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Melting Points of Ethane and Three of Its Deuterated Modifications

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A pulsed nuclear magnetic resonance method has been used to determine both the apparent melting point and the impurity correction for samples of ethane and three of its deuterated modifications. The true melting points were found to be: CH_3CH_3 89.82° K., CH_3CD_3 89.13° K., CHD_2CHD_2 89.89° K., and CHD_2CD_3 89.82° K.

IN THE PAST, considerable confusion has surrounded an accurate determination of the melting point of ethane. As late as 1960, the Handbook of Chemistry and Physics (*6*) quoted a value of 101.2° K., measured at the turn of the century (*7*). Results obtained later, notably 89.47° (*11*), 89.89° (*12*), and 90.35° K. (*3*), have slowly been incorporated into reference books during the last ten years. As late as 1949, Gutowsky *et al.* (*5*) quoted the melting point of ethane as 101.0° K., while reporting the observation of a narrow liquid-like nuclear magnetic resonance line at about 91° K.

In the course of attempts to understand spin-lattice relaxation in liquid and solid ethane (*4, 8*), the authors learned of this uncertainty in the ethane melting point and were unable to find any melting point measurements for the deuterated modifications of ethane. To measure these melting points, a nuclear magnetic resonance (NMR) technique (*1*) was developed which appears to give both the melting points of the samples and the true melting points as reliably as the conventional heat capacity method (*12*). By the true melting point of a substance, the authors mean the melting temperature of a sample of that substance whose impurity content is small enough or innocuous enough to have no measurable effect on the experimental determination of this temperature.

EXPERIMENTAL

The melting points and their impurity corrections were determined using this pulsed NMR method. According to the Raoult theory of impurity premelting (*10*), the fraction of the sample which is liquid, $A(T)$, at any temperature T below the apparent melting point, $(T_m)_A$, follows the equation

$$A(T) = \left[1 + \frac{(T_m)_A - T}{\Delta}\right]^{-1} \tag{1}$$

where Δ is equal to the difference between T_m, the true melting point, and $(T_m)_A$. Δ is also proportional to the fraction of impurity molecules which depress the melting point—that is, of a type soluble in the melt but not appreciably soluble in the crystals—and the proportionality constant is the (mole fraction) freezing point depression constant. $A(T)$ is measured directly by observing the amplitude of the spin echo of pulsed NMR. The two parameters, $(T_m)_A$ and Δ, are adjusted for a best fit to the experimental points and then added to provide the true melting point. For samples of ethane of reasonable purity, C.P. grade, neither the validity of the method nor the true melting points obtained depend upon the sample purity (*1*).

The CH_3CH_3 sample was prepared from Phillips Petroleum Co. research grade ethane. As with all the samples, it was exposed to a Misch metal getter in order to remove paramagnetic oxygen (*9*) and then sealed in a glass sample tube of 3.5-mm. i.d. and approximately 80-mm. length. Thus, all our measurements were taken along the vaporization curve. The melting range for this sample (Figure 1) was about 0.1° K., and its impurity correction was 0.007° K. Consequently, this sample is considerably purer than that of Witt and Kemp (*12*), and of comparable purity to that of Clusius and Weigand (*3*). The CH_3CD_3, CHD_2CHD_2, and CHD_2CD_3 samples were obtained from Merck, Sharp, and Dohme of Canada, Ltd. The overriding impurities in these samples were reported by the manufacturer to be other deuterated modifications of ethane. Analysis by the National Bureau of Standards of the lots from which our samples came indicated that each contained 93 to 95%

