$FeSn_2$ Phase.—The photograms of this phase indicate a very narrow homogeneity interval, corresponding almost exactly with the composition $FeSn_2$. The unit cell is probably hexagonal, having the following dimensions: a_1 = 5.317 Å., a_3 = 9.236 Å., a_3/a_1 = 1.737. It is likely that the cell contains twelve atoms, *i. e.*, 4 $FeSn_2$.

Sn Phase.—The diffraction pattern of this phase, as found in a number of our alloys, does not differ from that of pure tin. It follows from this that iron and the other phases in the system are insoluble in tin.

The discrepancies existing between the results of the x-ray analysis and the thermal diagram for the system as set up by Edwards and Preece, have been indicated and discussed.

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Thermodynamic Functions of Hydrocarbon Gases from Spectroscopic Data[1]

BY LOUIS S. KASSEL[2]

Methods

Within the last few years spectroscopic data for numerous diatomic molecules have been used to give very accurate values for those thermodynamic functions which do not involve the absolute value of *H*. The same methods may be applied to polyatomic molecules; here the spectroscopic data are usually both less accurate and less complete; nevertheless, there seem to be a number of cases in which such calculations may be usefully made. In the present article, methane, ethylene and acetylene will be considered.

The method used has been given in principle by Giauque,[3] but since there are a number of short cuts which may be used when making approximate calculations, the procedure to be followed will be described briefly.

For molecules with energy levels 0, ϵ_1, ϵ_2 . . . and associated quantum weights p_0, p_1, p_2 . . . the Maxwell–Boltzmann distribution law may be written in the form

$$H = -N\,(\mathrm{d}\log Q/\mathrm{d}\Theta) \qquad (1)$$

where

$$Q = \sum_i p_i\, e^{-\epsilon_i \sigma} \qquad (2)$$

and

$$\Theta = 1/kT \qquad (3)$$

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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[3] Giauque, THIS JOURNAL, **52**, 4808 (1930).

Here N is Avogadro's number, and H is the contribution of internal energy to the heat content; likewise, the contributions to other thermodynamic functions are

$$C_p = \partial H/\partial T = R\Theta^2\,\mathrm{d}^2 \log Q/\mathrm{d}\Theta^2 \tag{4}$$

$$\begin{aligned} S &= \int_0^T C_p \,\mathrm{d} \log T \\ &= R \log Q - R\Theta\,\mathrm{d} \log Q/\mathrm{d}\Theta - R \log p_0 \end{aligned} \tag{5}$$

$$\begin{aligned} F/T &= H/T - S \\ &= -R \log Q + R \log p_0 \end{aligned} \tag{6}$$

It is easily verified that whenever the energy splits up into a sum of independent terms, each of them contributes multiplicatively to Q, and additively to the thermodynamic functions. When the separate energy terms are sufficiently simple in form, the summation in (2) can be handled analytically. The terms into which the energy actually splits are the levels for a rotator or top, plus those for a number of oscillators; in the present treatment, the rotator will be considered rigid, and the oscillators harmonic.

For an harmonic oscillator

$$\begin{aligned} Q &= 1 + e^{-\varphi} + e^{-2\varphi} + \ldots \\ &= 1/(1 - e^{-\varphi}) \end{aligned} \tag{7}$$

where

$$\varphi = h\nu/kT \tag{8}$$

Then

$$H = RT\varphi/(e^{\varphi} - 1) \tag{9}$$

$$S = -R \log (1 - e^{-\varphi}) + R\varphi/(e^{\varphi} - 1) \tag{10}$$

$$F/T = R \log (1 - e^{-\varphi}) \tag{11}$$

It proves convenient in making calculations for polyatomic molecules to use a table of F/T as a function of φ, such as that given by Nernst.[4]

For a rigid rotator

$$Q = \sum_{j=0}^{\infty} (2j + 1)e^{-j(j+1)\sigma} \tag{12}$$

where

$$\sigma = h^2/8\pi^2JkT \tag{13}$$

For room temperature or higher, σ is quite small, and the greater part of the sum comes from a group of terms with large values of m, the change from term to term in this region being slight. It is then possible to approximate the sum by an integral; the most direct way to do this is to replace $(2j + 1)\ e^{-j(j+1)\sigma}$ by

$$\int_{j-1/2}^{j+1/2} (2x + 1)e^{-x(x+1)\sigma}\,\mathrm{d}x; \text{ this gives}$$

$$\begin{aligned} Q &= \int_{-\frac{1}{2}}^{\infty} (2x + 1)e^{-x(x+1)\sigma}\,\mathrm{d}x \\ &= (1/\sigma)e^{\sigma/4} \\ &= 1/\sigma + 1/4 + \ldots \end{aligned} \tag{14}$$

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(4) Nernst, "Grundlagen d. neuen Warmesätzes," 1918.

