231. *Certain Physical Properties of Cyanogen and its Halides.*

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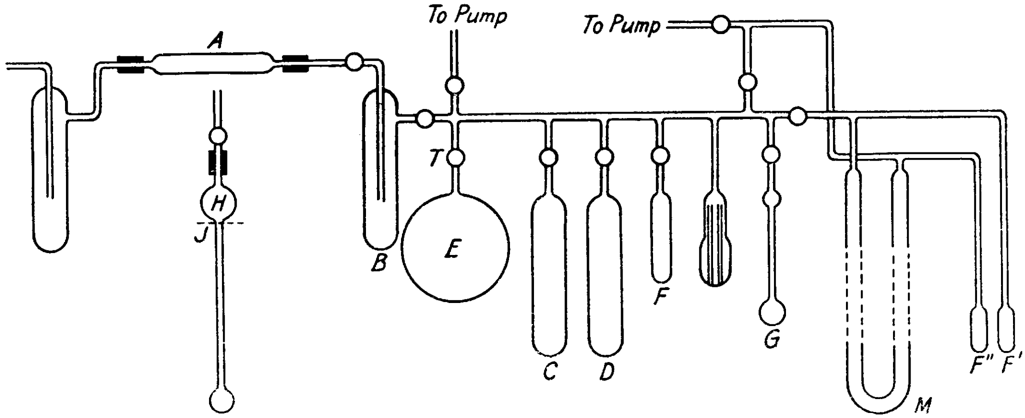
FARADAY (*Phil. Trans.*, 1845, **135**, 1, 155) measured the density of liquid cyanogen and its vapour pressure (his material probably contained carbon dioxide), and Perry and Bardwell (*J. Amer. Chem. Soc.*, 1925, **47**, 2629) determined the latter property over a range of temperature. Even fewer data are available on the properties of the cyanogen halides, and these probably relate to materials of doubtful purity. The present paper describes the preparation and purification of cyanogen and cyanogen chloride, bromide, and iodide, and the measurement of some of their physical properties, particularly liquid density and surface tension. The parachors and other constants have been determined and their significance is discussed.

EXPERIMENTAL.

Materials.—The dissociation of mercuric cyanide was unsatisfactory for the preparation of cyanogen, because the requisite temperature led also to formation of brown paracyanogen and sublimation of the starting material. After this method had been used to prepare one sample, which, incidentally, had the proper vapour pressure, it was replaced by methods involving (i) the reaction between potassium cyanide and copper sulphate (Davy and Faraday, *Phil. Trans.*, 1823, **2**, 196) and (ii) the dissociation of silver cyanide (Terwen, *Z. physikal. Chem.*, 1916, **91**, 469).

FIG. 1.



Silver cyanide was precipitated from saturated silver nitrate by the calculated weight of potassium cyanide (78% solution), rapidly filtered off, and immediately warmed with ammonia (*d*, 0·88). The argentocyanide which separated on cooling was twice recrystallised from ammonia, and kept at 140° for 4 days to remove water and ammonia. It was then a pale brown powder differing from freshly precipitated material in being insensitive to light. On dissociation in an evacuated Pyrex vessel heated by molten alkali nitrates, a little gas, presumably ammonia, was liberated between 220° and 330° and rejected; between 330° and 380° cyanogen was steadily evolved and, after passing over phosphoric oxide, was condensed. It was purified in the apparatus shown in Fig. 1, the stages being : treatment with phosphoric oxide, A, condensation in B, and finally 5 fractionations in a vacuum by using vessels B, C, and D, head and tail portions being rejected on each occasion. The effect of the fractionation was traced by condensing portions of certain fractions in the vessels F' and F'' respectively, which were connected together by the mercury manometer M. The vapour pressures of the samples were compared by immersion in liquid in the same vacuum flask, and it is evident that the material was very pure, since the later stages of fractionation did not effect any alteration in the vapour pressure.

