SEPTEMBER 1, 1931 PHYSICAL REVIEW VOLUME 38

THE LOW TEMPERATURE ROTATIONAL HEAT CAPACITIES AND THE RELATIVE AMOUNTS OF THE NUCLEAR SINGLET, TRIPLET AND QUINTET SYMMETRY MODIFICATIONS OF METHANE

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(Received July 11, 1931)

Abstract

There should be three noncombining varieties of methane, the nuclear singlet, triplet and quintet, and two of ammonia, the nuclear doublet and quadruplet, just as there are two of hydrogen, the nuclear singlet and triplet ("para" and "ortho" hydrogen). In this paper the statistical weights of the rotational states have been evaluated and used in conjunction with the Raman spectra data to calculate the heat capacities of each separate variety of methane, of the true equilibrium mixture and of the "frozen equilibrium" mixture. The feasibility of demonstrating experimentally the existence of these different varieties of methane is discussed in the light of the present calculations.

THE elegant experiments of Bonhoeffer, Harteck[1] and co-workers and of Eucken[2] who experimentally verified the predicted[3] existence of the two symmetry modifications of hydrogen, nuclear singlet and triplet (commonly designated by the perverted[4] nomenclature, para and ortho-hydrogen) led one to immediate speculations[1] concerning similar modifications of other compounds containing more than one hydrogen atom to the molecule. Owing to a discovery by one of us[5] of some peculiar differential vapor pressure effects with methane at liquid air temperature treated with and without active charcoal, it was deemed desirable to make calculations of the relative amounts of the different forms, their specific heats and the average specific heat of the mixture in true equilibrium and of the one in the frozen metastable equilibrium, since it was by such differences that Bonhoeffer was able to make his

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[1] Bonhoeffer and Harteck, Naturwiss **17**, 182 (1929); Zeits. f. phys. Chem. **B4**, 113 (1929)' Sitzb. Preuss. Akad. Wiss. **103**, (1929). Abhandl. a. d. Kaiser Wilhelm nst. f. Phys. u. El' Chem. **12**, 121, 129, 305 (1929).

[2] Eucken, Naturwiss **17**, 182 (1929); Eucken and Hiller, Zeits. phys. Chem. **B4**, 142–157 (1929).

[3] Heisenberg, Zeits. f. Physik **41**, 239 (1927); Hund, ibid. **42**, 93 (1927).

[4] Cf. Eucken and Hiller, Zeits. f. phys. Chem. **B4**, 142 (1927) their footnote 4; Mulliken, Trans. Faraday Soc. **25**, 634–645 (1929), especially p. 638 his footnote 16.

[5] G. S. These experiments were first made during the winter of 1929–30. Later experiments more carefully performed showed that the observed differences in vapor pressure might be ascribed to delay in reaching equilibrium between liquid and vapor as well as to a change from the "frozen" to the pure equilibrium which was at first postulated. A minor effect may still be found to exist by means of an improved differential method for determining the vapor pressure which we intend to apply. In the meanwhile Harteck and Schmidt (Naturwiss. **18**, 282 (1930) have looked unsuccessfully for such an effect in nitrogen, methane and chlorine.

famed experiments. In this paper we wish to present the results of this calculation, reserving for a possible subsequent one the description of the experimental work which has been in progress now for over a year.

THEORETICAL

In order to calculate the heat capacity of a gas, it is necessary to know the energy levels ϵ_i and their *a priori* probabilities. When these are known, use is made of the familiar equations:

$$n_i = n_0 p_i e^{-\epsilon_i/kT} \tag{1}$$

$$E = N\frac{\sum_i n_i\epsilon_i}{\sum_i n_i} \tag{2}$$

$$MC_v = \partial E/\partial T. \tag{3}$$

If we neglect stretching effects, the rotational levels are given by the formulae

$$\epsilon_j = j(j+1)h^2/8\pi^2 I \tag{4}$$

if the molecule is rod-shaped, or

$$\epsilon_{j,\tau} = (h^2/8\pi^2)[j(j+1)/A + (1/C - 1/A)\tau^2] \qquad \tau \leq j \tag{5}$$

if it is shaped like a symmetrical top.

