

**246. Studies on Hydrogen Cyanide. Part XVIII. Some Physical Properties of Anhydrous Hydrogen Cyanide.**

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The density, viscosity, and surface tension of anhydrous liquid hydrogen cyanide have been determined in the temperature range  $-13.3^{\circ}$  to  $25^{\circ}$ . The results obtained show some significant differences from values in the literature. The variation of these properties with temperature is expressed by equations and is discussed in relation to the linear association of hydrogen cyanide molecules due to hydrogen-bonding.

IN studies involving anhydrous hydrogen cyanide as a solvent, the need arose for accurate data for its physical properties, extending over the complete temperature range from the freezing point to the boiling point (f. p.  $-13.24^{\circ}$ ; b. p.  $25.7^{\circ}$ ; Giaque and Ruehrwein, *J. Amer. Chem. Soc.*, 1939, **61**, 2626). Dielectric constants for this temperature range have already been reported (Coates and Coates, *J.*, 1944, 77), and Giaque and Ruehrwein (*loc. cit.*) have recorded accurate heat capacity, vapour pressure, and related thermodynamic constants. A survey of the literature regarding the density, viscosity, and surface tension of the liquid showed that where independent measurements had been made on these properties the results of the different investigators were discordant and appeared unreliable when compared with some unpublished values obtained in this laboratory.

Numerous measurements have been made of the density of hydrogen cyanide. The work of Gay-Lussac (*Ann. Chim. Phys.*, **77**, 128) and of Bleekrode (*Jahresber. Chem.*, 1884, 284) is of historical interest only. The more recent measurements made by Meyer and Hopff (*Ber.*, 1921, **54**, 1709), Tromp (*Rec. Trav. chim.*, 1922, **41**, 278), Walker and Marvin (*Ind. Eng. Chem.*, 1926, **18**, 139), and Shirado (*J. Chem. Soc. Japan*, 1927, **48**, 280; *Bull. Chem. Soc. Japan*, 1927, **2**, 122) are either in a narrow temperature range or of low accuracy in view of the questionable purity of the liquid employed. Fredenhagen and Dahmlos (*Z. anorg. Chem.*, 1929, **179**, 77) claim an accuracy of only 1 : 700 for their values which cover the range  $-13^{\circ}$  to  $20^{\circ}$ . The most reliable and extensive results hitherto published appear to be those of Sinosaki and Hara (*Tech. Repts. Tôhoku Univ.*, 1929, **8**, 297). The density of the liquid at one temperature has also been recorded by Coates and Hartshorne (*J.*, 1931, 657), Lowry and Henderson (*Proc. Roy. Soc.*, 1932, *A*, **136**, 471), and Coates and Taylor (*J.*, 1936, 1245).

The only published results for the viscosity of hydrogen cyanide are those of Fredenhagen and Dahmlos (*loc. cit.*) for the temperature range  $-13^{\circ}$  to  $20^{\circ}$  and the value of 0.001986 c.g.s. unit at  $18^{\circ}$  reported by Coates and Taylor (*loc. cit.*).

The only values available for the surface tension of the liquid are derived from the "few ordering measurements" by Bredig and Teichmann (*Z. Elektrochem.*, 1925, **31**, 449).

The availability of highly purified hydrogen cyanide made it desirable to re-determine these properties, the temperature variation of which is of interest in view of the linear polymerization of the hydrogen cyanide molecule attributed to hydrogen-bonding (Kumler, *J. Amer. Chem. Soc.*,

1935, 57, 600; Pauling, "The Nature of the Chemical Bond," 2nd Edn., 1940, p. 294). The knowledge gained from these properties regarding the "structure" of the liquid is also of value in the treatment of ionic solvation in this solvent.

#### EXPERIMENTAL.

**Purification of Liquids.—Hydrogen cyanide.** The starting material supplied by Messrs. Imperial Chemical Industries Ltd. was of approx. 98% purity and stabilized with a little oxalic acid. The hydrogen cyanide was distilled from the oxalic acid and subsequently purified by the method of Coates and Taylor (*loc. cit.*), with use of an improved all-Pyrex glass fractionating apparatus. The specific conductance at 18° was less than  $1.5 \times 10^{-7}$  mho and the f. p.  $-13.25^\circ \pm 0.01^\circ$ .

