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# Nuclear Spin and Symmetry Effects in the Heat Capacity of Ethane Gas

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The heat capacity of ethane gas has been calculated for a number of values of the internal potential barrier from zero to high barriers. Detailed account of the presence of noncombining species and of the exact nuclear spin statistical weights was taken. It was found that down to temperatures at least as low as 90°K these phenomena are entirely unimportant and that the partition function calculated in the usual way is correct. It is concluded that the observed experimental data are best explained by the assumption of a high restricting potential. Tables of statistical weights for the rotational levels of  $C_2H_6$  and  $C_2D_6$  are given.

THE heat capacity of ethane gas at low temperatures<sup>1</sup> (100°K) provides a particularly important piece of evidence pointing to a high barrier of about 3000 calories restricting internal rotation in this molecule. This interpretation has, however, been challenged by Hunsmann,<sup>10</sup> who suggests that the observed result might be due to nuclear spin quantum effects such as occur in ortho- and parahydrogen. As previously pointed out in a preliminary report,<sup>2</sup> this suggestion is not acceptable since detailed calculations show that such spin effects are entirely negligible at the lowest temperatures at which measurements have been made. Although in a sense this conclusion is a negative one, it is an important link in the determination of the potential barrier, so that it seemed worth while to present the arguments which support it.

The method used is an extension of the group theory technique described earlier<sup>3</sup> for determining the statistical weights of the rotational levels of rigid molecules. The exact spin weight of each of the rotational states for each spin species is obtained and used to calculate the partition functions of the different noncombining species.

## THE WAVE EQUATION

The assumption is usually made that the internal potential energy is of the form

<sup>1</sup> (a) Eucken and Weigert, *Zeits. f. physik. Chemie* **B24**, 277 (1934). (b) G. B. Kistiakowsky and F. Nazmi, *J. Chem. Phys.* **6**, 18 (1938). (c) W. Hunsmann, *Zeits. f. physik. Chemie* **B39**, 1 (1938). (d) G. B. Kistiakowsky, J. R. Lacher, and Fred Stitt, *J. Chem. Phys.* **6**, 407 (1938). See also E. Teller and K. Weigert, *Gött. Nach.* (1933), p. 218, for a calculation of the heat capacity.

<sup>2</sup> E. B. Wilson, Jr., *J. Phys. Chem.* **6**, 408 (1938).

<sup>3</sup> E. B. Wilson, Jr., *J. Chem. Phys.* **3**, 276 (1935).

$$V = \frac{1}{2} V_0 (1 - \cos 3\chi'),$$

$\chi'$  being the internal angle and  $V_0$  the height of the potential barrier. The wave equation for ethane, treated as two connected rigid bodies, has been found<sup>4</sup> to be separable into two equations, one a function of the external Eulerian angles, the other a function of the angle between the methyl groups. The first equation is simply the wave equation for the ordinary rigid symmetrical rotator, whose solutions  $\psi_e = \psi_{JKM}(\theta, \chi, \varphi)$  have been amply studied. The other equation can be written in the form

$$(d^2\psi_i)/(d\gamma^2) + (\beta + 2\lambda \cos 6\gamma)\psi_i = 0, \quad (1)$$

where  $\gamma = \frac{1}{2}\chi'$ ,  $W_i = \frac{1}{2}V_0 + (h^2/8\pi^2C)\beta$ , and

$$\lambda = (8\pi^2C/h^2)V_0/4.$$

Here  $W_i$  is the internal energy,  $V_0$  is the height of the potential barrier,  $h$  is Planck's constant, and  $C$  is the moment of inertia of ethane about the principal symmetry axis.