The *a priori* probabilities measure the degeneracy of the energy levels and may be looked upon as the number of levels which happen to have exactly the same energy. The vector model of the molecule is an accurate guide in simple cases for finding the number of these levels, for it is the number of quantized orientations which the angular momentum may take on in a force field, $(2j+1)$ for the rod shaped molecule or $(2j+1)^2$ for the symmetrical top, if we lump all possible values of τ associated with each j. The rigorous rule is to be found from the application of the Pauli principle in quantum mechanics. The *a priori* probability is the number of *different ways* of combining subsidiary eigenfunctions to get a total eigenfunction completely antisymmetric[6] in the protons. The total eigenfunction may be ordinarily[7] taken as a product of the electronic, vibrational, rotational and nuclear eigenfunctions, which we call subsidiary.

$$\psi = \psi_{\text{el}}\psi_{\text{vibr}}\psi_{\text{rot}}\psi_{\text{nuclei}} \tag{6}$$

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[6] An antisymmetric function, A, is defined as one which has its sign changed by interchanging the designations of two like particles; a symmetric function, S, is defined as one which suffers no change from such an interchange. If the like particles are electrons, we speak of symmetry characteristics in (regard to) the electrons; if the like particles are protons, symmetry in the protons; if the like particles are nuclei, symmetry in the nuclei. Symmetry in the electrons is of interest to a discussion of the electron multiplicities. In the present problem we are interested only in the symmetry characteristics in the nuclei (or protons—the designations are equivalent for hydrogen) and hereafter shall be understood as referring only to the latter type.

[7] Hund, Zeits. f. Physik **43,** 805 (1927).

If the molecule is in its lowest electronic and vibrational state, they may be disregarded since they are symmetric (exceptions occur when there is an extra unlike atom in the molecule, with the result that the lowest vibrational state may be double, both A and S) and do not change the symmetry character of any function which they multiply. In the case of two equal nuclei, the products obey the rule

$$\left.\begin{aligned} S \times S &= S \\ S \times A &= A \\ A \times A &= S \end{aligned}\right\} \tag{7}$$

As an illustration of how these rules are applied to the problem of *a priori* probabilities, let us review the case for hydrogen. Hund[8] has shown that the even numbered rotational states are S in the nuclei and the odd ones are A. There are $(2j+1)$ different eigenfunctions which belong to each ϵ_j rotational level. For each successive value of j, there are therefore, beginning with zero, $1S$, $3A$, $5S$, $7A$, etc. eigenfunctions. Since to obey the Pauli principle, the total eigenfunction (6) must be A, each S eigenfunction listed above may combine with only an A function of the nuclear spin (and not with a S one) while each A above must combine with a S nuclear spin function. If we represent[9] the two spin eigenfunctions (corresponding to the two orientations) by α and β, we have the following possible combinations,

$$\left.\begin{aligned} &\alpha_1\alpha_2 \\ &\alpha_1\beta_2 + \alpha_2\beta_1 \\ &\beta_1\beta_2 \end{aligned}\right\} S \quad \alpha_1\beta_2 - \alpha_2\beta_1\, A \tag{8}$$

and see that there are $3S$ and $1A$ ones. This means that the *a priori* probabilities of the successive rotational states of hydrogen are 1, 3×3, 1×5, 3×7, 1×9, etc. and since there is very little coupling force to re-orient the nuclear spins in the molecule, a system of nuclear triplet molecules will act as a distinct molecular species entirely independently of a system of nuclear singlet molecules. If the temperature is lowered greatly, the triplet molecules fall into their lowest rotational state ($j=1$) and the singlet molecules into their lowest ($j=0$) and only after a catalytic action which involves a dissociation of the molecules into atoms will the triplet kind change into the singlet variety[10] until equilibrium is established.

When we wish to extend these considerations to the case of three like atoms, we find eigenfunctions which are not completely symmetric or antisymmetric, occurring along with those which are. Hund[11] has introduced the

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[8] Hund, Zeits. f. Physik **42,** 93 (1927).

[9] Pauli, Zeits. f. Physik **43,** 601–623 (1927).

[10] We hold with Rodebush that there are only two varieties of hydrogen and that the definition of Giauque (J. Am. Chem. Soc. **52,** 4812, 4822 (1930); Giauque and Johnston, ibid. **50,** 3221 (1928) which calls each molecule in a different energy level a different kind is an unjustified distortion of the word's commonly accepted meaning.

[11] Hund, Zeits. f. Physik **43,** 788 (1927).

term "symmetry character" to designate these different kinds and has discussed the rules of manipulating them. $S(3)$ is an eigenfunction, S in the interchange of two of any three particles; $S(2+1)$ is S in a certain pair but not for any other; and $S(1+1+1)$ is S in none. Hund has also shown that the latter character symmetric in no pair is completely antisymmetric $A(3)$, that the first completely symmetric is antisymmetric in no pair $A(1+1+1)$ and that the second is reciprocal to itself, i.e., is likewise $A(2+1)$.