Cyanogen (15 g.), prepared from potassium cyanide and copper sulphate solutions at 50° and dried with calcium chloride followed by phosphoric oxide, had a vapour pressure appreciably higher than the above material. This was doubtless due to carbon dioxide for, when it was removed by a more rigorous fractionation, the vapour pressure became identical with that of the silver cyanide preparation. The distillation of cyanogen is difficult because its vapour pressure is above atmospheric at practically all temperatures, and furthermore, the liquid invariably solidifies if evaporation is at all rapid. The pressure in the distillation vessel was allowed to rise until all the material liquefied, and the vapour was then permitted to escape at a rate which did not cause solid to separate.

Cyanogen chloride was prepared by saturating with chlorine at 0° the double cyanide formed by addition of sodium cyanide to excess of zinc sulphate in aqueous solution; it was distilled off and passed over calcium chloride, condensing as a white solid in an ice-salt freezing mixture (Held, *Bull. Soc. chim.*, 1887, 1727; Mauguin and Simon, *Ann. Chim. Phys.*, 1921, **15**, 19). Chlorine was removed by shaking with mercury, and the treated material was fractionated twice in a vacuum to give a final sample of 10 g.

Cyanogen bromide, obtained by adding sodium cyanide to well-stirred aqueous bromine below 15° ("Organic Syntheses," XI, 30), was distilled from the liquid, and purified by passage over calcium chloride and two vacuum fractionations; yield 10 g.

Cyanogen iodide was formed by shaking excess of powdered mercuric cyanide with ethereal iodine, and evaporating off the ether from the filtrate. It was thrice recrystallised, and finally sublimed; m. p. 146·0° (cf. 146·5°; Seubert and Pollard, *Ber.*, 1890, **23**, 1063).

Physical Properties.

Vapour Pressure.—Cyanogen. Material confined in F′ was allowed to reach a constant vapour pressure from about 1 cm. both below and above the particular value. The recorded results were constant for 45 mins. and have an accuracy of ± 0·5 mm. The two temperatures were the m. p.'s of carbon tetrachloride, — 22·9°, and methyl benzoate, — 14·4° (determined for the sample used). The vapour pressures (Table I and Fig. 2) agree with those calculated from Perry and Bardwell's (*loc. cit.*) equation, $\log_{10} p = -1818{\cdot}554/T - 5{\cdot}0183 \log_{10} T + 22{\cdot}30083$.

FIG. 2.

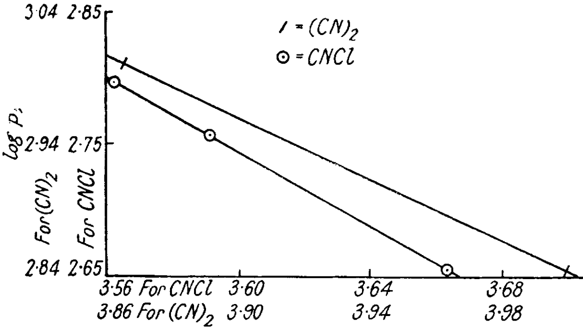
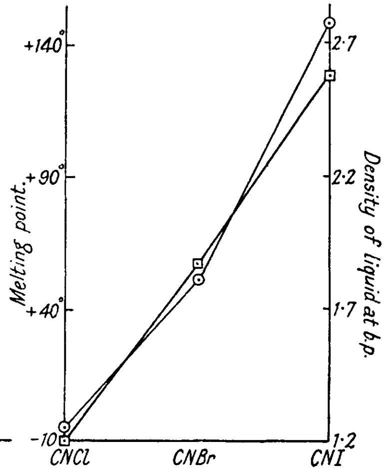


FIG. 3.



