Hindered Internal Rotation of Ethane

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LETTERS TO THE EDITOR

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Hindered Internal Rotation of Ethane

We have further improved the "hot wire" gaseous heat capacity apparatus of Kistiakowsky and Nazmi,[1] eliminating possible errors due to gas adsorption and "end conductance." Measurements on C_2H_6 and C_2D_6 near liquid oxygen temperature show that the observed heat capacity is independent of the nature of the wire, of the gas pressure, and of the temperature difference between the wire and the surrounding wall. The vibrational heat capacity of C_2H_6 at these temperatures is negligible, and that of C_2D_6 is certainly less than 0.05 cal./mole deg. By subtracting the vibrational, over-all rotational, and translational heat capacities from our measured values, we find for C_2H_6 the contribution of the hindered internal rotation to be 0.59 and 0.67 cal./mole deg. at 94° and 100°K. For C_2D_6 similarly we find 1.03 and 1.13 cal./mole deg. at 94° and 100°K. The values for light ethane are to be compared with Hunsmann's[2] data: 0.40 at 95° and 0.56 at 101°.

The theoretical dependence of the hindered internal rotational heat capacity upon the assumed magnitude of a restricting potential of the form $(1/2)V(1-\cos 3\theta)$ is shown in Fig. 1 for the temperatures in question. It will be seen that a barrier of about 3000 cal./mole is the only assumption consistent with the experimental data, provided this method of calculation[3] is not invalidated by quantum effects due to the existence of nuclear spin isomers—a point raised by Hunsmann.[2] In the following letter Professor Wilson reports that these quantum effects are completely negligible at these temperatures. It follows that the low temperature gaseous heat capacity of ethane cannot be interpreted in terms of a low potential barrier and these quantum effects as suggested by Hunsmann, but requires instead a high restricting barrier as indicated above. It also follows that the agreement of the entropy calculated semi-statistically by Hunsmann (i.e., statistically for over-all rotation and translation but graphically for the internal degrees of freedom) with the third law value is not accidental, as he suggests, but is a direct consequence of the existence of the high barrier. On the other hand the poor agreement of Hunsmann's calculated heat capacity of C_2H_6 for a high barrier with the experimental points between 100° and 200°K is due to an inadequate method of calculation. Using the hindered rotator model with $V=3000$ cal./mole, satisfactory agreement between theory and experiment is obtained over the entire temperature range for which the experimental data exist, provided the uncertain vibrational frequency in C_2H_6 is taken to be between 1000 and 1200 cm^{-1}. This frequency is not in accordance with Bartholomé and Karweil's[4] vibrational analysis, a point which will be discussed in papers soon to appear from this laboratory.

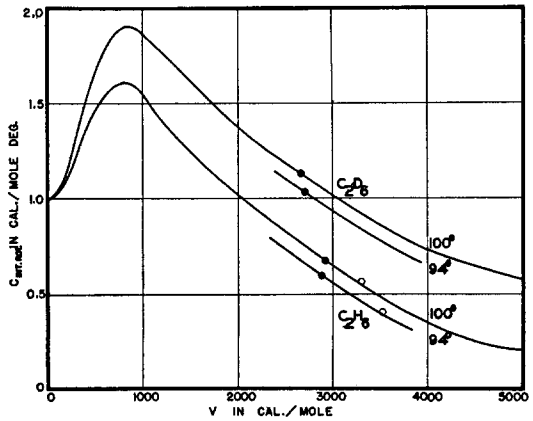

FIG. 1. Internal rotational heat capacity of ethane as a function of potential barrier. Filled circles, this work. Open circles, Hunsmann.

Thus, in addition to the other thermodynamic[5] and spectroscopic[6] evidence[7] for the existence of a fairly high barrier hindering internal rotation in ethane, the low temperature gaseous heat capacity leads directly to the conclusion that this barrier must be of the order of magnitude of 3000 cal./mole, without any other alternative.

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[3] K. S. Pitzer, J. Chem. Phys. **5**, 469 (1937).
[4] E. Bartholomé and J. Karweil, Zeits. f. physik. Chemie **B39**, 1 (1938).
[5] Kistiakowsky, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **58**, 137 (1936); J. D. Kemp and K. S. Pitzer, ibid. **59**, 276 (1937).
[6] J. B. Howard, J. Chem. Phys. **5**, 451 (1937).
[7] This evidence has not been generally regarded as conclusive. See Kassel, J. Am. Chem. Soc. **59**, 2745 (1937).