As an illustration, we take the three different eigenfunctions, a, b, and c as characterizing successively the three equal particles, 1, 2, and 3.

$$\begin{array}{llcccccccccc} S(3) & = a_1b_2c_3 & + & a_1b_3c_2 & + & a_2b_1c_3 & + & a_2b_3c_1 & + & a_3b_1c_2 & + & a_3b_2c_1 \\ S(2+1) & = & - & & + & & - & & + & & + & \\ S(1+1+1) & = & - & & - & & + & & + & & - & \end{array} \tag{9}$$

The reader may easily verify the fact that the sign of $S(3)$ remains unaltered on interchanging any two of the three particles, that of $S(1+1+1)$ is changed, and that of $S(2+1)$ remains unaltered if one interchanges particles 1 and 2, but a new function is obtained on interchanging 3 with one of the other two. Hund and others call the latter eigenfunction "degenerate." Whether we should count this degeneracy in computing statistical weights may be seen by setting up the spin functions for three like nuclei, and comparing the results with those given by the vector model, which we know gives the correct multiplicity. Each nucleus has two orientation possibilities. Therefore, there are 2^3 permutations of the eigenfunctions as well as orientations of the component vectors. In the following tabulations it may thus be seen that the complete degeneracy must be counted, otherwise a dissociation of the molecule into separate hydrogen atoms would create new nuclear spin statistical weights, which is impossible.

Three nuclei

$$\begin{array}{lll} \alpha\alpha\alpha & S(3) & \\ \alpha\alpha\beta & S(3) & S(2+1) \\ \alpha\beta\beta & S(3) & S(2+1) \\ \beta\beta\beta & S(3) & \\ \text{degeneracy} & & \text{two fold} \end{array} \tag{10}$$

Four nuclei

$$\begin{array}{llll} \alpha\alpha\alpha\alpha & S(4) & & \\ \alpha\alpha\alpha\beta & S(4) & S(3+1) & \\ \alpha\alpha\beta\beta & S(4) & S(3+1) & S(2+2) \\ \alpha\beta\beta\beta & S(4) & S(3+1) & \\ \beta\beta\beta\beta & S(4) & & \\ \text{degeneracy} & & \text{three} & \text{two} \end{array} \tag{11}$$

The two doublet systems represented are roughly analogous to the different systems of same multiplicity and like L so often encountered in a supermultiplet in electronic spectra. For four nuclei the total number of permutations including degeneracies is 16, as is also the total number of independent orientations of the four nuclei. The symmetry characters with more than two terms in the argument are excluded because, as Hund has shown, these do not occur when the spin can take on not more than two values. The $S(2+2)$ characters are missing from the $\alpha\beta\beta\beta$ case since there is only one pair of different eigenfunctions. How this works out can be seen by writing equation (9) with $b=a$. The function for $S(1+1+1)$ would come out identically zero.

The results of Hund show that in a molecule like NH_3 the number of ψ_{vibr}s of the lowest state are one $S(3)$ and one $S(1+1+1)$. The number and kind of rotational eigenfunctions are given in Table I.

TABLE I. *Rotational eigenfunctions of ammonia.*

τ	$=0$		$\equiv 1, 2$		$\equiv 3$	
j_{even}	$(2j+1)$	$S(3)$	$2(2j+1)$	$S(2+1)$	$(2j+1)$ $(2j+1)$	$S(3)$ $S(1+1+1)$
j_{odd}	$(2j+1)$	$S(1+1+1)$	$2(2j+1)$	$S(2+1)$	$(2j+1)$ $(2j+1)$	$S(3)$ $S(1+1+1)$

where $\tau\equiv 1$ means $(\tau-1)/3$ is a positive integer (can be zero). For each positive value of τ there is a negative one, which we take account of by the factor 2.

Likewise, the results of Elert[12] show that, in the ground vibrational state of methane, there is one $S(4)$ and one $S(1+1+1+1)$ function. In our discussion we shall discard the use of the "half system" proposed by Hund and used by Elert, and translate the latter's results into terms of the "complete" system, at the same time keeping account of the two different vibrational symmetry characters of the lowest vibrational state. This is less confusing in making the ultimate count of the different ways of getting a completely antisymmetric eigenfunction. As to the rotational states, all three moments of inertia are equal and hence formula (5) applies, giving an *a priori* weight of $(2j+1)^2$ to each j term, the fine structure being completely degenerate. Elert has demonstrated that the following distribution of these $(2j+1)^2$ characters among the different j states holds, at least for the first few states, and believes the rule is general, although he could not prove it.

