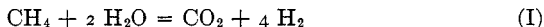


METHANE EQUILIBRIA FROM ABSOLUTE ENTROPIES, WITH A NOTE ON THE USE OF THE EHRENFEST SYMMETRY NUMBER

BY A. R. GORDON AND COLIN BARNES

The entropy of methane at 298°K was calculated from spectroscopic data by Giaque, Blue and Overstreet¹ who used the Ehrenfest formula which is strictly valid for the rotational entropy at this temperature. A calculation by Villars,² using the rotational symmetry characters of Elert,³ gave the same result when corrected for some numerical errors.⁴ The value so obtained for the entropy agreed moderately well with the free energy data derived by Storch⁵ from the measurements made by Randall and his associates on the two reactions



The calculations of Storch, however, involved specific heats which are not in agreement with those calculated from the vibration spectrum of methane. A consistent computation, using spectroscopic entropies and heat capacities of the gases, may now be carried out for these reactions; the only other quantities that are involved are the "third law" entropy of graphite and the calorimetric values of the heats of reaction.

1. The Entropy of Methane from 300° to 1200°K

In the calculations mentioned above, only a single temperature was considered; for the present purpose it is necessary to compute the entropy of methane up to 1200° in order to cover the equilibrium data on reactions I and II.

The molar translational entropy for temperature T and pressure 1 atmosphere for a gas of molecular weight M ($= 16.036$) is given by the usual Sackur-Tetrode formula⁶

$$S_T = -2.295 + 3R/2 \ln M + 5R/2 \ln T \quad (\text{r})$$

The values of this expression for the various temperatures are entered in Table I.

¹ Giaque, Blue and Overstreet: *Phys. Rev.*, (2) **38**, 196 (1931).

² Villars: *Phys. Rev.*, (2) **38**, 1552 (1931).

³ Elert: *Z. Physik*, **51**, 6 (1928).

⁴ MacDougall: *Phys. Rev.*, (2) **38**, 2074 (1931).

⁵ Storch: *J. Am. Chem. Soc.*, **53**, 1266 (1931).

⁶ The values of the constants used are (*Handbuch der Physik*, 1926): $R = 1.9858 \text{ cal./deg.}$; $k = 1.372 \times 10^{-16} \text{ ergs/deg.}$; $h = 6.55 \times 10^{-27} \text{ erg. sec.}$; $N = 6.06 \times 10^{23}$; 1 atmos. = $1.0133 \times 10^6 \text{ dynes/cm}^2$.

The methane molecule, considered as a completely symmetrical rigid rotator, has three equal moments of inertia $A = B = C = 5.17 \times 10^{-40}$, given by the measurements of Dickinson, Dillon and Rasetti¹ on the Raman effect in methane; if I be written for $\sqrt[3]{ABC}$, such a model gives a classical rotational entropy

$$S_R' = 3R/2 + 3R/2 \ln 8\pi^7/3 kT/h^2 \quad (2)$$

when *all* the rotational levels are taken into account. From the work of Elert,² however, it is known that only one-twelfth of the rotational states in methane are to be retained, for this is the fraction of all the molecular states which belong to a definite symmetry class, either completely symmetrical or completely antisymmetrical. For temperatures ranging from 300° to 1200°, the state sum (see note on symmetry number below) for the rotational entropy is just $1/12$ of the value used in the derivation of S_R' ; i.e. if S_R' is to be retained, we must subtract $R \ln 12$ from it to get the value of the rotational entropy of methane. This is, of course, what is meant by saying that the CH_4 molecule has a "symmetry number" 12.

