

2. Tests have shown the existence of other inner complexes of these and also other quinone oximes.

3. An increase in the complexity of the sub-

stituent groups on the organic compounds tested appears to cause a darkening in the color of the metal complexes.

SEATTLE, WASH.

RECEIVED JULY 12, 1939

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

The Entropy of Hydrogen Cyanide. Heat Capacity, Heat of Vaporization and Vapor Pressure. Hydrogen Bond Polymerization of the Gas in Chains of Indefinite Length

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

This paper reports the results of low temperature calorimetric measurements on solid and liquid hydrogen cyanide. The data have been used to calculate the entropy of hydrogen cyanide gas and the experimental result has been compared with the value calculated from available band spectrum data.

It has been shown by Sinosaki and Hara¹ and by Felsing and Drake² that hydrogen cyanide gas is partially polymerized, and it is therefore necessary to apply a correction in obtaining the entropy of HCN from the entropy of the actual gas.

The measurements were made in a calorimeter with the laboratory designation Gold Calorimeter III which has been described previously.³ The standard thermocouple which had been compared with a helium gas thermometer³ was compared with oxygen and hydrogen vapor pressures during the course of this work. Agreement was found to within 0.05° at all temperatures measured. The resistance thermometer was calibrated directly in terms of the vapor pressure of hydrogen for temperatures below 20°K.

Preparation and Purity of Hydrogen Cyanide.—Hydrogen cyanide was prepared by a method described by Perry and Porter.⁴ 18 Normal sulfuric acid was dropped on sodium cyanide until enough gas had been generated to make 300 cc. of liquid hydrogen cyanide. The gas from the generator was passed through 2 tubes of anhydrous calcium chloride and 3 tubes of phosphorus pentoxide. All of the tubes were 30 cm. long and 3 cm. in diameter. A considerable amount of a dark brown product was left in the reaction vessel.

The collected liquid was distilled three times, a portion being discarded at the beginning and end of each distillation. A purified portion of 135 cc. remained. This was distilled in a vacuum-jacketed column, for a reason

to be discussed later. The whole system could be subjected to a high vacuum and between each distillation the hydrogen cyanide was solidified by means of liquid air and pumped with a mercury diffusion pump.

The material was a clear colorless liquid and it remained so even after a portion had been allowed to stand at room temperature for about one year.

From the slight rise in heat capacity below the melting point, due to premelting, the liquid-soluble solid-insoluble impurity was estimated to be of the order of one mole in one hundred thousand moles of hydrogen cyanide.

An interesting phenomenon was observed when the solidified hydrogen cyanide was warmed from or cooled to liquid air temperatures in a glass bulb. Intense flashes of bluish-white light were emitted in the temperature range 100 to 200°K. both on warming or cooling. The static discharge probably was due to strains set up in the solid by an unequal rate of temperature change. The discharge was accompanied by a cracking sound characteristic of crystals breaking under strain. The temperature range of the effect was obtained roughly by sealing a well into the glass bulb so that a thermocouple could be introduced.

The above effect is an interesting demonstration of the necessity of providing glass bulbs with a protective sheath to prevent contact of such materials with liquid air in case of breakage. It appears that solid hydrogen cyanide cooling in contact with liquid air would be practically certain to explode although we did not try it. Electrostatic effects in some degree are to be expected when such materials are fractured.

The Melting Point and Vapor Pressure of Hydrogen Cyanide.—A summary of the melting point investigation is given in Table I.

The values of the vapor pressure are given in Table II. The measurements were made by means of a Société Générale cathetometer with a precision of 0.002 cm., used as a comparison instrument with a standard meter. 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. The meniscus height corrections were taken from the work of Cawood and Patterson⁵ and the corrections to international

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

(1) Sinosaki and Hara, *Tech. Repts. Tohoku Univ.*, **8**, 297 (1929).

(2) Felsing and Drake, *This Journal*, **58**, 1714 (1936).

(3) Glauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

(4) Perry and Porter, *This Journal*, **48**, 299 (1926).

TABLE I
MELTING POINT OF HYDROGEN CYANIDE
0°C. = 273.10°K.