TABLE II. *Rotational eigenfunctions of methane.*

j	$S(4)$	$S(3+1)$	$S(2+2)$
$\equiv 0$	$(j/6+1)(2j+1)$	$(3j/2)(2j+1)$	$(j/3)(2j+1)$
1	$[(j-1)/6](2j+1)$	$[(3j+3)/2](2j+1)$	$[(j-1)/3](2j+1)$
2	$(1/3)(j/2-1)(2j+1)$	$(3j/2)(2j+1)$	$[(2/3)(j/2-1)+2](2j+1)$
3	$[(j-3)/6+1](2j+1)$	$[(3j+3)/2](2j+1)$	$[(j-3)/3](2j+1)$
4	$(1/3)(j/2+1)(2j+1)$	$(3j/2)(2j+1)$	$(2/3)(j/2+1)(2j+1)$
5	$[(j-5)/6](2j+1)$	$[(3j+3)/2](2j+1)$	$[(j-5)/3+2](2j+1)$

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[12] Elert, Zeits. f. Physik **51**, 6–33 (1928).

In order to compute the *a priori* probabilities we now proceed as follows. From (11) we see there are five $S(4)$ spin eigenfunctions, three times three $S(3+1)$ and one times two $S(2+2)$. We desire to count the total number of ways we can combine the functions (6) to get a completely antisymmetric function, $S(1+1+1+1)$. In doing this we must keep in mind that, according to Hund and Elert only one-fourth of the products of two $S(2+1)$ or two $S(2+2)$ functions can be combined to a completely symmetric function and one-fourth to a completely antisymmetric one, while one-ninth of the combinations of two $S(3+1)$ functions multiplied together can be resolved into a completely symmetric function.[13] Table III gives the results, keeping separate those arising from each nuclear spin state, as these form different non-combining varieties of methane, just as they form the two non-combining varieties of hydrogen.

TABLE III. *Rotational weights of different varieties of methane.*

j	$S(4)$ Quintet	$S(3+1)$ Triplet	$S(2+2)$ Singlet
0	5×1	0	0
1	0	3·3	0
2	0	5·3	5·2
3	7	7·6	0
4	9	9·6	9·2
5	0	11·9	11·2
6	13·2	13·9	13·2
7	15	15·12	15·2
8	17	17·12	17·4
9	19·2	19·15	19·2
10	21·2	21·15	21·4

CALCULATIONS

Before making use of Eqs. (1) to (4), we shall introduce the substitution

$$\sigma = h^2/8\pi^2 IkT \tag{12}$$

$$= 0.716\Delta/T \tag{13}$$

where

$$\Delta = 2B = 2h/8\pi^2 cI \text{ cm}^{-1} \tag{14}$$

is the spacing in wave numbers of the lines in the normal band spectrum.

Unfortunately, in the case of methane, we are entangled with an ambiguity in interpretation of the experimental data. Cooley[14] found three different spacings, 5.41 (7.7μ band), 9.77 (3.31μ) and 15.3 cm^{-1} (3.5μ band), of which 9.77 most likely represents the moment of inertia of the molecule (5.66×10^{-40} gm. cm^2). This is near the value obtained from Raman spectra,[15] 5.17×10^{-40} corresponding to an absorption-emission line spacing of $\Delta=2$

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[13] Cf. Ludloff, Zeits. f. Physik **57**, 227–241 (1929).

[14] Cooley, Astrophys. J. **62**, 73–83 (1925).

[15] Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929).

[16] Mecke, Zeits. f. phys. Chem. **B7**, 108–129 (1930).

$\times 5.363$ cm^{-1}, and since this value was capable of the more accurate measurement we shall take it to translate σ into temperature.

$$\sigma = 0.716 \times 10.726/T.$$

Further support for the correctness of this moment of inertia as against that calculated from the other spacings 10.2 and 3.61×10^{-49}, lies in Mecke's[16] comparison of the CH, NH and OH nuclear distances in the free radicals with the corresponding distances in the saturated hydrides. The use of $I=10.2\times 10^{-40}$ would give a CH distance out of line with the trend in the other molecules of the series.

