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Thermodynamic Properties of Diiodoacetylene and Some Symmetrical-Top Acetylenes

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In this paper tables are presented of the thermodynamic functions—heat content, free energy, entropy, and heat capacity—of diiodoacetylene, methylchloroacetylene, methylbromoacetylene, methyliodoacetylene, methylacetylene, and methyldeuteroacetylene, for several temperatures from their boiling points up to 1000°K, for the ideal gaseous state at one atmosphere pressure. These functions were calculated from the Raman spectral data for all of the substances except methyldeuteroacetylene, for which the frequencies used were those calculated with force constants transferred from methylacetylene.

INTRODUCTION

THERMODYNAMIC properties can be calculated from spectroscopic data—to a rigid rotator, harmonic oscillator approximation—if the vibrational frequencies and their degeneracies are known and if the internuclear distances have been determined from spectroscopic or electron diffraction data. In the present investigation, such calculations have been made for diiodoacetylene, methylchloroacetylene, methylbromoacetylene, methyliodoacetylene, methylacetylene, and methyldeuteroacetylene. The thermodynamic properties calculated were the heat capacity, entropy, heat content, and free energy for several temperatures.

Previous calculations were made by Crawford¹ of the entropy, free energy, and heat capacity for methylacetylene, with results that are only slightly different from those obtained in the present investigation. Calculated values of the heat capacity for methylbromoacetylene and methyliodoacetylene also were reported previously by Cleveland and Murray;² each of their values was slightly greater than the corresponding value in the present results.

The values obtained for methyldeuteroacetylene are tentative since they were obtained from the calculated frequencies, with force constants transferred from methylacetylene. This was necessary because no Raman or infra-red data have been reported for this molecule.

TABLE I. Fundamental frequencies for diiodoacetylene.

Designation	Frequency (cm ⁻¹)	Degeneracy
ν_1	191	1
ν_2	2109	1
ν_3	710	1
ν_4	310	2
ν_5	115	2

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¹ Bryce L. Crawford, Jr., J. Chem. Phys. 8, 526 (1940).

² Forrest F. Cleveland and M. J. Murray, J. Chem. Phys. 11, 450 (1943); 12, 320 (1944).

The values of the physical constants used in the present calculations were:

$R = 1.98714$ cal. mole⁻¹ deg.⁻¹,
 $c_2 = hc/k = 1.4384$ cm deg.,
 $N_0 = 6.0228 \cdot 10^{23}$ mole⁻¹,
 Atomic weight of hydrogen = 1.0083,
 Atomic weight of deuterium = 2.01418,
 Atomic weight of carbon = 12.0146,
 Atomic weight of chlorine = 35.4570,
 Atomic weight of bromine = 79.916, and
 Atomic weight of iodine = 126.915.

SPECTROSCOPIC AND MOLECULAR DATA

Diiodoacetylene

Raman spectral data, for solutions in acetone and in absolute alcohol, have been obtained for diiodoacetylene by Glockler and Morrell³ and by Cleveland and Meister.⁴ Infra-red data, for the solid and for a carbon disulfide solution, were obtained by Emschwiller and Lecomte⁵ in the region 650 to 1450 cm⁻¹. Since the observed dipole moment for this molecule was nearly zero⁶ and since the electron diffraction data⁷ indicated a linear structure, Cleveland and Meister⁴ assumed that diiodoacetylene is linear and symmetrical and found that a satisfactory assignment of frequencies could be made upon this basis. As an aid in making the assignment, an *FG* matrix calculation of the frequencies was made, with force constants transferred from the similar molecule, methyliodoacetylene. According to this assignment, the fundamental frequencies and their degeneracies are those given in Table I.

The internuclear distances required for the calculation of the moments of inertia were taken from the electron diffraction results;⁷ they were 1.18Å for the

³ G. Glockler and C. E. Morrell, J. Chem. Phys. 2, 349 (1934); 4, 15 (1936).

⁴ Forrest F. Cleveland and Arnold G. Meister, paper presented at the international colloquium, Bordeaux, France, April 1948; see also J. Chem. Phys. 17, 212 (1949).

⁵ G. Emschwiller and J. Lecomte, J. de phys. et rad. 8, 130 (1937).

⁶ L. E. Sutton, R. G. A. New, and J. B. Bentley, J. Chem. Soc. 652 (1933).