The weight g of the lowest electronic configuration is 1 and will not enter into the complete expression for the entropy. The four hydrogen atoms in the methane molecule (for the temperature range considered) contribute, due to their intrinsic spins, an entropy $4R \ln 2$; thus the quantity S_R , entered for various temperatures in Table I, is given by

$$S_R = S_R' - R \ln 12 + 4R \ln 2 \quad (3)$$

The fundamental vibration frequencies have been given by Dennison;³ they are

$$4217 \quad (1) \qquad 1520 \quad (2) \qquad 3014 \quad (3) \qquad 1304 \quad (3)$$

in cm^{-1} , where the number in brackets after a frequency indicates its degree of degeneracy, i.e. the number of times it must be supposed to occur in calculating the state sum for the vibrational entropy S_V . S_V , computed in the usual way, is entered in Table I for the various temperatures. The total entropy is given by

$$S = S_T + S_R' + S_V - R \ln 12 + 4R \ln 2 = S_T + S_R + S_V \quad (4)$$

and is entered in Table I. The table also contains values of the heat capacity of methane at constant pressure for the temperatures considered; the vibrational contributions were computed from the fundamental frequencies of the molecule in the usual manner.

¹ Dickinson, Dillon and Rasetti: Phys. Rev., (2) **34**, 582 (1929).

² Elert: Loc. cit.

³ Dennison: Astrophys. J., **62**, 84 (1925); Dennison and Ingram: Phys. Rev., (2) **36**, 1451 (1930).

TABLE I

Molar Entropy and Heat Capacity at Constant Pressure (1 atmos) of Methane

T°K.	S _T	S _R	S _V	S	C _P
300	34.288	15.612	0.108	50.01	8.54
400	35.716	16.469	0.429	52.61	9.71
500	36.824	17.134	0.971	54.93	11.09
600	37.729	17.677	1.666	57.07	12.46
700	38.494	18.136	2.458	59.09	13.71
800	39.157	18.534	3.301	60.99	14.87
900	39.742	18.884	4.181	62.81	15.90
1000	40.265	19.198	5.066	64.53	16.83
1100	40.738	19.482	5.954	66.17	17.67
1200	41.170	19.741	6.833	67.74	18.45

2. The Equilibrium I

If P_X is the partial pressure of a component X in this reaction and if K be defined by

$$K = P_{CH_4} (P_{H_2O})^2 / P_{CO_2} (P_{H_2})^4$$

then

$$R \ln K = -Q/T + \Sigma S \quad (5)$$

where Q is the heat of reaction at temperature T and

$$\Sigma S = S_{CH_4} + 2S_{H_2O(g)} - S_{CO_2} - 4S_{H_2}$$

the entropies being all for temperature T and pressure 1 atmosphere.

The heat of combustion of methane¹ at 298° is 212790 cal., and the heat of formation of water¹ at the same temperature is 68313 cal.; from these two numbers and the heat of vaporization² of water at this temperature (10485 cal.), $Q_{298} = -39500$ cal. The values of Q for higher temperatures can now be found by integration of the specific heat curves, the heat capacities for methane being given in Table I and the values for the other gases having been previously calculated.³ The values of Q/T so obtained are given in Table II. Values of ΣS , obtained from the methane entropies in Table I and the known entropies of the other gases³ are entered in Table II, which also gives the resulting values of $R \ln K$. From the latter the curve in Fig. I was constructed.

TABLE II

The Equilibrium $CH_4 + 2 H_2O = CO_2 + 4 H_2$

T°K.	575	600	625	650	675	700
-Q/T	74.08	71.40	68.92	66.62	64.48	62.49
- ΣS	49.03	49.49	49.87	50.24	50.59	50.90
R ln K	25.05	21.91	19.05	16.38	13.89	11.59

¹ Rossini: Bur. Standards J. Research, (6) 1, 36 (1931).

² Int. Crit. Tables, 5, 138.

³ Gordon and Barnes: J. Phys. Chem., 36, 1143 (1932).

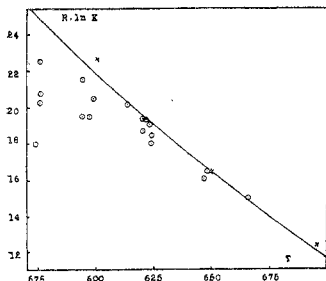
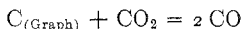


FIG. 1

discrepancy supposed to exist between the calculated and observed entropy change for the reaction. The values² suggested for this reaction are $-\Delta H_{298.1}^{\circ} = -39500$, $-\Delta S_{298.1}^{\circ} = -41.52$, $-\Delta F_{298.1}^{\circ} = -27120$.