Abbreviating the summation of the statistical weights by

$$Q = \sum_i n_i/n_0 = \sum_i p_i e^{-j(j+1)\sigma} \tag{15}$$

and changing the variable from T to σ in (3) we get

$$\begin{aligned} C_i/R &= (\sigma^2/Q_i^2)\left[Q_i d^2Q_i/d\sigma^2 - (dQ_i/d\sigma)^2\right] && (16)\\ &= \sigma^2 d^2 \ln Q/d\sigma^2 && (16a)\end{aligned}$$

where i refers respectively to the nuclear quintet, triplet and singlet forms. The values of Q_i are to be obtained from (15) and Table III and are, up to the 100σ power in the exponent:

$$\begin{aligned} {}^5Q_1/5 = {} & 1 + 7e^{-12\sigma} + 9e^{-20\sigma} + 26e^{-42\sigma} + 15e^{-56\sigma} \\ & + 17e^{-72\sigma} + 38e^{-90\sigma} \end{aligned} \tag{17}$$

$$\begin{aligned} {}^3Q_2 = {} & 9e^{-2\sigma} + 15e^{-6\sigma} + 42e^{-12\sigma} + 54e^{-20\sigma} \\ & + 99e^{-30\sigma} + 117e^{-42\sigma} + 180e^{-56\sigma} + 204e^{-72\sigma} \\ & + 285e^{-90\sigma} \end{aligned} \tag{18}$$

$$\begin{aligned} {}^1Q_3 = {} & 10e^{-6\sigma} + 18e^{-20\sigma} + 22e^{-30\sigma} + 26e^{-42\sigma} \\ & + 30e^{-56\sigma} + 68e^{-72\sigma} + 38e^{-90\sigma}. \end{aligned} \tag{19}$$

The coefficients of the terms in the above expressions as well as of those for the various derivatives are arranged in Table IV, at the bottom of which are given the calculated values of corresponding sums for four different values of σ, chosen to represent temperatures ranging from below the boiling point of liquid hydrogen to those of liquid air and above. In Table V are given the corresponding rotational specific heats obtained by applying Eq. (16). An idea of the rapidity of convergence of the different series for the least value of σ (0.0430) and the consequent accuracy of the summations may be gained from Table VI in which are given the ratio of the next to last to the last term taken and the percent of the whole sum (up to and including the last term) which the last term constitutes. From this we see that the series for Q_1 is still diverging where we stopped off, (although it converges later on) and that for Q_2 is just beginning to converge. At the other temperatures the series are on the whole satisfactorily convergent. The values in parentheses are those for $\sigma=0.0861$.

TABLE IV. *Summation coefficients.*

	Q_i			$-dQ_i/d\sigma$			$Q_i d^2Q_i/d\sigma^2-(dQ_i/d\sigma)^2$		
	$i=1$	2	3	1	2	3	1	2	3
	÷5			÷5			÷25		
m									
0	1								
2		9			18				
6		15	10		90	60			
8								2160	
12	7	42		84	504		1008		
14								37800	
18								22680	
20	9	54	18	180	1080	360	3600		
22								157464	
26								158760	35280
30		99	22		2970	660			
32							4032	843696	
36								855360	126720
42	26	117	26	1092	4914	1092	45864	1347192	
44								1684800	
48								2274480	336960
50								534600	39600
54							163800	4422600	
56	15	180	30	840	10080	1680	47040		
58								4723920	
62							113256	9807912	976512
68							203280	14636160	
72	17	204	68	1224	14688	4896	88128	1667952	82368
74								8996400	
76							174960	12597120	699840
78								13329360	2962080
84							428400	30844800	
86								12046320	446160
90	38	285	38	3420	25650	3420	307800		
92							413712	49650624	3309696
96								30164400	2681280
98							76440	4127760	152880
Sum									
$\sigma=0.0430$	16.168	145.614	32.239				72999	7543516	314364
.0861	5.970	53.733	11.940				6282.1	540870.	27062
.1937	1.880	16.369	3.576				201.92	10711	388.24
.3873	1.071	6.043	0.987				11.241	328.33	1.6087

$\text{Sum}_i=\sum_i a_i e^{-m\sigma}$ where a is value given in upper part of table.