Time	% melted	T. °K. resistance thermometer	T. °K. Thermocouple
1-26-38			
10:46 P.M.	Heated into melting point		
1-27-38			
1:20 P.M.	10	259.863	259.85
2:10 P.M.	10	259.854	259.85
3:48 P.M.	Supplied heat		
6:20 P.M.	40	259.850	259.86
7:02 P.M.	40	259.855	259.86
8:00 P.M.	Supplied heat		
10:00 P.M.	70	259.861	259.86
11:00 P.M.	70	259.857	259.86
11:35 P.M.	70	259.858	259.86
	Accepted value		259.86

cm. of Hg were made by means of data given in the "I.C.T."⁶

Several vapor pressure observations were made on the solid but it became evident that the results were slightly high due to the presence of a small amount of solid in the line just above the calorimeter. For this reason these observations are omitted. In solidifying the substance for calorimetric measurements this was avoided by the sudden introduction of an atmosphere of helium with the material at the freezing point and practically all solid. Cooling was then accomplished before diffusion could take place. The possibility that helium might be entrapped in the solid with subsequent diffusion during the vapor pressure measurements caused us to forego this method of keeping the tube open in that case.

TABLE II
VAPOR PRESSURE OF HYDROGEN CYANIDE
0°C. = 273.10°K.

T. °K. Resistance thermometer	P inter. cm. Hg	P _{obsd.} - P _{calcd.}	T _{obsd.} - T _{calcd.}	Remarks
259.854	14.040			Triple point
259.855	14.040			Triple point
259.858	14.048*			Triple point
259.856	14.040	0.000	0.000	Value accepted
265.083	18.170	-.006	.007	Liquid
268.017	20.915	.004	-.004	Liquid
272.004	25.178	.012	-.010	Liquid
276.221	30.411	-.008	.006	Liquid
280.090	36.003	.003	-.002	Liquid
285.020	44.284	-.012	.007	Liquid
289.929	54.043	.005	-.002	Liquid
295.015	65.873	-.016	.006	Liquid
298.801	76.016	.015	-.005	Liquid

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

The data in Table II have been represented by and compared with the equation

$$\log_{10} P \text{ (inter. cm. Hg)} = -\frac{1600.8}{T} - 0.0017835 T + 7.77114 \quad (1)$$

The temperatures are given to 0.001° only because of relative accuracy. The triple point value marked with an asterisk was given no weight because a slight superheating of the surface may have occurred when the solid was nearly all melted and that which remained was at the bottom of the container due to its greater density.

From Equation 1 the boiling point of hydrogen cyanide was determined to be 298.80°K.

The melting and boiling point temperatures obtained by various observers are given in Table III.

TABLE III
MELTING AND BOILING POINT TEMPERATURES OF HYDROGEN CYANIDE

M. P. T. °K.	B. P. T. °K.	Observer
259	299	Gautier ⁷ (1869)
262	298	Nef ⁸ (1895)
259.70	...	Tammann ⁹ (1899)
259.76	...	Lespieau ¹⁰ (1905)
259.70	298.7	Bredig and Teichmann ¹¹ (1925)
258.24	298.75	Perry and Porter ⁴ (1926)
260.08	298.8	Sinosaki and Hara ¹² (1927)
259.86	298.80	This research

The Heat Capacity of Hydrogen Cyanide.—The heat capacity data are given in Table IV, and are shown graphically in Fig. 1. The amount was determined by condensing the substance in an evacuated bulb which was weighed. This was especially convenient since hydrogen cyanide boils a little above room temperature. The molecular weight was taken as 27.026 and 3.3721 moles were used for the measurements; 4.1832 international joules was taken as one calorie. The heat capacity observations were corrected for vaporization into the small volume of calorimeter and line at all temperatures where the effect was appreciable. This correction which involves no appreciable inaccuracy utilized the data of Sinosaki and Hara¹ on the density of liquid hydrogen cyanide and the density of the

(7) Gautier, *Ann. chim. phys.*, [4] **17**, 121 (1869).

(8) Nef, *Ann.*, **287**, 325 (1895).

(9) Tammann, *Ann. Physik*, **68**, 576 (1899).

(10) Lespieau, *Compt. rend.*, **140**, 855 (1905).

(11) Bredig and Teichmann, *Z. Elektrochem.*, **31**, 449 (1925).

(12) Sinosaki and Hara, *Tech. Reports, Tohoku Univ.*, **6**, No. 3, 19 (1927).

TABLE IV

THE HEAT CAPACITY OF HYDROGEN CYANIDE

0°C. = 273.10°K. (molecular weight = 27.026) 3.3721 moles in calorimeter.