There are, however, other ways of replacing a sum by an integral (the inverse of the trapezoidal rule, the parabolic rule, etc.), and when these are used results are obtained which agree only in the leading term. The summation (12) has been treated by Mulholland[5] by more powerful methods; his result, in the present notation, is

$$Q = 1/\sigma + 1/3 + \ldots \tag{15}$$

Giauque and Overstreet[6] have considered the effect of molecular stretching, and given a convenient approximate method of handling the necessary summations; they show that neglect of this correction would produce an error of about 0.03 cal./mole/degree for hydrogen chloride at 2000°. An error of this magnitude is of course not permissible in their precise calculations, but it is of little importance for the present purposes.

Using Mulholland's result, we obtain for a rigid rotator

$$H = RT(1 - \sigma/3 + \ldots) \tag{16}$$

$$S = -R \log \sigma + R - R\sigma^2/90 + \ldots \tag{17}$$

$$F/T = R \log \sigma - R\sigma/3 + \ldots \tag{18}$$

For a rigid top with three equal moments of inertia we have

$$Q = \sum_{j=0}^{\infty} (2j + 1)^2 e^{-j(j+1)\sigma} \tag{19}$$

The first approximation may be obtained by replacing the sum with an integral, as before. In lieu of a correct treatment of this case, such as that given by Mulholland for the rotator, it proves possible to determine the second term in the expansion by numerical examples. The result is

$$Q = \sqrt{\pi}\, \sigma^{-3/2} (1 + \sigma/4 + \ldots) \tag{20}$$

This leads to

$$H = (3/2)RT(1 - \sigma/6 + \ldots) \tag{21}$$

$$S = (R/2) \log \pi - (3R/2) \log \sigma + 3R/2 + \ldots \tag{22}$$

$$F/T = -(R/2) \log \pi + (3R/2) \log \sigma - R\sigma/4 + \ldots \tag{23}$$

For a symmetrical top, with moments of inertia A, A and C, we encounter increasing difficulty. The rotational levels have been given by Reiche and Rademacher[7] as

$$\epsilon_{j,\kappa} = j(j + 1)\, \sigma + \kappa^2 \tau \quad |\kappa| \leqq j \tag{24}$$

where

$$\sigma = h^2\theta/8\pi^2 A \tag{25}$$

$$\tau = (h^2\theta/8\pi^2) \left(\frac{1}{C} - \frac{1}{A}\right) \tag{26}$$

$$\rho = \sigma + \tau \tag{27}$$

The multiplicity of each $\epsilon_{j,\kappa}$ is $2j + 1$. For this case

$$\begin{aligned} Q &= \sum_{\kappa=-\infty}^{\infty} e^{\kappa^2\tau} \sum_{m=|\kappa|}^{\infty} (2m + 1) e^{-m(m+1)\sigma} \\ &= 2 \int_{\kappa=0}^{\infty} e^{-\kappa^2\tau} \int_{m=\kappa-\frac{1}{2}}^{\infty} (2m + 1) e^{-m(m+1)\sigma}\, \mathrm{d}m\mathrm{d}\kappa \end{aligned}$$

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(5) Mulholland, *Proc. Cambridge Phil. Soc.*, **24**, 280 (1928).

(6) Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

(7) Reiche and Rademacher, *Z. Physik*, **39**, 444 (1926).

$$
\begin{aligned}
&= 2 \int_0^\infty e^{-\kappa^2\tau} \left[(1/\sigma)\, e^{-(\kappa^2 - 1/4)\sigma}\right] \mathrm{d}\kappa \\
&= (2/\sigma)\, e^{\sigma/4} \int_0^\infty e^{-\kappa^2\rho}\, \mathrm{d}\kappa \\
&= \sqrt{\pi}\, e^{\sigma/4}/\sigma \sqrt{\rho} \\
&= \frac{\sqrt{\pi}}{\sigma \sqrt{\rho}} (1 + \sigma/4 + \ldots) \qquad (28)
\end{aligned}
$$

It is unlikely that the expansion in (28) is exactly correct beyond the first term. Using only this term, we obtain

$$H = 3RT/2 \qquad (29)$$
$$S = (R/2) \log \pi - R \log \sigma - (R/2) \log \tau + 3R/2 \qquad (30)$$
$$F/T = -(R/2) \log \tau + R \log \sigma + (R/2) \log \tau \qquad (31)$$

For molecules with three different moments of inertia, it is not possible to express the energy levels by a formula; there is no real doubt, however, that for this case, to the same order of accuracy, it is merely necessary to replace σ in (30) and (31) by $(\sigma_1\sigma_2)^{1/2}$.