TABLE V. *Rotational heat capacities of separate forms of methane.*

T	σ	σ^2/Q_i^2			C_i/R		
		$i=1$	2	3	Quintet 1	Triplet 2	Singlet 3
178°K	0.00430	2.834×10^{-7}	8.737×10^{-8}	1.782×10^{-6}	0.5173	0.659	0.5603
89	.0861	8.316×10^{-6}	2.566×10^{-6}	5.196×10^{-5}	1.3059	1.3881	1.4067
40	.1937	4.244×10^{-4}	1.400×10^{-4}	2.934×10^{-3}	2.1433	1.4999	1.1380
19.8	.3873	5.232×10^{-3}	4.107×10^{-3}	1.540×10^{-1}	1.4701	1.3485	0.2477

TABLE VI. *Convergence data for series.*

	Ratio $\dfrac{\text{next to last}}{\text{last}}$ term		Percent of whole which last term constitutes	
	$\sigma=0.043$	(0.0861)	0.043	(0.0861)
Q_1	0.98	(2.1)	5	(0.3)
$Q_1d^2Q_1/d\sigma^2-(dQ_1/d\sigma)^2$	7	(9.1)	1.5	(0.3)
Q_2	1.5	(4.7)	4	(0.2)
$Q_2d^2Q_2/d\sigma^2-(dQ_2/d\sigma)^2$	8.	(8.7)	0.8	(0.2)
Q_3	4	(8.4)	2.5	(0.1)
$Q_3d^2Q_3/d\sigma^2-(dQ_3/d\sigma)^2$	20	(21)	0.6	(0.1)

In order to draw curves for the heat capacities we wish to know their asymptotic behavior at very low and very high temperatures. In the former case σ becomes large and the first terms in the series, the coefficients of which are given in Table IV, are the only important ones. Using solely these, the heat capacities were calculated for $\sigma = 0.5$ and 1.0 ($T = 15.4$ and 7.7°K respectively) and the corresponding points were used in plotting the curves.

The extrapolation of the curves in the other direction is more difficult. At high temperatures, σ becomes small and the series may be replaced by integrals

$$Q = \int_0^\infty p(2j+1)e^{-j(j+1)\sigma}dj \tag{20}$$

where $p(2j+1)$ is the number of rotational eigenfunctions of methane given in Table II. Since p is expressed analytically only for every sixth value of j and is a different function depending on whether one starts with 0, 1, 2, 3, 4 or 5 we must split the above integral into six.

$$Q = \int_0 (p_0) + \int_1 (p_1) + \int_2 (p_2) + \cdots \int_5 (p_5). \tag{21}$$

Changing variables in each case, we get for the $S(4)$ functions

$$\begin{aligned}
p_0 &= (j+6)/6 = q+1 & j &= 6q\\
p_1 &= (j-1)/6 = q & j &= 6q+1\\
p_2 &= (j-2)/6 = q & j &= 6q+2\\
p_3 &= (j+3)/6 = q+1 & j &= 6q+3\\
p_4 &= (j+2)/6 = q+1 & j &= 6q+4\\
p_5 &= (j-5)/6 = q & j &= 6q+5
\end{aligned} \tag{22}$$

and leaving all five intervening terms in the integral, for the other five integrals, $dj \to dq$ (not $\to 6\,dq$) we have

$$\begin{aligned}
\int_0^\infty (p_0) &= \int_0^\infty (q+1)(12q+1)e^{-6q(6q+1)\sigma}dq\\
\int_1^\infty (p_1) &= \int_0^\infty q(12q+3)e^{-(6q+1)(6q+2)\sigma}dq\\
\int_2^\infty (p_2) &= \int_0^\infty q(12q+5)e^{(6q+2)(6q+3)\sigma}dq\\
\int_3^\infty (p_3) &= \int_0^\infty (q+1)(12q+7)e^{-(6q+3)(6q+4)\sigma}dq\\
\int_4^\infty (p_4) &= \int_0^\infty (q+1)(12q+9)e^{-(6q+4)(6q+5)\sigma}dq\\
\int_5^\infty (p_5) &= \int_0^\infty q(12q+11)e^{-(6q+5)(6q+6)\sigma}dq.
\end{aligned} \tag{23}$$

It may be shown that

$$\int_0^\infty (q+a)[2(6q+b)+1]e^{-(6q+b)(6q+b+1)\sigma}dq$$

$$= (\tfrac{1}{6}\sigma^{-1})\{ae^{-b(b+1)\sigma} + e^{\sigma/4}\pi^{1/2}\sigma^{-1/2}/12$$

$$- (e^{\sigma/4}/6)[b+\tfrac{1}{2} - (b+\tfrac{1}{2})^3\sigma/3 + (b+\tfrac{1}{2})^5\sigma^2/10 - (b+\tfrac{1}{2})^7\sigma^3/42 \cdots]\}. \quad (24)$$