When either methyl group is turned through an angle of  $2\pi$  radians, the wave function must return to the original value. This rotation adds  $\pi$  to the external Eulerian angle  $\chi$  which is defined as one-half the sum of the Eulerian angles of the two methyl groups. It, therefore, multiplies the wave function by  $e^{iK\pi} = (-1)^K$ . The same rotation changes  $\chi'$  by  $2\pi$  and therefore  $\gamma$  by  $\pi$ . Consequently if  $K$  is even,  $\psi_i(\gamma + \pi)$  must equal  $\psi_i(\gamma)$ , while with  $K$  odd  $\psi_i(\gamma + \pi)$  must equal  $-\psi_i(\gamma)$ . Both of these are periodic in  $2\pi$ , so the problem is to find all solutions  $\psi_i$

<sup>4</sup> H. H. Nielsen, *Phys. Rev.* **40**, 445 (1932). See also J. B. Howard, *J. Chem. Phys.* **5**, 442, 451 (1937).

periodic in  $2\pi$ . Half of these are to be used when  $K$  is even, the other half when  $K$  is odd.

Equation (1) is invariant under the 12 operations  $\gamma \rightarrow \gamma$ ;  $\gamma \rightarrow \gamma + \pi$ ;  $\gamma \rightarrow \gamma \pm 2\pi/3$ ;  $\gamma \rightarrow \gamma \pm \pi/3$ ;  $\gamma \rightarrow -\gamma$ ,  $-\gamma \pm 2\pi/3$ ;  $\gamma \rightarrow -\gamma + \pi$ ,  $-\gamma \pm \pi/3$ ; which fall into the six classes indicated by the above arrangement. These operations form a group which is isomorphous with the standard symmetry point group  $D_6$ . The solutions of the differential equation (1) can therefore be classified according to their symmetry in terms of this group, as will be done below.

When  $\lambda = 0$ , there is complete free rotation and the solutions are

$$\psi_i = \sin m\gamma \text{ and } \cos m\gamma, \quad (2)$$

with  $\beta = m^2$ ,  $m = 0, 1, 2, 3, \dots$ . The normalizing constant has been omitted. These solutions may be classified according to their symmetries, since the solutions for any one energy must form a representation of the point group. It is quickly found that these symmetries are

$$\begin{array}{ll} m=0 & A_1 \\ m=6p & A_1 + A_2 \\ m=6p \pm 1 & E_1 \\ m=6p \pm 2 & E_2 \\ m=6p+3 & B_1 + B_2. \end{array} \quad (3)$$

Here  $p$  is a positive integer, while the symbols  $A_1, A_2$ , etc., represent the irreducible representations of the point group  $D_6$ , whose characters<sup>5</sup> are given in Table I. The result shows that when  $\lambda$  increases from zero, the levels with  $m$  a multiple of 3 will split into two levels (except the lowest level), while the others will retain their twofold degeneracies. For very high values of  $\lambda$ , the lower levels approach those of a harmonic oscillator. By expanding  $\cos 6\gamma$  in the expression for  $V$  and dropping higher terms it is found that as

$$\lambda \rightarrow \infty, \quad \beta \rightarrow (2k+1)6\sqrt{\lambda} - 2\lambda, \quad (4)$$

with  $k = 0, 1, 2, \dots$ . Each of these levels is six-fold degenerate in the limit but the boundary conditions previously mentioned require that for each  $K$  value only three of the solutions can be used, one set of three being used when  $K$  is even, the other set when  $K$  is odd.

For intermediate values of  $\lambda$ , no simple form

<sup>5</sup> J. E. Rosenthal and G. M. Murphy, Rev. Mod. Phys. 8, 317 (1936).

for  $\beta$  exists. The differential equation is a form of Mathieu's equation. Tables of values for  $\beta$  have been published<sup>6</sup> for the solutions with symmetries  $A_1, A_2, B_1$ , and  $B_2$  but the degenerate levels have not been tabulated, although estimates of their positions have been made.<sup>4, 7</sup> Some of these levels have been calculated by an extension of the method described by Goldstein.<sup>6</sup> The principle is as follows. The unknown function  $\psi_i$  is expanded in a Fourier series with

TABLE I. Character table for  $D_6$ .

