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THE ENTROPY OF POLYATOMIC MOLECULES[1]

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Abstract

By counting the total number of completely antisymmetric eigenfunctions which can be formed from the rotational states, the *a priori* probabilities of the different symmetry varieties of ammonia (nuclear doublet and quadruplet) and of methane (nuclear singlet, triplet and quintet) are derived and used to compute the corresponding entropies at 298.1°K. The relative proportions of the different varieties at high temperatures are found to be equal for ammonia and in the ratio of 2:9:5 for methane (respectively). The absolute entropy of the mixture of the different forms of ammonia is calculated to be 51.5 cal. degree^{-1}, the virtual entropy (the absolute minus the nuclear spin minus the frozen rotational entropy) 44.1; the absolute entropy of methane, 50.1, and its virtual entropy 44.2 cal. degree^{-1}

THE entropy of diatomic molecules has been extensively discussed[2] but so far no values for polyatomic molecules have yet been calculated according to the newer quantum mechanical theories. In this article I shall carry out such calculations for two typical gases, ammonia and methane. In molecules such as these where there are two or more equal nuclei, symmetry characteristics in the latter arise in the eigenfunctions bringing about, since the coupling of the nuclear spins with the outer forces in the molecule is very weak, a state of affairs where it is impossible for those rotational states which are associated with one nuclear configuration to change (by radiation or collision) to states associated with another nuclear configuration by any but exceedingly low velocities unless catalyzed in a way involving complete separation of the similar nuclei and subsequent rearrangement (dissociation catalysts). The ordinary gas is thus a mixture of different varieties which are noncombining and rarely in true equilibrium except when in the presence of a dissociation catalyst or at a high temperature. The application of the considerations of Hund[3] concerning symmetry characters and electronic spins to the problem of rotational *a priori* probabilites and nuclear spins has already been discussed in detail[4] in this journal in connection with the specific heats of the different symmetry forms of methane and the reader is referred to that article as a pre-

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[1] A preliminary announcement of the results contained herein was published in J. Am. Chem. Soc. **53**, L 2006 (1931). Unfortunately certain errors were made then, which are now corrected, cf. footnote 14.

[2] (a) Fowler, Proc. Roy. Soc. (London) **A118**, 52 (1928); (b) Giauque and Johnston, J. Am. Chem. Soc. **50**, 3221 (1928); (c) Rodebush, Proc. Nat. Acad. Sci. **15**, 678 (1929); (d) Villars, ibid. **15**, 705 (1929); **16**, 396 (1930); (e) Giauque and Johnston, Phys. Rev. **36**, 1592 (1930); (f) Giaque, J. Am. Chem. Soc. **52**, 4816 (1930); (g) MacGillavry, Phys. Rev. **36**, 1398 (1930); (h) Rodebush, Phys. Rev. **37**, 221 (1931); (i) Giauque, J. Am. Chem. Soc. **53**, 507 (1931).

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

[4] Villars and Schultze, Phys. Rev. **38**, 998 (1931). Hereafter to be designated as V and S.

face to the present one. In that work it was decided that there must be two different symmetry forms of ammonia (the nuclear doublet and quartet) and three of methane (the nuclear singlet, triplet and quintet) just as there are two of hydrogen (nuclear singlet—"para"—and triplet—"ortho-hydrogen"). Basing the work on Hund's[5] symmetry character assignment of the rotational terms of ammonia and Elert's[6] of methane, we there deduced the *a priori* probabilities for each of the rotational states of methane. (Tabulated in V and S, Table III).

ENTROPY

The general formula[7] for the entropy of a substance is

$$S = R \ln \sum_i p_i e^{-\epsilon_i/kT} + E/T \tag{1}$$

where p_i is the *a priori* probability of state i of energy ϵ_i and the other symbols have their usual significance. It is convenient and customary to split the total entropy, S, up into its component parts[2d], in which case E represents the corresponding part of the whole energy.

$$S = S_t + S_r + S_v + S_{el} + S_{\text{mix}}. \tag{2}$$

S_t is the Sackur-Tetrode translational entropy[8]

$$\begin{aligned} S_t &= R \ln \left\{ (2\pi mkT)^{3/2} h^{-3} V N^{-1} e^{5/2} \right\} \\ &= -\,2.2985 + R \ln M^{3/2} T^{5/2} P^{-1} \text{ cal. degree}^{-1} \end{aligned} \tag{3}$$

M being the molecular weight and P the pressure in atmospheres.

S_r is the rotational entropy and, for the polyatomic molecule of the symmetrical top form (three moments of inertia, two of which (A) are equal) is given by substituting for the rotational energy levels, ϵ_i

$$\epsilon_{j,\tau} = (h^2/8\pi^2)\left[j(j+1)/A + (1/C - 1/A)\tau^2\right] \qquad |\tau| \leqq j \tag{4}$$

and summing over all values of both τ and j.