3. The Equilibrium II

In this reaction the entropy of graphite gives rise to the most uncertainty, as there is always an element of risk when using a calorimetric entropy in conjunction with spectroscopic entropies. Fortunately an independent check is available here, since the equilibrium constant for the reaction



is fairly accurately known.³ Using the equation of Magnus⁴ for the heat capacity of graphite, and the value 1.22 calories per degree for the entropy of graphite⁵ at 273.1°, the entropy for the three temperatures 1123°, 1173° and 1223° is found to be 6.47, 6.70 and 6.92, respectively. The entropies of carbon monoxide and carbon dioxide can be found by interpolation from Gordon and Barnes' Tables IV and V,⁶ giving -41.58 , -41.47 and -41.35 as the values of $(S_{(\text{Graph.})} + S_{\text{CO}_2} - 2S_{\text{CO}})$ for the three temperatures. From the heat of combustion of graphite,⁷ viz. 94420 cal. at 291°, and that of carbon monoxide⁸ (67623 cal. at 298°), $Q_{298} = -40826$, so that Q/T for 1123°, 1173° and 1223° is -35.63 , -34.00 and -32.50 , respectively; hence, $R \ln (P_{\text{CO}_2})/(P_{\text{CO}})^2$ for the three temperatures is -5.95 , -7.47 and -8.85 . The corresponding experimental numbers are -5.26 , -7.47 and -8.54 , in reasonably good agreement.

¹ Randall and Gerard: Ind. Eng. Chem., **20**, 1335 (1928).

² The entropy of carbon dioxide at 300° is 51.09, not 51.19 as entered in Gordon and Barnes' Table V; the mistake arose from the value entered for S_V at this temperature; this should be 0.738, not 0.838 as printed.

³ Rhead and Wheeler: J. Chem. Soc., **97**, 2178 (1910).

⁴ Int. Crit. Tables, **5**, 94.

⁵ Int. Crit. Tables, **5**, 87.

⁶ Gordon and Barnes: Loc. cit.

⁷ Roth and Wallasch: Z. Elektrochemie, **21**, 1 (1915); Roth: **26**, 288 (1920).

⁸ Rossini: Loc. cit.

From the heats of combustion of methane and graphite, and the heat of formation of water, the heat of formation of methane at 298° is 18256 cal.; from this and the heat capacities of graphite, methane (Table I) and hydrogen,¹ the values of Q/T entered in Table III are found by tabular integration. The entropies of methane (Table I), of hydrogen¹ and of graphite² lead to the values of $\Sigma S = S_{(\text{Graph.})} + 2S_{\text{H}_2} - S_{\text{CH}_4}$ entered in that table. The resulting values of $R \ln (P_{\text{H}_2})^2/(P_{\text{CH}_4})$ are shown by the curve in Fig. II.

TABLE III

The Equilibrium $\text{C}_{(\text{Graph.})} + 2\text{H}_2 = \text{CH}_4$

T°K	700	800	900	1000	1100	1200
Q/T	29.68	26.51	23.96	21.87	20.10	18.58
ΣS	24.88	25.47	25.90	26.21	26.45	26.63
R ln K	-4.80	-1.04	+1.94	+4.34	+6.35	+8.05

The same figure shows the relation of the calculated curve to the experimental values obtained by Mayer and Altmayer,³ by Randall and Mohammed⁴ and by Coward and Wilson;⁵ the forward reaction, i.e. methane synthesis, gives the points indicated by the light symbols; the reverse reaction gives those indicated by the black symbols. For the lower part of the temperature range the calculated curve lies satisfactorily with regard to the experimental points, but the agreement is not so close at higher temperatures where the experimental curve would lie about 1 cal./degree below that of the figure.