⁷ H. de Laszlo, Trans. Faraday Soc. 30, 825 (1934); Nature 135, 474 (1935).

TABLE II. Fundamental frequencies for methylchloroacetylene.

Designation	Frequency (cm ⁻¹)	Degeneracy
ν_1	2926	1
ν_2	2263	1
ν_3	1380	1
ν_4	1078	1
ν_5	579	1
ν_1	2971	2
ν_2	1449	2
ν_3	1029	2
ν_4	353	2
ν_5	184	2

C \equiv C bond and 2.03Å for the C-I bond. The moments of inertia calculated from these bond distances were

$$I_1 = I_2 = 2.91 \cdot 10^{-37} \text{ g cm}^2,$$

and

$$I_3 = 0.$$

Methylchloroacetylene

Raman spectral data for a solution of methylchloroacetylene were obtained by Cleveland and Murray,² but no vibrational assignment could be made by them because of uncertainties introduced by the presence of the solvent lines. To overcome this difficulty, Meister⁸ calculated the frequencies for this molecule by the *FG* matrix method, assuming a C_{3v} symmetry and using force constants obtained in a previous investigation.⁹ The remaining force constants were determined from some of the observed frequencies and finally all of the frequencies were calculated and compared with the observed values. The agreement between the observed and calculated frequencies was within two percent. In this way, a rather certain assignment of the fundamental frequencies could be made. According to this assignment, the fundamental frequencies and their degeneracies are those given in Table II. The

TABLE III. Fundamental frequencies for methylbromoacetylene.

Designation	Frequency (cm ⁻¹)	Degeneracy
ν_1	2921	1
ν_2	2230	1
ν_3	1375	1
ν_4	1034	1
ν_5	464	1
ν_1	2968	2
ν_2	1443	2
ν_3	1026	2
ν_4	343	2
ν_5	171	2

⁸ Arnold G. Meister, J. Chem. Phys. 16, 950 (1948).

⁹ Arnold G. Meister and Forrest F. Cleveland, J. Chem. Phys. 15, 349 (1947).

TABLE IV. Fundamental frequencies for methyliodoacetylene.

Designation	Frequency (cm ⁻¹)	Degeneracy
ν_1	2913	1
ν_2	2197	1
ν_3	1375	1
ν_4	1008	1
ν_5	405	1
ν_1	2958	2
ν_2	1438	2
ν_3	1021	2
ν_4	343	2
ν_5	163	2

frequency designations are those used by Meister.⁸ No infra-red data have been reported for this molecule.

The bond distances and interbond angles used in calculating the moments of inertia were the ones used by Meister;⁸ they were: C-Cl, 1.68Å; C-H, 1.093Å; C \equiv C, 1.21Å; C-C, 1.462Å; and for the H-C-C angle, 109° 28'. The resulting values for the moments of inertia were

$$I_1 = I_2 = 386 \cdot 10^{-40} \text{ g cm}^2,$$

and

$$I_3 = 5.33 \cdot 10^{-40} \text{ g cm}^2.$$

Methylbromoacetylene

No infra-red data have been obtained for methylbromoacetylene, but Raman spectral data for the liquid state and an assignment of frequencies on the basis of a C_{3v} symmetry have been reported by Cleveland and Murray.² Later, Meister⁸ carried out an *FG* matrix treatment for this molecule and made some revisions in the previous assignment; his assignment of the fundamental frequencies and their degeneracies are given in Table III.

The bond distances and interbond angles used in calculating the moments of inertia for this molecule again were those used by Meister;⁸ they were: C-Br, 1.80Å; C \equiv C, 1.204Å; C-C, 1.462Å; C-H, 1.093Å; and for the H-C-C angle, 109° 28'. The

TABLE V. Fundamental frequencies for methylacetylene.

Designation	Frequency (cm ⁻¹)	Degeneracy
ν_1	2941	1
ν_2	2146	1
ν_3	1382	1
ν_4	928	1
ν_5	3429	1
ν_1	2982	2
ν_2	1448	2
ν_3	1038	2
ν_4	336	2
ν_5	642	2

TABLE VI. Fundamental frequencies for methyldeuteroacetylene.