S_v is the vibrational entropy, and is given by putting the energy level ϵ_i

$$\epsilon_v = vh\omega_k \tag{5}$$

(assuming harmonic oscillation—no appreciable error at room temperature) where ω_k is the frequency of the kth normal vibration of the molecule (in a diatomic molecule, there is only one such but in an n-atomic molecule there are $3n$–6 if it has three moments of inertia, or $3n$–5 if only two). The *a priori* probability p of each vibration is unity if one remembers to include an entropy for each of the $3n-\left\{ {6 \atop 5} \right.$ vibrations even though some happen to have the same frequency.

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[5] Hund, Zeits. f. Physik **43,** 805 (1927). Tabulated in V and S, Table I.

[6] Elert, Zeits. f. Physik **51,** 6 (1928). Tabulated in V and S, Table II.

[7] Cf. any text book, for example, Taylor, Treatise on Physical Chemistry, 1st ed. Vol II, p. 1202 by Rodebush (D. Van Nostrand Co. 1925).

[8] Cf. Birge, Rev. Mod. Phys. **1,** 65 (1929).

The electronic entropy, S_{el}, is zero in the present[9] case of chemically saturated molecules (presumably ${}^1\Sigma$ ones with p_{el} consequently unity).

Finally the entropy of mixing, S_{mix}, must be included in those cases where one computes that of a mixture of different symmetry varieties by calculating the entropy of each separate kind and adding them together in their proportionate amounts. It is given by the familiar[10] equation

$$S_{\text{mix}} = -N_1 R \ln N_1 - N_2 R \ln N_2 - \cdots . \tag{6}$$

That this method leads to an identical result in calculations with diatomic molecules to that obtained by correctly treating the gas as only one substance and not a mixture has been demonstrated elsewhere[2d]. The first method is, in certain respects, simpler, and by its use one is less likely to make mistakes. I shall therefore employ it.

For the sake of convenience, it is desirable from this point on to make use of certain abbreviations customary in the literature

$$Q \equiv \sum_n p_n e^{-\epsilon_n/kT} = \sum_{j,\tau} p_{j,\tau} e^{-j(j+1)\sigma_1 - \tau^2\sigma_2} \tag{7}$$

$$\sigma_1 \equiv h^2/8\pi^2 A kT \tag{8}$$

$$\sigma_2 \equiv (h^2/8\pi^2)(1/C - 1/A)/kT. \tag{9}$$

By differentiating Q partially with respect to σ_1 and σ_2 it may be readily shown that

$$E_r/T = -R(\sigma_1 \partial \ln Q/\partial\sigma_1 + \sigma_2 \partial \ln Q/\partial\sigma_2) \tag{10}$$

and

$$S_r = R[\ln Q - \sigma_1 \partial \ln Q/\partial\sigma_1 - \sigma_2 \partial \ln Q/\partial\sigma_2]. \tag{11}$$

In the case of a rotator like methane where all three moments of inertia are the same, Eq. (11) still applies with just one term in σ ($\sigma_2 = 0$).

A similar equation may be derived for vibrational entropy

$$S_v = R[\ln Q_v - \sigma_v d \ln Q_v/d\sigma_v] \tag{12}$$

if one assumes the motion to be harmonic and understands

$$\left.\begin{aligned} \sigma_v &\equiv h\omega/kT = \Theta/T \\ \epsilon_v &= vh\omega. \end{aligned}\right\} \tag{13}$$

If σ_v is large this may be further simplified to

$$\begin{aligned} S_v &= R(1 + \sigma_v)e^{-\sigma_v} \\ &= R(1 + \Theta/T)e^{-\Theta/T} \end{aligned} \tag{14}$$

where Θ is the "characteristic" temperature.

In the subsequent calculations of the entropy of ammonia and of methane we shall concern ourselves with moderate temperatures (298.1°K) at which, on the one hand, the rotational energy is almost fully developed, but, on the

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[9] A case where the electronic entropy must be considered was discussed in connection with hydroxyl[2d].

[10] Lewis and Randall, Thermodynamics, McGraw Hill Book Company (1923) p. 440.

other hand, very little vibrational energy has come into play (σ_v is large). For this reason, errors in assignment of fundamental vibrational frequencies will not affect the final result to any appreciable extent.

In order to compare our final results with experiment, one must subtract from them the entropy our gas would have at zero absolute, if it were not given time nor a catalyst to enable it to change over to its stable variety at that temperature. This is because most experimental low temperature measurements (for example, on specific heat) on which extrapolations to the absolute zero are based, are made under such conditions that true equilibrium never obtains, the proportion between the varieties remaining "frozen" in that obtaining at high temperature.

