by Moissan, phosphoryl difluoromonochloride boiling at 3.1° and a liquid, phosphoryl monofluorodichloride boiling at 52.9°. The freezing points, vapor pressure data, critical constants, gaseous and liquid densities have been determined and recorded along with a few of their chemical properties.

CLEVELAND, OHIO RECEIVED AUGUST 9, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Entropy of Cyanogen. Heat Capacity and Vapor Pressure of Solid and Liquid. Heats of Fusion and Vaporization

BY R. A. RUEHRWEIN AND W. F. GIAUQUE

This paper is a report on a low temperature calorimetric investigation on solid and liquid cyanogen, N—C≡C—N. The results have been used to calculate the entropy of the gas by means of the third law of thermodynamics and this value has been compared with one calculated from available molecular data. The two values agree within their respective limits of error.

The measurements were made in a calorimeter with the laboratory designation Gold Calorimeter III and temperatures were obtained by means of Standard Copper–Constantan Thermocouple W-25, both of which have been described previously.[1,2]

Preparation and Purity of Cyanogen.—Cyanogen was prepared by a method similar to one described by Cook and Robinson.[3] Silver cyanide was precipitated from a saturated silver nitrate solution by a slight excess of a 78% solution of potassium cyanide. The silver cyanide was filtered, washed free of excess cyanide and dried in an oven at 130° for twelve hours. The silver cyanide prepared in this way was a pale brown powder. It was then heated in a glass vessel and a temperature of approximately 380° was maintained.

The cyanogen, which was evolved steadily at a pressure of about half an atmosphere, was passed through two tubes containing phosphorus pentoxide and finally condensed in a bulb surrounded by liquid air but protected from it in case of breakage. The phosphorus pentoxide tubes were 3 cm. in diameter and 30 cm. long. The preparation system was evacuated to a pressure of 10^{-5} mm. before the cyanogen was generated; 180 cc. of liquid was prepared. The material was distilled twice, small end-fractions being discarded, and the solid was subjected to a high vacuum to remove any non-condensable gases; 135 cc. of liquid remained after this treatment.

From the effect of premelting on heat capacity measurements below the melting point the liquid-soluble solid-insoluble impurity was estimated to be 5 parts in 100,000 on a molal basis.

The Melting Point of Cyanogen.—A summary of the melting point investigation is given in Table I.

TABLE I

MELTING POINT OF CYANOGEN

0°C. = 273.10°K.

Time	% melted	T, °K. Resistance thermometer	T, °K. Thermocouple
7-27-38			
5:34 P. M.	Heated into melting point		
5:45 P. M.	10	245.281	245.26
8:25 P. M.	10	245.275	245.25
10:00 P. M.	10	245.265	245.27
11:12 P. M.	Supplied heat		
11:30 P. M.	40	245.264	245.30
7-28-38			
11:10 A. M.	40	245.278	245.27
12:08 P. M.	40	245.270	245.27
1:23 P. M.	Supplied heat		
1:45 P. M.	70	245.277	245.28
3:45 P. M.	70	245.269	245.27
5:35 P. M.	70	245.272	245.27
		Accepted value	245.27

The Vapor Pressure of Cyanogen.—The vapor pressure was measured with a Société Génévoise cathetometer with a precision of 0.002 cm. It was used as a comparison instrument for a standard meter suspended between the arms of the manometer, which was protected by a case with uniform temperature. The standard acceleration of gravity was taken as 980.665 cm. sec.$^{-2}$ and the acceleration at this location as 979.973 cm. sec.$^{-2}$. Data given in the "I. C. T."[4]

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(1) Giauque and Egan, *J. Chem. Phys.*, **5**, 47 (1937).

(2) Giauque and Ruehrwein, THIS JOURNAL, **61**, 2626 (1939).

(3) Cook and Robinson, *J. Chem. Soc.*, 1001 (1935).

