

Note on the Free Energy of Acetylene

A. R. Gordon

Citation: *The Journal of Chemical Physics* **6**, 219 (1938); doi: 10.1063/1.1750229

View online: <http://dx.doi.org/10.1063/1.1750229>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/6/4?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[An estimation of the isomerization energy of acetylene](#)

J. Chem. Phys. **110**, 1831 (1999); 10.1063/1.477890

[Vibrational energy levels of an acetylene molecule](#)

J. Chem. Phys. **61**, 1680 (1974); 10.1063/1.1682162

[Erratum: Correlation Energy of Ethylene and Acetylene](#)

J. Chem. Phys. **45**, 2338 (1966); 10.1063/1.1727942

[Correlation Energy of Ethylene and Acetylene](#)

J. Chem. Phys. **43**, 60 (1965); 10.1063/1.1696487

[Note on the Spectra of the Disubstituted Acetylenes and of the Mustard Oils](#)

J. Chem. Phys. **5**, 178 (1937); 10.1063/1.1750003



Note on the Free Energy of Acetylene

A. R. GORDON

Chemistry Department, University of Toronto, Toronto, Canada

(Received January 15, 1938)

ALTHOUGH acetylene is a reactant in a number of technically important gas reactions, moderately accurate free energy data are almost entirely lacking for it. Kassel¹ has computed F/T using the harmonic oscillator-rigid rotator approximation for its energy levels. Such an approximation, however, may introduce appreciable errors for high temperatures, and it is precisely the high temperature range that is of greatest experimental interest.

The most serious obstacle to a more exact calculation is the fact that attempts to represent the vibrational levels by an expression of the usual form

$$\epsilon_V = \sum_i v_i \omega_i + \sum_{ij} v_i v_j x_{ij} \quad (1)$$

have met with only moderate success. As is well known, acetylene has seven vibrational degrees of freedom divided among five fundamental frequencies, designated in Herzberg's notation as: ν_1 a C—C frequency, ν_2 and ν_3 symmetrical and antisymmetrical C—H frequencies, ν_4 and ν_5 antisymmetrical and symmetrical doubly degenerate deformation frequencies. Recently Mecke and Ziegler² have attacked the problem from a new angle. They assume only three fundamentals: a C—C frequency ν_{CC} , a doubly degenerate C—H frequency ν_{CH} , and a quadruply degenerate deformation frequency δ . Through anharmonicity and electrical and mechanical coupling, the degeneracy is wholly or partly removed, and they give equations by which the separations of the resulting levels may be computed. For example, for $v_\delta = 2$, there will be three energy states 1454, 1328 and 1218 cm^{-1} above the ground state, corresponding in the older notation to the levels $(v_4 = 2, v_5 = 0)$, $(v_4 = 1, v_5 = 1)$, $(v_4 = 0, v_5 = 2)$. This theory has been adversely criticized by Childs and Jahn,³ but the fact remains that it predicts energy levels in reasonably close agreement with those actually observed.

For the purposes of thermodynamic calculation, however, an expression of the type (1) is adequate provided the x_{ij} are average values determined from a large number of vibrational levels. The determination of such averages is a matter of some difficulty, but for the present purpose those selected are: $\omega_1 = 1977.5$, $\omega_2 = 3392$, $\omega_3 = 3315$, $\omega_4 = 732.4$, $\omega_5 = 612.8$, $x_{11} = -4.5$, $x_{22} = -20$, $x_{33} = -32$, $x_{44} = -3.2$, $x_{55} = -1.0$, $x_{12} = x_{13} = -8$, $x_{23} = -100$, $x_{14} = x_{15} = 0$, $x_{24} = x_{25} = x_{34} = x_{35} = x_{45} = -12.5$, all expressed in cm^{-1} . This choice is consistent with the most recent values of the fundamentals listed by Funke and Lindholm⁴ viz. 1973, 3372, 3283, 729.2 and 611.8 cm^{-1} ; for the energy states with $v_\delta = v_4 + v_5 \leq 5$, $v_{CH} = v_2 + v_3 \leq 5$, it introduces at most an error of 0.005 in F/T if it be assumed that the levels computed by Mecke and Ziegler's equations are the correct ones. Moreover, for some 40 levels listed by Funke and Lindholm, the use of this approximate expression instead of the experimentally observed values causes at most an error of 0.006 in F/T .

The rotational constants⁴ are $B = 1.1764 - 0.0051(v_{CH} + v_{CC}) + 0.0020v_\delta$; $D = -1.83 \times 10^{-6}$. For consistency with earlier free energy calculations, the universal constants are $R = 1.9869$, $hc/k = 1.4324$, additive constant for the translational free energy = -7.267 . The resulting values⁵ of $(F^0 - E_0^0)/T$ for a few temperatures and of $S^0_{298.1}$ are given in Table I; in none of these entries is the nuclear spin contribution of the two hydrogen atoms in the molecule included. For purposes of interpolation, the entries can be represented within one or two units in the last decimal place as printed by the empirical equations below. These equations have been checked at numerous intermediate temperatures.

$$\begin{aligned} (400-1200^\circ\text{K}) - (F^0 - E_0^0)/T = & 0.223 \\ & + 16.0125 \log T - 18.3 \log (1 - \exp[-900/T]) \\ & - 1.068 \times 10^{-3} T + 0.817 \times 10^{-6} T^2, \end{aligned}$$

¹ Kassel, J. Am. Chem. Soc. **55**, 1351 (1933).

