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The Vapor Pressure Constant of Methane

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§1. It can be shown by statistical quantum mechanics that the vapor pressure constant of a molecule whose principal moments of inertia are all equal to A is

$$i = \log (64\pi^5 k^4 m^{3/2} A^{3/2}/h^6) + \Sigma_r D_r \log (G_r/{}_r\omega_0)$$

at ordinary temperatures; where m is the mass, k is Boltzmann's constant, h is Planck's constant, the D_r's are the gram molecular fractions of the two varieties, and where the G_r's and ${}_r\omega_0$'s are constants.

§2. It is found that G_1 for methane is 5/12, G_2 is 9/12 and G_3 is 2/12.

§3 and §4. It is shown by quantum mechanics that ${}_1\omega_0$ for methane is 5, ${}_2\omega_0$ is 9, and ${}_3\omega_0$ is 2; if the spins of the hydrogen nuclei are taken into consideration but the spin of the carbon nucleus neglected, which is permissible.

§5. With the value $A = 5.17 \times 10^{-40}$ c.g.s. units, it is found that the vapor pressure constant in atmospheres and common logarithms of methane at ordinary temperatures should be -1.94. The experimental result given by Eucken, -1.97 ± 0.05, agrees with this.

INTRODUCTION

IN RECENT papers[1,2,3,4] the author has studied the vapor pressures of diatomic vapors. The work was an extension of that of R. H. Fowler,[5] who first investigated, theoretically, the vapor pressure of hydrogen made up of the two non-combining varieties para-hydrogen and ortho-hydrogen. In a subsequent paper[6] the author investigated the vapor pressure constant of a polyatomic vapor, ammonia. It was shown that the vapor pressure constant i of a molecule such as ammonia, two of the principal moments of inertia of which, A and B, were equal with the third C differing from A and B, should be given by

$$i = \log \frac{64\pi^5 m^{3/2} k^4 A C^{1/2}}{h^6} + \Sigma_r D_r \log \frac{G_r}{{}_r\omega_0}$$

at ordinary temperatures for which the constant part of the specific heat of the vapor at constant pressure was equal to $4R$ per gram molecule. There R was the gas constant; m was the mass of the molecule; k was Boltzmann's constant; h was Planck's constant; the D_r's were the gram molecular fractions of the different sorts r of molecules present (there were two varieties of ammonia molecules); G_r was the numerical factor by which the expres-

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[1] T. E. Sterne, Proc. Roy. Soc. **A130**, 367 (1931).

[2] T. E. Sterne, Proc. Roy. Soc. **A130**, 551 (1931).

[3] T. E. Sterne, Proc. Roy. Soc. **A131**, 339 (1931).

[4] T. E. Sterne, Proc. Roy. Soc. **A133**, 303 (1931).

[5] R. H. Fowler, Proc. Roy. Soc. **A118**, 52 (1928).

[6] T. E. Sterne, Phys. Rev. **39**, 993 (1932).

sion $16(2^{\frac{1}{2}})\pi^{7/2}A\,C^{1/2}k^{3/2}T^{3/2}/h^3$ must be multiplied in order to obtain the rotational partition function R_r for the gas molecule of type r; and ${}_r\omega_0$ was the statistical weight of the lowest quantum state of a molecule of ammonia in the crystalline phase "at the absolute zero."

This theory yielded a value for the vapor pressure constant of ammonia in satisfactory agreement with experiment. It therefore becomes interesting to investigate next the vapor pressures of substances for which all three principal moments of inertia of the polyatomic vapor molecules, A, B and C, are equal to each other. We shall therefore in this paper consider the vapor pressure constant of methane, CH_4. The methane molecule appears to consist of four hydrogen nuclei placed at the vertices of a regular tetrahedron, together with a carbon nucleus at the centroid of the tetrahedron; and the three principal moments of inertia appear to be equal. The Raman spectrum has been studied by Dickinson and others.[7]