(4) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1926, Vol. I.

were used to correct the observations to international cm. of Hg, and the meniscus corrections were taken from the work of Cawood and Patterson.[5]

The data have been represented by the equations

Solid cyanogen 202 to 245.27°K. $\log_{10} P(\text{inter. cm. Hg}) = (-1795.9/T) - 0.001464T + 9.42442$ (1)

Liquid cyanogen 245.27 to 253°K. $\log_{10} P(\text{inter. cm. Hg}) = (-1525.7/T) - 0.0040842T + 8.96542$ (2)

TABLE II

VAPOR PRESSURE OF CYANOGEN

Boiling point 251.95°K. (0°C. = 273.10°K.)

T, °K., resistance thermometer	P inter. cm. Hg	$P_{\text{obsd.}}-P_{\text{calcd.}}$	$T_{\text{obsd.}}-T_{\text{calcd.}}$	Remarks
202.422	1.802	−0.001	0.006	Solid
202.660	1.842	− .003	.017	Solid
210.189	3.740	.003	− .009	Solid
215.299	5.861	.002	− .004	Solid
220.090	8.760	.003	− .004	Solid
225.037	13.023	.005	− .005	Solid
229.953	18.960	− .004	+ .003	Solid
235.054	27.533	− .005	+ .003	Solid
240.108	39.191	− .015	+ .006	Solid
245.270	55.360	.000	.000	Triple point
247.350	61.252	.016	− .005	Liquid
250.311	70.452	.001	.000	Liquid
253.068	79.988	.001	.000	Liquid

In Table II the observations have been compared with values calculated from Equations 1 and 2. From Equation 2 the boiling point was found to be 251.95°K.

The vapor pressure of cyanogen has been measured by Terwen,[6] Perry and Bardwell,[7] and Cook and Robinson.[3] Taking pressures as a reference, Terwen's data correspond to temperatures about 0.2° below the present results over the liquid and most of the solid ranges; however, the deviation increases at lower temperatures to 1.3° below when the pressure is about 2 cm.

The results of Perry and Bardwell and the present work agree within a few hundredths of a degree in the liquid and upper solid range but the deviation gradually increases until the observed temperature is 0.8° below the temperature obtained in this research when the pressure was about 2 cm.

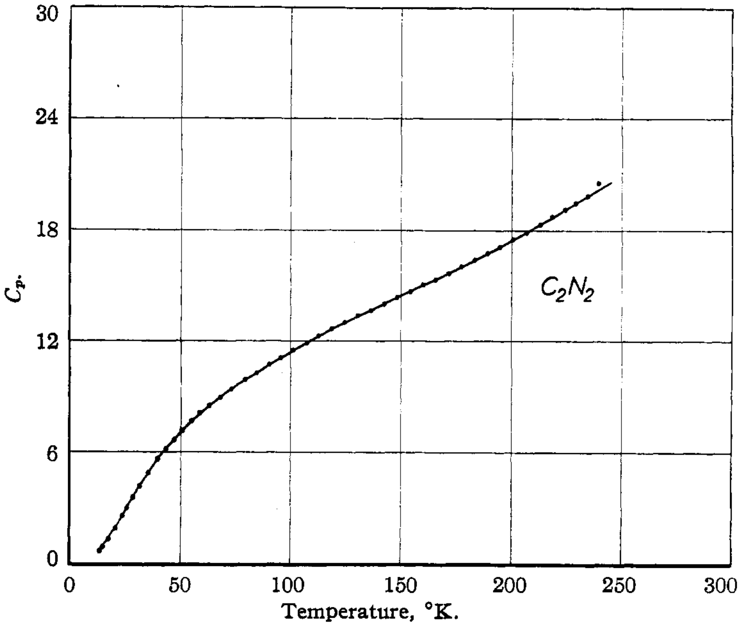

Fig. 1.—Heat capacity in calories per degree per mole of cyanogen.

Cook and Robinson made only one vapor pressure measurement below the boiling point and the present work is in agreement with this observation within 0.01°.