² Mecke and Ziegler, Zeits. f. Physik **101**, 405 (1936).

³ Childs and Jahn, Zeits. f. Physik **104**, 804 (1937).

⁴ Funke and Lindholm, Zeits. f. Physik **106**, 518 (1937).

⁵ For the method of calculation, see Gordon, J. Chem. Phys. **3**, 259 (1935).

$$(1200-2800^\circ\text{K}) - (F^0 - E_0^0)/T = -1.642 \\ + 16.0125 \log T + 6.256 \times 10^{-3}T \\ - 0.475 \times 10^{-6}T^2.$$

A comparison of the data of Table I with Kassel's values (after subtracting the nuclear spin contribution 2.754 cal./deg. from his numbers) shows that the values given here are slightly less than his for low temperatures, principally due to the fact that he used a slightly smaller value of ν_5 , namely 600 cm^{-1} ; for high temperatures, the values of Table I are definitely greater than his, owing primarily to the contribution of x_{45} to the state sum. For example, for 2000°, Kassel gives 61.59 cal./deg. (64.34 before subtracting the spin contribution) which is 0.24 cal./deg. less than the entry in Table I.

Kassel in his calculation adopts a heat of combustion for acetylene at 18°C of 311,000 cal.; from this and the known heats of combustion of hydrogen⁶ and graphite⁷ (68313 cal. and 94,240 cal. at 25°C) ΔH_{298} for the reaction $2C + H_2 = C_2H_2$ is 54150. From this and the thermodynamic data for hydrogen⁸ and graphite⁹ $\Delta F_{298.1}^0$ is 49970 cal. and ΔE_0^0 is 54280 cal. The resulting values for $\log K_1 = \log (P_{C_2H_2})/(P_{H_2})$ are given in the table. Fig. 1 gives a comparison

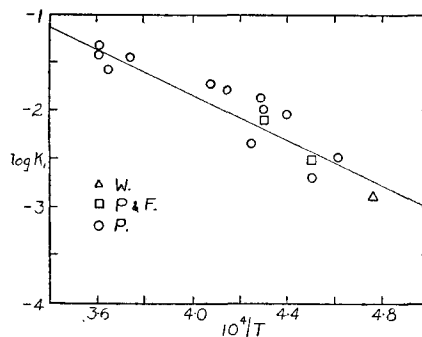


FIG. 1.

of the experimental values of $\log K_1$ obtained by Von Wartenburg,¹⁰ by Pring¹¹ and by Pring and Fairlie¹² with the data of the table. The agreement is excellent, and is well within the limits of error of the experiments.

From the data for acetylene, nitrogen¹³ and hydrogen cyanide¹⁴ it is also possible to compute the equilibrium constant for the reaction $C_2H_2 + N_2 = 2 HCN$. If the heat of formation of gaseous hydrogen cyanide at 298° be taken¹⁴ as 31000 cal., ΔH_{298} for the reaction is 7850 cal.; $\Delta S_{298.1}^0$ is 2.659, hence $\Delta F_{298.1}^0$ is 7060 cal. $\log K_2 = \log (P_{HCN})^2/(P_{C_2H_2})(P_{N_2})$ is given in the last column of the table.

All the equilibrium constants of Table I are of course subject to correction as a result of the uncertainty in the heats of formation of acetylene and hydrogen cyanide. The former may be in error to the extent of 1 kcal. per mole, with a resulting uncertainty in $\log K_1$ of 0.09 at 2500°. The uncertainty for hydrogen cyanide must be considerably less than this, in view of the excellent agreement between the value computed for its free energy of formation from thermal and spectroscopic data, and that obtained from entirely independent equilibrium measurements.¹⁴

TABLE I. $K_1 = (P_{C_2H_2})/(P_{H_2})$; $K_2 = (P_{HCN})^2/(P_{C_2H_2})(P_{N_2})$.

$T^\circ\text{K}$	$-(F^0 - E_0^0)/T$	$-\log K_1$	$-\log K_2$
298.1	39.993	36.64	5.18
300	40.044	36.39	5.14
400	42.477	26.53	3.71
600	46.368	16.69	2.29
800	49.499	11.78	1.59
1000	52.157	8.85	1.17
1200	54.49	6.90	0.90
1600	58.47	4.47	0.56
2000	61.83	3.01	0.37
2400	64.75	2.04	
2800	67.35	1.35	
$S_{298.1}^0$	48.029		

⁶ Rossini, Nat. Bur. Stand. J. Research 6, 1 (1931).

⁷ Roth and Naeser, Zeits. f. Elektrochem. 31, 461 (1925) as corrected by Clayton and Giauque, reference 9.

⁸ Giauque, J. Am. Chem. Soc. 52, 4816 (1930); Davis and Johnston, J. Am. Chem. Soc. 56, 1045 (1934).

⁹ Clayton and Giauque, J. Am. Chem. Soc. 54, 2610 (1932).

¹⁰ Von Wartenburg, Zeits. f. anorg. allgem. Chemie 52, 299 (1907).

¹¹ Pring, J. Chem. Soc. 89, 1601 (1906); 97, 498 (1910).

¹² Pring and Fairlie, Ind. Eng. Chem. 4, 812 (1912).

¹³ Giauque and Clayton, J. Am. Chem. Soc. 55, 4875 (1933).

¹⁴ Gordon, J. Chem. Phys. 5, 30 (1937).