	$E$	$C_2$	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$
$A_1$	1	1	1	1	1	1
$A_2$	1	1	1	1	-1	-1
$B_1$	1	-1	1	-1	1	-1
$B_2$	1	-1	1	-1	-1	1
$E_1$	2	-2	-1	1	0	0
$E_2$	2	2	-1	-1	0	0

undetermined coefficients:

$$\psi_i = A_1 \cos \gamma + A_5 \cos 5\gamma + A_7 \cos 7\gamma + A_{11} \cos 11\gamma + \text{etc.} \quad (5)$$

It is necessary to use only those cosines which have the desired symmetry, in this case  $E_1$ . This series is substituted into the differential equation and the coefficient of  $\cos k\gamma$  in the reduced result equated to zero. This yields the following recursion formulas

$$\begin{aligned} (\beta - 1)A_1 + \lambda A_5 + \lambda A_7 &= 0, \\ (\beta - 25)A_5 + \lambda A_1 + \lambda A_{11} &= 0, \\ (\beta - 49)A_7 + \lambda A_1 + \lambda A_{13} &= 0, \\ (\beta - m^2)A_m + \lambda A_{m-6} + \lambda A_{m+6} &= 0, \\ m &= 7, 11, 13, \text{etc.} \end{aligned} \quad (6)$$

Let  $v_m = A_{m+6}/A_m$ ,  $u_0 = A_5/A_1$ . Then

$$\begin{aligned} \beta - 1 + \lambda u_0 + \lambda v_1 &= 0, \\ (\beta - 25)u_0 + \lambda + \lambda v_5 u_0 &= 0, \\ (\beta - m^2)v_{m-6} + \lambda + \lambda v_m v_{m-6} &= 0, \quad m > 5. \end{aligned} \quad (7)$$

To determine the value of the lowest root  $\beta$  of symmetry  $E_1$  for a given value of  $\lambda$ , assume that  $v_m = 0$  for some sufficiently high value of  $m$ . Then from Eq. (7) calculate the lower ratios

<sup>6</sup> E. L. Ince, Proc. Roy. Soc. Edin. 52, 355 (1932). S. Goldstein, Trans. Camb. Phil. Soc. 23, 303 (1927).  
<sup>7</sup> K. S. Pitzer, J. Chem. Phys. 5, 469 (1937).

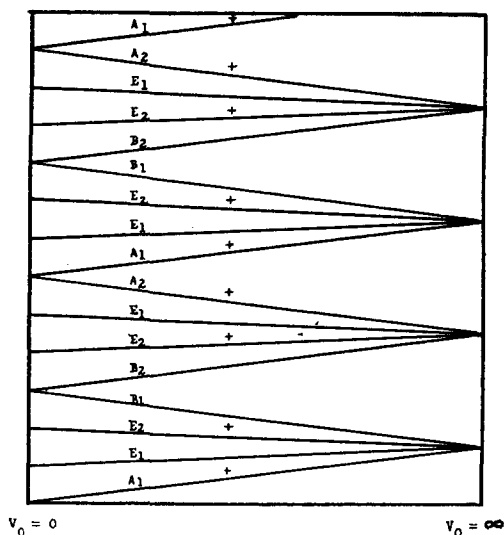


FIG. 1. Diagram showing the way in which the energy levels for free rotation connect with those for oscillation. + signs indicate levels which go with  $K$  even. Letters represent symmetry of level with respect to  $D_6$ . This is not a plot of energy against potential.

$v_{m-6}$ , etc., using an estimated value of  $\beta$ . It is necessary to come down both the  $6p+1$  and the  $6p-1$  series in this way until  $u_0$  and  $v_1$  have been calculated. Then a better approximation to  $\beta$  is calculated from the first equation of Eq. (7). This new value is used in repeating the process for a better approximation. To obtain higher levels, the same method is used except that the estimated value of  $\beta$  is substituted in all the equations except the one containing  $\beta-k^2$ ,  $k^2$  being the value of  $\beta$  for  $\lambda=0$  for the level of interest. Solution of this equation for  $\beta$  gives the next approximation to the root. This method is quite rapid if the barrier is not too high. For high barriers the lower  $E_1$  and  $E_2$  levels are so narrowly limited by the other previously calculated levels above and below them, that they do not need to be computed.