The contribution from translation is given by the Sackur–Tetrode equation; at 1 atm. pressure

$$S = (5R/2) \log T + (3R/2) \log M - 2.300 \qquad (32)$$
$$S_{298} = 6.8625 \log_{10} M + 26.000 \qquad (33)$$
$$F/T = 7.267 - (3R/2) \log M - (5R/2) \log T \qquad (34)$$

Actual molecules differ from the simple models we have so far considered because nuclei have spins and obey non-classical statistics. As a result, some rotational levels are actually not occupied, while others have quantum weights greater than those which we have assigned. For diatomic molecules these changes are relatively simple; thus for oxygen the even-numbered rotational levels are missing, while for hydrogen the odd-numbered levels (ortho-hydrogen) are relatively three times as abundant as the even. For polyatomic molecules, the changes are much more complex, and their determination is a matter of considerable difficulty. It is fortunate that for most purposes a much less detailed analysis will suffice; this comes about in the following way. Whenever it is permissible to replace the simple rotational Q-sum by an integral, the correct Q-sum, with an error only slightly larger, can be replaced by the same integral, with a numerical multiplier which gives the ratio of the actual number of rotational levels to the number for a simple rotator or top. At low temperatures this will no longer be permissible, and detailed calculations must be made. For room temperature and higher, however, it will always be a fair approximation to multiply the Q integral with a correction factor μ. Ludloff[8] has shown that this factor is the product of the spin multiplicities for the nuclei, divided by the number of equivalent rotational orientations for the molecule. For oxygen, this factor is just 1/2, since the O atom has no spin; for hydrogen it is $2^2/2 = 2$; for ammonia it is $3 \times 2^3/3 = 8$,

(8) Ludloff, *Z. Physik*, **57**, 227 (1929).

assuming a pyramid structure; for methane, tetrahedral, $2^4/12 = 4/3$; for acetylene, linear, $2^2/2 = 2$; ethylene, with a plane structure, $2^4/4 = 4$; ethane, probably $2^6/6 = 32/3$, though a more detailed analysis is desirable where bond rotation can occur.

In making calculations, it is conveninent to combine the contributions from translation, rotation and nuclear spin. We thus get the following formulas

Rotator

$$S = (7/2)R \log T + (3/2)\, R \log M + 175.375 + R \log J + R \log \mu \tag{35}$$

$$S_{298} = (3/2)\, R \log M + R \log J + R \log \mu + 214.995 \tag{36}$$

$$F/T = -(7/2)\, R \log T - (3/2)\, R \log M - R \log J - R \log \mu - 168.421 \tag{37}$$

Top

$$S = 4\, R \log T + (3/2)\, R \log M + (1/2)\, R \log ABC + R \log \mu + 265.349 \tag{38}$$

$$S_{298} = (3/2)\, R \log M + (1/2)\, R \log ABC + R \log \mu + 310.629 \tag{39}$$

$$F/T = -4R \log T - (3/2)\, R \log M - (1/2)\, R \log ABC - R \log \mu - 257.401 \tag{40}$$

Here J is the moment of inertia of the rotator, and A, B, C the three principal moments of the top. In using the formulas, $R \log_e 10$ is a conventional constant with the value 4.57500. Other physical constants are taken from "International Critical Tables."

Calculations

Methane is presumably a symmetrical tetrahedron, and should have all three moments of inertia equal. Actually Cooley[9] observed three different spacings in the three infra-red bands that he measured. It is uncertain how this result should be interpreted, as a molecule with two or three different moments of inertia would not lead to such a result. In the present calculations we shall use the value obtained from Raman spectra,[10] 5.17×10^{-40} g. cm.^{2}, which leads to a reasonable CH distance, and must certainly be almost correct.[10a]

Methane has nine modes of vibration, with four distinct frequencies. The first analysis was made by Dennison[11] who found two triple vibrations at 1304 cm.$^{-1}$ and 3014 cm.$^{-1}$, a double vibration at 1520 cm.$^{-1}$, and a single one at 4217 cm.$^{-1}$. The Raman observations of Dickinson, Dillon and Rasetti show clearly that 4217 cm.$^{-1}$ is a combination frequency, and that the fourth normal frequency is 2915 cm.$^{-1}$.[12] The vibrational analysis has been made in a different way by Mecke.[13] He used a treatment based on the concepts of valence and bending vibrations which is probably preferable to the central force analysis of Dennison. The result is that 1304 cm.$^{-1}$ becomes a double vibration and 1520 cm.$^{-2}$ a triple vibration;

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(9) Cooley, *Astrophys. J.*, **62**, 73 (1925).

(10) Dickinson, Dillon and Rasetti, *Phys. Rev.*, **34**, 582 (1929).

(10a) Teller and Tisza, *Z. Physik*, **73**, 791 (1932), have explained the variable spacings in the infrared bands by rotation–vibration interaction, thus making the Raman moment of inertia still more likely.