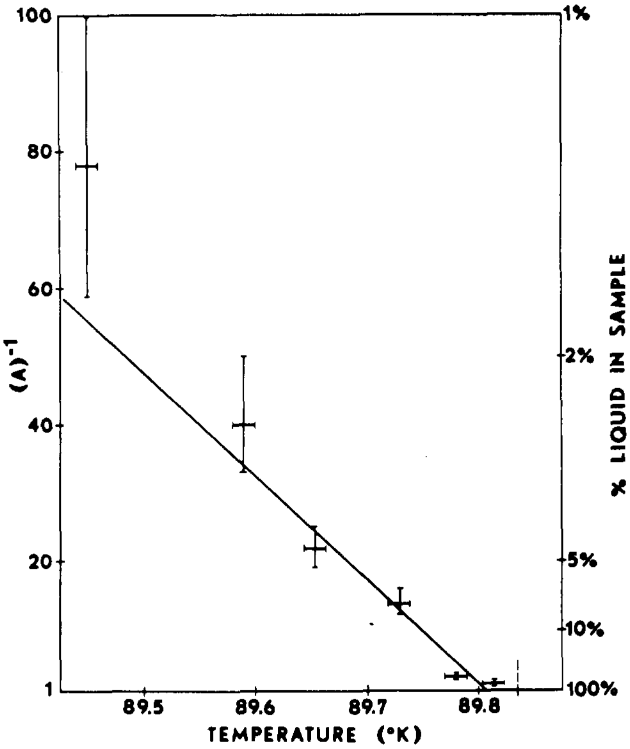

Figure 1. Reciprocal of liquid fraction as a function of temperature for CH_3CH_3

——— Fit of Equation 1 to points

— — — Temperature of a data point obtained for sample just after it had been liquified. This represents an upper bound to $(T_m)_A$

of the appropriate deuteration and approximately 7 to 5% of a deuteration containing one less deuteron. The impurity corrections and X, the inferred mole per cent of liquid-soluble solid-insoluble impurities present in these samples as found in this work, are given in Table I. To obtain the impurity content, the freezing point depression constant for ethane was calculated to be 23.5° K. from a knowledge of the heat of fusion (*12*), assumed to be the same for all the ethanes. While the heat of fusion is dependent to some extent on the impurity content, the consequent variation of the heat of fusion has a negligible effect on our measurements.

The most important considerations for any melting point measurement are the homogeneity and stability of the temperature of the sample and the accuracy of the determination of the sample temperature. A liquid oxygen bath was used to control the sample temperature, as the boiling point of oxygen is very close to the melting point of ethane. A block diagram of the system used to control and measure the temperature of the sample is shown in Figure 2. The pressure over the oxygen bath was controlled by a Cartesian manostat, which will maintain a differential pressure to within ±0.1 mm. of mercury. In this application, where the fluctuations in pressure from the evaporating liquid were very small, control of the differential pressure was considerably better.

The copper NMR coil and a copper sheath encased the sample tube with wires extending from the sheath to the copper sample case. These wires were in direct thermal contact with a National Bureau of Standards calibrated platinum resistance thermometer (Figure 3).