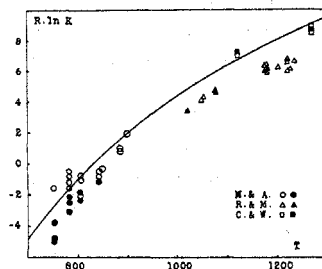


Fig. 2

Villars⁶ has recently suggested frequencies for the methane molecule somewhat different from those used above, but in better agreement with observed Raman lines; he replaces Dennison's single frequency 4217 cm^{-1} by the Raman frequency 2914.8 but leaves the other frequencies unchanged. This makes an appreciable difference in the entropy and heat capacity of methane⁷ only for

¹ Gordon and Barnes: Loc. cit.

² The graphite entropies were computed from the entropy at 273.1° by tabular integration of $(C_p/T).dT$; they are

T°K	700	800	900	1000	1100	1200
S	4.15	4.76	5.33	5.86	6.36	6.83

³ Mayer and Altmayer: Ber., 40, 2134.

⁴ Randall and Mohammed: Ind. Eng. Chem., 21, 1048 (1929).

⁵ Coward and Wilson: J. Chem. Soc., 115, 1380 (1919).

⁶ Villars: Preprint of papers to be presented at the New Orleans meeting of the American Chemical Society, March 30, 1932, Paper No. 32.

⁷ Using Villars' frequencies, the numbers are (cf. Table I):

T°K	700	800	900	1000	1100	1200
S	59.12	61.05	62.90	64.66	66.33	67.94
C_p	13.86	15.11	16.22	17.21	18.09	18.90

temperatures greater than 700° . As far as the calculation of $R \ln K$ for Reaction II is concerned, however, the changes introduced in Q/T and ΣS partly cancel, and thus the equilibrium constant is only slightly altered; the use of Villars' frequencies would change -1.04 for 800° into -1.05 and $+8.05$ for 1200° into $+8.00$, far too small a correction to account for the discrepancies shown in Fig. II.

The satisfactory agreement in the case of Reaction I would indicate that the quantities used in the calculations are not very seriously in error. A reasonable explanation for the drift in $R \ln K$ for Reaction II at the higher temperatures lies in the experimental conditions under which equilibrium was attained; side reactions leading to the formation of hydrocarbons other than methane undoubtedly occur,¹ particularly at high temperatures, and low values of K would result from the measured excess of methane. In view of the experimental difficulties on the one hand, and the uncertainties inherent in the calculation of a vibration-rotation entropy on the other, the agreement in this case also is probably as close as can be expected.

The value of $-\Delta F^\circ_{298.1}$ for methane,² calculated from the heat of formation and the entropies, is 12490 cal.

4. Note on the use of the "Symmetry Number"

From the work of Gibson and Heitler³ and of Ludloff,⁴ it is now known that the Ehrenfest symmetry number, σ , originally introduced as a geometrical concept into the classical phase space of a gas, is merely a convenient way of expressing what fraction of all the energy states of a molecule have a certain symmetry character; the expression "symmetry character" is to be understood in the sense of quantum mechanics as applied to molecules containing two or more identical nuclei. If the energy states ϵ_n of a molecule occur with the weight factors p_n , the familiar entropy expression is

$$S = R(\Sigma_2/\Sigma_1) + R \ln \Sigma_1 \quad (6)$$

where Σ_1 (the state sum) and Σ_2 (the energy sum) are defined by

$$\Sigma_1 = \sum_n p_n \cdot e^{-\epsilon_n/kT}; \quad \Sigma_2 = \sum_n p_n \cdot (\epsilon_n/kT) \cdot e^{-\epsilon_n/kT} \quad (7)$$

For temperatures above 300°K , the evaluation of these sums, for practically all types of molecules, leads to the classical expression for the rotational entropy, provided no states are rejected on a basis of selection of some definite type of symmetry. In the computation of such an entropy, however, we must select only those states of a certain symmetry; the correction to the classical expression is then summarized in a symmetry number. It appears that when no enumeration of the rotational symmetry characters can be made, no symmetry number can be deduced with certainty from an assumed geometrical

¹ See Storch: *Loc. cit.*; Pring and Fairlie: *J. Chem. Soc.*, **101**, 91 (1912).