Figure 1 shows the way in which the energy levels  $W_i$  for  $V_0=0$  connect with those for  $V_0$  large. It does not represent the variation of  $W_i$  with  $V_0$ . It is to be remembered that for a given rotational state only half these levels occur. Levels which go with even  $K$  values are marked +.

#### PERMUTATION GROUP AND STATISTICAL WEIGHTS

The permutations of the hydrogen atoms in ethane which are equivalent to rotations of the

molecule (including internal rotation) form a group of 18 operations, hereafter called group  $G$ . This is not isomorphous with any of the standard symmetry point groups, so that it was necessary to determine its classes, irreducible representations, and their characters by the standard group theory methods.<sup>8</sup> The results are contained in Table II. In Table II,  $C_3'$  and  $C_3''$  refer to rotations by  $2\pi/3$  of one methyl group and the other, respectively;  $C_3'^{1/2}$ ,  $C_3''^{1/2}$  are similar

TABLE II. Character table for pure rotation group for ethane (18 elements). Group  $G$ ,  $\omega = \exp(2\pi i/3)$ .

	$E$	$C_3', C_3'^{1/2}$	$C_3'^{1/2}, C_3''^{1/2}$	$C_3, C_3^2$	$C_3' C_3$	$C_3'' C_3$	$3C_2$	$3C_2 C_3'$	$3C_2 C_3''$
$\Gamma_1$	1	1	1	1	1	1	1	1	1
$\Gamma_2$	1	1	1	1	1	1	-1	-1	-1
$\Gamma_3$	1	$\omega$	$\omega^2$	1	$\omega$	$\omega^2$	1	$\omega$	$\omega^2$
$\Gamma_4$	1	$\omega^2$	$\omega$	1	$\omega^2$	$\omega$	1	$\omega^2$	$\omega$
$\Gamma_5$	1	$\omega$	$\omega^2$	1	$\omega$	$\omega^2$	-1	$\omega$	$\omega^2$
$\Gamma_6$	1	$\omega^2$	$\omega$	1	$\omega^2$	$\omega$	-1	$\omega^2$	$\omega$
$\Gamma_7$	2	$-\omega$	$-\omega^2$	-1	$2\omega$	$2\omega^2$	0	0	0
$\Gamma_8$	2	$-\omega^2$	$-\omega$	-1	$2\omega^2$	$2\omega$	0	0	0
$\Gamma_9$	2	-1	-1	-1	2	2	0	0	0
$h$	1	2	2	2	1	1	3	3	3

rotations by  $4\pi/3$ ;  $C_3$  and  $C_3^2$  are rotations by  $2\pi/3$  and  $4\pi/3$  of both methyl groups simultaneously;  $C_2$  is an end over end rotation by  $\pi$ .  $C_2 C_3'$ , for example, represents the product of  $C_2$  and  $C_3'$ , when written without a comma.  $\Gamma_i$  is the symbol for the  $i$ th irreducible representation and  $h$  is the number of operations in each class.

The next step is to find the number of nuclear spin wave functions in each irreducible representation. There are  $2^6=64$  spin functions for  $C_2H_6$ . The methods previously described<sup>3</sup> quickly show that the symmetry of these spin functions is

$$10\Gamma_1 + 6\Gamma_2 + 3\Gamma_3 + 3\Gamma_4 + \Gamma_5 + \Gamma_6 + 8\Gamma_7 + 8\Gamma_8 + 4\Gamma_9.$$

Since  $\Gamma_7$ ,  $\Gamma_8$  and  $\Gamma_9$  are each doubly degenerate, this accounts for all 64 functions. The same treatment of  $C_2D_6$  gives

$$66\Gamma_1 + 55\Gamma_2 + 36\Gamma_3 + 36\Gamma_4 + 28\Gamma_5 + 28\Gamma_6 + 88\Gamma_7 + 88\Gamma_8 + 64\Gamma_9.$$

The effect of the symmetry operations of group  $G$  on  $\psi_i$ , the internal wave function, is best obtained by a consideration of the rotational subgroup  $C_6$  of the group  $D_6$ . The characters for

<sup>8</sup> See, for example, E. Wigner, *Gruppentheorie*.

