Table III. Comparison of Protonation and Formation Constants with Related Compounds

	T, °C.	Ionic Strength	H^+ Log K_1	H^+ Log K_2	Cu^{+2} Log K_1	Cu^{+2} Log K_2	Ref.
N-(2-aminoethyl)morpholine	30	→0	9.15	4.06	6.56	5.30	
N-(2-aminoethyl)morpholine	30	1.0*M* KNO_3	9.45	4.84	6.60	3.96	(*2*)
N-(2-aminoethyl)piperidine	30	→0	9.89	6.38	7.77	5.83	(*7*)
N-(2-aminoethyl)pyrrolidine	30	→0	9.74	6.56	8.77	6.05	(*7*)
1,2-Ethanediamine	30	→0	9.81	6.79	10.36	8.93	(*5*)
N-(2-aminoethyl)piperazine	30	→0	9.40	8.37	5.49	(3.7)	(*6*)
N,N-dimethyl-1,2-ethanediamine	25	0.1*M* KCl	9.53	6.63	9.23	6.73	(*4*)
N,N-diethyl-1,2-ethanediamine	25	0.1*M* KCl	10.02	7.07	8.17	5.55	(*4*)
2-Picolylamine	30	→0	8.51	3.1	9.45	7.80	(*1*)

LITERATURE CITED

(1) Goldberg, D.E., Fernelius, W.C., *J. Phys. Chem.* **63**, 1246 (1959).

(2) Hares, G.B., Fernelius, W.C., Douglas, B.E., *J. Am. Chem. Soc.* **78**, 1816 (1956).

(3) Hulquist, M.E., Nortbeg, E.H., *Ibid.*, **62**, 447 (1940).

(4) Irving, H., Griffiths, J.M.M., *J. Chem. Soc.* **1954**, 213.

(5) McIntyre, G.H., Jr., Block, B.P., Fernelius, W.C., *J. Am. Chem. Soc.* **81**, 529 (1959).

(6) Pagano, J.M., Goldberg, D.E., Fernelius, W.C., *J. Phys. Chem.* **65**, 1062 (1961).

(7) Reichard, R.E., Fernelius, W.C., *Ibid.*, **65**, 380 (1961).

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Thermodynamic Functions of Acetylene

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Thermodynamic functions were computed for an ideal gas of C_2H_2 molecules under standard conditions incorporating the effects of anharmonicities, rotational stretching, and vibration-rotation interaction over the temperature range 298° to 6000° K.

BELL AND NIELSEN (*2*) have determined the vibrational fundamentals, the rotational constants, and the 15 first-order anharmonicity terms. Allen, Tidwell, and Plyler (*1*) redetermined some of these. Wiggins, Plyler, and Tidwell (*7*) have recently determined the five vibration-rotation interaction coefficients αi as well as redetermining B_0, D_0, and v_5. Somewhat different values for the Raman-active vibration-rotation data are given by Stoichieff (*6*). Thermodynamic functions were computed by the Bendix G20 Electronic Data Processing Machine for an ideal gas of C_2H_2 molecules at 1 atm. using a modification of the triatomic molecules program described earlier (*4*, *5*). In these calculations, R is 1.98726 cal. per mole degree, the dimensionless factor hc/k is 1.4388, and the Sackur-Tetrode constant K_6 is −7.28353 (*3*). Previous tables for C_2H_2 were based on the rigid rotor-harmonic oscillator (RRHO) approximation. Consideration of the anharmonicities and rotational effects raises C_p^0 (6000° K.) 9.3% beyond the RRHO result.

The separate effects of the anharmonicities, etc., on the free energy function at 6000° K. were also determined as follows:

RRHO part	80.024
Rotational stretch	0.020
Overtone anharmonicities X_{ii}	−0.493
Combination anharmonicities X_{ij}	1.107
Rotation-vibration terms αi	−0.034
Total	80.624

Of course, the other thermodynamic functions are more sensitive to these effects than the free energy function, and at lower temperatures the effects are less in magnitude. The net negative contribution from the X_{ii} terms may seem at first surprising, but is caused by the large negative value of the quantity $-X_{44}/\sigma_{42}$ which corresponds to overtones of the lowest energy, doubly degenerate vibration. Likewise, the net negative contribution from the αi arises from the shortening of the molecule (increase in B) when it

Table I. Thermodynamic Functions of C_2H_2 (g.)