(11) Dennison, *Astrophys. J.*, **62**, 84 (1925).

(12) Villars was apparently one of the first to adopt this change; New Orleans meeting, American Chemical Society, March, 1932.

(13) Mecke, *Z. physik. Chem.*, **17B**, 1 (1932).

aside from this one point, there seems to be no doubt about the frequencies. We shall make the calculations using both the Dennison–Villars and the Mecke assignment.[14]

The thermal values necessary are known with quite sufficient accuracy in this case. The heat of combustion of graphite at 25° is 94,240 cal.,[15] and this value is unchanged when corrected to 18°. The heat of combustion of hydrogen[16] at 18° is 68,367 cal., and that of methane[17] is 212,946 cal. The heat content of graphite at 18° is 239 cal.;[18] the heat content of hydrogen at 18° is given by Giauque's[19] spectroscopic calculations as 1975 cal. The heat content of methane at 18° is calculated by (9) and (21) as 2335 cal. From these data the heat of formation of methane gas from hydrogen gas and β-graphite at the absolute zero is +16,174 cal.

The spectroscopic values of $(F^\circ - E_0^\circ)/T$ for hydrogen have been given by Giauque.[19] Values of this function for β-graphite have been computed by Clayton and Giauque[20] from specific heat data. An independent calculation, with a presumably different choice of specific heat equations, gave a maximum deviation of 0.009 cal./deg. up to 1500°K., rising to 0.039 at 3000°K. For the sake of uniformity, Clayton and Giauque's values are adopted here.

Table I gives the absolute value (including nuclear spin) of $(F^\circ - E_0^\circ)/T$ for methane, from spectroscopic data alone, and the values of $\Delta F/T$ and $\log_{10} K$ for its formation from the elements, based also on the foregoing heat of reaction. No entirely reliable equilibrium measurements are available. At the lower temperatures, it is very difficult to attain equilibrium with any catalyst, and there is also some uncertainty as to whether or not the effective solid phase is β-graphite. At the higher temperatures, hot carbon rods in non-isothermal systems have been used, and there is the possibility of perturbing reactions in the cooler parts of the systems. At the highest temperatures attained, there is clearly a very considerable formation of methane from acetylene in this way. Figure 1 shows the results of a number of workers; it is clear that the present calculations agree with the bulk of the data fairly well; the early work of Pring and his

(14) Since this paper was written, it has been suggested by Ruedy [*Canada J. Research*, **7**, 328 (1932)] that the 1520 cm.$^{-1}$ frequency should be replaced by 1100 cm.$^{-1}$ Neither of these has been directly observed, and it is doubtful whether or not the change is desirable. If the change is made, methane becomes more stable at all temperatures, the effect increasing with the temperature; at 2000°K. the free energy of formation would be increased 2334 cal. and the equilibrium constant increased 80%; the agreement with experiment would be appreciably less good than at present.

(15) Roth and Naeser, *Z. Elektrochem.*, **31**, 461 (1925); Giauque, THIS JOURNAL, **54**, 2623 (1932). Since this paper was submitted for publication, Gordon and Barnes, *J. Phys. Chem.*, **36**, 2601 (1932), have made spectroscopic calculations of the methane equilibrium up to 1200°K. They have used for the heat of combustion of graphite the older value 94,420 cal., and they have followed also the original Dennison assignment of frequencies.

(16) Rossini, *Bur. Standards J. Research*, **6**, 1 (1931).

(17) Rossini, *ibid.*, **6**, 37 (1931).

(18) "International Critical Tables," Vol. V.

(19) Giauque, THIS JOURNAL, **52**, 4816 (1930).

(20) Clayton and Giauque, *ibid.*, **54**, 2610 (1932).

associates is surprisingly correct. With this assurance that there is no unsuspected gross error, it seems reasonable to assume that the calculated equilibrium constant is not in error by more than 25% up to the highest temperature given.