$C_6$  are given in Table III. Comparing Table I and Table III, one sees that the representations of  $D_6$  are related to those of  $C_6$  as follows:  $A_1, A_2 \rightarrow A$ ;  $B_1, B_2 \rightarrow B$ ;  $E_1 \rightarrow E_1$ ;  $E_2 \rightarrow E_2$ . Furthermore, the operations of the group  $G$  are related to those of  $C_6$  by their effect on  $\gamma$  as follows:  $E \rightarrow E$ ,  $C_3' \rightarrow C_6$ ,  $C_3'^2 \rightarrow C_3$ ,  $C_3 \rightarrow E$ ,  $C_3' C_3 \rightarrow C_6$ ,  $C_3'' C_3 \rightarrow C_6^5$ . These operations affect  $\chi$  as follows:  $E\chi \rightarrow \chi$ ,  $C_3'\chi \rightarrow \chi + \pi/3$ ,  $C_3'^2\chi \rightarrow \chi + 2\pi/3$ ,  $C_3\chi \rightarrow \chi + 2\pi/3$ ,  $C_3' C_3\chi \rightarrow \chi + \pi$ ,  $C_3'' C_3\chi \rightarrow \chi + \pi$ . Since

TABLE III. Character table for  $C_6$ .

	$E$	$C_6$	$C_3$	$C_2$	$C_3^2$	$C_6^5$
$A$	1	1	1	1	1	1
$B$	1	-1	1	-1	1	-1
$E_1$	$\begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$	$\omega$	$\omega^2$	1	$\omega$	$\omega^2$
		$\omega^2$	$\omega$	1	$\omega^2$	$\omega$
$E_2$	$\begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$	$-\omega^2$	$\omega$	-1	$\omega^2$	$-\omega$
		$-\omega$	$\omega^2$	-1	$\omega$	$-\omega^2$

$\psi_e = e^{iK\chi} f_{JK}(\theta, \varphi)$ , this enables one to calculate the effect of the operations of  $G$  on  $\psi_e$ . Table IV contains the characters of the representations formed by  $\psi_e \psi_i$  for various quantum numbers, as well as their symmetries calculated therefrom.

There now remains the problem of combining the spin and rotation functions in such a way that the whole function has the correct symmetry. For  $C_2H_6$  this correct symmetry is  $\Gamma_2$  of  $G$ , since this is the antisymmetric representation. For  $C_2D_6$ , it is  $\Gamma_1$ , the symmetric representation. Table V gives the necessary multiplication relations between the representations of  $G$ . The use of these, together with the symmetries of the rotational and spin functions previously obtained, yields the statistical weights of the rotational levels given in Table VI. The assumption

has been made that the electronic and vibrational wave functions are completely symmetrical. This is not always true for excited vibrational states, but they do not contribute appreciably to the thermodynamic properties at low temperatures; also, since it will be found that spin effects are negligible, the general conclusions will hold even with vibrational excitation. Table VI, however, will be different for states with  $\psi_v$  not completely symmetrical.

TABLE V. Multiplication table for group  $G$ .

$\Gamma_1 \times \Gamma_2 = \Gamma_3 \times \Gamma_6 = \Gamma_4 \times \Gamma_5 = \Gamma_2$ ;
$\Gamma_1 \times \Gamma_1 = \Gamma_2 \times \Gamma_2 = \Gamma_3 \times \Gamma_4 = \Gamma_5 \times \Gamma_6 = \Gamma_1$ ;
$\Gamma_7 \times \Gamma_8 = \Gamma_1 + \Gamma_2 + \Gamma_9$ ; $\Gamma_9 \times \Gamma_9 = \Gamma_1 + \Gamma_2 + \Gamma_9$

### NONCOMBINING SPECIES

The group  $G$  has 9 irreducible representations but  $\Gamma_3$  and  $\Gamma_4$ ,  $\Gamma_5$  and  $\Gamma_6$ , and  $\Gamma_7$  and  $\Gamma_8$  are complex conjugate pairs. Consequently, states with spin symmetry  $\Gamma_3$  have the same rotational weights as those with spin symmetry  $\Gamma_4$ , etc. Therefore there can be only 6 species of ethane whose proportions could be altered in the same way as is done with ortho- and parahydrogen. Later it will be shown that these species divide into two sets such that only at very low temperatures could there be any possible segregation of members of the same set. Finally it will be shown that there is no change in the proportions of even the two sets of species at temperatures as high as 90°K.