§1. THE VAPOR PRESSURE OF METHANE

There should be three varieties of methane molecules, which should retain their separate identities over fairly long periods at ordinary and low temperatures. If we use the notation of the article on ammonia, we say that the first variety is characterized by wave functions which are completely symmetrical $S(4)$ in the spins of the four hydrogen nuclei; the second variety is characterized by wave functions $S(3+1)$ in the spins of the four hydrogen nuclei; and the third variety is characterized by wave functions $S(2+2)$ in the spins of the four hydrogen nuclei. A simpler notation is to follow Dirac's procedure[8] by introducing the observable s, which describes the magnitude of the total proton spin angular momentum, $\frac{1}{2}\Sigma_r\boldsymbol{\sigma}_r$ in units of $h/2\pi$, through the formula

$$s^2 - \tfrac{1}{4} = (\tfrac{1}{2}\Sigma_r\boldsymbol{\sigma}_r,\ \tfrac{1}{2}\Sigma_t\boldsymbol{\sigma}_t)$$

where the scalar product is meant. Then the first variety corresponds to the eigenvalue $s'=5/2$, the second variety to $s'=3/2$, and the third variety to $s'=\frac{1}{2}$. By methods similar to those employed in the article on ammonia,[6] §1, it is easy to show that the vapor pressure constant i of a polyatomic vapor, for which the three principal moments of inertia of the molecules are equal to A, is given by

$$i = \log\,(64\pi^5k^4m^{3/2}A^{3/2}/h^6) + \Sigma_rD_r\log\,(G_r/{}_r\omega_0)\,. \tag{1.0}$$

Here the symbols have the same meanings as in the INTRODUCTION to this paper. Number G_r is here the factor by which the expression $16(2^{\frac{1}{2}})\pi^{7/2}A^{3/2}k^{3/2}T^{3/2}/h^3$ must be multiplied in order to obtain the rotational partition function R^5 for a gas molecule of the rth sort. The derivation of the Eq. (1.0) above proceeds in the same fashion as the derivation of Eq. (1.92) in the author's paper on ammonia, except that since a number of selector variables has to be used equal to one more than the number of non-combining groups of terms, we are obliged to use four selector variables in the case of methane although

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

[8] Dirac, *Principles of Quantum Mechanics*, first edition, Chap. XI.

three were sufficient in the case of ammonia. A quadruple integral must occur in the case of methane in the equation analogous to the Eq. (1.1) of the article on ammonia. To find the G_r's, we shall have to determine the rotational partition functions R_1, R_2 and R_3 for the three sorts of methane molecules, respectively.

§2. THE ROTATIONAL PARTITION FUNCTIONS OF FREE METHANE MOLECULES

The rotational energy levels are given by[9]

$$W = (h^2/8\pi^2A)j(j+1) \tag{2.0}$$

where j can take on positive integral values. There is another quantum number K, which can take on the values $0, 1, 2, 3, \cdots, j$ for each value of j. The weights of the levels are given by Villars and Schultze,[10] and are taken from the work of Elert.[11] The rotational partition functions R_1, R_2 and R_3 for the three sorts of methane molecules, respectively appear to have been calculated correctly by Villars and Schultze, at least insofar as the asymptotic expressions

$$R_1 \sim (5/12)\Omega, \quad R_2 \sim (9/12)\Omega, \quad R_3 \sim (2/12)\Omega \tag{2.1}$$

where

$$\Omega = 16(2^{\frac{1}{2}})\pi^{7/2}A^{3/2}k^{3/2}T^{3/2}/h^3,$$

are concerned. In deriving Eqs. (2.1) we may use methods similar to those used for obtaining the corresponding expressions in the case of ammonia, given in considerable detail in the paper[6] on ammonia.

It appears, therefore, that

$$G_1 = 5/12, G_2 = 9/12, G_3 = 2/12. \tag{2.2}$$

In this paper the spin of the carbon nucleus is neglected, since the vapor pressure constant of methane could not depend upon its value in any case, and since further the spin is zero.

We must now determine the values of ${}_1\omega_0$, ${}_2\omega_0$ and ${}_3\omega_0$.