Designation	Frequency (cm ⁻¹)	Degeneracy
ν_1	2941	1
ν_2	2009	1
ν_3	1376	1
ν_4	914	1
ν_5	2674	1
ν_1	3059	2
ν_2	1454	2
ν_3	1037	2
ν_4	309	2
ν_5	518	2

resulting values for the moments of inertia were

$$I_1 = I_2 = 541 \cdot 10^{-40} \text{ g cm}^2,$$

and

$$I_3 = 5.33 \cdot 10^{-40} \text{ g cm}^2.$$

Methyliodoacetylene

No infra-red data have been obtained for methyl-iodoacetylene, but Raman data for the liquid state and a frequency assignment were given by Cleveland and Murray² on the basis of a C_{3v} symmetry. Later, Meister⁸ carried out an FG matrix treatment for this molecule also and made some revisions in the previous assignment; his assignment of the fundamental frequencies and their degeneracies is given in Table IV.

The bond distances and interbond angles used in calculating the moments of inertia for this molecule were those used by Meister;⁸ they were: C—I, 2.03A; C≡C, 1.18A; C—C, 1.462A; C—H, 1.093A; and the H—C—C angle, 109° 28'. The resulting

TABLE VII. Heat content, free energy, entropy, and heat capacity of diiodoacetylene for the ideal gaseous state at one atmosphere pressure.*

T	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$	S^0	C_p^0
373.16	13.90	64.75	78.65	17.44
400	14.14	65.72	79.86	17.61
600	15.47	71.73	87.20	18.55
800	16.32	76.32	92.63	19.17
1000	16.94	80.02	96.96	19.60

* In this and subsequent tables, T is in °K and the other four quantities are in cal. deg.⁻¹ mole⁻¹.

TABLE VIII. Heat content, free energy, entropy, and heat capacity of methylchloroacetylene for the ideal gaseous state at one atmosphere pressure.

T	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$	S^0	C_p^0
400	14.04	59.27	73.31	19.72
600	16.66	65.47	82.13	23.87
800	18.87	70.57	89.44	26.98
1000	20.74	74.99	95.73	29.32

values for the moments of inertia were

$$I_1 = I_2 = 673 \cdot 10^{-40} \text{ g cm}^2,$$

and

$$I_3 = 5.33 \cdot 10^{-40} \text{ g cm}^2.$$

Methylacetylene

Raman spectral data have been reported by Glockler and Davis¹⁰ and both Raman and infra-red data by Crawford.^{1,11} An assignment of the frequencies was made by Crawford¹ upon the basis of a C_{3v} symmetry, which was also the structure which was found to be consistent with the electron diffraction data.¹² The fundamental frequencies have been calculated by Crawford¹ and by Meister.⁸ The values of the fundamental frequencies^{1,8} and their degeneracies used in the present work are given in Table V. The frequency designations are those of Meister.

The bond distances and interbond angles^{13,12} used in calculating the moments of inertia were: C—H (methyl), 1.093A; C—H (terminal), 1.057A; C—C, 1.462A; C≡C, 1.204A; and the H—C—C angle, 109° 28'. These values yield the following moments of inertia:

$$I_1 = I_2 = 97.87 \cdot 10^{-40} \text{ g cm}^2,$$

and

$$I_3 = 5.333 \cdot 10^{-40} \text{ g cm}^2.$$

Methyldeuteroacetylene

As yet no Raman or infra-red spectral data have been reported for methyldeuteroacetylene. How-

TABLE IX. Heat content, free energy, entropy, and heat capacity of methylbromoacetylene for the ideal gaseous state at one atmosphere pressure.

T	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$	S^0	C_p^0
400	14.36	61.80	76.16	20.02
600	16.96	68.13	85.08	24.08
800	19.13	73.31	92.44	27.13
1000	20.98	77.79	98.76	29.43

TABLE X. Heat content, free energy, entropy, and heat capacity of methylchloroacetylene for the ideal gaseous state at one atmosphere pressure.

T	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$	S^0	C_p^0
400	14.54	63.44	77.97	20.18
600	17.12	69.85	86.96	24.19
800	19.28	75.08	94.36	27.22
1000	21.11	79.59	100.60	29.51

¹⁰ G. Glockler and H. M. Davis, J. Chem. Phys. 2, 881 (1934).

¹¹ Bryce L. Crawford, Jr., J. Chem. Phys. 7, 140 (1939).

¹² L. Pauling, H. D. Springall, and K. J. Palmer, J. Am. Chem. Soc. 61, 927 (1939).