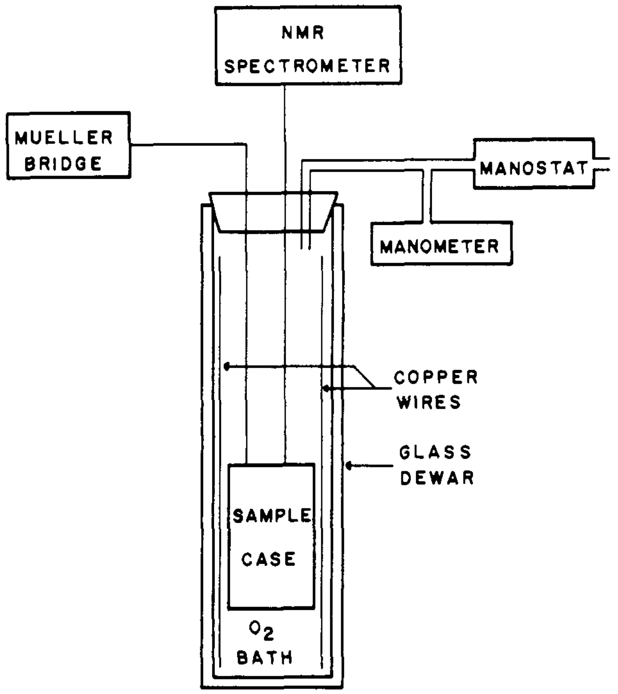

Figure 2. Diagram of melting point measurement system

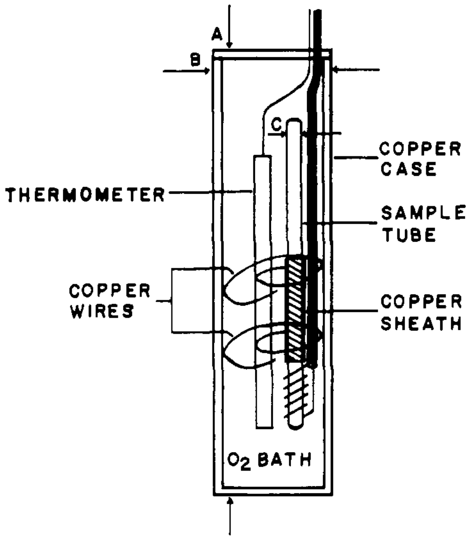

Figure 3. Cross section of sample case showing sample and thermometer placement

A, 108 mm.; B, 18 mm.; C, 5 mm.

The resistance of the platinum thermometer was read on a Honeywell Rubicon Model 1551 Mueller bridge, recently calibrated by the Honeywell Co. The copper case minimized temperature gradients in the immediate oxygen bath. To minimize the hot spots common to temperature-controlling baths, copper wires were also strung longitudinally along the Dewar.

An indication of the stability of this temperature system is provided by the experimental points obtained directly below the apparent melting point for some of the purer samples. In CH_3CH_3, for example, the NMR spin echo signal height changes by a factor of 5—e.g., from 2 to 10 volts—over the 0.02° K. immediately below the apparent melting point. During the taking of data

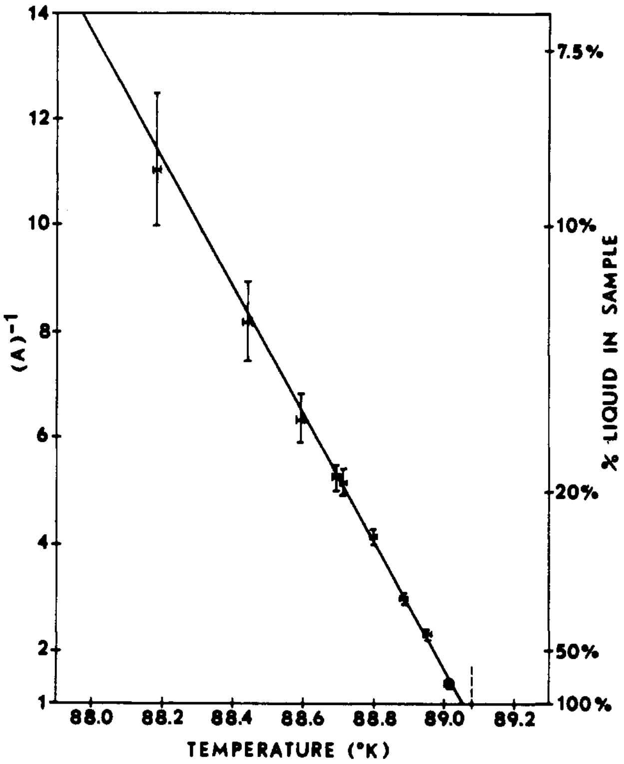

Figure 4. Reciprocal of liquid fraction as a function of temperature for CH_3CD_3