² Giauque, Blue and Overstreet's value (*loc. cit.*) is 12440 .

³ Gibson and Heitler: *Z. Physik*, **49**, 465 (1928).

⁴ Ludloff: *Z. Physik*, **57**, 227 (1929).

model; even in simple cases the geometrical concept can only be made to give the desired number by some device or other, which essentially involves a knowledge of the rotational characters themselves.

In the case of models of some exact geometrical figure, e.g. a regular tetrahedron, it is often possible from the wave equation of the molecule, to find the fraction of the rotational levels which are, say, symmetrical in the nuclei; this fraction is one-twelfth in methane, one-third in ammonia, and so on. But if the molecule only roughly approximated to a regular figure, it would then possess no symmetry number suggested by geometry. A small continuous deformation of the regular figure will change its moments of inertia continuously, and it is known that the rotational energy values are continuous functions of the moments of inertia, so that the energy values will themselves change continuously; for example, if the deformation of a symmetrical methane molecule (three equal moments of inertia $A = B = C$) be such that A , B and C are no longer equal, the $(2J + 1)^1$ originally coincident rotational levels for a given J will proceed to separate under the deformation into $(2J + 1)$ distinct levels each $(2J + 1)$ -fold degenerate. Now the symmetry character of a level (and therefore its weight) is invariant for a deformation of the molecule; thus Hund² used the deformation of a symmetrical top to establish the symmetry characters for an unsymmetrical rotator; hence the entropy given by Eq. 6 must be a continuous function of the moments of inertia, and must only change slightly as a result of a small deformation. All geometric symmetry has by now been lost, however, and no symmetry number in the Ehrenfest sense can be assigned. Of course, when one keeps in mind the quantum significance of σ , this difficulty vanishes; the fraction of states of given symmetry character will be conserved for small deformations from geometric symmetry, and it would still be necessary in Eq. 3 to use $\sigma = 12$ for a methane molecule which need only roughly approximate to a regular tetrahedron.

¹ Giauque, Blue and Overstreet: Loc. cit.

² Hund: Z. Physik, 43, 822 (1927). To be precise, permissible deformations must result from perturbations symmetrical in the like particles.

The necessity for the invariance of the symmetry characters during a deformation is evident when one considers the question of nuclear spin. With four hydrogen nuclei in the molecule, Villars (loc. cit.) has shown that there are five $S(4)$ spin wave functions, three $S(3+1)$ each threefold degenerate, and one doubly degenerate $S(2+2)$ —sixteen in all. From the work of Elert (loc. cit.) one twelfth of the rotational states in methane are $S(4)$, nine twelfths are $S(3+1)$ and two twelfths are $S(2+2)$. If Σ is the value of the State Sum in the absence of symmetry and spin (see Eq. 2), then its high temperature value (to a close approximation) in the presence of symmetry and spin will be

$$5 \times \Sigma/12 + 9 \times 1/9 \times \Sigma/12 + 2 \times (1/4 + 1/4) \times 2\Sigma/12 = 16\Sigma/12$$

(The factors $1/9$ and $(1/4 + 1/4)$ arise from the fact that only one ninth of the products of two $S(3+1)$ functions are $S(4)$, while one quarter of the products of two $S(2+2)$ are $S(4)$ and one quarter $A(4)$ both of which may be retained owing to the double character of the ground vibrational state). It is for this reason that the classical formula gives the rotational entropy of methane correctly if the classical expression is corrected by a symmetry term— $R \ln 12$ and a spin term $+R \ln 16$. That the spin contribution is just $R \ln 16$ is in conformity with the rule that at high temperatures spin entropy must cancel in the entropy of reaction.

