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Hindered Rotation of the Methyl Groups in Ethane

A reliable value of the entropy of ethane from calorimetric measurements extending to 15°K has been obtained by Witt and Kemp.¹ Several investigators^{2, 3} have given the treatment for obtaining the entropy of ethane from statistical-mechanical considerations, assuming a model with freely rotating methyl groups. The value of the entropy of ethane obtained from such a treatment, however, differs from the experimental value by 1.57 E.U. The reason for this disagreement could be either the assumption of an incorrect molecular model or an incorrect experimental entropy due to the persistence of rotation in the crystal at low temperatures, as suggested by Aston and Messerly⁴ and Kassel⁵ for disagreements in the values for other hydrocarbons.

A further discrepancy has been found between an accurate determination of the heat of hydrogenation of ethylene by Kistiakowsky and co-workers,^{5, 6} and a large number of concordant experiments on the free energy of hydrogenation of ethylene. Using a model of ethane requiring free rotation of the methyl groups, Teller and Topley⁷ and Smith and Vaughan,⁸ have been unable to correlate these data by a statistical-mechanical calculation. The assumption that ethane rotates in the crystal at low temperatures would not remove this discrepancy.

Confronted with these disagreements, we felt that the trouble lay perhaps in the assumption of completely free rotation of the methyl groups. Accordingly, we have made statistical-mechanical calculations⁹ assuming various potential barriers of the form $\frac{1}{2}V_0(1 - \cos 3\phi)$. Table I gives a preliminary survey of the results of these calculations, together with the experimental values of the entropy of ethane and the heat of hydrogenation of ethylene.

The values of ΔH_{755° calculated for the reaction $C_2H_4 + H_2 = C_2H_6$ were obtained using the best value of

the free energy of reaction selected by Teller and Topley.⁷ It is seen that agreement between the various data is obtained only for a potential barrier of about 3150 cal., which, with suitable selection of the uncertain vibration frequency, we have found to be in accord with the heat capacity of ethane gas determined by Eucken and co-workers.^{10, 11}

In view of these considerations, we feel that the entropies of ethane and similar hydrocarbons obtained with the aid of the third law of thermodynamics from calorimetric data extending to low temperatures are the correct ones for use in thermodynamic calculations. Thus the disagreements found by Aston and Messerly⁴ for tetramethylmethane and by Kassel⁵ for *n*-butane are due probably to an incorrect assumption of completely free rotation of the methyl groups. A potential barrier of 3150 cal. in no way conflicts with the existing knowledge of organic chemistry concerning isomerism.

A more detailed discussion of both the experimental data and statistical-mechanical calculation will be published later.

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October 2, 1936.

¹ To be published.

² Mayer, Brunauer and Mayer, *J. Am. Chem. Soc.* **55**, 37 (1933).

³ Kassel, *J. Chem. Phys.* **4**, 276 (1936).

⁴ Aston and Messerly, *J. Chem. Phys.* **4**, 391 (1936).

⁵ Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughn, *J. Am. Chem. Soc.* **57**, 65 (1935).

⁶ Kistiakowsky, Ruhoff, Smith and Vaughn, *J. Am. Chem. Soc.* **58**, 137 (1936).

⁷ Teller and Topley, *J. Chem. Soc.* 876 (1935).

⁸ Smith and Vaughan, *J. Chem. Phys.* **3**, 341 (1935).

⁹ A quantum-mechanical treatment of this model has been given by Nielsen, *Phys. Rev.* **40**, 445 (1932).

¹⁰ Eucken and Parts, *Zeits. f. physik. Chemie* **B20**, 184 (1933).

¹¹ Eucken and Weigert, *Zeits. f. physik. Chemie* **B23**, 265 (1933).

TABLE I. *The heat of hydrogenation of ethylene and the entropy of ethane.*

Calc. with	ΔH_{755° (cal.)	$S_{184.1^\circ K}$ (1 atmos.) cal./deg./mole
$V_0 = 0$ cal.	$-31,500 \pm 300$	51.21 ± 0.2
$V_0 = 315$ cal.	$-31,560 \pm 300$	51.10 ± 0.2
$V_0 = 3150$ cal.	$-32,940 \pm 300$	49.44 ± 0.2
experimental	$-32,824 \pm 50^5$	49.64 ± 0.15^1

Infrared Evidence for the Existence of Hydrogen Bonds

The possibility of the formation of hydrogen bonds has been emphasized by many recently.¹ Acetic and formic acids, most of the alcohols, water and some other substances, because of their unusual thermodynamic behavior and their high dielectric constants, are generally supposed to be associated, possibly through the formation of hydrogen bonds. Hydrogen fluoride is associated in the vapor state, and in solution is thought to give rise to $[HF_2]^-$ ions. This is evidence favoring the formation of hydrogen bonds.

The writer has undertaken a series of experiments on mixtures of liquids in which association of the two liquids may be anticipated through the formation of hydrogen bonds. Liquids, such as water, alcohols, aniline, were mixed with acetone, ethers, methyl cyanide, ethyl formate, ethyl acetate, etc. Changes in the electric moment of the group which carry the hydrogen would be expected if hydrogen bonds are formed. These variations would be evidenced by changes in the infrared spectra. Preliminary results show that changes in the spectrum actually exist, which may be attributed to this. For example, in mixtures of methyl alcohol and ethyl acetate, the fundamental vibrational band of the OH alcohol group is shifted to the shorter wave-length and its intensity is appreciably increased, while the vibrational band of the CO group in the

ethyl acetate is shifted to the longer wave-length with a corresponding increase in intensity. Other bands appear to remain constant. Similar results were obtained for other alcohol mixtures and for aniline with several other organic liquids. Also changes in the water spectrum indicate association between water and methyl cyanide, and water and other organic liquids.

It is expected that these results will be ready for publication soon.

WALTER GORDY

Mary Hardin-Baylor College,
Belton, Texas,
October 12, 1936.

¹ L. Pauling, J. Am. Chem. Soc. **57**, 2680 (1935); *ibid.* **58**, 94 (1936); L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936); R. H. Gillette and A. Sherman, J. Am. Chem. Soc. **58**, 1135 (1936); R. H. Gillette and F. Daniels, J. Am. Chem. Soc. **58**, 1139 (1936).