§3. THE SPHERICAL OSCILLATORY MOTION OF METHANE MOLECULES IN CRYSTALLINE METHANE

It appears from the considerations advanced by L. Pauling[12] that at very low temperatures, and *a fortiori* at the absolute zero, molecules of methane are not rotating in crystalline methane, but on the contrary are oscillating about orientations of minimum potential energy in the crystal lattice. It will be necessary for us to consider the nature of these motions in some detail in order to be able eventually to evaluate the ${}_r\omega_0$'s for methane.

It is not necessary, however, to solve in detail in this paper the quantum mechanical problem which is involved. Taking into account the geometrical symmetry of the methane molecule, we can generalize at once the results

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[9] Dennison, Rev. Mod. Phys. **3**, 280 (1931)

[10] Villars and Schultze, Phys. Rev. **38**, 998 (1931).

[11] Elert, Zeits. f. Physik **51**, 6 (1928).

[12] L. Pauling, Phys. Rev. **36**, 430 (1930).

obtained in the case of the ammonia-type molecule considered in the paper on the vapor pressure of ammonia.[6] We take the origin, O, at the mass center of the molecule; and fixed orthogonal axes OX, OY, OZ such that the orientation of minimum potential energy for the methane molecule corresponds to the presence of the hydrogen nuclei 1, 2, 3, 4 at the points $(0, 0, 6^{\frac{1}{2}}a/2)$, $(-2\cdot 3^{\frac{1}{2}}a/3, 0, -6^{\frac{1}{2}}a/6)$ $(3^{\frac{1}{2}}a/3, -a, -6^{\frac{1}{2}}a/6)$ and $(3^{\frac{1}{2}}a/3, a, 6^{\frac{1}{2}}a/6)$ respectively; the carbon nucleus being of course at O. Let us investigate the forms of the potential and kinetic energies of the molecule, regarded as rigid, for small displacements of the molecule from this orientation of minimum potential energy. As in the case of ammonia, we specify a displacement by the small rotations x, y and z of the molecule about the axes OX, OY and OZ respectively. The Hamiltonian for the methane molecule is similar to the Hamiltonian for the ammonia molecule, but its form is simpler than the latter because of the higher degree of symmetry of the methane molecule. We see therefore as in the case of the ammonia-type molecule that the lowest energy level of the methane-type molecule, when the arrangement of the hydrogen nuclei is that specified above, can be represented by only a single linearly independent wave function describing its spherical oscillatory motion.

In order to find the values of the ${}_r\omega_0$'s, we must now study the symmetry properties of the complete wave functions of the methane molecule, taking into account the spins of the hydrogen nuclei and the various possible distributions of the hydrogen nuclei among the neighborhoods of the four points whose coordinates are specified above.

§4. THE VALUES OF ${}_1\omega_0$, ${}_2\omega_0$ AND ${}_3\omega_0$

The discussion of the symmetry properties of the spherical oscillatory wave functions of a methane molecule in crystalline methane is somewhat more involved than the discussion of the case of an ammonia molecule in crystalline ammonia, because a methane molecule contains one more hydrogen nucleus than an ammonia molecule. There are 24 possible permutations of the protons in a methane molecule as compared with the 6 which are possible in the case of ammonia. For the sake of simplicity and elegance we shall therefore use the methods described by Dirac[13] in order to consider the symmetry properties of the wave functions of methane. Dirac's procedure can be followed as easily for protons as for electrons, because both protons and electrons have one-half quantum spins. We shall accordingly depart here from the methods which we used for considering ammonia, and in what follows we shall assume that the reader is already familiar with Dirac's theory of the permutation observables.