——— Fit of Equation 1 to points

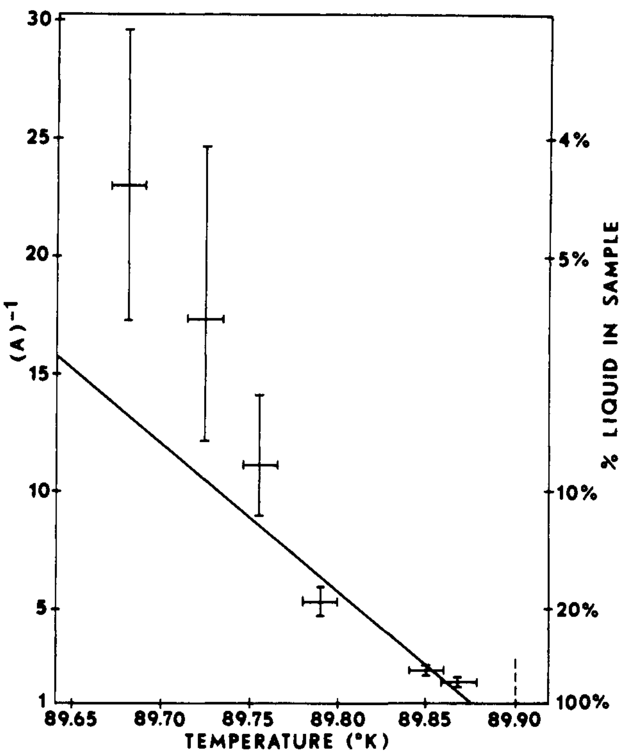

Figure 5. Reciprocal of liquid fraction as a function of temperature for CHD_2CHD_2

——— Fit of Equation 1 to points

points in this region, the signal height did not change by more than 0.2 volt during a 10-minute period. This corresponds to a short-term stability of better than 0.5 millidegree Kelvin. Long-term stability over hours is evidenced by the fact that, while taking these points, the temperature of the sample never drifted above its apparent melting point. Since ethane supercools, the sample, once melted, would have remained all liquid and the amplitude of the NMR signal would have made this obvious.

By the same technique—i.e., the use of the NMR signal from the sample as a very sensitive thermometer—the thermal relaxation time of the temperature system was measured. After a change of temperature from $T = (T_m)_A - 0.1°$ K. to approximately $T = (T_m)_A - 0.02°$ K., the time for establishing equilibrium was on the order of 30 to 45 minutes. Consequently, approximately 4 hours were allowed to lapse before a data point was taken.

RESULTS AND DISCUSSION

Figures 1, 4, 5, and 6 present the melting data observed for CH_3CH_3, CH_3CD_3, CHD_2CHD_2, and CHD_2CD_3, respectively. These are plots of $[A(T)]^{-1}$ *vs.* T which yield, according to Equation 1, straight lines with slopes $-\Delta^{-1}$ and intercepts of $(T_m)_A$ at $A(T) = 1$. Estimated errors for the temperature (±0.01° K.) and for the reciprocal of the amplitude of the signal are shown for each point. During the time of a NMR reading, about 15 minutes, the temperature as determined by the platinum resistance thermometer wandered typically by 0.001° K. and never by more than 0.003° K. Thus, 0.01° K. is a conservative estimate of the random error in the temperature. Uncertainties in $[A(T)]^{-1}$ reflect the decreasing signal-to-noise ratio of the NMR signal as the liquid fraction decreases.

The solid lines on these graphs were obtained by the "Least-Squares Fitting of a Straight Line" method of York (*13*). This method minimizes the sum in the following equation:

$$S = \sum_i \{\omega(X_i)\,(x_i - X_i)^2 + \omega(Y_i)\,(y_i - Y_i)^2\}$$

where X_i, Y_i are the observations, $\omega(X_i)$, $\omega(Y_i)$ are the

Table I. Melting Points of Ethane and Three of Its Deuterated Modifications

Sample	Apparent Melting Point, $(T_m)_A$, ° K.	Impurity, Correction, Δ, ° K.	Mole % Impurity, X	True Melting Point, T_m, ° K.
CH_3CH_3	89.809 ± 0.009	0.007 ± 0.001	0.03%	89.82 ± 0.03
CH_3CD_3	89.050 ± 0.005	0.083 ± 0.002	0.36%	89.13 ± 0.03
CHD_2CHD_2	89.876 ± 0.011	0.017 ± 0.003	0.07%	89.89 ± 0.03
CHD_2CD_3	89.798 ± 0.004	0.023 ± 0.001	0.09%	89.82 ± 0.03