TABLE I

FREE ENERGY OF METHANE

		Dennison–Villars		Mecke
T	$-(F^\circ - E_0^\circ)/T$	$\Delta F/T$	$\log_{10} K$	$-(F^\circ - E_0^\circ)/T$
250	40.525	....	...	40.525
300	41.986	−40.879	8.935	41.982
350	43.232	−32.175	7.033	43.226
400	44.334	−25.529	5.580	44.323
450	45.325	−20.153	4.405	45.309
500	46.228	−15.956	3.488	46.205
550	47.073	−12.387	2.708	47.043
600	47.867	− 9.367	2.047	47.829
650	48.621	− 6.782	1.482	48.576
700	49.336	− 4.534	0.991	49.284
750	50.023	− 2.564	.560	49.963
800	50.686	− 0.821	.180	50.617
850	51.322	+ 0.732	− .160	51.247
900	51.949	+ 2.115	− .462	51.865
950	52.548	+ 3.369	− .736	52.458
1000	53.134	+ 4.504	− .985	53.037
1050	53.704	+ 5.536	−1.210	53.601
1100	54.258	+ 6.481	−1.417	54.150
1150	54.804	+ 7.344	−1.605	54.690
1200	55.336	+ 8.141	−1.779	55.217
1250	55.863	+ 8.870	−1.939	55.738
1300	56.373	+ 9.548	−2.087	56.243
1400	57.361	+10.767	−2.354	57.222
1500	58.316	+11.828	−2.585	58.168
1600	59.238	+12.763	−2.790	59.083
1700	60.132	+13.586	−2.970	59.970
1800	60.999	+14.313	−3.129	60.830
1900	61.831	+14.966	−3.271	61.656
2000	62.645	+15.542	−3.397	62.465
2100	63.431	+16.065	−3.511	63.246
2200	64.197	+16.542	−3.616	64.006
2300	64.937	+16.988	−3.713	64.743
2400	65.667	+17.390	−3.801	65.470
2500	66.371	+17.770	−3.884	66.170
2600	67.068	+18.115	−3.960	66.864
2700	67.730	+18.451	−4.033	67.521
2800	68.389	+18.750	−4.098	68.177
2900	69.031	+19.029	−4.159	68.815
3000	69.649	+19.296	−4.218	69.431
3500	72.568	....	...	72.339
4000	75.212	....	...	74.971
4500	77.589	....	...	77.342
5000	79.799	....	...	79.544

The tabular method of presenting free energy values, which has been used exclusively in Giauque's publications, does not appear to be entirely satisfactory; interpolation, even using third and fourth differences, is not accurate to 0.001 of a unit. Accurate values may be obtained by fitting an equation of the type

$$\Delta F/T = A/T + B + CT, \text{ or } \Delta F/T = A/T + B + C \log T$$

to three successive entries in the tables. The derivative of such an equation, preferably one of the second kind, will give a fairly satisfactory value of ΔH, the error in the worst cases being only about 50 cal.; the second derivative will give a very rough estimate of ΔC_p. The use of such a procedure would be very laborious in some cases, and it seems that an attempt should be made to give a single equation applicable over the entire range of temperature. It proves to be almost impossible to accomplish this with the usual form of equation. Closer consideration of the problem suggests that since $\Delta F/T$ is changing rapidly when T is small and slowly when it is large, a power series in T should not be expected to fit well; the inclusion of terms of the form $1/T^2$ and $1/T^3$, in addition to the usual $1/T$, leads to much better results. The most satisfactory equation which has been found for methane, with the Dennison–Villars choice of frequencies, is

$$\Delta F/T = -24{,}903.5/T + 1{,}763{,}748/T^2 - 1501 \times 10^5/T^3 - 0.4607 \log_{10} T - 9.194 \times 10^{-5}\, T + 29.2749 \qquad (41)$$

This equation reproduces the tabulated values with a maximum deviation of 0.026 in $\Delta F/T$, or 62 cal. in ΔF, or 1.3% in K. It has been made to give a value of ΔH_{291} correct within 6 cal., but at other temperatures the agreement is less good, the possible error being about 100 cal. It seems probable that more accurate ΔH values than this cannot be obtained from ΔF, and must be directly calculated when needed. A 5-constant equation only slightly less satisfactory than the preceding one is

$$\Delta F/T = -25{,}714.6/T + 2{,}041{,}540/T^2 - 1890 \times 10^5/T^3 - 1.5051 \log_{10} T + 32.8813 \qquad (42)$$

The maximum deviation in $\Delta F/T$ is 0.030, but ΔH_{291} is 160 cal. in error. This difference is probably due only in a small degree to the extra term in the former equation; (41) was fitted by least squares to $\Delta F/T$ at ten points and to ΔH at 291°, while the five constants of (42) were determined from only five values of $\Delta F/T$; it is this difference in procedure which is responsible for a large part of the superiority of (41).

Acetylene is undoubtedly a linear molecule; its moment of inertia is known very accurately as 23.509 g. cm^2.[21] A molecule of this type has three valence vibrations and two double bending vibrations. The original assignment of these vibrations, made by Mecke,[22] has been justly criticized by Olson and Kramers.[23] These authors pointed out that a simple treat-

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[21] Levin and Meyer, *J. Opt. Soc. Am.*, **16**, 137 (1928).

[22] Mecke, *Z. Physik*, **64**, 173 (1930).