We must take account of the spins of the hydrogen nuclei and also of the spherical vibrational factors in the wave functions. In dealing with the vibrational factors we must now take account of the different arrangements of the hydrogen nuclei which are possible among the four mean positions, a, b, c and d, say, which we specified in §3. If the vibrational factor in a wave func-

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[13] Dirac, *Principles of Quantum Mechanics*, first edition, §66.

tion for the lowest vibrational level with which we are concerned is denoted by f, then $f(1, 2, 3, 4)$ would refer to a state in which nucleus 1 was in the vicinity of position a, 2 in the vicinity of position b, 3 in the vicinity of position c, 4 in the vicinity of position d; with analogous meanings for the other 23 f's which are possible. In accordance with §66 of Dirac's book, let us denote the z-component σ_z of the spin vector $\boldsymbol{\sigma}$ of the i 'th hydrogen nucleus by σ_i, so that the representative of a state will be $(x_1, x_2, x_3, x_4, \sigma_1, \sigma_2, \sigma_3, \sigma_4 |\quad)$; the single variable x being written instead of x, y, z and the suffix z being dropped from the σ_z's that occur in representatives. Then in accordance with Dirac's equation (32) it is sufficient to study the permutations P^σ which operate only on the σ's, and this results in a considerable simplification since it allows us to ignore the x's. There are five types of permutations of four particles, namely: the types 4, 3+1, 2+2, 2+1+1 and 1+1+1+1. There are thus five independent commuting observables χ^σ which are constants of the motion:

$$\begin{aligned}
\chi_1^\sigma &= (1/6)\Sigma P^\sigma{}_4 \\
\chi_2^\sigma &= (1/8)\Sigma P^\sigma{}_{3+1} \\
\chi_3^\sigma &= (1/3)\Sigma P^\sigma{}_{2+2} \\
\chi_4^\sigma &= (1/6)\Sigma P^\sigma{}_{2+1+1} \\
\chi_5^\sigma &= \Sigma P^\sigma{}_{1+1+1+1} \equiv 1.
\end{aligned}$$

Here, for instance, $\Sigma P^\sigma{}_{2+2}$ is the sum of all permutations which operate on the spin variables σ, of type 2+2. We shall find it easier to study the χ^σ's than the χ's. There are 15 simultaneous equations like Dirac's Eq. (22) involving the χ^σ's; if we notice that $\chi_5{}^\sigma \equiv 1$ we have merely the 10 equations

$$\begin{aligned}
(\chi_1^\sigma)^2 &= \tfrac{2}{3}\chi_2^\sigma + \tfrac{1}{6}\chi_3^\sigma + \tfrac{1}{6} & (\chi_1^\sigma\chi_3^\sigma) &= \tfrac{1}{3}\chi_1^\sigma + \tfrac{2}{3}\chi_4^\sigma \\
(\chi_2^\sigma)^2 &= \tfrac{1}{2}\chi_2^\sigma + \tfrac{3}{8}\chi_3^\sigma + \tfrac{1}{8} & (\chi_1^\sigma\chi_4^\sigma) &= \tfrac{2}{3}\chi_2^\sigma + \tfrac{1}{3}\chi_3^\sigma \\
(\chi_3^\sigma)^2 &= \tfrac{2}{3}\chi_3^\sigma + \tfrac{1}{3} & (\chi_2^\sigma\chi_3^\sigma) &= \chi_2^\sigma \\
(\chi_4^\sigma)^2 &= \tfrac{2}{3}\chi_2^\sigma + \tfrac{1}{6}\chi_3^\sigma + \tfrac{1}{6} & (\chi_2^\sigma\chi_4^\sigma) &= \tfrac{1}{2}\chi_1^\sigma + \tfrac{1}{2}\chi_4^\sigma \\
(\chi_1^\sigma\chi_2^\sigma) &= \tfrac{1}{2}\chi_1^\sigma + \tfrac{1}{2}\chi_4^\sigma & (\chi_3^\sigma\chi_4^\sigma) &= \tfrac{2}{3}\chi_1^\sigma + \tfrac{1}{3}\chi_4^\sigma
\end{aligned}$$

and when we solve them for the sets of simultaneous eigenvalues $\chi^{\sigma\prime}$ of the observables χ^σ we obtain the values given in Table I, where the sets are denoted by S, α, β, A and γ.