Since the spin wave functions are independent of the geometrical arrangement of the particles, it is necessary that the rotational symmetries be unaltered during the deformation, since otherwise the spin contribution would no longer be $R \ln 16$.

In Cooley's measurements¹ on the infra red adsorption spectrum of methane, different fine structure separations are found for the bands 3.31μ and 7.7μ , corresponding to the existence of at least two different moments of inertia; this result is of course quite incompatible with a regular tetrahedral structure. Asymmetry is also indicated by the work of Langseth² on the Raman effect in carbon tetrachloride and carbon tetrabromide. If it should prove that only two of the methane moments of inertia are equal to 5.17×10^{-40} , while the third is, say, ten per cent larger, the rotational entropy given by Eq. 3 would be only 0.1 cal./degree greater than that entered in Table I, the symmetry number 12 being retained in accordance with the preceding argument. Conversely, if the use of a given symmetry number leads to an entropy in approximate agreement with experiment, this must not be used as evidence as to the exact "shape" of the molecule.

The use of the symmetry number, where geometrical symmetry is excluded, is illustrated by the following simple calculation:

(a) Consider an unsymmetrical pyramidal molecule RX_3 whose moments of inertia are such that $(h^2/8\pi^2 kT) \cdot (1/A, 1/B, 1/C) = 0.10, 0.09, 0.08$; the energy levels can then be found from the equations for an unsymmetrical rotator. Assume that the three X nuclei have no spin and are slightly different, e.g. three different isotopes. Then the weight factor for each of the $2J + 1$ rotational levels for a given J is simply $2J + 1$ since symmetry considerations are entirely excluded. The values of the energy and state sums are entered in the column *a* of the table below, together with the resulting value of the entropy obtained from Eq. 6; the expression S_R' (Eq. 2) is here applicable without correcting terms.

(b) If the three X nuclei are identical but non-spinning, then from a consideration of the limiting case as $A \rightarrow B < C$, for a given J the levels $\tau = J, J-5, J-6, J-11, J-12, \dots$ will be either symmetrical or antisymmetrical in the X nuclei, while for other values of τ the levels will have degenerate symmetry; thus since the lowest vibrational state is double, having both a completely symmetric and a completely antisymmetric character, the levels $\tau = J, J-5, J-6, \dots$ will have the weight $2J + 1$, the other levels having the weight zero. If Eq. 2 is to be used, a term $R \ln 3 (= 2.182)$ must be subtracted from the value of S_R' for case *a*, for the fraction one-sixth of the rotational levels can be associated with one of the lowest vibration symmetries, and a further fraction one-sixth with the second of the lowest vibration symmetries, so that one-third of the rotational-vibrational states are of a definite symmetry character.

(c) Finally, let each of the three X nuclei have one half unit of spin; the weights³ of the levels $\tau = J, J-5, J-6, \dots$ are then $4(2J + 1)$, the other levels receive the weights $2(2J + 1)$. If Eq. 2 is to be used, $-R \ln 3 + 3R \ln 2 (= 1.947)$ must be added to the expression on its right.

¹ Cooley: *Astrophys. J.*, **62**, 73 (1925).

² Langseth: *Z. Physik*, **72**, 350 (1931).

³ Villars: *Loc. cit.*, Table II.

	(a)	(b)	(c)
Σ_1	67.54	22.43	179.93
Σ_2	99.82	33.21	266.06
S_R (Eq. 6)	11.301	9.117	13.247
S_R (Eq. 2)	11.301	9.119	13.248
corrected.			

The table shews clearly that the rotational entropy, calculated by the classical Eq. 2, agrees with that obtained by evaluating the exact sums, when the classical expression receives the necessary corrections in the form of a symmetry number and a spin term. The table also shews that geometrical symmetry is a sufficient but not necessary condition for the existence of a symmetry number. It must be remembered, however, that the use of the classical formula for the rotational entropy, quite apart from corrections due to spin or to symmetry properties, is restricted to temperatures high enough for almost complete classical "excitation" of the rotational degrees of freedom. At lower temperatures the accurate summation formula must necessarily be used.

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