**Water.** "Conductivity" water of specific conductance  $1.0\text{--}1.2 \times 10^{-4}$  mho at 18° was employed.

**Benzene.** An "AnalaR" specimen was purified by the method of Linton (*J. Amer. Chem. Soc.*, 1940, 62, 1945); f. p.  $5.50^\circ$ .

**Ethyl ether.** Ether of a good grade was stored over flaked sodium hydroxide for a week, with occasional shaking. After distillation it was kept over sodium wire. The ether was fractionated from the sodium as required and the middle fraction boiling within  $0.02^\circ$  collected (b. p.  $34.5^\circ/756$  mm.;  $d_4^{20}$  0.7192<sub>g</sub>).

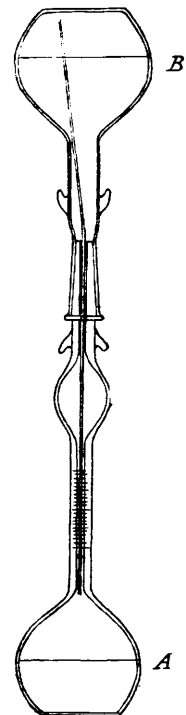
The weights and thermometers employed were compared with N.P.L. certified standards.

**Temperature Control.**—The thermostat consisted of an unsilvered Dewar vessel of about 5-l. capacity. The temperature was controlled by means of an electronic relay in conjunction with a sensitive mercury-toluene regulator. For temperatures down to  $5^\circ$ , cooling was effected by the flow of ice-chilled water through a copper coil immersed in the thermostat, the constancy of temperature being better than  $\pm 0.01^\circ$ . Temperatures below  $5^\circ$  were maintained to within  $\pm 0.02^\circ$  by the addition of small pieces of solid carbon dioxide. A few density measurements were also made in a Dewar vessel containing either finely crushed ice or a potassium chloride-ice freezing mixture.

**Density Measurements.**—These were made by means of a silica dilatometer *A* (see figure) of about 36-ml. capacity with a capillary arm 12 cm. long and 1.7 mm. in diameter, provided with a ground joint which accurately fitted a ground cap as well as the joint on the neck of the filling flask *B*. The upper part of the capillary arm was enlarged into a bulb of about 5-ml. capacity to allow for the expansion of the liquid when measurements were made at temperatures below that of the room. The capillary was graduated in mm. over a length of 2 cm. Filling of the dilatometer was effected by a simple procedure which has been adopted for some years in this laboratory and proved to be very convenient for measurements on volatile and hygroscopic liquids. A loose-fitting capillary tube inserted in the dilatometer reached to the bottom of the neck and nearly to the top of the filling vessel when the latter was in the filling position as shown in the figure. A slight kink in the capillary tube prevented it from slipping down into the dilatometer. The flow of liquid from flask *B* into the dilatometer causes the displaced air to be forced up the inserted capillary tube. The filling was always carried out at a temperature which was a few degrees below that at which measurements were to be made. The method is also very convenient for measurements on volatile solutions since composition changes are minimized. The dilatometer may be emptied by reversing the above procedure.

The dilatometer was calibrated at  $25^\circ$  with freshly-boiled conductivity water. For use at lower temperatures small corrections were applied to allow for the contraction of the silica glass, and for this purpose the data of Beattie *et al.* (*Proc. Amer. Arts Sci.*, 1941, 74, 371) for the coefficient of expansion of silica glass were employed. The calibrations were reproducible to 0.0003 ml. This uncertainty would not affect the fifth significant figure in the density of hydrogen cyanide, a limit to the degree of accuracy fixed by the extent to which the temperature of measurement was absolutely known, *viz.*,  $\pm 0.01^\circ$ . In measurements on hydrogen cyanide it was necessary to boil the liquid for a short time before filling the dilatometer, otherwise troublesome bubbles of air were produced. All weighings were reduced to vacuum, and the densities calculated as described by Reilly and Rae ("Physico-Chemical Methods," 1940, Vol. 1, p. 496), the density of silica glass being taken as 2.2 (Internat. Crit. Tables, 1927, Vol. II, p. 82). No allowance was made for the hydrogen cyanide vapour in the space above the liquid since its density and that of air are approximately equal. The density values were reproducible to  $\pm 0.00002$ .