I shall now proceed to calculate the various types of entropy for ammonia and methane at 298.1°K.

The Entropy of Ammonia at 298.1°K

Translational

Substituting in Eq. (3) values for ammonia at 298.1°K and one atmosphere, I get

$$S_t^{298.1} = 34.45 \text{ cal. degree}^{-1}$$

Vibrational

For the fundamental vibrational frequencies of ammonia I take those derived from Dennison,[11] but corrected to agree with Badger and Mecke[12] from whose work I shall later use also the moments of inertia. Calculation gives (Table I)

$$S_v^{298.1} = 0.06 \text{ cal. degree}^{-1}$$

Table I. *Vibrational entropy of ammonia.*

k	$\tilde{\omega}_k$cm^{-1}	Θ B & M	(Dennison)	$\Theta/298.1$	S_k
1	966	1380	(1346)	4.79	0.047
2, 3	1630	2330	(2330)	7.82	0.004 (×2)
4, 5	3336	4770	(4810)	16.0	0.000 (×2)
6	(4450)		(6370)		0.000
					$0.055 = S_v$

Rotational

The difficult part of the calculation of the entropy of ammonia lies in the evaluation of the rotational entropy. At room temperature where σ is small, the estimation of the double sum Q, may be carried out only by replacing it with a double integral, after which four steps are necessary to compare the calculated entropy with experiment; (1) decide upon the *a priori* probabilities, (2) compute the double integral, (3) determine the relative amounts of the different forms at high temperatures, and (4) subtract the "zero point" entropy.

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[11] Dennison, Phil. Mag. **1,** 195 (1926).

[12] Badger and Mecke, Zeits. f. physik. Chem. **135,** 333 (1929). $A = 2.79 \times 10^{-40}$, $C = 3.40 \times 10^{-40}$ gm·cm^2.

The *a priori* probabilities of the different rotational energy states of ammonia are obtained by the following considerations.[4,5,6,13] There are four $S(3)$ (quadruplet) and two $S(2+1)$ (doublet) nuclear spin eigenfunctions, the latter type being doubly degenerate, making four in all. One may look upon this degeneracy as corresponding roughly to the case where more than one doublet of the same total L occurs in a supermultiplet in electronic spectra. The total of eight is thus exactly equal to the total *a priori* weight one would get from the hydrogen nuclei by dissociating the ammonia into its three hydrogen atoms. There is one $S(3)$ and one $S(1+1+1)$ vibrational eigenfunction for the ground vibrational level. Of the rotational levels, there are $(2j+1)$ eigenfunctions for $\tau=0$ which are alternately $S(3)$ for even j and $S(1+1+1)$ for odd j. When τ is divisible by three, there are $(2j+1)$ $S(3)$ and $(2j+1)$ $S(1+1+1)$ functions for each value of j. When τ is not divisible by three, there are $2(2j+1)$ degenerate $S(2+1)$ rotational functions for each value of j. By multiplying together all combinations and discarding any but those which come out completely antisymmetric, $S(1+1+1)$, (Pauli exclusion principle), and remembering that, according to Hund,[5] only one-fourth of the combinations of two degenerate functions, $S(2+1)$, will result in a completely antisymmetric one, $S(1+1+1)$, and another fourth will give a completely symmetric one, $S(3)$, we get the values given in Table II.

TABLE II. *Rotational weights of different varieties of ammonia.*

j	τ	Nuclear quartet $S(3)$	Nuclear doublet $S(2+1)$
0	0	4×1	4×0
1	0	3	0
1	1	0	3
2	0	5	0
2	1	0	5
2	2	0	5
3	0	7	0
3	1	0	7
3	2	0	7
3	3	7×2	0
4	0	9	0
4	1	0	9
4	2	0	9
4	3	9×2	0
4	4	0	9
		$4(2j+1)$ for $\tau=0$ $8(2j+1)$ for τ divisible by three	$4(2j+1)$ for τ indivisible by three

Generalizing the *a priori* probabilities, p, as is done at the end of Table II, one can write for the Q sums

$$ {}^4Q = \sum_{j=0}^{\infty} 4(2j+1)e^{-j(j+1)\sigma_1} + \sum_{j=0}^{\infty} \sum_{\tau\equiv 0}^{(\tau\equiv 3)\leq j} 8(2j+1)e^{-j(j+1)\sigma_1-\tau^2\sigma_2} \quad S(3) \quad (15)$$

$$ {}^2Q = \sum_{j=0}^{\infty} \sum_{\tau\equiv 1,2}^{(\tau\equiv 1,\,2)\leq j} 4(2j+1)e^{-j(j+1)\sigma_1-\tau^2\sigma_2} \quad S(2+1). \quad (16)$$