The melting and boiling points are compared with the values obtained by previous observers in Table III.

TABLE III

MELTING AND BOILING POINT TEMPERATURES OF CYANOGEN

M. p., °K.	B. p., °K.	Observer
....	252.7	Bunsen[8] (1814)
238.7	....	Faraday[9] (1845)
245.18	251.75	Terwen[6] (1916)
245.20	251.94	Perry and Bardwell[7] (1925)
245.27	251.95	This research

The Heat Capacity of Cyanogen.—The amount of cyanogen used for the heat capacity measurements was measured by condensing it in a steel bomb and weighing at room temperature. The bomb was equipped with a gas tight double seated valve and a ground glass joint through which it could be evacuated and filled. The bomb weighed 450 g. and had a capacity of 150 cc., a weight of 119.516 g., which is equivalent to 2.2980 moles of cyanogen, was used for the measurements.

The heat capacity observations are given in Table IV and are shown in Fig. 1. The value marked with an asterisk is high due to premelting. One international joule was taken as 4.1832 cal-

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[5] Cawood and Patterson, *Trans. Faraday Soc.*, **29**, 514 (1933).

[6] Terwen, *Z. physik. Chem.*, **91**, 469 (1916).

[7] Perry and Bardwell, THIS JOURNAL, **47**, 2629 (1925).

[8] Bunsen, *Ann. Physik*, **46**, 101 (1814).

[9] Faraday, *Ann. chim. phys.*, [3] **15**, 277 (1845).

ories in calculating energy. The calorimetric observations were corrected for vaporization into the small unoccupied volume in the calorimeter and the attached line. In making the correction the density of the liquid was taken from the work of Cook and Robinson[3] and the density of the solid was estimated with sufficient approximation for this small correction.

TABLE IV

MOLAL HEAT CAPACITY OF CYANOGEN

(0°C. = 273.10°K.)

Molecular weight, 52.036, 2.9280 moles in calorimeter.

T, °K.	ΔT	C_p, cal./deg./mole	T, °K.	ΔT	C_p, cal./deg./mole
14.89	1.950	0.840	130.53	5.751	13.39
17.56	2.868	1.268	136.46	6.180	13.67
20.72	3.395	1.883	142.47	5.874	14.04
23.62	2.470	2.534	148.24	5.607	14.39
25.87	2.040	2.993	154.14	5.998	14.71
28.66	3.507	3.501	160.15	5.737	15.05
31.83	2.895	4.135	165.94	5.509	15.34
35.59	4.681	4.846	171.81	5.875	15.68
39.83	3.915	5.544	177.78	5.626	16.06
43.69	3.833	6.133	183.59	5.392	16.44
47.28	3.424	6.625	189.19	5.197	16.77
51.03	4.096	7.142	195.02	5.994	17.15
55.06	4.004	7.675	201.17	5.758	17.54
58.97	4.025	8.115	207.13	5.641	17.90
63.28	4.678	8.506	213.28	5.432	18.34
68.24	5.265	8.965	218.87	5.214	18.74
73.49	5.264	9.435	224.35	5.020	19.14
79.11	5.746	9.929	229.62	4.861	19.49
84.71	5.335	10.27	234.71	4.676	19.88
90.26	5.783	10.73	239.89	4.450	20.59*
95.85	5.410	11.12	245.27	Melting point	
101.49	5.875	11.52	246.32	1.606	25.15
107.20	5.532	11.89	248.46	2.386	25.08
112.96	5.972	12.28	251.07	2.577	25.12
118.77	5.640	12.67	253.82	2.532	25.35
124.64	6.064	13.02	251.95	Boiling point	

TABLE V

MOLAL HEAT CAPACITY OF CYANOGEN

Molecular weight, 52.035. Values taken from a smooth curve through the observations.