**Viscosity Measurements.**—These measurements were made in an Ostwald viscometer, constructed in Pyrex glass and adapted for use with volatile liquids as well as designed to conform with recent recommendations on viscometry. The essential dimensions of the viscometer were: volume of efflux, 5.146 ml.; loading volume, approx. 8 ml.; length of capillary,  $20.02 \pm 0.02$  cm.; radius of capillary,  $0.01571 \pm 0.00003$  cm.; average hydrostatic head, approx. 21 cm.; radii of upper and lower bulbs, 0.8 cm. These dimensions are such that the maximum kinetic energy correction term amounts to less than 1% of the viscosity value. The minimum time of flow was 567 seconds so that drainage errors are negligible (Jones and Stauffer, *J. Amer. Chem. Soc.*, 1937, 59, 1630; Jones and Ferrel, *J.*, 1939, 325). By incorporating features of design recommended by Jones and Fornwalt (*J. Amer. Chem. Soc.*, 1938, 60, 1684) and Cannon and Fenske (*Ind. Eng. Chem. Anal.*, 1938, 10, 297), surface tension effects were reduced to a minimum. Barr (*Proc. Phys. Soc.*, 1946, 58, 575) has recently emphasised the surface tension error in viscometry but it was estimated by comparison with the instrument of Jones and



Fornwalt (*loc. cit.*) that in the present work surface tension effects would not influence the result by more than 0.03%.

Measurements on hydrogen cyanide were found to be more conveniently made by introducing known weights of the liquid into the viscometer (cf. Jones and Fornwalt, *loc. cit.*), so that the loading volume was not always the same. Further the large coefficient of expansion of the liquid leads to an appreciable variation in the working volume with temperature. The instrument was therefore calibrated by making observations with different volumes of water (approx. 7–8 ml.) which included the range of working volumes experienced with hydrogen cyanide at the different temperatures. The observed times of flow for water at varying temperatures from 0° to 70°, and the viscosity data for water (Internat. Crit. Tables, 1929, Vol. V, p. 10) enabled the constants  $A, B, C$  in the following equation to be evaluated (Barr, "A Monograph of Viscometry," 1930, p. 127) :

$$\eta = (A - Bv)dt - Cd/t$$

where  $\eta$  is the viscosity,  $v$  the loading volume,  $t$  the time of efflux,  $d$  the density of the liquid. Calculation showed that in the temperature range involved in this work there was negligible variation in the dimensions of the viscometer.

In introducing the hydrogen cyanide into the viscometer, atmospheric contamination of the liquid was avoided by distilling the liquid from a small weight-pipette into the evacuated viscometer cooled to about  $-13^\circ$  by solid carbon dioxide-alcohol. By means of a small pressure bulb attached to one limb of the viscometer, the liquid could be forced up into the efflux bulb without opening the viscometer to the atmosphere. In computing the volume of liquid in the viscometer from the weight of hydrogen cyanide added, a small correction was made for the weight of hydrogen cyanide present as vapour. This correction could be made with sufficient accuracy by means of a relation derived from the data of Sinosaki and Hara (*loc. cit.*) and the vapour pressure values of Giaque and Ruehrwein (*loc. cit.*).

Times of flow were observed with a Venner stopwatch reading to 0.1 second. For most temperatures five determinations were made on different samples. As a check on the procedure and calibration of the viscometer, a measurement was made on ethyl ether, a liquid of comparable viscosity and volatility. The observed value of 0.002474 c.g.s. unit at  $15^\circ$  is in good agreement with that of 0.00247 reported by Timmermans and Martin (*J. Chim. physique*, 1928, **25**, 411).

*Surface Tension Measurements.*—These were made for the whole temperature range by the maximum bubble pressure method, and also for temperatures above  $10^\circ$  by the capillary rise method.