Inserting the appropriate values of a and b from (23) and repeating the calculation in a similar fashion for the $S(3+1)$ and $S(2+2)$ functions we get

$$^5Q_1 = 5(\pi^{1/2}\sigma^{-3/2}/12)\{1+\sigma/4 - 30\pi^{-1/2}\sigma^{3/2} + \sigma^2/32 + 302.4\pi^{-1/2}\sigma^{5/2} \cdots\} \quad (25)$$

$$^3Q_2 = (9\pi^{1/2}\sigma^{-3/2}/12)\{1+\sigma/4 - 74\pi^{-1/2}\sigma^{3/2} + \sigma^2/32 + 840.4\pi^{-1/2}\sigma^{5/2} \cdots\} \quad (26)$$

$$^1Q_3 = (2\pi^{1/2}\sigma^{-3/2}/12)\{1+\sigma/4 - 78\pi^{-1/2}\sigma^{3/2} + \sigma^2/32 + 1094.4\pi^{-1/2}\sigma^{5/2} \cdots\}. \quad (27)$$

Whence we obtain by differentiation of ln Q, remembering that σ is small

$$^5C_1/R = 1.5 - 12.7\sigma^{3/2} + 655.8\sigma^{5/2} \quad (28)$$

$$^3C_2/R = 1.5 - 31.3\sigma^{3/2} + 1817\sigma^{5/2} \quad (29)$$

$$^1C_3/R = 1.5 - 33.01\sigma^{3/2} + 2357\sigma^{5/2}. \quad (30)$$

From these expansions the heat capacities of each form was calculated for $\sigma = 0.01 (T = 768°\mathrm{K})$.

It is possible now to estimate the relative amounts of each form at high temperature from equations 25–7. They are

Nuclear quintet $5(\pi^{1/2}\sigma^{-3/2}/12)/(5\pi^{1/2}\sigma^{-3/2}/12 + 9\pi^{1/2}\sigma^{-3/2}/12 + 2\pi^{1/2}\sigma^{-3/2}/12)$

$$^5F = 5/(5+9+2) = 31.2 \text{ percent} \quad (31)$$

Nuclear triplet $^3F = 9/(5+9+2) = 56.2$ percent
Nuclear singlet $^1F = 2/(5+9+2) = 12.5$ percent.

This relative proportion should remain unaltered if we cool ordinary methane gas down to extremely low temperatures, but should change over into the equilibrium proportion obtaining at that temperature on exposure of the methane to suitable catalysts ("dissociation catalysts"). The latter proportion

$$F_i = Q_i/(Q_1 + Q_2 + Q_3) \quad (32)$$

is to be determined by substituting the appropriate values already calculated.

The results are all summarized in Table VII which gives the relative equi-

TABLE VII. *Heat capacities of frozen and true equilibrium mixtures of methane.*

T	σ	$^5F_1$	$^3F_2$	$^1F_3$	$^5C_1/R$	$^3C_2/R$	$^1C_3/R$	C_r/R frozen	C_r/R equil.
7.7°K	1	80.1	19.5	0.3	0.006	0.488	0.0003	0.28	0.10
15.4	0.5	56.8	37.6	5.7	.626	.902	.0804	.71	.70
19.8	0.3873	43.3	48.8	8.0	1.47	1.349	.248	1.25	1.31
40	.1937	32.0	55.7	12.2	2.143	1.500	1.138	1.65	1.66
89	.0861	31.2	56.2	12.5	1.306	1.388	1.407	1.36	1.36
178	.043	31.2	56.2	12.5	0.517	0.659	0.560	0.60	0.60
768	.01	31.2	56.2	12.5	1.493	1.487	1.491	1.49	1.49

librium proportions of the different symmetry forms, their separate heat capacities, the average heat capacity of the mixture in frozen equilibrium and that of the mixture in true equilibrium. Figs. 1 , 2 and 3 portray the same data graphically. The average heat capacity is calculated from the formula

