

Internal Rotation in Dimethyl Acetylene

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LETTERS TO THE EDITOR

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Internal Rotation in Dimethyl Acetylene

A preliminary comparison of calculated and observed heat capacities for gaseous dimethyl acetylene indicates that the internal rotation of the methyl groups against one another is essentially free, the restricting potential barrier being less than 500 cal./mole. This result agrees with that expected from the large distance between methyl groups.¹

A study of the infra-red and Raman spectra of this molecule, to be published soon by one of us, gives a basis for the calculation of the heat capacity for the ideal gas, C_p^0 , exclusive of the contribution from the internal rotation, C_r . This quantity ($C_p^0 - C_r$) is compared with the other data in Table I.

Measurements on the heat capacity of the gas have been made by the adiabatic expansion method recently described.² The values of C_p' obtained are given in Table I. In order to correct C_p' to C_p or to C_p^0 , it is necessary to use equation-of-state data. Since these are not available for dimethyl acetylene, the following procedure was used to obtain an estimate of the correction. A plot of critical pressure vs. critical temperature was made for a number of hydrocarbons; the plot showed satisfactory regularity, and was used to obtain the critical pressure of dimethyl acetylene from the known critical temperature.³ These critical data were then used in the Keyes equation⁴ to evaluate the correction ($C_p^0 - C_p'$). As a check on the reliability of the results, the same method was used for a number of hydrocarbons for which equation-of-state data are available; the comparisons with the known values indicate that the corrections ($C_p^0 - C_p'$) for dimethyl acetylene are probably good to 0.10 cal./mole degree.

The resulting values for C_r , the contribution from the internal rotation, are consistent with the value 0.99 cal./mole degree expected for a completely free motion; i.e., a restricting potential of 0. Using the data at 369°, with the limit of error of 0.12 cal./mole degree indicated, a maximum value of 500 cal./mole is found for the restricting potential. (Values from Pitzer's tables⁵ were used.)

The validity of this result depends on the correctness of the vibrational assignment used in calculating ($C_p^0 - C_r$)

as well as on the accuracy of the correction for gas imperfection. A study of the heat capacity of the gas over a wider temperature range, using the hot-wire method,⁶ is now in progress; it is hoped that this work will serve to check the vibrational analyses and the correction used here, and to determine the restricting potential more accurately.

In concluding, we wish to thank Professors G. B. Kistiakowsky and E. B. Wilson, Jr. for their continued interest in this work and for many helpful contributions thereto.

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¹ See, for example, G. B. Kistiakowsky, J. R. Lacher, and W. W. Ransom, *J. Chem. Phys.* **6**, 900 (1938).

² G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.* **7**, 281 (1939).

³ F. R. Morehouse and O. Maass, *Can. J. Research* **11**, 640 (1934).

⁴ F. G. Keyes, *J. Am. Chem. Soc.* **60**, 1761 (1938).

⁵ K. S. Pitzer, *J. Chem. Phys.* **5**, 471 (1937).

⁶ G. B. Kistiakowsky, J. R. Lacher, and F. Stitt, *J. Chem. Phys.* **7**, 289 (1939); and references therein.

* National Research Fellow in Chemistry.

Errata: The Electrostatic Influence of Substituents on the Dissociation Constants of Organic Acids. I and II

(*J. Chem. Phys.* **6**, 506, 513 (1938))

The title of Table II, p. 511 should read "Values of $\sqrt{x D_E(x)}$." Eq. (2), p. 514, should contain the factors $[1 - (D_i/D)C_n]^{-1}$ rather than $[1 + (D_i/D)C_n]^{-1}$. Similarly, the negative sign is proper in the corresponding term of Eqs. (3), (14), (17) and (18), pp. 514, 516 and 517. Further, Eq. (2) should read

$$U_n = 2(2n+1) \frac{Q_n(\lambda_0)}{P_n(\lambda_0)} (-1)^n$$

and Eq. (3)

$$Y_n = -2n(n+1)(2n+1) \frac{Q_n(\lambda_0)}{P_n(\lambda_0)} (-1)^n.$$

In Eq. (19), $(-1)^n$ rather than $(-1)_n$ should appear. The correct equations were employed for the numerical calculations.

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TABLE I. Heat capacity data for gaseous dimethyl acetylene, in cal./mole degree.

$T, ^\circ K$	$(C_p^0 - C_p')$	C_p'	$(C_p^0 - C_p')$	C_p^0	C_r
336	19.14	19.41 ± 0.03	0.80 ± 0.10	20.21 ± 0.11	1.07 ± 0.12
369	20.47	20.76 ± 0.04	0.67 ± 0.10	21.43 ± 0.11	0.96 ± 0.12