¹³ G. Herzberg, F. Patat, and H. Verleger, J. Phys. Chem. 41, 123 (1937).

TABLE XI. Heat content, free energy, entropy, and heat capacity of methylacetylene for the ideal gaseous state at one atmosphere pressure.

T	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$	S^0	C_p^0
250	9.75	47.06	56.81	13.05
298.16	10.40	48.84	59.23	14.55
400	11.81	52.09	63.89	17.32
600	14.43	57.38	71.81	21.79
800	16.70	61.85	78.55	25.12
1000	18.66	65.79	84.45	27.69

ever, Meister⁸ has calculated frequencies for this molecule with force constants transferred from methylacetylene; from the nature of the potential function used, one would expect these frequencies to be reliable to within two percent. Consequently, it seemed worth while to include this molecule in the present series in order that tentative results for its thermodynamic properties might be available. The values of the fundamental frequencies and their degeneracies are given in Table VI.⁸

The bond distances and interbond angles were assumed to be the same as for methylacetylene. The calculated values for the moments of inertia were

$$I_1 = I_2 = 107.4 \cdot 10^{-40} \text{ g cm}^2,$$

and

$$I_3 = 5.333 \cdot 10^{-40} \text{ g cm}^2.$$

THERMODYNAMIC FUNCTIONS

The frequencies, degeneracies, and moments of inertia listed in the above sections were used to calculate the heat capacity, free energy, heat content, and entropy for the diiodoacetylene, methylchloroacetylene, methylbromoacetylene, methyliodoacetylene, methylacetylene, and methyldeuteroacetylene molecules. The calculations were made to the rigid rotator, harmonic oscillator approximation and nuclear spins and the effect of isotopic mixing were neglected. The calculated values are for the ideal gaseous state at one atmosphere pressure. The symmetry number σ for diiodoacetylene is 2 and for the methylacetylenes it is 3. The molecular weights for diiodoacetylene, methylchloroacetylene, methylbromoacetylene, methyliodoacetylene, methylacetylene, and methyldeuteroacetylene were respectively 277.86, 74.526, 118.98, 165.98, 40.077, and 41.083.

The results obtained for diiodoacetylene are given in Table VII. The first column gives the temperatures in °K for which calculations were made and the

TABLE XII. Tentative values of the heat content, free energy, entropy, and heat capacity of methyldeuteroacetylene for the ideal gaseous state at one atmosphere pressure.

T	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$	S^0	C_p^0
250	10.15	47.52	57.67	13.78
298.16	10.85	49.36	60.22	15.16
400	12.29	52.76	65.04	17.84
600	14.90	58.24	73.14	22.20
800	17.16	62.85	80.00	25.55
1000	19.11	66.90	86.01	28.13

next four columns give in succession the heat content, free energy, entropy, and heat capacity in calories per degree per mole.

The results for methylchloroacetylene are given in Table VIII.

The results for methylbromoacetylene and methyliodoacetylene are given in Tables IX and X, respectively. The present results for the heat capacity should replace those obtained in earlier calculations;² the present values are, on the average, 1.5 percent smaller than the previous values.

The results for methylacetylene are given in Table XI. The present values are in excellent agreement with the values calculated by Crawford¹ for the entropy, free energy, and heat capacity at constant volume. (Since the present heat capacities were calculated for constant pressure, rather than constant volume, it is necessary to add 1.99 to each of Crawford's heat capacities in order to obtain values comparable with the present heat capacities.) Rossini *et al.* also list some values¹⁴ for the thermodynamic properties of methylacetylene.

The results for methyldeuteroacetylene are given in Table XII. These results must be regarded as tentative since they were determined with calculated frequencies in the absence of observed values; it seems probable, however, that they should be reliable to within about two percent.

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The authors wish to express their appreciation to Dr. Arnold G. Meister for giving them the assignments of the fundamental frequencies for the methylacetylenes prior to publication.

¹⁴ F. D. Rossini, K. S. Pitzer, W. J. Taylor, J. P. Ebert, J. E. Kilpatrick, C. W. Beckett, M. G. Williams, and H. G. Werner, A. P. I. Research Project 44, Circular of the National Bureau of Standards C461, "Selected Values of Properties of Hydrocarbons," (U. S. Government Printing Office, Washington, D. C., 1947), pp. 184, 202, 220, 226, and 291.