$$C = {}^5F_1{}^5C_1 + {}^3F_2{}^3C_2 + {}^1F_3{}^1C_3 \qquad (33)$$

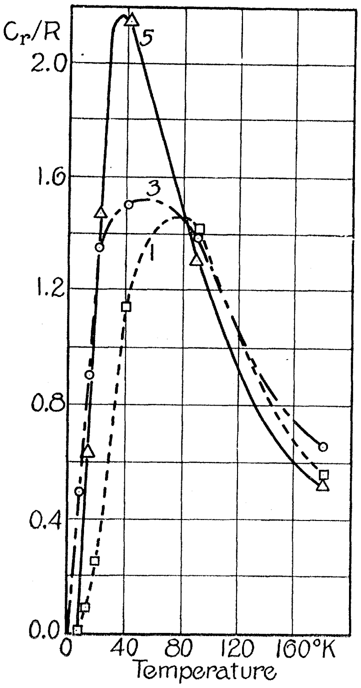

Fig. 1. Rotational heat capacities of methane.
△ Quintet ○ Triplet □ Singlet

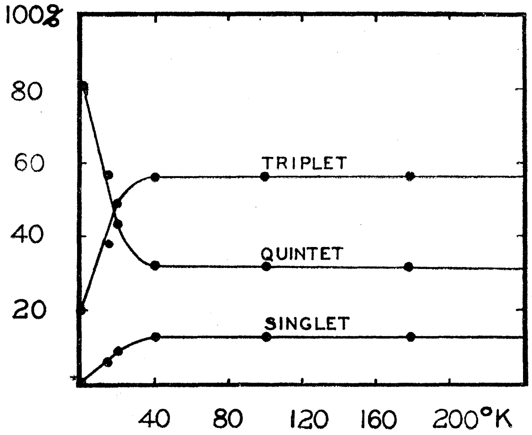

Fig. 2. Equilibrium amounts of different symmetry forms of methane.

Conclusions

A study of Table VII and Fig. 3 shows that according to our calculations, there should be two regions propitious for detecting a change in specific heat after catalytic treatment, were it not for vapor pressure limitations. The more practical would be that at the temperature of boiling hydrogen where the specific heat should increase some five or six percent. The other region should be at the much lower temperature of ~8°K where the heat capacity should *decrease* some 64 percent. The inaccuracies involved in the cessation of our sums at a possibly too early point (Table VI) affect only the values obtained at 178°K, where the frozen equilibrium proportions are practically identical with those at true equilibrium. From the standpoint of these calculations it seems that experimental difficulties of working with methane vapor at such low temperatures would be almost insurmountable in view of the fact that it cannot be held in the gaseous state in concentrations greater than those cor-

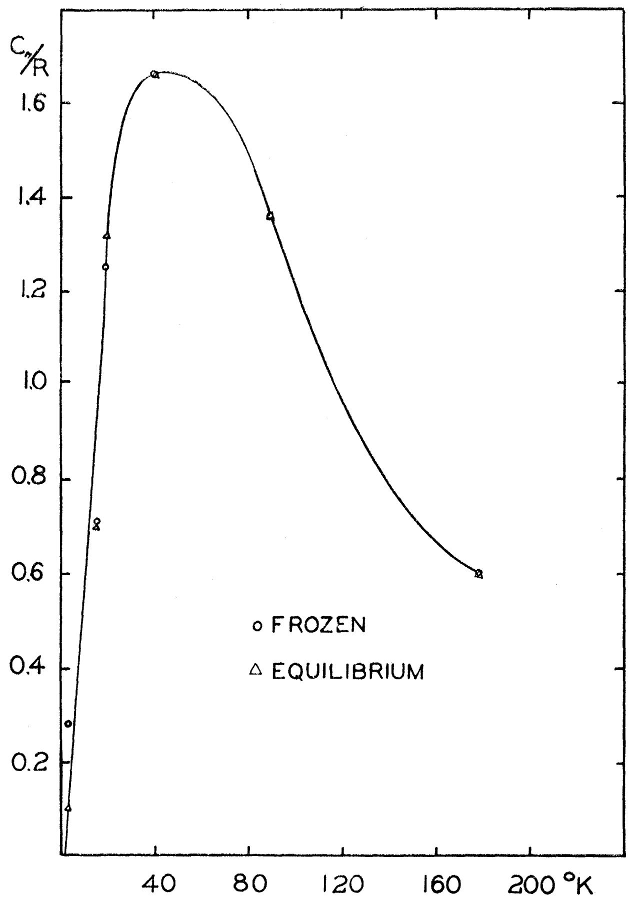

Fig. 3. Average rotational heat capacity of methane.

responding to its vapor pressure, which indeed must be less than 0.1 mm even at 40°K. Whether the same distribution would hold among the different varieties in the solid crystal as we have calculated for the gas, we are not prepared to state. A catalytic change in the solid state might perhaps be detected by raising the temperature to a test temperature accurately controlled and observing any alteration in the heat capacity of the vapor. Such changes should however be exceedingly minute. These considerations lead one to become exceedingly pessimistic concerning any method of demonstrating the different varieties by means of the specific heats of the vapor.