Cyanogen chloride. The temperatures were given by the m. p.'s of (i) ice, 0°, (ii) benzene, + 5·48°, and (iii) *o*-chlorophenol, + 7·75° (determined for the sample used). The results (Table I and Fig. 2) conform to $\log_{10} p = 7{\cdot}80477 - 1406{\cdot}4/T$ (cf. $\log_{10} p = 7{\cdot}840 - 1415{\cdot}4/T$; Regnault, *Mem. Acad. Roy. Sci. Franç.*, 1862, **26**, 339). Extrapolation of the present data gives b. p. 12·55°/760 mm. [cf. 12·5°/755 mm. (Mauguin and Simon, *loc. cit.*); 12·7°/760 mm. (Regnault); and contrast 13·0° (uncorr.), Price and Green, *J. Soc. Chem. Ind.*, 1920, **39**, 98T]. The b. p. calculated from Regnault's equation is 11·2° and not 12·7°, which was presumably determined.

TABLE I.

	Temp.	Pressure, mm.		Pressure, mm.	
Cyanogen	−22·9°	701·60	Cook and Robinson	701·50	Perry and Bardwell
	−14·4	1030·4		1032·3	
Cyanogen chloride	0·00	451·5	Cook and Robinson	451·6	Regnault
	+ 5·48	568·6		574·8	
	+ 7·75	626·2		630·4	

Vapour Density.—This was measured for cyanogen, as a check on its purity, by confining the gas at known pressure in the known volume E (Fig. 1), which was kept constant to within ± 0·2°, and subsequently weighing the sample. For this purpose, tap T was closed and the rest of the system evacuated, then the material in E was condensed in F, which was sealed off and removed. (We found it possible to weigh many materials above their critical temperature provided suitable vessels are used, this having been done for cyanogen fluoride and silicon tetrafluoride.) With F at *ca.* − 180°, the pressure of the gas in the system could be reduced to about 1 mm., and a correction was applied for this residue and also for the air displaced in F. The following results show an anticipated departure from the gas laws, but support our belief that the material is reasonably pure.

				Density, g./l. at N.T.P.	
$(CN)_2$, g.	Vol., c.c.	Press., mm.	Temp.	Found.	Calc.
0·7405	820·7	316·60	19·4°	2·321	2·337
0·7616	820·7	326·12	19·9	2·321	

Liquid Density.—This was determined by sealing off a quantity of liquid in G, which had been previously weighed and calibrated as to volume, weighing it, and determining the weight of liquid present (with corrections for air displaced), and subsequently determining the volume of the liquid at a series of temperatures.

Cyanogen. Data for material prepared by the two methods agreed excellently (see below) : $D_{t^\circ} = 0{\cdot}91506(1 - 0{\cdot}00203t)$, from the m. p. to + 20°. The only earlier measurement, made at 17° (Faraday, *loc. cit.*), is low, *viz.*, 0·866 against 0·8835 g./c.c. The compound was kept in the liquid state for 3 weeks without alteration in density.

Density of Liquid Cyanogen.

From AgCN.				From KCN and $CuSO_4$.			
Temp.	*D*, g./c.c.	Temp.	*D*, g./c.c.	Temp.	*D*, g./c.c.	Temp.	*D*, g./c.c.
−26·39°	0·95777	+ 7·68°	0·90072	−20·03°	0·95130	− 1·43°	0·91313
−20·85	0·95284	+13·69	0·88996	−16·70	0·94587	+12·29	0·89039
−16·50	0·94522	+17·39	0·88093	− 8·03	0·93068	+13·79	0·88986
− 8·02	0·93003	+18·69	0·87870	− 3·15	0·92113	+18·69	0·87974
− 3·02	0·91987	+19·39	0·87897				

Cyanogen chloride. Results obtained by the same method conform to $D_{t^\circ} = 1{\cdot}2223(1 - 0{\cdot}001677t)$, from the m. p. to 18° :

Temp.	−5·80°	0·00°	5·05°	5·40°	6·00°	9·70°	11·40°	14·00°
D, g./c.c.	1·235	1·222	1·212	1·211	1·210	1·201	1·199	1·193

D_{0° is the same as that of Mauguin and Simon (*loc. cit.*), and our coefficient of expansion from 0° to 45°, 0·001677, is close to theirs, 0·0015. D_{4° and D_{9° agree well with Price and Green's values (*loc. cit.*), *viz.*, 1·218 and 1·207.