### PARTITION FUNCTIONS

The partition functions for each of the six noncombining species of  $C_2H_6$  are given below.

TABLE IV. Characters for the representations formed by  $\psi_e \psi_i$  and their symmetries.  $p = \text{integer}$ .

$K$	$J$	$\psi_i$	$E$	$C_3', C_3'^2$	$C_3'^2, C_3'$	$C_3, C_3^2$	$C_3' C_3$	$C_3'' C_3$	$3C_2$	$3C_2 C_3'$	$3C_2 C_3''$	Sym.
0	even	$A$	1	1	1	1	1	1	1	1	1	$\Gamma_1$
0	odd	$A$	1	1	1	1	1	1	-1	-1	-1	$\Gamma_2$
0	even	$E_1$	2	-1	-1	2	-1	-1	2	-1	-1	$\Gamma_3 + \Gamma_4$
0	odd	$E_1$	2	-1	-1	2	-1	-1	-2	1	1	$\Gamma_5 + \Gamma_6$
$6p$		$A$	2	2	2	2	2	2	0	0	0	$\Gamma_1 + \Gamma_2$
$6p$		$E_1$	4	-2	-2	4	-2	-2	0	0	0	$\Gamma_3 + \Gamma_4 + \Gamma_5 + \Gamma_6$
$6p \pm 1$		$B$	2	-1	-1	-1	2	2	0	0	0	$\Gamma_9$
$6p \pm 1$		$E_2$	4	1	1	-2	-2	-2	0	0	0	$\Gamma_7 + \Gamma_8$
$6p \pm 2$		$A$	2	-1	-1	-1	2	2	0	0	0	$\Gamma_9$
$6p \pm 2$		$E_1$	4	1	1	-2	-2	-2	0	0	0	$\Gamma_7 + \Gamma_8$
$6p \pm 3$		$B$	2	2	2	2	2	2	0	0	0	$\Gamma_1 + \Gamma_2$
$6p \pm 3$		$E_2$	4	-2	-2	4	-2	-2	0	0	0	$\Gamma_3 + \Gamma_4 + \Gamma_5 + \Gamma_6$

TABLE VI. Statistical weights and symmetries of rotational levels (not including factor  $2J+1$  in weights) for symmetrical vibrational states.

K	J	$\psi_i$	C <sub>2</sub> H <sub>2</sub>		C <sub>2</sub> D <sub>2</sub>	
			$\psi_s$	Wt.	$\psi_s$	Wt.
0	even	A	$\Gamma_2$	6	$\Gamma_1$	66
0	odd	A	$\Gamma_1$	10	$\Gamma_2$	55
0	even	E <sub>1</sub>	$\Gamma_3+\Gamma_4$	2	$\Gamma_3+\Gamma_4$	72
0	odd	E <sub>1</sub>	$\Gamma_3+\Gamma_4$	6	$\Gamma_3+\Gamma_4$	56
6p		A	$\Gamma_1+\Gamma_2$	16	$\Gamma_1+\Gamma_2$	121
6p+3		B	$\Gamma_1+\Gamma_2$	16	$\Gamma_1+\Gamma_2$	121
6p		E <sub>1</sub>	$\Gamma_3+\Gamma_4+\Gamma_5+\Gamma_6$	8	$\Gamma_3+\Gamma_4+\Gamma_5+\Gamma_6$	128
6p+3		E <sub>2</sub>	$\Gamma_3+\Gamma_4+\Gamma_5+\Gamma_6$	8	$\Gamma_3+\Gamma_4+\Gamma_5+\Gamma_6$	128
6p±1		B	$\Gamma_3$	4	$\Gamma_3$	64
6p±2		A	$\Gamma_3$	4	$\Gamma_3$	64
6p±1		E <sub>2</sub>	$\Gamma_7+\Gamma_8$	16	$\Gamma_7+\Gamma_8$	176
6p±2		E <sub>1</sub>	$\Gamma_7+\Gamma_8$	16	$\Gamma_7+\Gamma_8$	176