Series	T, °K.	ΔT	C _p , cal./deg./mole	Series	T, °K.	ΔT	C _p , cal./deg./mole
I	14.77	1.029	0.372	II	166.30	1.812	10.70
I	16.85	2.333	0.523	III	166.40	3.370	10.72
I	19.04	1.669	0.746	II	168.23	1.784	10.81
I	21.64	3.410	1.013	III	169.55	2.665	11.93*
I	25.82	5.047	1.423	II	170.20	1.920	12.19*
I	29.79	2.818	1.864	III	171.27	0.674	11.68*
I	32.85	3.104	2.232	II	172.31	2.022	11.23*
I	36.10	3.260	2.607	III	172.73	2.074	10.93
I	39.43	3.321	3.005	II	174.42	2.041	10.95
I	43.43	4.532	3.477	III	175.81	3.789	10.96
I	47.67	3.883	3.940	I	177.04	6.334	11.01
I	51.72	4.060	4.412	II	177.58	3.720	11.04
I	56.15	4.649	4.877	II	181.51	3.611	11.19
I	60.53	4.161	5.275	I	183.61	6.065	11.23
I	65.00	4.775	5.628	I	190.30	5.788	11.52
I	69.81	4.885	6.042	I	196.32	5.569	11.76
I	74.68	4.868	6.428	I	202.10	5.350	12.02
I	79.79	5.377	6.795	I	207.76	5.272	12.22
I	84.93	4.958	7.158	I	213.43	5.542	12.49
I	89.95	5.029	7.456	I	224.74	5.254	13.08
I	94.97	5.150	7.718	I	230.94	5.440	13.42
I	102.06	4.725	8.126	I	236.66	5.228	13.77
I	106.94	4.485	8.349	I	242.51	5.525	14.09
I	111.60	4.809	8.599	I	248.43	5.304	14.47
I	116.85	5.482	8.833	I	254.14	5.110	14.79
I	122.48	5.215	9.034		259.86		Melting point
II	124.67	8.848	9.121	IV	266.57	4.112	16.92
I	127.73	4.976	9.244	V	271.33	6.049	16.85
II	133.19	8.234	9.453	IV	271.76	4.870	16.82
I	133.34	4.736	9.468	IV	277.15	4.790	16.84
I	138.42	5.219	9.631	V	277.97	5.898	16.95
II	141.10	7.705	9.780	IV	282.77	5.083	16.86
I	143.62	4.986	9.882	V	284.63	5.784	16.92
I	148.75	5.012	10.04	IV	288.48	4.978	16.93
II	149.34	8.852	10.12	V	291.12	5.648	17.01
I	154.04	5.242	10.27	IV	294.02	4.509	16.94
II	157.89	8.319	10.42	V	297.12	5.090	16.96
I	159.29	5.053	10.44	IV	298.34	2.976	16.88
II	163.70	3.346	10.63		298.80		Boiling point
I	164.43	4.869	10.62				

solid was estimated with sufficient accuracy from rough observations during the preparation of the material. A smooth curve through the data should give the heat capacity to within 0.2% above 35°K. At 20°K. the inaccuracy may be about ±1% and at 15°K. about ±5%. Values taken from a smooth curve are given in Table V.

TABLE V

THE HEAT CAPACITY OF HYDROGEN CYANIDE

Values taken from smooth curve through the data. Molecular weight, 27.026.

T, °K.	C _p , cal. deg. ⁻¹ mole ⁻¹	T, °K.	C _p , cal. deg. ⁻¹ mole ⁻¹
15	0.382	160	10.48
20	0.835	170	11.20
25	1.336	170.37	31 maximum
30	1.886	180	11.12
35	2.470	190	11.50
40	3.069	200	11.90
45	3.646	210	12.32
50	4.214	220	12.82
60	5.230	230	13.37
70	6.058	240	13.95
80	6.817	250	14.55
90	7.456	259.86	Melting point
100	8.008	260	16.82
110	8.520	270	16.86
120	8.938	280	16.90
130	9.333	290	16.94
140	9.730	298.80	Boiling point
150	10.11	300	16.97

A narrow region of high heat capacity occurred near 170°K. as is shown in Fig. 1. The points marked with asterisks in Table IV are not plotted in Fig. 1 because the temperature interval used was too large to allow them to be considered as values of differential heat capacity in this region of rapid variation. When the effect was first noted, during some preliminary observations, it was thought that it might be due to impurity, so the hydrogen cyanide was removed and fractionated in a vacuum-jacketed column. This produced no change in the effect.

Attainment of thermal equilibrium was a little less rapid in the region 140 to 170°K. and in order to determine whether the region of high heat capacity was due to some false equilibrium in the solid, the material was allowed to stand at approximately 165°K. for three days. No change in the effect was found.

