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The Heat Capacity Anomaly in Phenanthrene; Effects of Deuteration, Purification and Dissolution†

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Arndt and Damask[1] reported a heat capacity anomaly of 380 cal/mole in phenanthrene around 70° C. An electrical anomaly occurs at the same temperature and has also been described in detail.[2] No explanation as yet exists for these phenomena. Further studies being conducted involve the use of fully deuterated phenanthrene but, since this is available only in limited quantities, some of the purification procedures had to be omitted. It was of interest to see if these omitted procedures suppressed the heat capacity anomaly to any extent, since it has been reported that impurities and radiation suppress the electrical anomaly.[2] Accordingly, the heat capacity anomaly of phenanthrene was remeasured under different conditions.

Measurements were performed using an isochronal differential microcalorimeter.[3] One side of the calorimeter was loaded with 0.2–0.4 grams of the sample in a sealed copper cylinder and the other side was iron, which is essentially inert at these temperatures and serves as a dummy. Pure gallium was used to calibrate the instrument and, because of possible errors in estimating the base line, the results are accurate to about 5%.

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Deuterated phenanthrene (99.4 atom % D), which had been recrystallized from ethanol, was obtained from Merck Sharp and Dohme of Canada. Its anomaly, as received, was 355 cal/mole. Zone refining (twenty passes) in 2 mm pyrex tubing with ½ atm. of purified nitrogen caused the anomaly to be increased to 423 cal/mole. The pure phenanthrene mentioned above in which the anomaly was 380 cal/mole had been purified by chromatographic columns and vacuum sublimation as well as by zone refining. For comparison some "as received" phenanthrene was recrystallized from ethanol and zone refined in an effort to duplicate the processes performed on the deuterated material. Following this procedure the anomaly was 310 cal/mole. Thus the omission of the chromatographic and sublimation steps caused about 20% reduction of the heat capacity anomaly. This result compares favorably with that of Matsumoto[4] who reported a magnitude of 260 cal/mole in phenanthrene after purification by recrystallization from ethanol and zone refining. It does not agree at all with the report of 607 cal/mole by Ueberreiter and Orthmann[5] on phenanthrene of unstated purity. It is clear from these measurements that the heat capacity anomaly in deuterated phenanthrene is larger than that in the nondeuterated material and that its magnitude is probably larger than the 423 cal/mole reported here for the partially purified sample. That the purification steps which were performed had considerable value was demonstrated by measuring the anomaly in the "as received" phenanthrene. It was 150 cal/mole.

As a further part of the continuing study of this anomaly in phenanthrene, an experiment was performed to see if this phenomenon is a property of the molecules themselves or of the crystalline state. High purity phenanthrene was dissolved in xylene. The solution was sealed in a bomb for the calorimeter. The quantity used was about 15% of that used in the other measurements. This amount was well within the detectability range of the calorimeter, since it can detect 0.005 cal in a 10 minute interval. No anomaly was observed for the solution, indicating that the anomaly arises from the crystalline state of the molecule.

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