The Pyrex-glass capillarimeter employed was of the type recommended by Richards and Coombes (*J. Amer. Chem. Soc.*, 1915, **37**, 1656). The capillary consisted of a "Veridia" brand precision-bore tube. The uniformity of the tube was checked by measurements on the length of a mercury thread at different parts along the tube and its radius calculated by two independent methods, (a) from the weight of a thread of mercury of known length, and (b) from the capillary rise for benzene, the surface tension of which was taken as 28.88 dynes/cm. at  $20^\circ$  (Internat. Crit. Tables, 1928, Vol. IV, p. 454). The values so obtained were 0.018512 and 0.018529 cm. respectively. The latter value was adopted as the more reliable. The capillary rise was measured by means of a travelling microscope reading to 0.001 cm. The method of illuminating and observing the meniscus was similar to that described by Richards and Coombes (*loc. cit.*). A few readings were made later in a capillarimeter after the design of Jasper and Herrington (*J. Amer. Chem. Soc.*, 1946, **68**, 2142). This apparatus was found to be more convenient for measuring the capillary rise and confirmed the results previously obtained. The surface tension was calculated by means of the following relation (Harkins, "Physical Methods of Organic Chemistry," Interscience Publishers, Vol. 1, p. 160) :

$$\gamma = \frac{1}{2}rg(D - d)(h + r/3)$$

where  $\gamma$  is the surface tension (dynes/cm.),  $r$  the radius of the capillary (cm.),  $g$  the gravitational constant (981.2 cm./sec.<sup>2</sup>),  $h$  the capillary rise (cm.),  $D$  and  $d$  the density of the liquid and vapour phase respectively.

The bubble-pressure apparatus was similar to that described by Quayle and Smart (*J. Amer. Chem. Soc.*, 1944, **66**, 937), the wider tube having an internal radius of 0.155<sub>5</sub> cm. The precautions listed by Harkins (*loc. cit.*) were observed. The bubbles were formed by connecting the apparatus to a compressed-air cylinder provided with a fine-adjustment needle valve. Ethyl alcohol tinted with a little magenta was employed as the manometric liquid. The manometer was immersed in a thermostat maintained at  $25^\circ$  to avoid fluctuations in room temperature influencing the manometric head. The manometric head could be observed to  $\pm 0.2$  mm. on a glass scale, and from the previously determined density of the liquid the pressure could be calculated in absolute units. The apparatus was calibrated at  $10^\circ$ ,  $18^\circ$ , and  $25^\circ$  with benzene as standard liquid, and the constant calculated as described by Sugden ("The Parachor and Valency," Routledge, London, 1930, p. 211). Confirmation of the calibration and procedure was obtained from measurements on ethyl ether, a liquid comparable in volatility and surface tension with hydrogen cyanide. The values of 16.54 and 17.10 dynes/cm. at  $25^\circ$  and  $20^\circ$  respectively agreed well with published data, *viz.*, 16.51 and 17.06 dynes/cm. ("Ann. Tables of Physical Constants," Timmermans, 1941, sect. 700(C), p. 3; cf. Vogel, *J.*, 1948, 619).

The results obtained with independent samples of hydrogen cyanide were reproducible to 0.3%, this being the extent of agreement between the values obtained by the two methods in the temperature range where the measurements overlapped. No measurements were made on the influence of small amounts of water on the values obtained by the bubble-pressure method, but it was observed by the capillary-rise method that the addition of 0.5% of water increased the surface-tension values of hydrogen cyanide by about 1%. All precautions were therefore taken in the course of manipulations to prevent the liquid from being contaminated by traces of moisture.

*Results.*—The values obtained for the density, viscosity and surface tension are given in Table I. Values obtained at intermediate temperatures have been omitted but have been employed to derive the equations which express the variation of these properties with temperature. Parachor values at some of the temperatures have been evaluated and are listed in column 5.

TABLE I.