In order to determine the entropy connected with the above effect, the total energy absorbed over a temperature of several degrees was measured. While the heat absorption was not sharp,

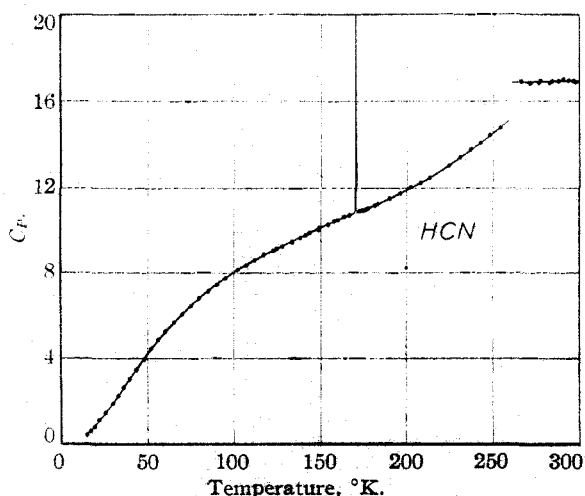


Fig. 1.—Heat capacity in calories per degree per mole of hydrogen cyanide.

it was possible, without much arbitrariness, to subtract what may be considered the normal $\int C_p dT$ over the interval and thus assign a value to the heat effect accompanying the phenomenon. These values are given in Table VI. The first three values given correspond to the measurements made before the material was removed for fractionation in the column. The differences between the several values are somewhat greater than might be expected but we do not feel that any significance is to be attached to the variations.

The effect was also studied by means of cooling rate observations in this region. The temperature of the heavy metal cylinder which surrounded the calorimeter was set a little below that of the calorimeter, which thus cooled very slowly. The rate of cooling in the region of normal heat capacity was 0.0103° per minute while at the maximum of the heat capacity curve the rate decreased to 0.0044° per minute. The cooling rates give the best available information as to the character of the curve. The maximum heat capacity of $31 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ occurred at 170.37°K . The cooling curve data, which are shown in Fig. 2, were also used to calculate a value for the total heat effect. This value is included in Table VI. The agreement of the results obtained by heating and cooling shows that no appreciable irreversibility is involved.

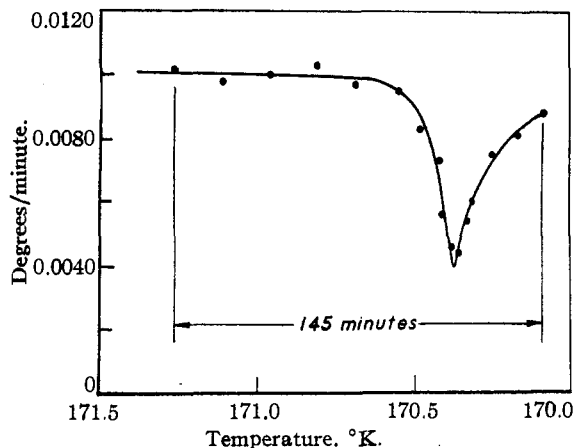
TABLE VI

MOLAL ENERGY ABSORPTION OF HYDROGEN CYANIDE NEAR 170°K .

Amounts given are in calories per mole above the heat corresponding to the "normal" heat capacity. Maximum heat capacity at 170.37°K .

No. of energy increments	Temp. interval	Heat input cal. mole ⁻¹	$\int C_p dT$	ΔH cal. mole ⁻¹
Before fractionation				
1	167.166-173.499	99.34	94.80	4.5
A few % melted, stood 10 hrs. resolidified				
2	169.231-173.320	64.93	61.15	3.8
3	168.198-173.759	87.48	83.15	4.3
Material removed from calorimeter and fractionated				
0	From graphical integration of cooling rate			3.2
2	168.224-171.969	59.36	55.26	4.1
10	167.690-171.749	63.43	59.89	3.5
1	168.574-172.490	61.30	58.22	3.1
Mean value 3.8				

The entropy change corresponding to the $3.8 \text{ cal. mole}^{-1}$ is only $0.022 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. The physical process which results in such a small change in entropy must be one involving the actions of large groups of hydrogen cyanide molecular units.

Fig. 2.—Cooling rate curve for hydrogen cyanide near 170°K .

As has been pointed out by Smyth and McNeight,¹⁸ the low dielectric constant of the solid precludes any possibility of appreciable molecular rotation in the crystalline state and the hydrogen bond polymerization to be discussed later in this paper should be effective in preventing rotation.

The Heat of Fusion of Hydrogen Cyanide.

The determinations were made in the usual manner, each measurement was started somewhat below the melting point and ended somewhat above. Corrections for the $\int C_p dT$ were made. The results are given in Table VII.

TABLE VII

MOLAL HEAT OF FUSION OF HYDROGEN CYANIDE

Melting point 259.86°K . $0^\circ\text{C.} = 273.10^\circ\text{K}$. Molecular weight, 27.026.