Cyanogen bromide. The solid was introduced into H (Fig. 1), which was evacuated and isolated by closing a tap. The material was melted with precaution against decomposition, and caused to flow into the lower bulb, which was sealed off at J. Measurements were done up to 76°, at which some decomposition became apparent; well-stirred, hot water formed the bath. $D_{t^\circ} = 2{\cdot}0246(1 - 0{\cdot}00130t)$.

Temp.	54·0°	58·0°	60·0°	64·5°	66·60°	68·75°	76·00°
D, g./c.c.	1·881	1·873	1·867	1·855	1·847	1·844	1·823

Cyanogen iodide. Only an approximate determination was possible, as the material decomposes at its m. p. : $D_{146^\circ} = 2{\cdot}59 \pm 0{\cdot}02$ g./c.c.

Surface Tension.—This was determined for the liquid under its own vapour pressure, two capillary tubes being used.

Cyanogen, cyanogen chloride and bromide. The density of cyanogen vapour was computed by extrapolation of Perry and Bardwell's data (*loc. cit.*); in the other cases this was not necessary. For the three compounds, γ_{t° (dynes/cm.) = $18{\cdot}50(1 - 0{\cdot}008873t)$, $25{\cdot}80(1 - 0{\cdot}005837t)$, and $36(1 - 0{\cdot}004785t)$ respectively.

Surface Tensions and Parachors of Cyanogen, Cyanogen Chloride and Bromide.

Cyanogen.

From AgCN.						From KCN and $CuSO_4$.		
Temp.	γ.	P.	Temp.	γ.	P.	Temp.	γ.	P.
+16·25°	15·82	117·1	− 9·06°	19·79	117·7	+19·20°	15·08	116·5
+10·80	16·72	117·5	−14·58	20·88	118·0	+ 6·06	17·56	117·8
+ 6·51	17·37	117·7	−18·88	21·81	118·3	− 3·16	19·21	118·2
+ 1·31	18·20	117·6	−25·0	22·82	118·2	−14·58	20·98	118·2
− 4·12	18·87	117·4		Mean	117·7	−24·24	22·52	118·0
							Mean	117·7

The calculated value for the parachor, P, of cyanogen is 125·0.

Cyanogen chloride.

Temp.	γ.	P.	Temp.	γ.	P.
−6·3°	26·53	113·1	+10·0°	24·61	114·1
0·0	25·79	113·4	+24·7	22·08	113·6
+5·8	25·03	113·6	—	Mean	113·6

Cyanogen bromide.

Temp.	γ.	P.	Temp.	γ.	P.
+55·0°	27·26	128·9	+70·0°	24·65	128·2
+60·0	26·37	128·7	+75·0	23·75	127·8
+65·0	25·45	128·4	—	Mean	128·4

DISCUSSION AND SUMMARY.

The physical properties of these compounds and of hydrogen cyanide are given in Table II.

TABLE II.

The Physical Properties of Cyanogen Compounds.

Compound	$(CN)_2$.	CNCl.	CNBr.	CNI.	CNH.
B. p.	−21·17°	+12·6°	+61·3°	—	+25·70°
$\lambda_{b.p.}$ *	5778	6358	—	—	6760
M. p.	−27·9°	−6·5°	+51·3°	+146°	−14·0°
D of liquid at b. p.	0·9537	1·1963	1·8633	(*ca.* 2·59)	0·6820
Coeff. of expansion × 10^5	209·6	168·5	145·2	—	288·0
Mol. vol. at b. p.	54·55	51·38	56·85	(*ca.* 58·8)	39·50
Mol. diameter × 10^9	9·809	8·882	9·186	(*ca.* 9·29)	9·656
$d\gamma/dt$ (obs.)	0·213	0·150	0·176	—	0·133
Ramsay–Shields const., K †	2·18	—	—	—	1·10
Trouton's constant	22·94	22·26	—	—	22·49
Chemical constant, i ‡	2·947	2·988	3·030	—	3·000
$\gamma_{b.p.}$	21·98	2·390	25·84	—	17·10
$\gamma_{b.p.}$ (Walden) §	23·85	29·36	31·91	—	40·27
Mean mol. parachor (obs.)	117·7	113·6	128·4	—	81·5
,, ,, ,, (calc.)	125·0	116·3	130·5	—	79·6
Parachor of CN (obs.)	58·9	59·8	60·4	—	64·4
,, ,, (calc.) = 62·5.					