If we introduce the observable s, which we defined in §1, to describe the magnitude of the total spin angular momentum we find by the methods of §66 in Dirac's book that

$$\begin{aligned}
\chi_1^\sigma &= [1/192][(4s^2 - 13)^2 + 8(4s^2 - 13) - 48] \\
\chi_2^\sigma &= (1/16)(4s^2 - 9) \\
\chi_3^\sigma &= [1/96][(4s^2 - 13)^2 - 48] \\
\chi_4^\sigma &= (1/24)(4s^2 - 1) \\
\chi_5^\sigma &= 1.
\end{aligned}$$

There is therefore one set of numerical values $\chi^{\sigma\prime}$ for the χ^{σ}'s, and thus one exclusive set of states, for each eigenvalue s' of s. The eigenvalues of s are 5/2, 3/2, and 1/2; we readily find that corresponding to these eigenvalues of s the exclusive sets of states are those which we have denoted by S, β and T respectively. There are no other sets possible; the sets α and A being impossible in the case of a set of four protons. The relationship between s' and the $\chi^{\sigma\prime}$'s is shown in Table I.

TABLE I.

Exclusive sets of states.	S	α	β	A	γ
Eigenvalues					
s'	5/2	—	3/2	—	1/2
$\chi_1^{\sigma\prime}$	1	1/3	−1/3	−1	0
$\chi_2^{\sigma\prime}$	1	0	0	1	−1/2
$\chi_3^{\sigma\prime}$	1	−1/3	−1/3	1	1
$\chi_4^{\sigma\prime}$	1	−1/3	1/3	−1	0
$\chi_5^{\sigma\prime}$	1	1	1	1	1

The three sets, however, may be degenerate; and in fact they are degenerate. Corresponding to any s' there are $2s'$ possible values for the z-component of total spin angular momentum $\Sigma_{r=1}^{4}\sigma_r$ which we may denote by s_z. Thus for the exclusive set of states S, s_z' may be 4, 2, 0,–2 or −4. Similarly for the set β, s_z' may be 2, 0 or −2. For the set γ, s_z' must be 0. Each of the states so defined may itself be degenerate, and some of them are in fact degenerate. These latter degeneracies are essential and cannot be removed by perturbations which are symmetrical between the particles; but we must study them in order to enumerate our representatives correctly and thus obtain our ω_0's.

Let us choose a representation whose fundamental states are the eigenstates of the z-components σ of the spin vectors of the hydrogen nuclei, corresponding to the simultaneous eigenvalues of all four σ's. There will of course be $2^4=16$ fundamental states, since the eigenvalues of the σ's are independent and can each be $+1$ or -1. We wish to find the number of linearly independent eigenstates corresponding to each choice of simultaneous eigenvalues for s_z and s; that is, we wish to find the number of linearly independent wave functions or representatives capable of representing each of these eigenstates of s_z' and s' in the σ representation. Denoting states by ψ's, we have

$$\psi(s_z', s') = \Sigma\psi(\sigma')(\sigma' \mid s_z', s')$$

and also

$$(s'^2 - \tfrac{1}{4})(\sigma' \mid s_z', s') = \Sigma(\sigma' \mid s^2 - \tfrac{1}{4} \mid \sigma'')(\sigma'' \mid s_z', s'). \tag{4.1}$$

To calculate the matrix elements $(\sigma' \mid s^2 - \frac{1}{4} \mid \sigma'')$ we use the relation

$$s^2 - \tfrac{1}{4} = 6\chi_4^{\sigma}; \tag{4.2}$$

to calculate the matrix elements $(\sigma' \mid \chi_4^{\sigma} \mid \sigma'')$ we allow the observable χ_4^{σ} to operate on the various $\psi(\sigma')$'s in turn and we write down the matrix elements by comparison with the equation

$$\chi_4^\sigma \psi(\sigma'') = \Sigma \psi(\sigma')(\sigma' \,|\, \chi_4^\sigma \,|\, \sigma''). \tag{4.3}$$

If we write down the set of simultaneous Eqs. (4.1) for any set of eigenvalues S_z' and s' and solve it, we shall find thereby a linear relation or linear relations obeyed by the representative $(\sigma' \,|s_z', s')$ and from this we can find the number of linearly independent eigenfunctions $(\sigma' \,| \quad)$ which are possible; or in other words, the number of independent $\psi(s_z', s')$'s. The following calculations should make this clear.