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}
15	0.86	140	13.91
20	1.76	150	14.47
25	2.82	160	15.02
30	3.78	170	15.58
35	4.74	180	16.20
40	5.57	190	16.82
45	6.33	200	17.45
50	7.02	210	18.11
60	8.20	220	18.82
70	9.13	230	19.54
80	9.97	240	20.27
90	10.71	245.27	Melting point
100	11.41	250	25.17
110	12.08	251.95	Boiling point
120	12.73	255	25.27
130	13.35		

Heat capacity values taken from a smooth curve through the data are given in Table V. The curve should give the heat capacity to within 0.2% above 35°K. At 20°K. the error may be about 1% and at 15°K. as much as 5%.

The Heat of Fusion of Cyanogen.—A summary of the heat of fusion data is given in Table VI. The measurements were started a little below the melting point and ended somewhat above. A correction was applied for the $\int C_p\,dT$ and for the small amount of premelting that had occurred at the starting temperature due to the five thousandths of one mole per cent. impurity.

TABLE VI

MOLAL HEAT OF FUSION OF CYANOGEN

Melting point 245.27° K. (0°C. = 273.1°K.)

Temperature interval	Heat added per mole	$\int C_p\,dT$	Premelting	ΔH, cal. mole^{-1}
242.403–249.404	2142.8	208.0	3.6	1938
242.471–247.672	2084.7	151.7	3.7	1937
242.503–247.575	2082.5	147.7	3.7	1939
			Mean value	1938 ± 1

The Heat of Vaporization.—The heat of vaporization was measured by evaporating the cyanogen at constant pressure and absorbing the gas in a bulb containing 10 M sodium hydroxide. The absorption bulb had a small mercury trap. The rate of absorption of cyanogen in sodium hydroxide solution of lower concentration than 10 M was somewhat slow but the absorption was easily completed when the 10 M solution was used. The results are summarized in Table VII.

TABLE VII

MOLAL HEAT OF VAPORIZATION OF CYANOGEN

Boiling point 251.95°K. (0°C. = 273.10°K.). Molecular weight, 52.036.

Moles vaporized	Time of energy input, min.	ΔH, cal. mole^{-1}
0.20791	48	5568
.21620	48	5580
.21630	48	5579
.21737	48	5576
	Mean	5576 ± 5
From vapor pressure equation 2, assuming a Berthelot gas		5624

The value of the heat of vaporization obtained from the vapor pressure observations and given in Table VII includes a gas imperfection correction of −151 cal. mole^{-1}. In obtaining the gas imperfection, Berthelot's equation was used with $T_c = 401.4$°K.[10] and $P_c = 59.7$ atm.[10]

The value obtained from the vapor pressure measurements is given no weight in comparison with the direct calorimetric result.

The Entropy of Cyanogen.—A summary of the calculation of the entropy from calorimetric data is given in Table VIII. The correction for gas imperfection was calculated from the Berthelot gas expression

$$S_{\text{ideal}} - S_{\text{actual}} = 27\ RT_c^3P/32T^3P_c$$

The entropy of cyanogen gas has recently been calculated from molecular data by Stevenson,[11] who obtained 57.90 cal. deg.$^{-1}$ mole^{-1} at 298.1°K.

TABLE VIII

THE MOLAL ENTROPY OF CYANOGEN FROM CALORIMETRIC DATA

0–15°K. Debye function, $h c\nu/k = 118$	0.307
15–245.27°K., graphical	24.298
Fusion 1938/245.27	7.901
245.27–251.95°K., graphical	0.678
Vaporization 5576/251.95	22.131
Entropy of actual gas at boiling point	55.32 ± 0.1
Correction for gas imperfection	0.11
Entropy of ideal gas at 1 atm. and 251.95°K.	55.43 cal. deg.$^{-1}$ mole^{-1}

The moment of inertia, $I = 176 \times 10^{-40}$ g. cm.^{2}, is obtained from the electron diffraction measurements of Pauling, Springall and Palmer,[12] who find the C–C distance to be 1.37 Å. and the C–N distance 1.16 Å.