Temp. (°c.).	$d_4^t$ , g./ ml.	$\eta \times 10^5$ , poises.	$\gamma$ , dynes/ cm.	[P.]	Temp. (°c.).	$d_4^t$ , g./ ml.	$\eta \times 10^5$ , poises.	$\gamma$ , dynes/ cm.	[P.]
25.00	0.67972	183.4	17.78	81.8	5.00	0.70893	222.8	20.02	—
22.00	0.68414	188.5	18.12	—	0.00	0.71618	235.5	20.62	80.4
20.00	0.68708	—	18.33	—	-5.00	0.72341	249.2	21.20	—
18.00	0.69001	195.5	18.56	—	-10.00	0.73058	264.4	21.78	80.0
15.00	0.69438	201.4	18.89	—	-13.30	0.73521	275.6	22.16	—
10.00	0.70167	211.4	19.45	80.9					

## DISCUSSION.

The values obtained for the density of hydrogen cyanide are claimed to be correct to better than 3 parts in  $10^5$ , this limit to the accuracy being determined mainly by the precision to which the temperature was absolutely known. Barr (*J.*, 1924, 1043) states that it is doubtful whether an accuracy better than 1 in  $10^5$  for the density of a volatile liquid can be obtained by the pycnometric method. The result at  $18^\circ$  confirms the values previously reported from this laboratory (*loc. cit.*). The following equation reproduces the density of the liquid to better than 5 in the fifth decimal place over the complete range of temperature :

$$d_4^t = 0.71618 - 1.4457 \times 10^{-3}t - 5.50 \times 10^{-7}t^2 + 1.6 \times 10^{-9}t^3.$$

As indicated earlier, of the published data, those of Sinosaki and Hara are in best agreement with present values. The divergence between their values and present values is more marked at the lower temperatures. Thus their result at  $25^\circ$  is identical with that obtained in this work, whereas at  $0^\circ$  their value is 1 part in 3,500 higher. Below  $0^\circ$  the results of Fredenhagen and Dahmlos (*loc. cit.*) are subject to an error much greater than the 1 in 700 which they claim.

The viscosity results are claimed to be correct to within 0.1% (relative to the absolute values for water) and are lower than any values previously recorded, being approximately 5% lower than the results of Fredenhagen and Dahmlos (*loc. cit.*). The value of 0.001986 poise at  $18^\circ$  reported by Coates and Taylor (*loc. cit.*) is about 1.5% higher than that obtained at the same temperature in the present work. The measurements of Coates and Taylor were carried out with a liquid of high purity and a quartz viscometer of the Washburn and Williams type (*J. Amer. Chem. Soc.*, 1913, **35**, 737). Following the recommendations of the latter workers, no kinetic energy correction was applied to the result. This neglect of the kinetic energy correction is questionable, even for measurements with water, and is certainly unjustifiable in measurements on a liquid such as hydrogen cyanide of viscosity only a fifth that of water, especially when the latter is used as the calibrating liquid. The need for applying this correction to the result of Coates and Taylor is indicated by the fact that if a viscometer involving a longer time of flow is employed, thereby reducing the magnitude of the correction, the observed viscosity is less than that reported by these workers. The design of the viscometer employed in the present work enabled the kinetic energy correction to be reduced to a minimum and the method of calibration eliminated any uncertainty regarding its magnitude. The discrepancy of 1.5% between the value at  $18^\circ$  reported by Coates and Taylor and that recorded in this work may be attributed almost entirely to the kinetic-energy term.

The viscosity of a liquid depends on the shape and size of the molecules as well as the strength of the forces between them. The magnitudes of the physical properties of hydrogen cyanide such as the boiling point, dielectric constant, etc., are very much higher than would be expected of a substance of similar molecular dimensions, *e.g.*, hydrogen chloride. These differences have been attributed to the association of the hydrogen cyanide molecule into linear polymers as a consequence of hydrogen-bonding (Pauling, *op. cit.*). Friend (*Chem. and Ind.*, 1944, 179) and Kendall (*ibid.*, p. 211) have both drawn attention to the close connection between viscosity and hydrogen-bonding, the viscosity of liquids involving such bonds being abnormally high, since energy is required to break these bonds in addition to overcoming any dipolar and van der Waals forces. It is therefore of interest to compare the viscosity of hydrogen cyanide with that of hydrogen fluoride which is similarly associated. Simon and Dresdner (*J. Amer. Chem. Soc.*, 1944, **66**, 1070) found that at  $0^\circ$  the viscosity of hydrogen fluoride was 0.00256, which compares with the value of 0.002355 for hydrogen cyanide at the same temperature. Thus the viscosities of the two liquids, like certain other physical properties such as boiling point, dielectric constant, molar heat of vaporisation, etc., present a close parallelism. Some differences are to be expected since the hydrogen bonds in hydrogen fluoride are stronger than those in hydrogen cyanide (Pauling, *op. cit.*, p. 333) while the hydrogen fluoride chains