* $\lambda_{b.p.}$ = Molecular heat of vaporisation at the b. p.

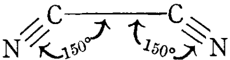
† $K = d[\gamma(M/D)^{2/3}]/dt$.

‡ $i = 1{\cdot}33 \log T_{b.p.} - 0{\cdot}00098\, T_{b.p.}$.

§ $\gamma_{b.p.}$ (Walden) $= T_{b.p.}\, 2{\cdot}15 \log T_{b.p.}/MV_{b.p.}$.

The Ramsay–Shields constant indicates no association in cyanogen, and Trouton's constant is normal, not only for this and for the chloride, but also for the hydride, which is known to be associated. The considerable association of hydrogen cyanide is, however, best shown by comparing $\gamma_{b.p.}$ with that calculated from Walden's relationship: this would appear to indicate that the compound is largely bimolecular at its b. p. (compare Robinson and Scott, J., 1932, 972; Durrant, Pearson, and Robinson, J., 1934, 731). The absence of association in cyanogen as compared with the chloride and bromide is similarly confirmed: a view supported by its feeble solvent powers (Centnerszwer, *Z. physikal. Chem.*, 1901, **39**, 217) and small dipole moment (Braune and Asche, *ibid.*, 1931, *B*, **14**, 18).

Ring structures for cyanogen, such as that of Dixon and Taylor (J., 1913, **103**, 974) based on the assumption (subsequently disproved by Braekken, *Norsk. Videnskab. Selskab. Forh.*, 1930, **48**, 169) that silver cyanide had the structure Ag·N⁚C, are rendered improbable by the predictions of Mecke (*Z. Physik*, 1930, **64**, 182) which were realised by Mooney and Reid spectroscopically (*Proc. Roy. Soc. Edin.*, 1932, **52**, 152), and by the electron-diffraction observations of Wierl (*Ann. Physik*, 1932, **13**, 453) and of Brockway (*Proc. Nat. Acad.*

Sci., 1933, **19**, 868). Wierl gives a structure 

, but Brockway's results implied that all the atoms lie in a straight line, $N \overset{1\cdot16\text{ Å.}}{\text{———}} C \overset{1\cdot43\text{ Å.}}{\text{———}} C \overset{1\cdot16\text{ Å.}}{\text{———}} N$. The sequence of the atoms and the low dipole moment make highly probable the structure N⋮C·C⋮N, predicted by Pauling and Hendricks (*J. Amer. Chem. Soc.*, 1926, **48**, 641). The observed parachors of CN (mean 59·7) in the several compounds, though definitely below the calculated, 62·5, show little variation among themselves and are in accordance with a triple bond. The constants used in calculating the parachors were supplied by Professor Sugden, F.R.S., with whom we had the advantage of discussing our results.

The discrepancy between the observed and the caculated values of the surface tension at the boiling point indicates that the chloride and bromide are both slightly associated in the liquid state. A plot of melting points and densities against period number of the halogen (Fig. 3) shows no irregularities. These compounds are apparently associated to a similar degree, which is, however, much less than that of hydrogen cyanide. The observed parachors of the chloride and bromide agree fairly well with the calculated values, and establish the existence of a triple bond in these substances.

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