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

The double sum in (15) is to be taken only for values of $\tau = 3$, 6, 9 etc. up to one which may equal but not exceed the particular value of j assumed in the first summation. The double sum in (16) is taken for the remaining values of $\tau = 1$, 2, 4, 5, 7, 8, etc. up to j but not exceeding it. When the summations extend over a great many terms (σ small) these equations may be written in the integral form

$$^4Q = 4\int_0^\infty (2j+1)e^{-j(j+1)\sigma_1}dj + \int_0^\infty (2j+1)e^{-j(j+1)\sigma_1}dj \int_{\tau\equiv 3}^{\tau\leq j} e^{\leq \tau^2\sigma_2}d\tau \quad (17)$$

$$^2Q = 4\int_0^\infty (2j+1)e^{-j(j+1)\sigma_1}dj \int_{\tau\equiv 1,2}^{\tau\leq j} e^{-\tau^2\sigma_2}d\tau. \quad (18)$$

The first term of (17) is readily integrated. In order to compute the double integral in (17) one must introduce some simplifying approximation. Making use of Badger and Mecke's[12] data (which gives $\sigma_1 = 0.0476$; $\sigma_2 = -0.00854$) I find that the ratio $\sigma_1 : \sigma_2$ is -5.6. This suggests the possibility that σ_2 may be neglected with no appreciable error. Thus, the second integral in the second term of (17) could be taken as approximately $j/3$ as long as $j(j+1)\sigma_1$ is small; when the latter becomes large, the first exponential would have approached quite a small value before the second integral could have changed materially. The use of this approximation would give a lower limit to the sum Q (since σ_2 is negative). Likewise, the second integral in (18) might be taken as $2j/3$. Obviously, the next approximation is to be obtained by expanding the exponential in $\tau^2\sigma_2$ and integrating by parts. Carrying out this integration one gets the following, the last term in braces representing the second approximation.

$$^4Q = (4/3)\pi^{1/2}\sigma_1^{-3/2}e^{\sigma_1/4}\left[\left\{1 - 4\pi^{-1/2}\sigma_1^{1/2} + (5/6)\pi^{-1/2}\sigma_1^{3/2}\right\} - (\sigma_2/2\sigma_1)\left\{1 - 2\pi^{-1/2}\sigma_1^{1/2} + \sigma_1/2\right\}\right] \quad (19)$$

$$^2Q = (4/3)\pi^{1/2}\sigma_1^{-3/2}e^{\sigma_1/4}\left[\left\{1 - 4\pi^{-1/2}\sigma_1^{1/2} + (5/6)\pi^{-1/2}\sigma_1^{3/2}\right\} - (\sigma_2/2\sigma_1)\left\{1 - 3\pi^{-1/2}\sigma_1^{1/2} + \sigma_1/2\right\}\right] \quad (20)$$

This shows immediately that the proportions of the two forms at high temperature (σ small) are equal.

$$^4Q : {}^2Q = 4/4. \quad (21)$$

Differentiating the natural logarithm of (19) and (20) and applying (11), one obtains for the absolute rotational entropies

$$\begin{aligned} ^4S_r &= R\left[1.5 + \ln 4\pi^{1/2}/3 - 1.5\ln\sigma_1 - 2\pi^{-1/2}\sigma_1^{1/2} - \sigma_2/2\sigma_1 + \tfrac{1}{2}\sigma_2\pi^{-1/2}\sigma_1^{-1/2}\right] = 2.98 + 1.70 + 9.08 - 0.49 + 0.18 - 0.02 \quad (22)\\ &= 13.43 \text{ at } 298.1°K \end{aligned}$$

$$^2S_r = R\left[1.5 + \ln 4\pi^{1/2}/3 - 1.5\ln\sigma_1 - 2\pi^{-1/2}\sigma_1^{1/2} - \sigma_2/2\sigma_1 + (3/4)\sigma_2\pi^{-1/2}\sigma_1^{-1/2}\right] = 13.42 \text{ at } 298.1°K. \quad (23)$$

The total absolute rotational entropy is (cf 21)

$$\begin{aligned} S_r &= \tfrac{1}{2}\,{}^4S_r + \tfrac{1}{2}\,{}^2S_r - \tfrac{1}{2}R\ln\tfrac{1}{2} - \tfrac{1}{2}R\ln\tfrac{1}{2} \\ &= 13.425 + 1.377 \\ &= 14.80 \text{ cal. degree}^{-1} \text{ at } 298^\circ K \end{aligned} \tag{24}$$

while the entropy of the gas at the absolute zero under conditions of "frozen" equilibrium would be

$$\begin{aligned} S_r' &= \tfrac{1}{2}R\ln 4 + \tfrac{1}{2}R\ln 12 + S_{\text{mix}} \\ &= 1.377 + 2.468 + 1.377 \\ &= 5.22 \text{ cal. degree}^{-1}. \end{aligned} \tag{25}$$

The latter must be subtracted from the absolute entropy to obtain what we shall call the "virtual" entropy, which corresponds to the calorimetrically measured quantity.†

$$\begin{aligned} S_r^* &= S_r - S_r' = 14.80 - 5.22 \\ &= 9.58 \text{ at } 298^\circ. \end{aligned} \tag{26}$$

It is evident from the foregoing that the entropy of mixing does not enter into the final value of the virtual rotational entropy since it cancels out in the "zero point" correction, but that it is quite important to the value of the absolute entropy.