Case 1,

$s'=5/2$, $s_{z'}=4$. The only $\psi(\sigma')$ which can be concerned is $\psi(1, 1, 1, 1)$ and there is thus only one eigenfunction possible: $(\sigma_1', \sigma_2', \sigma_3', \sigma_4' \,|\, 4, 5/2)$ is a constant when all the σ''s are 1, and vanishes for all other values of the σ''s.

Case 2,

$s'=5/2$, $s_z'=2$. The only fundamental $\psi(\sigma')$'s which can be concerned when $s_z'=2$ are those which $\Sigma\sigma'=2$; they are $\psi(1, 1, 1, -1)$, $\psi(1, 1, -1, 1)$, $\psi(1, -1, 1, 1)$ and $\psi(-1, 1, 1, 1)$. We shall denote these states by $\psi(1)$, $\psi(2)$, $\psi(3)$ and $\psi(4)$, respectively, for brevity. We find easily from Eqs. (4.2) and (4.3) that the matrix representing $s^2-\frac{1}{4}$ is

$$\begin{array}{c|c|c|c|c|} & 1 & 2 & 3 & 4 \\ \hline 1 & 3 & 1 & 1 & 1 \\ \hline 2 & 1 & 3 & 1 & 1 \\ \hline 3 & 1 & 1 & 3 & 1 \\ \hline 4 & 1 & 1 & 1 & 3 \\ \hline \end{array}\,. \tag{4.4}$$

The set of Eqs. (4.1) in this case becomes

$$\begin{array}{r} -3(1| \quad)+(2| \quad)+(3| \quad)+(4| \quad)=0 \\ (1| \quad)-3(2| \quad)+(3| \quad)+(4| \quad)=0 \\ (1| \quad)+(2| \quad)-3(3| \quad)+(4| \quad)=0 \\ (1| \quad)+(2| \quad)+(3| \quad)-3(4| \quad)=0 \end{array}$$

and hence

$$(1| \quad) = (2| \quad) = (3| \quad) = (4| \quad)$$

so that only one linearly independent eigenfunction exists, given by $(r\,|2,5/2)=\text{const.}$, $r=1, 2, 3, 4$.

Case 3,

$s'=5/2$, $s_z'=0$. The $\psi(\sigma')$'s concerned when $s_z'=0$ are $\psi(1, 1, -1, -1)$, $\psi(1, -1, 1, -1)$, $\psi(-1, 1, 1, -1)$, $\psi(1, -1, -1, 1)$, $\psi(-1, 1, -1, 1)$ and $\psi(-1, -1, 1, 1)$; denoted by $\psi(1)$, $\psi(2)$, $\psi(3)$, $\psi(4)$, $\psi(5)$ and $\psi(6)$ respectively. The other $\psi(\sigma')$'s can be ignored. The matrix representing $s^2-1/4$ is

$$
\begin{array}{c|cccccc}
 & 1 & 2 & 3 & 4 & 5 & 6 \\
\hline
1 & 2 & 1 & 1 & 1 & 1 & 0 \\
2 & 1 & 2 & 1 & 1 & 0 & 1 \\
3 & 1 & 1 & 2 & 0 & 1 & 1 \\
4 & 1 & 1 & 0 & 2 & 1 & 1 \\
5 & 1 & 0 & 1 & 1 & 2 & 1 \\
6 & 0 & 1 & 1 & 1 & 1 & 2
\end{array}
\tag{4.5}
$$

and we find after solving the Eqs. (4.1) in this case that $(r\,|0,\ 5/2)=\text{const.}$; $r=1,\ 2,\ 3,\ 4,\ 5,\ 6$. This is the only eigenfunction possible.