[23] Olson and Kramers, THIS JOURNAL, **54**, 136 (1932).

ment gave for the ratio of the antisymmetric to the symmetric bending frequency the value $\delta_a/\delta_s = 0.816$, while Mecke's assignment, $\delta_s = 730$ cm.$^{-1}$, $\delta_a = 1326$ cm.$^{-1}$ gave $\delta_a/\delta_s = 1.88$; there was the further criticism that 730 cm.$^{-1}$ was observed in absorption, and hence should not be symmetric. Apparently, independently of this criticism, Mecke[24] has now revised his assignment. He puts $\delta_a = 729$ cm.$^{-1}$ and $\delta_s = 600$ cm.$^{-1}$. The former of these is observed in the infra-red, but the latter is not directly observed anywhere; it occurs in four combination frequencies, one of which is a difference combination, and one a triple combination. The ratio δ_a/δ_s is still somewhat out of line with Olson and Kramers' treatment, though less than before, and Mecke believes that the difference can be accounted for by more complete treatment of the coupling terms, such as he has given. It must be admitted, however, that this part of the assignment is not free from doubt. The valence vibrations are very probably given correctly; two of them, 1975 cm.$^{-1}$ and 3370 cm.$^{-1}$, are observed in the Raman spectrum; the third, 3277 cm.$^{-1}$, is observed in the infra-red, and should, on theoretical grounds, be very close to one of the Raman frequencies, both being essentially C–H vibrations. Since there seems to be no way of rearranging the observed frequencies more satisfactorily, we shall follow Mecke and take 1974 cm.$^{-1}$, 3277 cm.$^{-1}$, 3370 cm.$^{-1}$ and double vibrations at 600 cm.$^{-1}$ and 729 cm.$^{-1}$.

The uncertainty in the vibrational frequencies has at least the compensation that one is spared the pain of contaminating precise spectroscopic data by the inaccurate heat of combustion of acetylene. On the authority of Rossini[25] I have adopted 311,000 cal. in preference to 312,000 cal. given by the "International Critical Tables." It seems entirely possible that this value may be in error by as much as 2000 cal. The heat content of

TABLE II

FREE ENERGY VALUES FOR ACETYLENE

T	$-\frac{F^\circ - E_0^\circ}{T}$	$\frac{\Delta F^\circ}{T}$	$\log_{10} K$
300	42.809	166.445	−36.381
400	45.249	121.340	−26.522
500	47.320	94.310	−20.614
600	49.140	76.311	−16.680
700	50.776	63.470	−13.873
800	52.258	53.873	−11.776
900	53.626	46.425	−10.148
1000	54.893	40.485	− 8.849
1200	57.188	31.600	− 6.907
1500	60.182	22.773	− 4.978
2000	64.343	14.025	− 3.066
2500	67.784	8.848	− 1.934
3000	70.752	5.472	− 1.196

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(24) Mecke, *Z. physik. Chem.*, **17B**, 1 (1932).

(25) Private communication.

acetylene gas at 18° may be calculated to be 2331 cal.; with these figures and the thermal data given previously, ΔE_0° for the formation of acetylene is 54,275 cal.

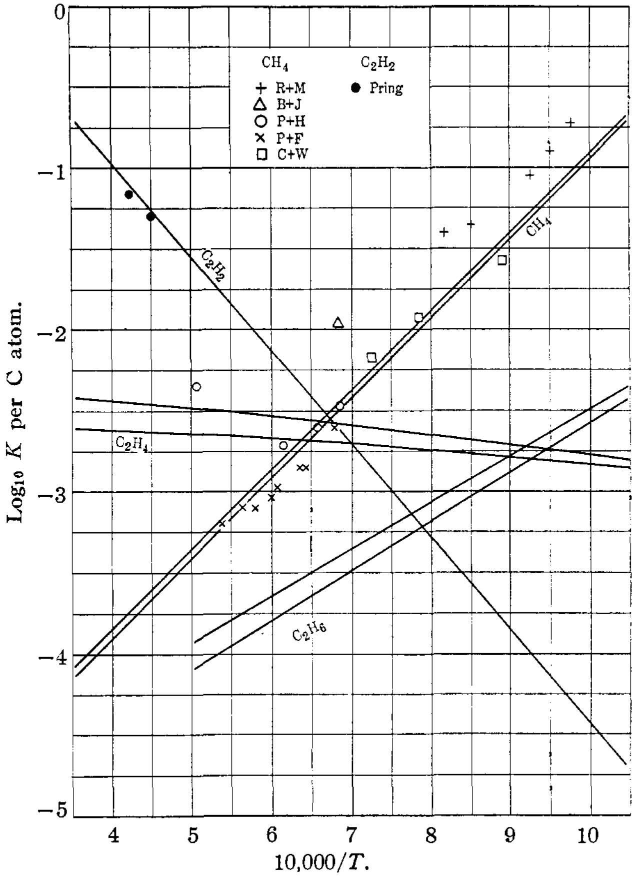

Fig. 1.—The curves give the calculated equilibrium constants, per gram atom of carbon, for the formation from hydrogen and β-graphite. For methane the upper curve is based on the Dennison–Villars frequencies, the lower curve on those of Mecke. For ethylene, the upper curve is based on 950 cm.$^{-1}$ for the torsional frequency, while the lower curve neglects this frequency. The curves for ethane are obtained by combining the two calculations for ethylene with the measured equilibrium constant for ethane dissociation.[26] The sources of the experimental equilibrium constants for methane are: R + M, Randall and Mohammad; B + J, Bone and Jerdan; P + H, Pring and Hutton; P + F, Pring and Fairlie; C + W, Coward and Wilson.[27]

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(26) Pease and Durgan, THIS JOURNAL, **50**, 2715 (1928).