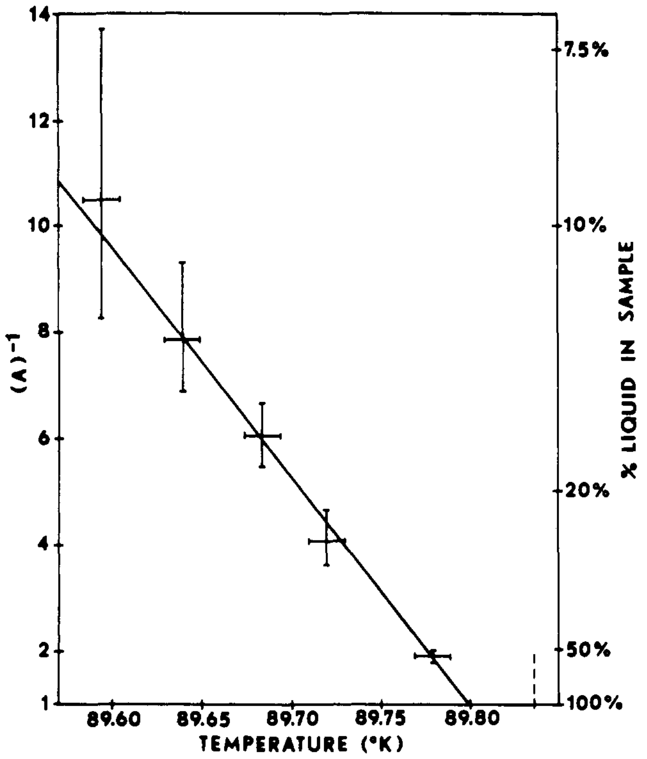

Figure 6. Reciprocal of liquid fraction as a function of temperature for CHD$_2$CD$_3$

——— Fit of Equation 1 to points

weights of the various observations, and x_i, y_i are the adjusted values of X_i, Y_i which lie on a straight line and make S a minimum. The weight of each observation was taken to be the reciprocal of the square of its estimated uncertainty. This method takes into account errors in both X_i and Y_i in a natural manner. The uncertainties presented for Δ and for $(T_m)_A$ are the standard deviations given by this least-squares program.

The melting point measurements are presented in Table I. The uncertainties quoted in the last column are estimates of the total inaccuracy, reflecting both the uncertainty in the fit of Equation 1 to the data and an estimate (±0.02° K.) of the uncertainty in absolute temperature. The calibration of the platinum resistance thermometer was accurate to within ±0.01° K. and the Mueller bridge error of ±0.02% leads to a temperature uncertainty of ±0.01° K.

Although no other melting point measurements exist for the deuterated ethanes, the present results for CH$_3$CH$_3$ may be compared with the two commonly quoted values. These two measurements yielded 89.89° ± 0.10° K. (*12*) and 90.350 ± 0.03° K. (*3*), and were determined by the most common method—i.e., during heat capacity measurements. The present value of 89.82° ± 0.03° K. is consistent with the former, but differs significantly from the latter.

Melting point measurements have been made on methane and some of its deuterated modifications (*2*, *3*) ; the melting point differences between isotopic variations of methane are roughly the same as those for ethane. However, as pointed out by Ubbelohde (*10*), the melting process is not well enough understood to explain the melting point differences observed for isotopic variations of molecules.

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