Temp. interval	Heat added per mole	$\int C_p dT$	ΔH_f cal. mole ⁻¹
257.400-263.844	2142.5	132.8	2010
257.388-263.975	2144.7	135.8	2009
257.030-264.166	2155.3	147.0	2008
Average value 2009			

The Heat of Vaporization of Hydrogen Cyanide.

The heat of vaporization was measured at constant pressure, the gas being absorbed in a bulb containing 150 cc. of 4 M sodium hydroxide and arranged with a mercury trap at the bottom. Only the lower half of the calorimeter heater was used to supply energy and hydrogen cyanide was evaporated only from the upper part of the calorimeter. The data are given in Table VIII, which also lists a value obtained from the vapor pressure observations represented by Equation 1. In using the equation

$$\Delta H_{\text{vaporization}} = \frac{dP}{dT} T \Delta V$$

(18) Smyth and McNeight, *THIS JOURNAL*, **58**, 1723 (1936).

we have made use of the liquid and gas density data of Sinosaki and Hara¹ which are discussed later in this paper. $(PV/RT) = 0.9239$ at 1 atmosphere and 298.80°K ., which leads to a gas volume of 22,655 cc. per mole of HCN at the boiling point. The molal volume of the liquid is 40 cc. at this temperature.

TABLE VIII

HEAT OF VAPORIZATION OF HYDROGEN CYANIDE
Boiling point 298.80°K . 0°C . = 273.10°K . Molecular weight, 27.026.

Moles evap.	Time, min.	ΔH cal., deg. ⁻¹ mole ⁻¹
0.21455	45	6007
.22473	45	6031
.22549	45	6033
.22656	45	6035
Average value		6027

Calcd. from vapor pressure Equation 1 6083

The value of the heat of vaporization obtained from the vapor pressure data is given in weight in comparison with the calorimetric value.

The Entropy of Hydrogen Cyanide from Calorimetric Data.—A summary of the entropy calculation for the equilibrium mixture of hydrogen cyanide and its associated forms at the boiling point is given in Table IX.

TABLE IX

THE ENTROPY OF HYDROGEN CYANIDE

0-15°K., Debye extrapolation, $hcv/k = 160$	0.126
15-259.86°K., Graphical	16.770
Heat absorption above normal C_p near 170.37 = $3.8/170.37$	0.022
Fusion, 2009/259.86	7.731
259.86-298.80°K., Graphical	2.360
Entropy of liquid at 298.80°K .	27.01
Vaporization, 6027/298.80	20.17
	47.18
Gas imperfection correction	0.03
Entropy of 27.026 g. of gas at 298.80°K .	47.21

The correction for gas imperfection was made by assuming Berthelot's equation of state and the critical constants for hydrogen chloride

$$T_c = 324.5^\circ\text{K}.,^{14} P_c = 83 \text{ atm}.,^{14}$$

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

$$= 0.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

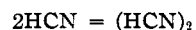
Although Berthelot's equation does not hold for an associated gas, the above estimate should be fairly accurate since the gas consists largely of the monomer.

(14) Pickering, *J. Phys. Chem.*, **28**, 97 (1924).

The Polymerization of Hydrogen Cyanide Gas.—In order to calculate the entropy of monomeric hydrogen cyanide gas from the above results, it is necessary to consider the association of the substance. Sinosaki and Hara¹ have made a very extensive investigation of the gas density of hydrogen cyanide as a function of temperature and pressure and more recently Felsing and Drake² have reported single observations at each of three temperatures which show that association exists.

The results in this paper are based on the work of Sinosaki and Hara and we have not used their observations at pressures below 0.3 atmosphere because the accuracy limitations of gas density measurements make them unsuitable for the accurate determination of the extent of association. In making corrections for gas imperfection the equation $PV = RT(1 + \lambda P)$ was used and λ was taken as -0.0056 at the boiling point of hydrogen cyanide, this being the value for hydrogen chloride considered to be a Berthelot gas. Similarly values of λ were obtained at other temperatures. The value of λ for associated forms is undoubtedly larger but it may be shown readily that it is unimportant to consider the difference. The critical data of hydrogen cyanide were not used to calculate λ because it may be shown that a considerable amount of the polymer is present at the critical point. The effect of variation of λ will be discussed later.