The nuclear spin symmetries are enclosed in parentheses.

$$Q_a = 10R_A(P_1+S_0) + 10R_B S_3, (\Gamma_1)$$

$$Q_b = 6R_A(P_2+S_0) + 6R_B S_3, (\Gamma_2)$$

$$Q_c = 6R_{E_1}(P_1+S_0) + 6R_{E_2} S_3, (\Gamma_3+\Gamma_4)$$

$$Q_d = 2R_{E_1}(P_2+S_0) + 2R_{E_2} S_3, (\Gamma_5+\Gamma_6)$$

$$Q_e = 16R_{E_1}(S_2+S_4) + 16R_{E_2}(S_1+S_5), (\Gamma_7+\Gamma_8)$$

$$Q_f = 4R_A(S_2+S_4) + 4R_B(S_1+S_5), (\Gamma_9)$$

in which the symbols have the following meaning.

$R_x = \sum e^{-W_{ix}/kT}$ , summed over all the internal energy levels of symmetry  $x=A, B, E_1$  or  $E_2$ .  $E_1$  and  $E_2$  levels are to be counted once each in these sums.

$$P_1 = \sum_J (2J+1) \exp [-J(J+1)h^2/8\pi^2 A kT],$$

summed over all odd values of  $J$  from 1 to  $\infty$ .  $A$  is the moment of inertia about an axis perpendicular to the C-C axis.  $P_2$  is the similar sum over the even values of  $J$  from zero to  $\infty$ .

$$S_n = \sum_{J, K} (2J+1) \exp [-(h^2/8\pi^2 A kT) \times \{J(J+1) + K^2[(A/C)-1]\}],$$

where  $J$  runs from zero to  $\infty$ , and  $K=6p+n$  with  $p=0, 1, 2, \dots$ , etc., but  $K \leq J$  and  $K > 0$ .

The sums  $P_1$ ,  $P_2$  and  $S_n$  have been evaluated with the aid of their Euler-MacLaurin expansions,<sup>9</sup> the first terms of which are given below.

<sup>9</sup> L. S. Kassel, Chem. Rev. 18, 277 (1936). Whittaker and Watson, *Modern Analysis*, Sec. 7.21.

$$P_1 = \frac{1}{2\sigma} \left\{ 1 + \frac{1}{3}\sigma + \frac{1}{15}\sigma^2 + \frac{4}{315}\sigma^3 + \dots \right\},$$

$$P_2 = P_1 \text{ to terms in } \sigma^3,$$

$$S_n = \frac{1}{12\sigma} (\pi/\nu)^{\frac{1}{2}} \left\{ 1 + \frac{1}{3}\sigma - \frac{1}{12}(\sigma^2/\nu) + \dots \right\} - (\alpha/\sigma),$$

with  $\alpha = \frac{1}{2}$  for  $n=0$ ,  $\frac{1}{3}$  for  $n=1$ ,  $\frac{1}{6}$  for  $n=2$ , 0 for  $n=3$ ,  $-\frac{1}{6}$  for  $n=4$ ,  $-\frac{1}{3}$  for  $n=5$ . Here

$$\sigma = (h^2/8\pi^2 A kT), \quad \nu = (h^2/8\pi^2 C kT).$$

At 90°K or higher, it is sufficient to take the first term of  $P_1$  and  $P_2$ . To this order of accuracy,  $P_1+S_0$ ,  $P_2+S_0$ ,  $S_2+S_4$ ,  $S_1+S_5$ , and  $S_3$  are all equal so that  $Q_a$ ,  $Q_b$ ,  $Q_f$  are proportional to each other as are  $Q_c$ ,  $Q_d$  and  $Q_e$ . There can be no shift in relative proportions, therefore, inside these groups, but there might be a change in the relative proportions of the two groups, depending on whether or not  $R_A+R_B$  is always proportional to  $R_{E_1}+R_{E_2}$ .