The fundamental frequency assignment was taken from the work and summary of Woo and Badger[13]: $\nu_1 = 860$, $\nu_2 = 2336$, $\nu_3 = 2150$, $\nu_4 = 230$, $\nu_5 = 512$ cm.$^{-1}$. ν_4 and ν_5 refer to deformation vibrations and have an *a priori* weight of 2. ν_5 is estimated from Raman observations on liquid cyanogen and ν_4 has not been observed directly, the 230 cm.$^{-1}$ value having been obtained from differences in ultraviolet bands. Unfortunately, ν_4 and ν_5 are the values of greatest importance in calculating the entropy. An error of 10 cm.$^{-1}$ in the 230 cm.$^{-1}$ value is equivalent to 0.15 cal. deg.$^{-1}$ mole^{-1} in the entropy. The symmetry number is 2.

The values are compared in Table IX.

The absolute entropy is obtained by adding $R \ln 9 = 4.366$ cal. deg.$^{-1}$ mole^{-1}, the nuclear spin entropy, to the values given in column 4 of Table IX.

TABLE IX

COMPARISON OF ENTROPY VALUES FROM CALORIMETRIC AND FROM MOLECULAR DATA

Cal. deg.$^{-1}$ mole^{-1}.

	Calorimetric data		Molecular data	
T, °K.	Actual gas	Ideal gas	Less nuclear spin entropy	Absolute entropy
251.95	55.32	55.43	55.67	60.04
298.10	...	57.64	57.88	62.25

The agreement of the two entropy values is within the limit of error of the result based on molecular data. However, the agreement is sufficiently close to show that cyanogen approaches zero entropy as the absolute zero is approached.

Until a more complete investigation and analysis of the cyanogen band spectrum is available, the most reliable value of the entropy is the one based on the third law of thermodynamics, 57.64 cal. deg.$^{-1}$ mole^{-1} at 1 atm. and 298.1°K.

We thank Dr. T. M. Powell for assisting with the measurements.

Summary

The heat capacity of solid and liquid cyanogen has been measured from 15°K. to the boiling point.

The melting and boiling point temperatures were found to be 245.27 and 251.95°K., respectively (0°C. = 273.10°K.).

The heats of fusion and vaporization were determined by calorimetric observation to be 1938 and 5576 cal. mole^{-1}, respectively.

The vapor pressure of solid and liquid was measured and the data have been represented by the equations

Solid cyanogen 202 to 245.27°K. $\log_{10}P(\text{inter. cm. Hg}) = (-1795.9/T) - 0.001464T + 9.42442$

Liquid cyanogen 245.27 to 253°K. $\log_{10}P(\text{inter. cm. Hg}) = (-1525.7/T) - 0.0040842T + 8.96542$

The calorimetric data have been used to calculate the entropy of cyanogen gas and this value has been compared with one obtained from molecular data and it is found that the entropy of cyanogen approaches zero near the absolute zero of temperature.

Until more complete information concerning the vibrations of the cyanogen gas molecule is

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[10] Pickering, *J. Phys. Chem.*, **28**, 97 (1924).

[11] Stevenson, *J. Chem. Phys.*, **7**, 171 (1939).

[12] Pauling, Springall and Palmer, THIS JOURNAL, **61**, 927 (1939).

[13] Woo and Badger, *Phys. Rev.*, **39**, 932 (1932).

available the most reliable value of the entropy of cyanogen is the calorimetric one, 57.64 cal. deg.$^{-1}$ mole^{-1} at 298.1°K. and one atmosphere. This value does not include the nuclear spin entropy.

BERKELEY, CALIF. RECEIVED AUGUST 1, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ALBERTA]

The Decomposition of Some Iodonium Salts. Reactions with Mercury, Tellurium and Antimony

BY R. B. SANDIN, F. T. MCCLURE[1] AND F. IRWIN[2]

Recently H. J. Lucas and co-workers[3] have shown that di-*o*-tolyliodonium iodide decomposes at 155° into *o*-iodotoluene, uncontaminated by any isomeric product. They suggest that the mechanism involves a decomposition which proceeds through an intermediate, positively charged *o*-tolyl ion in which the positive charge is carried by a carbon atom. The positive *o*-tolyl ion then combines with the negative iodide ion of the iodonium salt to form a molecule of *o*-iodotoluene.