We are now ready to add together all our results in order to get the total entropy of ammonia.

$$\begin{aligned} S_{\text{NH}_3}^{298.1} &= 34.45 + 0.06 + 14.80 + 2.18 \\ &= 51.5 \text{ cal. degree}^{-1} \text{ absolute entropy.} \end{aligned}$$

(The entropy, $R \ln 3 = 2.18$, due to the nitrogen nucleus, hitherto neglected, is here included.)

$$\begin{aligned} S_{\text{NH}_3}^{298.1*} &= 34.45 + 0.06 + 9.58 \\ &= 44.1 \text{ cal. degree}^{-1} \text{ virtual entropy}^{14} \text{ at } 298.1^\circ K. \end{aligned}$$

The absolute minus nuclear spin entropy ($R \ln 24 = 6.31$) is 45.2.

Comparison with experiment.

To compare these calculated values with experiment requires extreme caution. By using the equations of Lewis and Randall,[10] p. 557, for the heat and free energy of formation of ammonia, one may get the entropy change of the reaction

$$\Delta S_{\text{NH}_3}^{298.1} = -23.7.$$

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† Cf. comments added in proof.

[14] The difference between these values and those announced in the preliminary statement (reference 1) arose from a discovery of certain fundamental errors which had been made in counting eigenfunctions.

It at first seemed justifiable to add to this the experimental (virtual) entropies of nitrogen and hydrogen to get an experimental value for the virtual entropy of ammonia (43.6) and it was on this basis that comparisons were made in the preliminary notice of this work.[1] Giauque, Blue and Overstreet,[15] in a letter to the Editor of this journal state that this calculation "is evidently in error," after giving theirs to be 46.1. This is a rather unfair statement, in that it implies an arithmetical error where in reality the difference lies in the manner of definition.††

Mature consideration shows that the entropy change of the reaction of formation which was obtained above is in reality the change in *absolute* entropy. Least confusion will therefore arise if one talks in terms of absolute entropy.

$$S_{\mathrm{NH_3}} = \Delta S + \tfrac{1}{2}S_{\mathrm{N_2}} + 1.5\, S_{H_2} \tag{27}$$

where the absolute entropy

$$\begin{aligned} S_{H_2} &= 33.98 \\ &= S_{\mathrm{H_2}}{}^* + R \ln 4 + \tfrac{3}{4}R \ln 3 \end{aligned} \tag{28}$$

and similarly

$$\begin{aligned} S_{\mathrm{N_2}} &= S_{\mathrm{N_2}}{}^* + R \ln 9 \\ &= 2 \times 22.9 + 4.37 \\ &= 50.2. \end{aligned} \tag{29}$$

The term ($\tfrac{1}{3}R \ln 3 = 0.73$) corresponding to the odd rotating variety of nitrogen which I know to constitute one-third of the total from the intensity ratio of the band lines[16] and from the Raman effect,[17] I have stricken out (in proof) on the authority of a private communication from Giauque who states that experimental work by himself and Clayton has shown that the calorimetric value of the entropy of nitrogen is absolute entropy (as computed from band spectra) minus only the nuclear spin entropy. With (28) and (29) one gets as an "experimental" value for the absolute entropy of ammonia

$$\begin{aligned} S_{\mathrm{NH_3}}^{298\ 1} &= -\ 23.7 + 25.08 + 50.97 \\ &= 52.3 \text{ cal. degree}^{-1}. \end{aligned}$$

My calculated value of the absolute entropy, 51.5, thus agrees fairly well

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[15] Giauque, Blue and Overstreet, Phys. Rev. **38,** 196–7 (1931). I wish to thank Professor Giauque for a copy of this letter which was furnished me while the present manuscript was being prepared. As far as I can tell, Giauque Blue and Overstreet have calculated the entropy of methane and ammonia by means of the old quantum theory involving the sometimes ambiguous symmetry number, to obviate the necessity for which was the especial virtue of the Gibson-Heitler[15a] theory. I shall show that the two methods are in agreement when the same data are used.

[15a] Gibson and Heitler, Zeits. f. Physik **49,** 465 (1928).

†† Added in Proof—This has been recognized by Bryant. J. Am. Chem. Soc. **53,** 3014 (1931).