(27) Randall and Mohammad, *Ind. Eng. Chem.*, **21**, 1048 (1929); Bone and Jerdan, *J. Chem. Soc.*, **71**, 41 (1897); **79**, 1042 (1901); Pring and Hutton, *ibid.*, **89**, 1591 (1906); Pring and Fairlie, *ibid.*, **101**, 91 (1912); Coward and Wilson, *ibid.*, **115**, 1380 (1919).

The results for acetylene are given in Table II and shown in part in Fig. 1. For comparison, determinations by Pring[28] are plotted also. The close agreement is somewhat accidental, since the experiments from which these constants were obtained gave values much too high for methane and ethylene. One must assume that these latter gases were formed from acetylene in the colder parts of the apparatus.

The moments of inertia of ethylene are not known, but can be estimated in various ways. By assuming a C–C distance of 1.18×10^{-8} cm., C–H, 1.08×10^{-8} cm., and a tetrahedral valence angle for carbon, the moments may be calculated as 28.73, 23.69 and 5.03×10^{-40} g. cm.^{2}, giving a product of 3423×10^{-120}. Badger and Binder[29] interpreted their absorption measurements in the near infra-red in accordance with preliminary theoretical results of Nielsen. They give provisional values for the moments of 31, 27 and 3.8×10^{-40}, leading to a product of 3181×10^{-120}. Badger and Binder state, however, in a note added in proof, that the complete results of Nielsen[30] alter this interpretation somewhat, and lead to slight changes in the moments. In the present calculations the value 3423×10^{-120} will be used for the product of the three principal moments; this may well be in error by 25%. The resultant error in F/T would be 0.22 cal./deg.; the error in K would be only 12%. Our final values for ethylene will undoubtedly contain other errors of greater magnitude than this.

Ethylene has five valence vibrations, six bending vibrations and a torsional vibration about the double bond. Mecke[31] has assigned frequencies to all of these except the torsion. For ease in calculation we shall lump his eleven frequencies into five groups: a triple vibration at 950 cm.$^{-1}$, single at 1100 cm.$^{-1}$, double at 1400 cm.$^{-1}$, single at 1620 cm.$^{-1}$ and quadruple at 3090 cm.$^{-1}$. The resistance of the double bond to torsion is probably not great, but since the moment of the molecule about the C–C axis is small, the torsional frequency is presumably of moderate value.

TABLE III

FREE ENERGY VALUES FOR ETHYLENE

	Without torsional frequenc			With torsional frequency, 950 cm.$^{-1}$		
T	$-\frac{F^\circ - E_0^\circ}{T}$	$\frac{\Delta F}{T}$	$\log_{10} K$	$-\frac{F^\circ - E_0^\circ}{T}$	$\frac{\Delta F}{T}$	$\log_{10} K$
300	49.085	42.487	−9.287	49.106	42.379	−9.263
500	53.652	31.748	−6.939	53.787	31.613	−6.910
700	57.206	27.969	−6.113	57.513	27.662	−6.046
1000	61.680	25.730	−5.624	62.279	25.141	−5.495
1500	67.854	24.478	−5.350	68.882	23.450	−5.126
2000	72.986	24.082	−5.264	74.390	22.678	−4.957
2500	77.394	23.948	−5.235	79.120	22.222	−4.857
3000	81.263	23.983	−5.242	83.271	21.975	−4.803

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(28) Pring, *J. Chem. Soc.*, **101**, 498 (1910).

(29) Badger and Binder, *Phys. Rev.*, **38**, 1442 (1931).

(30) Nielsen, *Phys. Rev.*, **38**, 1432 (1931).

(31) Mecke, *Z. physik. Chem.*, **17B**, 1 (1932).

We shall make computations both neglecting this frequency, and assigning it the value 950 cm.$^{-1}$. The true contribution is probably within these limits, though they may very well be too narrow to compensate for errors in the other frequencies.

We shall take the heat of combustion of ethylene at 18° to be 334,000 cal.; the heat content of the gas we calculate as 2414 cal. On this basis, the heat of formation of ethylene gas at the absolute zero is $-10{,}800$ cal.

The calculated values are given in Table III and shown in part in Fig. 1. There are no experimental data with which comparison is possible.