This plausible mechanism fits in with the fact that it is now known definitely that the I–I bond in diphenyliodonium iodide is an ionic, not a covalent, bond.[4] However, the authors of this paper became interested in the possibility that the decomposition of iodonium salts might, to some extent at least, be a non-ionic one and might proceed through the intermediate formation of free radicals. A non-ionic mechanism might explain the fact that the decomposition temperature of an iodonium salt depends upon the nature of the anion as well as the cation. For example, di-*o*-tolyliodonium bromide decomposes at 178°, the iodide at 155° and the sulfide at room temperature. If the decomposition involved only the positive ion, it is conceivable that the decomposition temperatures would lie closer together. Keeping the positive ion the same, we find roughly that the decomposition temperature of an iodonium salt varies directly with the electronegativity of the negative ion. Again, it is in a reaction such as this where one might look for the formation of free radicals. The latter are likely to be formed from those molecules which readily tend to undergo thermal self-decomposition at comparatively low temperatures (*e. g.*, explosives, endothermic compounds, etc.). Finally, the recent work of Waters[5] and co-workers on the decomposition reactions of the aromatic diazo compounds gave the present workers some hope in the idea that iodonium salts might behave similarly to diazonium salts.[6] Waters has shown that the diazonium chlorides can decompose by a non-ionic mechanism $(PhN_2)^+Cl^- \longrightarrow$ Ph-N=N-Cl $\longrightarrow Ph\cdot + N_2 + \cdot Cl$, giving transient free neutral aryl radicals which are identical in chemical behavior with the neutral alkyl radicals[7] which have been studied in the gaseous phase.

The authors of this paper have carried out the decomposition of diphenyliodonium chloride and sulfide and di-*p*-tolyliodonium chloride in the presence of mercury, tellurium and antimony. In all cases, reactions have occurred which suggest the intermediate formation of free aryl radicals. Similarly, Waters[5] has found that benzenediazonium chloride decomposes under acetone kept neutral with chalk, in such a way that mercury, tellurium and antimony are attacked. Waters concludes that in the reaction mixture the free phenyl radical has a transient existence and that the phenyl radical is formed by thermal or photochemical decompositions of organic molecules in the liquid phase as well as in the gaseous phase.[8]

In view of the results obtained, it seems especially tempting to assume that in the decomposition of an iodonium salt, part of it at least can decompose by way of a non-ionic mechanism. The assumption is made that in the iodonium salt the

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(1) Present address, 625 Mendota Ct., Madison, Wisconsin.

(2) Honors student in Chemistry, University of Alberta.

(3) H. J. Lucas, E. R. Kennedy and C. A. Wilmot, THIS JOURNAL, **58**, 157 (1936).

(4) Medlin, *ibid.*, **57**, 1026 (1935).

(5) (a) Waters, *J. Chem. Soc.*, 1077 (1938); (b) Makin and Waters, *ibid.*, 843 (1938); (c) Waters, *ibid.*, 113, 2007, 2014 (1937). For a thorough review on free radicals in solution, see Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

(6) There is a fundamental relationship between diazonium salts and iodonium salts in that the former are quaternary ammonium salts (*i. e.*, fully substituted ammonium salts) and the latter are fully substituted derivatives of the hypothetical $(H_2I)^+X$.

(7) For an excellent treatise see F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.

(8) (a) Zartman and Adkins, THIS JOURNAL, **54**, 3398 (1932); (b) Dull and Simons, *ibid.*, **55**, 3898, 4328 (1933); (c) Glazebrook and Pearson, *J. Chem. Soc.*, 589 (1939).