[16] Mulliken, Trans. Farady Soc. **25,** 634 (1929).

[17] Rasetti, Nature **124,** 792 (1929).

with the above. Giauque, Blue and Overstreet[15] suggest that my choice of Badger and Mecke's[12] moments of inertia may have led to a small divergence in results for ammonia. One may readily calculate this effect from our Eqs. (22) and (23). They prefer the values of 5.47×10^{-40} and 2.792×10^{-40} gm cm^2 obtained by Barker.[18] This would give a ratio of $\sigma_1:\sigma_2$ of -2.04 instead of -5.6 as before. The terms in (22) and (23) corresponding to the second approximation are therefore 5.6/2.04 greater and this would give a greater entropy by 0.2 cal. degree.$^{-1}$ If their estimate of the vibrational entropy 0.3 prove to be better founded than that used above 0.06 (Table I), the remainder of the difference 0.3, might perhaps be largely that arising from neglect of the stretching effects of the rotation, although part of it is to be accounted for by the higher terms in the expansions (19) and (20).†††

THE ENTROPY OF METHANE AT 298.1°K

Translational

Substituting in Eq. (3) values for methane at 298.1°K and one atmosphere, I get

$$S_t^{298.1} = 34.27 \text{ cal. degree}^{-1}.$$

Vibrational

For the fundamental vibrational frequencies of methane I take those from Dennison.[19] Some doubt has been cast on the correctness of his assignment by Dickinson, Dillon and Rasetti[20] who find a very strong Raman line of frequency 2914.8 cm^{-1}, which is exactly equal to the difference between two of Dennison's fundamentals, 4217 and 1304 cm^{-1}. As they point out, this indicates that it either owes its origin to molecules in thermal vibration (highly improbable for the strongest line) or else that the choice of the fundamentals is wrong. For want of better information however, I shall use Dennison's data, with the assurance that the vibrational entropy at most only amounts to a small fraction of the whole. Calculation gives (Table III)

$$S_v^{298.1} = 0.11 \text{ cal. degree}^{-1}$$

TABLE III. *Vibrational entropy of methane.*

k	$\tilde{\omega}_k$cm^{-1}	Θ	$\Theta/298.1$	S_k
1, 2, 3	1304	1870	6.275	0.0274 (×3)
4, 5	1520	2180	7.31	.0112 (×2)
6, 7, 8	3014	4310	14.45	$.0_417$ (×3)
9	4217	6040	20.3	—
				0.105 S_v

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[18] Barker, Phys. Rev. **33**, 684 (1929).

††† Added in Proof—The remainder of the discrepancy between my value for the absolute entropy, 51.5, and theirs, 52.7, is probably to be ascribed to the fact that my series is carried out to the second approximation which is farther than theirs has been.

[19] Dennison, Astrophys J. **62**, 84 (1925).

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

Rotational

The rotational equations for the three different forms of methane have already been derived (V and S). Differentiating only once the natural logarithm of the expressions (25), (26) and (27) of that paper and applying (11) of the present article, one obtains for absolute rotational entropies

$$\begin{aligned} {}^5S_r &= R[-1.5 \ln \sigma + \ln 5\pi^{1/2}/12 + 1.5 + 15\pi^{-1/2}\sigma^{3/2} \cdots] \\ &= 10.91 - 0.61 + 2.98 + 0.07 \\ &= 13.35 \text{ at } 298.1^\circ \end{aligned} \tag{30}$$

$$\begin{aligned} {}^3S_r &= R[-1.5 \ln \sigma + \ln 9\pi^{1/2}/12 + 1.5 + 37\pi^{-1/2}\sigma^{3/2} \cdots] \\ &= 10.91 + 0.57 + 2.98 + 0.17 \\ &= 14.63 \text{ at } 298.1^\circ \end{aligned} \tag{31}$$

$$\begin{aligned} {}^1S_r &= R[-1.5 \ln \sigma + \ln 2\pi^{1/2}/12 + 1.5 + 39\pi^{-1/2}\sigma^{3/2} \cdots] \\ &= 10.91 - 2.43 + 2.98 + 0.18 \\ &= 11.64 \text{ cal. degree}^{-1} \text{ at } 298.1^\circ K. \end{aligned} \tag{32}$$

As before, I shall use the Raman value of the moment of inertia which gives $\sigma = 0.0258$ at 298.1°K. The average absolute rotational entropy is, making use of the proportions found in (31) of V and S.

$$\begin{aligned} S_r &= (5/16)\,{}^5S + (9/16)\,{}^3S + (2/16)\,{}^1S + S_{\text{mix}} \\ &= 4.17 + 8.23 + 1.46 + 1.89 \\ &= 15.75 \text{ cal. degree}^{-1}. \end{aligned} \tag{33}$$