T, ° K.	$\frac{-(F^0 - E_0^0)}{T}$	$\frac{(H^0 - E_0^0)}{T}$	S^0	C_p^0 Cal. Mole^{-1} Deg.$^{-1}$	$H_T^0 - H_{298}^0$ Kcal. Mole^{-1}
298.15	39.972	8.030	48.002	10.531	
300	40.022	8.046	48.067	10.564	0.019
400	42.451	8.873	51.324	12.054	1.155
500	44.513	9.620	54.133	13.104	2.416
600	46.326	10.271	56.596	13.917	3.768
700	47.953	10.842	58.794	14.605	5.195
800	49.434	11.351	60.785	15.219	6.687
900	50.798	11.812	62.611	15.780	8.237
1000	52.065	12.235	64.300	16.295	9.841
1100	53.250	12.626	65.876	16.768	11.495
1200	54.364	12.990	67.354	17.199	13.193
1300	55.417	13.329	68.746	17.590	14.933
1400	56.417	13.646	70.063	17.946	16.710
1500	57.369	13.944	71.312	18.267	18.521
1600	58.277	14.223	72.500	18.558	20.363
1700	59.148	14.485	73.634	18.821	22.232
1800	59.984	14.733	74.716	19.060	24.126
1900	60.786	14.967	75.753	19.278	26.043
2000	61.559	15.188	76.747	19.476	27.981
2100	62.305	15.396	77.701	19.657	29.938
2200	63.026	15.594	78.620	19.823	31.912
2300	63.723	15.781	29.504	19.976	33.902
2400	64.399	15.959	80.357	20.117	35.907
2500	65.054	16.128	81.181	20.248	37.925
2600	65.689	16.288	81.978	20.370	39.956
2700	66.307	16.442	82.749	20.483	41.999
2800	66.908	16.588	83.496	20.589	44.052
2900	67.492	16.728	84.220	20.689	46.116
3000	68.062	16.861	84.923	20.783	48.190
3100	68.616	16.989	85.606	20.873	50.273
3200	69.158	17.112	86.270	20.956	52.364
3300	69.686	17.230	86.916	21.036	54.464
3400	70.202	17.343	87.545	21.112	56.571
3500	70.707	17.451	88.158	21.185	58.686
3600	71.200	17.556	88.756	21.254	60.808
3700	71.682	17.657	89.339	21.321	62.937
3800	72.154	17.754	89.909	21.386	65.072
3900	72.617	17.848	90.465	21.448	67.214
4000	73.070	17.939	91.009	21.508	69.361
4100	73.514	18.027	91.540	21.566	71.515
4200	73.949	18.112	92.061	21.622	73.675
4300	74.376	18.194	92.570	21.676	75.839
4400	74.795	18.274	93.069	21.730	78.010
4500	75.207	18.351	93.558	21.781	80.185
4600	75.611	18.426	94.037	21.832	82.366
4700	76.008	18.499	94.507	21.881	84.552
4800	76.398	18.570	94.969	21.930	86.742
4900	76.782	18.639	95.421	21.977	88.938
5000	77.159	18.706	95.866	22.023	91.138
5100	77.530	18.772	96.302	22.068	93.342
5200	77.896	18.836	96.731	22.113	95.551
5300	78.255	18.898	97.153	22.157	97.765
5400	78.609	18.959	97.567	22.201	99.983
5500	78.957	19.018	97.975	22.244	102.205
5600	79.300	19.076	98.376	22.286	104.431
5700	79.638	19.133	98.771	22.327	106.662
5800	79.972	19.188	99.160	22.368	108.897
5900	80.300	19.242	99.543	22.409	111.136
6000	80.624	19.295	99.919	22.449	113.379

Table II. Molecular Constants of C_2H_2 (g.), Cm.$^{-1}$

Molecular weight = 26.038
Symmetry No. = 2
$B_0 =$ 1.17654
$D_0 =$ 1.51×10^{-6}
$\sigma_1 = 3373.7$
$\sigma_2 = 1973.8$
$\sigma_3 = 3281.9$
$\sigma_4 = 611.6^a$
$\sigma_5 = 729.11^a$
(band center frequencies)^a

$-X_{11} = 24.08$
$-X_{12} = 16.94$
$-X_{13} = 99.01$
$-X_{14} = 16.46$
$-X_{15} = 11.75$
$-X_{22} = 7.92$
$-X_{23} = 1.38$
$-X_{24} = 6.15$

$-X_{25} = 0.85$
$-X_{33} = 25.69$
$-X_{34} = 9.06$
$-X_{35} = 5.73$
$-X_{44} = -5.38$
$-X_{45} = 12.65$
$-X_{55} = 2.27$
$g_{44} = 1.10$
$g_{55} = 2.49$

$\alpha_1 = 0.00685$
$\alpha_2 = 0.00622$
$\alpha_3 = 0.00419$
$\alpha_4 = -0.00131$
$\alpha_5 = -0.00215$

[a] Double degeneracy.

is vibrating in the perpendicular modes v_4 and v_5, each of which is doubly degenerate.

A complete vibrational analysis for the related molecule C_2N_2 would be worthwhile project. The C_2H_2 and C_2N_2 molecules occur in significant amounts in oxygen-deficient flames, or in graphite-moderated reactors cooled by hydrogen, nitrogen, or the hydrides; or in carbon-tube furnaces with flowing or stagnant atmospheres. With halogen-containing atmospheres, additional molecules such as C_2F_2, HCCF, C_2H, C_2F become important.

LITERATURE CITED

(1) Allen, H.C., Tidwell, E.D., Plyler, E.K., *J. Research Natl. Bureau Standards* **57**, 213 (1956).

(2) Bell, E.E., Nielsen, H.H., *J. Chem. Phys.* **18**, 1382 (1950).

(3) Cohen, E.R., DuMond, J., Layton, T.W., Rollet, J.S., *Rev. Mod. Phys.* **27**, 363 (1955).

(4) (a) Gordon, J.S., J. CHEM. ENG. DATA **6**, 390 (1961). (b) Gordon, J.S., Proceedings of Second Conference, Kinetics, Performance and Equilibria of High Temperature Systems, Western States Section, Combustion Institute, pp. 42–113. New York: Gordon and Breach (1963).

(5) Pennington, R.E., Kobe, K.A., *J. Chem. Phys.* **22**, 1442 (1954).

(6) Stoichieff, B.P., in H.W. Thompson, Ed., "Advances in Spectroscopy," New York, Interscience Pub., Vol. 1, 123 (1959).

(7) Wiggins, T.A., Plyler, E.K., Tidwell, E.D., *J. Opt. Soc. Am.* **51**, 1219 (1961).

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