Cases 4 and 5,

for $s'=5/2$, $s_z'=-2,\ -4$ respectively, are similar to cases 1 and 2 and in each case only one eigenfunction exists.

Case 6,

$s'=3/2$, $s_z'=2$. When we solve the set of Eqs. (4.1) in this case, using the matrix for $s^2-1/4$ given by (4.4), we find that

$$(1\,|\,2,\ 3/2)+(2\,|\,2,\ 3/2)+(3\,|\,2,\ 3/2)+(4\,|\,2,\ 3/2)=0. \tag{4.6}$$

We can choose three and only three linearly independent eigenfunctions obeying Eq. (4.6). All other possible eigenfunctions obeying (4.6) can be expressed as linear combinations of these three. Thus we might choose the 3 eigenfunctions $(r\,|\quad)_1$, $(r\,|\quad)_2$, $(r\,|\quad)_3$ defined by the following table:

r	1	2	3	4
$(r\,\vert\quad)_1$	1	-1	0	0
$(r\,\vert\quad)_2$	1	0	-1	0
$(r\,\vert\quad)_3$	1	0	0	-1

Any fourth function $(r\,|\quad)_4$ obeying (4.6) would be in the form

r	1	2	3	4
$(r\,\vert\quad)_4$	a	b	c	$-a-b-c$

and we should have

$$(r\,|\quad)_4=-b(r\,|\quad)_1-c(r\,|\quad)_2+(a+b+c)(r\,|\quad)_3$$

so that it would not be linearly independent.

Case 7,

$s'=3/2$, $s_z'=0$. Using the matrix (4.5) we find eventually that $(1\,|\quad)=-(6\,|\quad)$; $(2\,|\quad)=-(5\,|\quad)$; $(3\,|\quad)=-(4\,|\quad)$. There are three and only three linearly independent eigenfunctions.

Case 8,

$s'=3/2$, $s_z'=-2$. This is similar to case 6, and there are three linearly independent eigenfunctions.

Case 9,

$s'=1/2$, $s_z'=0$. Using the matrix (4.5) we find that

$$(1|\ ) = (6|\ );\ (2|\ ) = (5|\ );\ (3|\ ) = (4|\ );\ (1|\ ) + (2|\ ) + (3|\ ) = 0.$$

There are two and only two linearly independent eigenfunctions possible, which might be for instance the functions $(r|\ )_1$ and $(r|\ )_2$ given by

r	1	2	3	4	5	6
$(r\|\ )_1$	1	-1	0	0	-1	1
$(r\|\ )_2$	1	0	-1	-1	0	1

Recapitulating, we can prepare Table II showing the numbers ω_0 of eigenfunctions which are possible in the different cases:

TABLE II.

s'	s_z'	ω_0	Totals
5/2	4	1	5
	2	1	
	0	1	
	-2	1	
	-4	1	
3/2	2	3	9
	0	3	
	-2	3	
1/2	0	2	2

and we see therefore that ${}_1\omega_0=5$; ${}_2\omega_0=9$; ${}_3\omega_0=2$.

§5. THE VAPOR PRESSURE CONSTANT OF METHANE

From the results of §2, we have at once that $D^1=5/16$, $D^2=9/16$, $D_3=2/16$. Hence it follows from the results of the last section and §2 that the last term in Eq. (1.0) is log 1/12. We are now in a position to calculate the vapor pressure constant of methane. Taking the molecular weight with sufficient accuracy to the 16.04 and the moment of inertia A to be[7] 5.17×10^{-40} c.g.s. units, we find that the vapor pressure constant i' at ordinary temperatures, in atmospheres and common logarithms,[14] is $i'=-1.94$. This is in good agreement with the experimental value given by Eucken[15] $i'=-1.97\pm.05$.

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[14] We merely use Eq. (1.0) with common logarithms instead of natural logarithms, and subtract the quantity 6.006 from the right-hand member.

[15] Eucken, Phys. Zeits. **31**, 361 (1930).