The first calculations were based on the assumption that



represented the polymerization with

$$K = \frac{\alpha/2(1 - \alpha/2)}{(1 - \alpha)^2 P}$$

where α represents the fraction of the material in the dimeric form and

$$1 - \alpha/2 = \frac{(PV)_{\text{observed}}}{RT(1 + \lambda P)}$$

$(PV)_{\text{observed}}$ was taken as the volume of one mole on a monomeric basis. The values of K calculated showed a very considerable decrease with decreasing pressure at the several temperatures and even impossibly large values of λ could not appreciably alter the trend. Calculations based on the presence of some hydrogen isocyanide assumed to be out of equilibrium with hydrogen cyanide and the formation of dimers in the various possible combinations did not satisfy the data.

The assumption of specific formation of a trimer

gave impossible results and indicated that the average polymer was intermediate between a dimer and trimer and thus the presence of both.

It is evident that if the equilibrium constants calculated on the assumption of dimer formation are plotted, the true constant for the formation of $(\text{HCN})_2$ will be obtained by extrapolating the values to zero pressure. Values so obtained are shown in Table X, together with the false values corresponding to one atmosphere to show the trend.

TABLE X
EQUILIBRIUM CONSTANTS FOR THE REACTION $2\text{HCN} = (\text{HCN})_2$

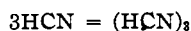
T, °K.	$K(p=0) \times 10^3$	$K(p=1) \times 10^2$
	True	False
273.1	9.5	...
303.0	5.6	8.6
333.1	3.4	4.2
373.1	2.0	2.3
462.3	1.0	1.0

The logarithms of the values of the constants given in the second column of Table X fall nearly on a straight line when plotted against the reciprocal of the absolute temperature and may be represented by the equation

$$\log_{10} K_D = (717/T) - 3.616 \quad (2)$$

where K_D is the equilibrium constant for dimer formation.

K_T for the reaction



was then calculated at the several temperatures.

$$K_T = \frac{\beta/3(1-\alpha/2-2\beta/3)^2}{(1-\alpha-\beta)^2 P^2} \quad (3)$$

where α and β are the fractions associated to dimer and trimer, respectively, and

$$(1 - \alpha/2 - 2\beta/3) = \frac{(PV)_{\text{observed}}}{RT(1 + \lambda P)} \quad (4)$$

Values of K_T obtained by means of the above equations decreased somewhat with decreasing pressure. Again extrapolating to zero pressure, the values 0.055, 0.0087, 0.0030 and 0.0013 atm.⁻² are found for K_T at the temperatures 273.1, 303.0, 333.1 and 373.1°K., respectively. These results can be represented by the equation

$$\log_{10} K_T = (1905/T) - 8.320 \quad (5)$$

If hydrogen cyanide forms both a dimer and trimer, one might reasonably ask whether higher polymers are not present also and there are good reasons for believing this to be the case. The trend in K_T with pressure is in the right direction

to indicate higher polymers but this places too great a strain on the gas density to be considered as more than a suggestion. However, Kumler¹⁵ has explained the phenomenally high dielectric constants of such liquids as hydrogen cyanide and hydrogen fluoride by assuming chains due to hydrogen bond formation and it is difficult to see any other explanation for the high electric moment.

There is no evident limit to the length of the hydrogen cyanide chains possible by such a mechanism except that the longer groupings are less stable thermodynamically. Equations 2 and 5 may be used as a basis for estimating the fractions of higher polymers.

Bauer, Beach and Simons¹⁶ recently have presented electron diffraction evidence which indicates that hydrogen fluoride gas consists principally of zig-zag chains due to hydrogen bonds.

There are two simple tests which may be applied to Equations 2 and 5 to judge their reasonableness. First: the entropy change in the formation of the dimer should roughly approximate the Trouton value for the reduction by one of the number of moles of gas by a condensation process and the change for trimer formation should be about twice that for the above quantity. Second: the heat of formation for the trimer from the monomer should be of the order of twice the value for the dimer. The following values are found

$$\Delta S_D^\circ = -16.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta S_T^\circ = -38 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_D^\circ = -3,280 \text{ cal. mole}^{-1}$$

$$\Delta H_T^\circ = -8,720 \text{ cal. mole}^{-1}$$

Taking the increments between the dimer and trimer values as more representative of further additions, a general equation may be written as

$$\Delta F^\circ = -RT \ln K_n = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

$$= 7600 - 5440n - T(26.5 - 21.5n) \quad (7)$$

where n is the number of molecules combined in the polymer.

From Equation 7 and equations similar to Equation 3, the fractions associated in the various polymers have been calculated and are given in Table XI.

Since deuterium bonds would be expected to be stronger than those of hydrogen gas density measurements on deuterium cyanide should show a larger, more easily studied, polymerization.

(15) Kumler, *THIS JOURNAL*, **57**, 600 (1935).

(16) Bauer, Beach and Simons, *ibid.*, **61**, 19 (1939).

