The Entropy of Dimethyl Acetylene from Low Temperature Calorimetric Measurements. Free Rotation in the Dimethyl Acetylene Molecule

The separation of the methyl groups in the dimethyl acetylene molecule, $H_3C-C\equiv C-CH_3$, is much greater than it is in ethane, and if the potential barrier[1] of about 3000 cal./mole restricting internal rotation in the latter is due to interactions between the methyl groups, then this barrier should be much smaller in dimethyl acetylene. If, on the other hand, the restricting potential in ethane is largely due to resonance with double bonded structures as proposed by Gorin, Walter and Eyring,[2] the fact that the length of the C−C single bonds in dimethyl acetylene[3] is such as to indicate considerable double bond character might lead one to expect a barrier about as large as in ethane. In order to determine the magnitude of this barrier we have calculated the entropy of dimethyl acetylene from low temperature calorimetric measurements and have compared this experimental value with that computed from molecular data.

The heat capacities, heat of fusion, and heat of vaporization were determined in an adiabatic calorimeter in the temperature range 15 to 291°K. The amount of material in the calorimeter was 0.8671 mole, and there was an impurity of 0.23 mole percent, as estimated from the change in melting point with proportion melted. Temperatures were measured with a platinum resistance thermometer which was compared with a National Bureau of Standards platinum thermometer down to 90°K and with a helium gas thermometer between 14 and 90°K. It is believed that our temperature scale agrees with that adopted at the National Bureau of Standards[4] to about 0.01°. Measurements of energy and resistance were made with an autocalibrated White double potentiometer and standards recently calibrated at the National Bureau of Standards. A detailed account of the apparatus and results will be published later.

In Table I are presented in itemized form the entropy changes calculated from our calorimetric data. The correction for gas imperfection was made under the assumptions that the gas follows a Berthelot equation of state, that the critical temperature is 489°K, as estimated by Morehouse and Maas,[5] and that the pressure of 41 atmos. obtained by extrapolation of the vapor pressure equation[6] to 489°K is the critical pressure.

TABLE I. *Molal entropy of dimethyl acetylene from calorimetric data.*

0–14.70°K, Extrapolation	0.25
14.70–240.93°K, Graphical	31.01
Fusion, 2206.7/240.93	9.16
240.93–291.00°K, Graphical	5.45
Vaporization at 291.00°K and 536 mm, 6440/291.00	22.13
Entropy of actual gas at 291.00°K and 536 mm	68.00 ±0.1
Correction for gas imperfection	0.14
Entropy of ideal gas at 291.00°K and 536 mm	68.14 cal./deg. mole

A summary of the calculation of the entropy from molecular data by the methods of statistical mechanics is given in Table II. For the vibrational entropy the frequencies used were those given by Crawford.[7] In the calculation of the rotational entropy it was assumed that the configuration of the methyl groups is the same as in methane and that the methyl groups are entirely free to rotate. The interatomic distances used, C−H = 1.09A, C−C = 1.47A, and C≡C = 1.20A, are due to Pauling, Springall and Palmer.[3]

The deviation of the calorimetric from the statistical entropy, namely 0.32 cal./deg. mole, is greater than our estimated experimental error, ±0.1 cal./deg. mole, and is possibly to be ascribed to an error of a few cm^{-1} in the lowest frequency, 213 cm^{-1}, to neglect of any anharmonicity in the vibrations, and to uncertainty in the correction for gas imperfection.

TABLE II. *Molal entropy of gaseous dimethyl acetylene from molecular data, for 291.00°K and 536 mm.*

S_{trans}	38.47
S_{vib} (harmonic)	6.72
S_{rot} (with free internal rotation)	22.63
Total entropy	67.82 cal./deg. mole

It appears from the agreement between the calorimetric entropy, 68.14 cal./deg. mole, and that calculated from the existing molecular data on the assumption of free internal rotation, 67.82 cal./deg. mole, that within the limits of experimental error there is no appreciable barrier restricting the rotation of the methyl groups with respect to each other. Indeed, the assumption of any barrier would result in a decrease in the value of the statistical entropy, and this in turn would make the deviation from the experimental value still greater. Crawford and Rice[8] have reached essentially the same conclusion from the results of their gas heat capacity measurements. The results presented above, however, are less dependent on the correction for gas imperfection and on the vibrational frequencies above 1000 cm^{-1}.

We wish to express our indebtedness to Professor Alexander Goetz for supplying us with liquid hydrogen, and to Mr. Thurston Skei and Mr. Russell Doescher for preparing and purifying the dimethyl acetylene.

DARRELL W. OSBORNE*
CLIFFORD S. GARNER**
DON M. YOST

Gates Chemical Laboratory,
California Institute of Technology,
Pasadena, California,
December 10, 1939.

[1] J. D. Kemp and K. S. Pitzer, J. Am. Chem. Soc. **59**, 276 (1937).
[2] E. Gorin, J. Walter and H. Eyring, J. Am. Chem. Soc. **61**, 1876 (1939).
[3] L. Pauling, H. D. Springall and K. J. Palmer, J. Am. Chem. Soc. **61**, 927 (1939).
[4] H. J. Hoge and F. G. Brickwedde, Nat. Bur. Stand. J. Research **22**, 351 (1939).
[5] F. R. Morehouse and O. Maas, Can. J. Research **11**, 637 (1934).
[6] G. B. Heisig and H. M. Davis, J. Am. Chem. Soc. **57**, 339 (1935).
[7] B. L. Crawford, Jr., J. Chem. Phys. **7**, 555 (1939).
[8] B. L. Crawford, Jr. and W. W. Rice, J. Chem. Phys. **7**, 437 (1939).
* A. A. Noyes Fellow in Chemistry.
** A. A. Noyes Fellow in Chemistry. Present address: Chemistry Department, University of Texas, Austin, Texas.