The "zero point" entropy correction under conditions of frozen equilibrium would be

$$\begin{aligned} S_r' &= (5/16)R \ln 5 + (9/16)R \ln 9 + (2/16)R \ln 10 + S_{\text{mix}} \\ &= 1.00 + 2.45 + 0.57 + 1.89 \\ &= 5.91 \text{ cal. degree}^{-1}. \end{aligned} \tag{34}$$

Subtracting this from the absolute entropy, one gets the virtual entropy which may now be compared with experiment.†

$$\begin{aligned} S_r^* = S_r - S_r' &= 15.75 - 5.91 \\ &= 9.84 \text{ cal. degree}^{-1}. \end{aligned} \tag{35}$$

The total entropy is the sum of the foregoing amounts

$$\begin{aligned} S_{\text{CH}_4}^{298.1} &= 34.27 + 0.11 + 15.75 \\ &= 50.1 \text{ absolute entropy or} \\ S_{\text{CH}_4}^{298.1*} &= 34.27 + 0.11 + 9.84 \\ &= 44.2 \text{ cal. degree}^{-1} \text{ virtual entropy}^{14}. \end{aligned}$$

The absolute minus nuclear spin entropy ($R \ln 16 = 5.51$) is 44.6.

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† Cf. comments added in proof.

Comparison with experiment.

The above value for the virtual entropy of methane (44.2) may be compared with an experimental entropy recently recalculated by Storch[21] from the specific heat measurements of Clusius[22] (43.39). Much better agreement of our calculated value is found when it is compared with the one computed by Giauque, Blue and Overstreet[15] (44.3) from the data of Clusius,[22] of Stock, Henning and Kuss[23] and of Keyes, Taylor and Smith.[24]

The reaction of formation may also be employed for comparison purposes. In this case, as before with ammonia one should compare absolute entropies, not experimental, if one is to avoid confusion. Storch[21] has recalculated the data of Randall and Mohammad[25] to agree with the later specific heat measurements of Eastman[26] and of Eucken and Luede[27] and gives us the values

$$\Delta H_{\mathrm{CH_4}}^{298.1} = -\ 18062 \text{ cal./mole}$$

$$\Delta F_{\mathrm{CH_4}}^{298.1} = -\ 12542 \text{ cal./mole.}$$

From these I compute

$$\Delta S_{\mathrm{CH_4}}^{298.1} = -\ 18.52 \text{ cal. degree}^{-1}$$

and add 2×33.98 (the absolute entropy of hydrogen) plus 1.39 (I. C. T. value for entropy of graphite) to get

$$S_{\mathrm{CH_4}}^{298.1} = 50.8 \text{ cal. degree}^{-1}$$

which compares quite favorably with my calculated value of the absolute entropy of methane (50.1). This last estimate is uncertain in that we do not know whether the experimental entropy of graphite (1.39) differs from its absolute entropy. If it were a diatomic gas, one could say definitely that there would be no difference, since its nuclear spin entropy is zero and its lowest rotational level is the one of zero rotation (in C_2, the odd levels are missing).[16] It is quite probable that the lowest levels in the graphite crystal correspond to zero rotation, and if this is true, the above comparison is justified; if it is not true, then the corresponding entropy of rotation should be added to 50.8 and that value be compared with my theoretical one of 50.1

It may be noted in passing that 0.4 cal. degree^{-1} of the 1.9 units divergence noted by Storch as existing between the reaction of formation data and the specific heat data on methane has been removed in the above analysis, on the interpretation involving virtual entropies as I have defined them. This is not removed if the experimental entropies differ from their absolute values only

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[21] Storch, J. Am. Chem. Soc. **53,** 2166 (1931).

[22] Clusius, Zeits. f. physik. Chem. **B3,** 41 (1929).

[23] Stock, Henning and Kuss, Ber. **54,** 1119 (1921).

[24] Keyes, Taylor and Smith, J. Math. Phys. Mass. Inst. Tech. **1,** 191 (1922).

[25] Randall and Mohammad, Ind. Eng. Chem. **21,** 1048 (1929).

[26] Eastman, Bureau of Mines Circular **6125,** May (1929).

[27] Eucken and Luede, Zeits. f. physik. Chem. **B5,** 436 (1929).

by their nuclear spin entropies. (The entropy indicated from the $CO_2 \rightarrow CH_4$ reaction is still in disagreement with the other values.)††

CONCLUSION

Before concluding, it might be briefly pointed out that the common factor multiplying all the *a priori* probabilities of a distinct symmetry variety affects the relative proportions (mole fraction) of the different varieties and their absolute entropies; not, however, the virtual entropy.