TABLE XI

FRACTIONS OF HYDROGEN CYANIDE GAS IN THE STRAIGHT CHAIN SERIES OF POLYMERS

$T = \text{boiling point} = 298.80^\circ\text{K.}$, $P = 1 \text{ atmosphere.}$

Polymer	Fraction
Dimer	0.0988
Trimer	.0268
Tetramer	.0064
Pentamer	.0015
Hexamer	.0003
Heptamer	.00004

The question also arises as to whether hydrogen bond polymerization does not occur to a small extent in gaseous water and we believe that it can be answered in the affirmative in the following way. From the gas density data as summarized by Keenan and Keyes,¹⁷ $\lambda = -0.016 \text{ atm.}^{-1}$ for saturated vapor at the boiling point. If the specific effects due to hydrogen bonds could be eliminated, the λ for hydrogen sulfide should be larger than that for water at the same temperature. Berthelot's equation of state represents the gas density of hydrogen sulfide quite accurately at ordinary temperatures and it seems safe to assume that it does so at the boiling point of water. λ is found to be -0.004 and from this we conclude that hydrogen bond association exists to the extent of about 3% in gaseous water at one atmosphere and 373.1°K. A larger effect would be anticipated in the case of deuterium oxide gas.

The Entropy of Monomeric Hydrogen Cyanide.—The entropy of the equilibrium mixture in hydrogen cyanide gas is given by the expression

$$S^\circ_{\text{mixture}} = (1 - \alpha - \beta - \dots) S^\circ_{\text{HCN}} + \alpha/2 S^\circ_{\text{D}} + \beta/3 S^\circ_{\text{T}} + \dots - R(1 - \alpha/2 - 2\beta/3 - \dots) [N_{\text{M}} \ln N_{\text{M}} + N_{\text{D}} \ln N_{\text{D}} + N_{\text{T}} \ln N_{\text{T}} + \dots] \quad (8)$$

$$= S^\circ_{\text{HCN}} + \alpha/2 \Delta S^\circ_{\text{D}} + 2\beta/3 \Delta S^\circ_{\text{T}} + \dots + R(1 - \alpha/2 - 2\beta/3 - \dots) \sum N \ln N \quad (9)$$

$$S^\circ_{\text{HCN}} = S^\circ_{\text{mixture}} - \alpha/2 \Delta S^\circ_{\text{D}} - \beta/3 \Delta S^\circ_{\text{T}} - \dots + R \left[(1 - \alpha - \beta - \dots) \ln \frac{(1 - \alpha - \beta - \dots)}{(1 - \alpha/2 - 2\beta/3 - \dots)} + \alpha/2 \ln \frac{\alpha/2}{(1 - \alpha/2 - 2\beta/3 - \dots)} + \beta/3 \ln \frac{\beta/3}{(1 - \alpha/2 - 2\beta/3 - \dots)} + \dots \right] \quad (10)$$

The total entropy correction to be added to the value for the entropy of the equilibrium mixture on account of polymerization is $0.73 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, of which only $0.05 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ is due to all polymers higher than the trimer.

To test the importance of the particular choice of λ , the calculations were repeated with $\lambda = -0.025 \text{ atm.}^{-1}$. With the larger λ the $0.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ correction for ordinary gas imperfection, given in Table IX, is increased to $0.12 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. It is sufficient to include only polymers up to and including the trimer in making the comparison. The following result was obtained

$$\lambda = -0.025: \text{ correction} = 0.12 + 0.57 = 0.69 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\lambda = -0.0056: \text{ correction} = 0.03 + 0.68 = 0.71 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

The difference of $0.02 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ for such a large variation of λ makes it evident that the final result does not depend appreciably on the particular value selected as the best estimate.

Comparison of the Entropy Values from Calorimetric and Spectroscopic Data.—The necessary molecular data for calculating the entropy were taken from the band spectrum observations of Bartunek and Barker,¹⁸ who give a summary of previous observers. The moment of inertia, I , is $18.72 \times 10^{-40} \text{ g. cm.}^2$ and the observed vibrational quanta for excitation to the first level of each type are 2089.0 , 712.1 and 3312.9 cm.^{-1} respectively. The 712.1 cm.^{-1} corresponds to the bending motion and has a weight of 2.

$$S_{\text{Translation}} = 3/2 R \ln M + 5/2 R \ln T - R \ln P - 2.300$$

$$S_{\text{Rotation}} = R \ln IT + 177.676$$

The vibrational entropy was calculated by means of the Einstein formula. The nuclear spins of H, C and N are $1/2$, 0 and 1, respectively; thus the spin contribution is $R \ln (2 \times 1/2 + 1) (2 \times 1 + 1) = R \ln 6 = 3.560 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. A comparison of the entropy values at the boiling point 298.80°K. and at 298.10°K. is given in Table XII. The value $48.23 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ for 298.10°K. is identical with the result of a similar calculation made by Gordon,¹⁹ who also considered