Some support for the frequencies assigned to ethylene, and hence to the foregoing calculations, is provided by recent specific heat measurements for ethylene gas from 0 to 70°.[32] The experimental results are represented by

$$C_p = 4.064 + 0.02022\ T$$

Table IV shows how the vibrational part of the specific heat compares with that calculated.

TABLE IV

VIBRATIONAL SPECIFIC HEAT OF ETHYLENE

Temp., °K.	Calcd. with torsion	Calcd. without torsion	Exptl.
300	2.349	1.901	2.182
350	3.567	2.925	3.193

It seems likely that with the rise of these spectroscopic methods, there will be a diminution of the importance of entropy in routine equilibrium calculations. We shall, however, give entropy values for these hydrocarbons. Our calculation of the absolute translational plus rotational entropy of methane at 25° gives 49.867 entropy units, in excellent agreement with 49.86 given by Giauque, Blue and Overstreet.[33] Upon adding the vibrational contribution, the total absolute entropy becomes either 49.974 or 49.955 entropy units for the Dennison–Villars and the Mecke frequencies, respectively. The agreement with the low-temperature specific heat value of 49.8 is good. For acetylene, the absolute translational plus rotational entropy is 49.359 at 25°; the vibrational contribution is 1.474, making a total of 50.833. For ethylene, the absolute translational plus rotational entropy is 56.903; the vibrational entropy is 0.452 or 0.569, the torsional frequency being omitted or taken as 950 cm.$^{-1}$; this gives a total of 57.355 or 57.472. For both acetylene and ethylene, the calculated values are probably in error by several tenths of an entropy unit.

It is planned to extend these calculations to other organic substances of scientific and technical interest. There appears to be some possibility of making orienting calculations even for the higher hydrocarbons.

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(32) Haas and Stegeman, *J. Phys. Chem.*, **36**, 2127 (1932).

(33) Giauque, Blue and Overstreet, *Phys. Rev.*, **38**, 196 (1931).

Summary

1. Methods have been given for the convenient calculation of free energies and entropies from spectroscopic data for polyatomic molecules.

2. Calculations have been made for methane, acetylene and ethylene.

3. The problem of representing the results of spectroscopic calculations by simple equations has been considered. It is shown that this can only be done satisfactorily by including in $\Delta F/T$ terms in $1/T^2$ and $1/T^3$.

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The Reactions of Atomic Hydrogen with Several Alkyl Halides

BY H. MARSHALL CHADWELL AND TOSHIZO TITANI[1]

The chemical behavior at ordinary temperatures of atomic hydrogen has been the subject of numerous investigations[2] during the past decade. The present investigation deals with the reactions of atomic hydrogen, produced by the Wood discharge tube, upon simple alkyl halide vapors: methyl fluoride, chloride, bromide and iodide, and ethyl chloride and bromide. The reactions with methane and ethane were also investigated. Boehm and Bonhoeffer[2] found that methyl chloride was attacked, but did not investigate the products. Of particular interest in connection with our results are the experiments of Hartel and Polanyi[3] on the reaction of sodium vapor with the alkyl halides.

Our experiments have shown that the reactions concerned are complicated, that in the series methyl fluoride, chloride, bromide and iodide, the amount decomposed under the experimental conditions varies from 0 to 100%. Both methyl and ethyl halides form methane, ethane and a small amount of ethylene. The chlorides produce only hydrogen chloride, while the bromides and iodides yield both hydrogen halide and free halogen.

Experimental Manipulation

Purification of Materials

Methyl Fluoride.—The methyl fluoride was prepared by the method of Moissan[4]

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(2) For a review of the early literature see Bonhoeffer, *Ergebnisse Exakten Naturwissenschaften*, **6**, 201 (1927), and Taylor, THIS JOURNAL, **48**, 2840 (1926). For reactions with hydrogen produced by the Wood discharge tube, Bonhoeffer and Boehm, *Z. physik. Chem.*, **119**, 385 (1926); Bonhoeffer and Harteck, *ibid.*, **139**, 64 (1928); Wartenberg and Schultze, *ibid.*, **B2**, 1 (1929); Urey and Lavin, THIS JOURNAL, **51**, 3286, 3290 (1929); Geib and Harteck, *Z. physik. Chem.*, *Bodenstein Festband*, 849 (1931); Dixon, THIS JOURNAL, **54**, 4262 (1932). See also Smallwood, *ibid.*, **51**, 1985 (1929); Bichowsky and Copeland, *ibid.*, **50**, 1315 (1928); Harteck, *Z. physik. Chem.*, **139**, 98 (1928).

(3) Hartel and Polanyi, *Z. physik. Chem.*, **B11**, 97 (1931).

(4) Moissan, *Jahresber. Chem.*, **41**, 931 (1888).