In conclusion I wish to emphasize my belief that comparisons between theory and experiment should be made, wherever possible, with the absolute entropies. If these are uncertain in symmetrical molecules, then this uncertainty will almost invariably be carried over to the calculated value which is being compared with experiment, except where the relative proportions of the different symmetry varieties are already known in advance. In only one case may the virtual theoretical value be compared with the actual calorimetric one and that is when the latter has been determined from specific heat measurements on that substance alone (not in connection with a reaction). In this case, the absolute entropy must be calculated beforehand, at any event. An important corollary of the conclusions developed above is that the experimental entropy change in a reaction (obtained from the free energy and heat change) is equal to the change in absolute entropy and in some cases may be distinctly different from that computed from the algebraic sum of the experimental entropies derived from specific heat measurements on the separate reactants.

Comments added in proof: (9/15/31)

The foregoing calculations of the absolute entropy by the application of quantum mechanics are seen to be in good agreement with those obtained from classical theory. In all fairness it should be stated however that the method of comparison with experiment is not at all certain. If calorimetric measurements were made on the *gas* all the way down to near the absolute zero, or if the liquid and crystal carry over the rotational states of the gas without material changes in the relative rotational and vibrational energy level spacings, the experimental calorimetric entropy should correspond to the virtual entropy (absolute minus nuclear spin minus frozen rotational entropy). This is true of hydrogen if too low temperatures are not attained. However, there is a second class of substances (Giauque, ref. 2f, p. 4825 believes all substances belong to this class except hydrogen) such as iodine[2i] in which the degenerate rotational levels become so widely separated (perturbed) by the crystal forces as the molecule passes into the crystalline state that the ratio, Σ/kT, is no longer negligible but becomes quite appreciable

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†† Added in proof—The difference between my calculated value of the absolute entropy of methane, 50.13, and that of Giauque, Blue and Overstreet, 49.86, may be shown to be due to the fact that I have not neglected vibrational entropy (0.11) and have computed my series to a further degree of approximation than that used by these authors. My last approximation amounts to 0.15 and fully accounts for the difference between our results.

for all but the lowest of the resolved degenerate levels with the result that all molecules settle into the lowest state which is now of unit statistical weight. Under such conditions, the frozen rotational entropy is removed and the experimental value should correspond to the absolute minus nuclear spin entropy.

Finally, a third class has been proposed recently by Ludloff[28] in which even the entropy of nuclear spin is partially or wholly resolved, in solids of great crystal forces. He points out that even under such circumstances, the entropy of mixing will remain associated with the state of zero temperature. Of course substances may also belong to the in-between classes. Examples of class III given by him are N_2O, NH_3, Br_2 and Cl_2. In such a case, it will be necessary to know the relative amounts of the different symmetry forms in order to compute the entropy of mixing, and here the method of calculation I have chosen possesses distinct advantage over the one used by Gibson and Heitler [15a] and by Giauque, Blue and Overstreet.[15]

The calorimetric value of ammonia given by the latter, computed from data of Eucken and Karwat[29] and Henning and Stock[30] is 47.2. My four calculated values of entropy are summarized as follows: absolute, 51.5; absolute minus mixing (Ludloff, class III), 50.1; absolute minus nuclear spin (Giauque, class II) 45.2; absolute minus nuclear spin minus frozen rotational (virtual—class I), 44.1.

The same data for methane, which, according to Ludloff, belong to class II are: experimental calorimetric, 43.39 (Storch) or 44.3 (Giauque, Blue and Overstreet); absolute, 50.1; absolute minus mixing, (class III), 48.2; absolute minus nuclear spin (class II), 44.6; absolute minus nuclear spin minus frozen rotational (virtual—class I), 44.2

In this connection, Rodebush[2h] maintains that the only entropy worthy of consideration is that of the equilibrium mixture. To measure this, it is necessary to find a catalyst which establishes equilibrium at all temperatures down to near the absolute zero. I wish to point out that the discovery of such a catalyst serviceable at these low temperatures will probably be the exception rather than the rule in view of the recent proof by Taylor[31] that activation heats are associated with adsorption processes. While the equilibrium value of the entropy (absolute entropy) is the one which should be used in thermodynamic discussions, it seems to me more practicable, at least until such catalysts are universally assured to make the experimental measurements on the metastable mixture of the proportions existing at high temperature down to a temperature at which the resolution of the frozen rotational or the nuclear spin entropy just begins to become evident, extrapolate from there to the absolute zero and correct for the omission of this type of entropy by adding the suitable theoretical amount.

[28] Ludloff, Zeits. f. Physik **68,** 433–46 (1931).

[29] Eucken and Karwat, Zeits. f. phys. Chem. **112,** 467 (1924).

[30] Henning and Stock, Zeits. f. Physik **4,** 226 (1921).

[31] Taylor, J. Am. Chem. Soc. **53,** 578 (1931).