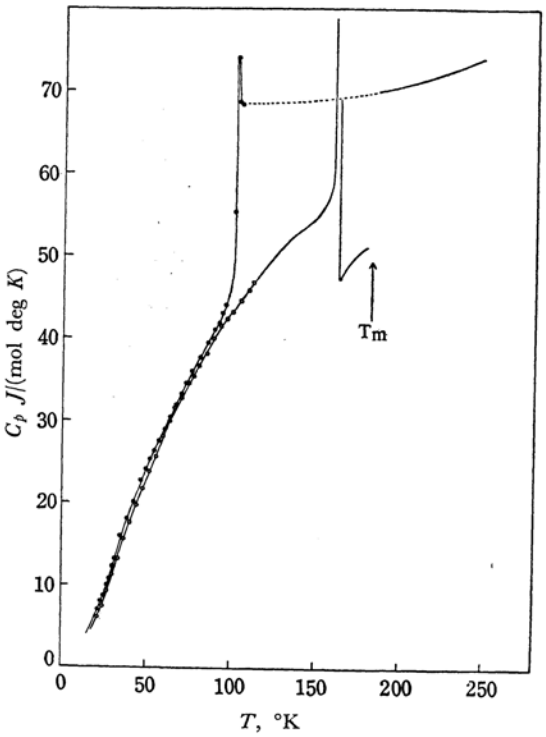
According to Staveley *et al.*,[1] methanol is supercooled to 95°K, without the scintillation effect which is characteristic of crystalline powder, when a liquid droplet is used as a sample. This fact is not, however, direct evidence of the obtaining of the glassy state. Another experiment has been reported by Pimentel *et al.*[2] using the infrared method; in this experiment the spectra of glassy state were reported with no recognition of the difference between the supercooled liquid and glassy states.

In order to verify the existence of the glassy state in general, we should distinguish the supercooled liquid and glassy states by the direct observation of the glass-transition phenomena, which may then be compared to the characteristic transition point (melting point) between crystalline and liquid states.

For the study of the glass-transition phenomena of materials with rather simple molecular structures, we have constructed a novel type of calorimeter suitable for obtaining the glassy sample by the vapor deposition method. Here we should like to give an outline of the calorimeter and describe the results of our heat-capacity measurements.

The calorimeter consists of a filling tube, a copper cell with a platinum resistance thermometer, inner and outer radiation shields, a copper block as a thermal station, and a vacuum jacket. The filling tube is made of monel metal and soft copper and is wound closely with a constantan heater. During sampling, this apparatus is immersed into a liquid nitrogen bath and helium gas is introduced as a conduction gas into the vacuum jacket. When the filling tube is heated to around 200°K, the temperature of the wall of the cell falls to 90—93°K. Under this conditioning the rate of deposition is regulated at 0.11 g per hour, and the sample obtained amounts to about 1.4 g. The measurements of the heat capacities were made from 20°K to 120°K, for vitreous and crystalline states respectively. Crystallization takes place just above the glass-transition point (102°K), so there is a temperature region (102—175°K) where heat-capacity measurements of the supercooled liquid are impossible. The results are shown in the accompanying figure, where an anomalous rapid rise in the heat capacity, characteristic of glass-transition phenomena, is verified at 102°K.



Heat capacity curve of methyl alcohol
● glassy state } present work
○ crystalline state }
—— above 120°K by K. K. Kelley[3]

The values of heat capacity just above the glass transition point can be well situated on the curve extrapolated from the values for a liquid. The details of our experiment will be published elsewhere in due course.

1) H. J. de Nordwall and L. A. K. Staveley, *J. Chem. Soc.*, **1954**, 224.
2) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco and London (1960), p. 103.
3) K. K. Kelley, *J. Am. Chem. Soc.*, **51**, 180 (1929).