TABLE XII

COMPARISON OF CALORIMETRIC AND SPECTROSCOPIC VALUES FOR THE ENTROPY OF HYDROGEN CYANIDE

Temperature, °K.	298.80	298.10
Equilibrium gas, actual	47.18 ± 0.1	...
Equilibrium gas, ideal	47.21	...
Correction for polymerization	0.73	...
HCN ideal, experimental	47.94	47.92
HCN spectroscopic less nuclear spin contribution	48.25	48.23
Correction for nuclear spin	3.56	3.56
Absolute entropy, cal. deg. ⁻¹ mole ⁻¹	51.81	51.79

(17) "Thermodynamic Properties of Steam," Keenan and Keyes, John Wiley and Sons, Inc., New York, 1936.

(18) Bartunek and Barker, *Phys. Rev.*, **48**, 516 (1935)

(19) Gordon, *J. Chem. Phys.*, **5**, 30 (1937).

the effect of polymerization. However, Gordon was unaware of the experiments of Sinosaki and Hara¹ and thus was led to assume that only a dimer was formed.

The experimental value is 0.31 cal. deg.⁻¹ mole⁻¹ lower than the one obtained from molecular data. We believe that not more than 0.1 cal. deg.⁻¹ mole⁻¹ of this can be attributed to calorimetric error. The weakest point in the calculation appears to be the strain placed on the gas density observations in obtaining the temperature coefficients of the association constants. The density measurements of Sinosaki and Hara¹ have been made with great care but the amounts of polymeric forms decrease so rapidly with increasing temperature that high accuracy is not to be expected when the data are used to calculate association constants. Here, as in so many other cases of equilibrium measurements, the onset of error is gradual and the straight line obtained with a $\log K$ vs. $1/T$ plot must not be taken too seriously.

The net correction for the presence of polymers is only 0.73 cal. deg.⁻¹ mole⁻¹; the entropy terms in Equation 10 which are based on the temperature coefficient of gas density amount to 1.28 cal. deg.⁻¹ mole⁻¹. Thus we conclude that the entropy obtained from the third law of thermodynamics is in agreement with the value obtained from molecular data.

The entropy value 48.23 cal. deg.⁻¹ mole⁻¹, which does not include the nuclear spin effect, is the one which should be used in ordinary thermodynamic calculations for monomeric hydrogen cyanide. The entropy of liquid hydrogen cyanide at 298.1 is 26.97 cal. deg.⁻¹ mole⁻¹.

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

Summary

The heat capacity of solid and liquid hydrogen cyanide has been measured from 14 to 300°K.

The melting and boiling points were found to be 259.86 and 298.80°K., respectively (0°C. = 273.10°K.).

The heat of fusion is 2009 cal. mole⁻¹.

An energy absorption of 3.8 cal. mole⁻¹ occurred over a small temperature range with a maximum at 170.37°K.

The heat of vaporization at the boiling point was determined calorimetrically to be 6027 cal. mole⁻¹.

The vapor pressure of liquid hydrogen cyanide has been measured and the data have been represented by the equation liquid, 259.86 to 298.9°K.

$$\log_{10}P \text{ (inter. cm. Hg)} = -(1600.8/T) - 0.0017835 T + 7.77114$$

The triple point pressure is 14.040 inter. cm. Hg.

The available gas density data on hydrogen cyanide have been used to show that multiple polymerization exists. The data are taken to indicate indefinite straight chain hydrogen bond polymerization in the gas, as suggested by Kumler for the liquid, in explanation of its abnormally high dielectric constant. The fraction of the gas in the various polymeric forms up to the heptamer has been calculated.

It has been estimated that hydrogen bond polymerization occurs in saturated water vapor to the extent of 3% at the boiling point.

The data and the third law of thermodynamics have been used to calculate the entropy of monomeric hydrogen cyanide gas at 298.10°K. and 1 atm. The experimental value 47.92 cal. deg.⁻¹ mole⁻¹, which contains a small possible error on account of uncertainty in the temperature coefficients of the polymerization reactions, is in agreement with the value 48.23 cal. deg.⁻¹ mole⁻¹, calculated from the band spectrum data.

The entropy of liquid hydrogen cyanide at 298.1°K. is 26.97 ± 0.05 cal. deg.⁻¹ mole⁻¹.

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RECEIVED JULY 5, 1939