The evaluation of  $R_A+R_B$  and  $R_{E_1}+R_{E_2}$  was carried out for barriers of height zero, 300 and about 3000 cal. For zero barrier, the functions are theta-functions<sup>10</sup> so that

$$R_A+R_B = \frac{1}{3}(\pi/\nu)^{\frac{1}{2}} \{1 + 2 \exp(-\pi^2/9\nu) + \dots\},$$

$$R_{E_1}+R_{E_2} = \frac{1}{3}(\pi/\nu)^{\frac{1}{2}} \{1 - 2 \exp(-\pi^2/9\nu) - \dots\}.$$

Since  $\nu \approx 0.043$  at 100°K, these functions differ by less than 1 in  $10^9$ .

For a barrier of 300 cal.,  $R_A+R_B$  and  $R_{E_1}+R_{E_2}$  were obtained by actual summation over the energy levels and were found to be the same, at least to 1 part in a thousand, even at 50°K. For this barrier the heat capacity was calculated for several temperatures above 90°K and no difference was found between the two species.

For high barriers the two types of energy levels ( $A, B$  and  $E_1, E_2$ ) coincide so closely that it is not necessary to carry out the numerical calculations to see that there can be no difference in the partition functions and heat capacities of the two species above 90°K.

Where comparisons were made, it was found that the values for the thermodynamic quantities which were obtained agreed with those tabulated by Pitzer.<sup>7</sup>

<sup>10</sup> Whittaker and Watson, *Modern Analysis*, Sec. 21.51.

## DISCUSSION

These calculations show that no appreciable change in the equilibrium proportions of the several species of ethane can take place unless the temperature is reduced considerably below 50°K. It is therefore impossible to account for the low value of the observed heat capacity of  $C_2H_6$  at 94°K by postulating such spin effects. Since  $C_2D_6$  is heavier, spin effects will not occur in this molecule until still lower temperatures are considered. The only other explanation which has been proposed for the low temperature heat capacity is the existence of a barrier of about 3000 cal., an explanation which is compatible with all the known experimental data on ethane, including the heat capacity, Raman and infra-red vibrational spectra, infra-red rotational spectrum, entropy from the third law and from equilibrium measurements, etc. Some of these data are also compatible with the low value of the barrier, but not all of them, so that the evidence at present seems quite strong for the high barrier.

It should be emphasized, however, that this "barrier height" is a rather arbitrary quantity, being the value of the parameter  $V_0$  in the function  $V = \frac{1}{2} V_0 (1 - \cos 3\chi')$  chosen so as to give the best fit with certain observed thermodynamic properties. If a different shape for the potential barrier is assumed, the "height" may need to be changed considerably in order to obtain agreement with experiment. For example,

rough calculations with a square shape of barrier in which the width of the "valleys" is equal to the width of the "hills" shows that in order to fit the heat capacity at 100° a very high "barrier" is needed—over ten thousand calories. Such a calculation means very little, however, because at 100°K, even the second level above the ground level contributes but slightly to the heat capacity (assuming roughly equal spacing), so that this experimental value can give very little information about the nature of the barrier except that it must yield no level nearer than about 280 wave numbers or 800 cal. from the ground state. Heat capacity data at higher temperatures would yield information about higher levels but there is the difficulty that the importance of these higher levels is possibly of the same order of magnitude as that of the unknown, low lying fundamental frequency of vibration. Until this frequency is definitely located from spectroscopic arguments it is not safe to draw too refined conclusions from the heat capacity data at higher temperatures.

Nevertheless, whatever the shape, it seems evident that the barrier must be fairly high in order that the lowest excited state may be as high as 280 cm.\*

\* *Note added in proof:* Since the above was submitted, a paper by K. Schäfer, *Zeits. f. physik. Chemie* **40**, 357 (1938), has been received, belonging to the same series as that of Hunsmann, ref. 1. In it methods similar to those used above lead to the same conclusion, and as a consequence, Schäfer accepts the high value of the barrier.