are zig-zag shaped (Bauer, Beach, and Simons, *J. Amer. Chem. Soc.*, 1939, **61**, 19) as compared with the linear hydrogen cyanide chains.

Since an exponential equation of the form  $\eta = Ae^{E_{\text{visc.}}/RT}$  is known to represent with fair accuracy the variation of viscosity with temperature for most liquids and has further been shown to have a theoretical basis (*e.g.*, Andrade, *Phil. Mag.*, 1934, **17**, 497, 698; Ward, *Trans. Faraday Soc.*, 1937, **33**, 88; Eyring *et al.*, *J. Chem. Physics*, 1936, **4**, 283; 1937, **5**, 726), it was applied to the present results.  $A$  and  $E_{\text{visc.}}$  were evaluated by the method of least squares, and the equation

$$\log \eta = (357.927/T) - 3.93816$$

or

$$\eta = 1.153 \times 10^{-4} e^{1637/RT}$$

was found to reproduce the results to better than 0.3%. The value of 1637 cal. for  $E_{\text{visc.}}$ , the energy of activation for viscous flow, compares with that for hydrogen fluoride in the same temperature range (*viz.*, 1690 cal.) and is less than half that for other hydrogen-bonded liquids. Thus the structure of the liquid does not undergo appreciable break-down before flow can occur. The slope of the plot of  $\log \eta$  against  $1/T$  is slightly greater at lower than at higher temperatures indicating that  $E_{\text{visc.}}$  is not quite independent of temperature. On the views of Ward (*loc. cit.*) this small variation of  $E_{\text{visc.}}$  with temperature, amounting to about 3% for the normal liquid range, implies little change of co-ordination in the liquid state with temperature.

Since in the aliphatic cyanide series hydrogen cyanide is unique in displaying association due to hydrogen-bonding, it is of interest to compare the respective values of  $A$  and  $E_{\text{visc.}}$  for some of the lower members of the cyanide series. Values of  $1/A$  and  $E_{\text{visc.}}$  for a number of such cyanides have been derived from the viscosity data given by Friend and Hargreaves (*Phil. Mag.*, 1944, **35**, 619) and are included in Table II for comparison with the corresponding values obtained for hydrogen cyanide in the present work.

TABLE II.

	HCN.	CH <sub>3</sub> ·CN.	C <sub>2</sub> H <sub>5</sub> ·CN.	n-C <sub>3</sub> H <sub>7</sub> ·CN.	n-C <sub>4</sub> H <sub>9</sub> ·CN.	n-C <sub>5</sub> H <sub>11</sub> ·CN.
1/A .....	8674	5960	6040	7130	6960	7590
$E_{\text{visc.}}$ , kcals./mole ...	1.64	1.81	1.89	2.18	2.30	2.50

Barrer (*Trans. Faraday Soc.*, 1943, **39**, 48) has drawn attention to relationships involving  $E_{\text{visc.}}$  and  $1/A$  in homologous series of compounds. The plot of  $E_{\text{visc.}}$  against chain length is linear for the six cyanides in Table II. The increment in  $E_{\text{visc.}}$  over that for hydrocarbons due to the introduction of the —CN group is comparable with that for the —CO<sub>2</sub>R group. Thus the value of  $E_{\text{visc.}}$  for hydrogen cyanide appears to fit regularly in the cyanide series. On the other hand the value of  $1/A$  for this liquid is seen to be abnormally high. The transition-state method (Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," Chap. 9) interprets the factor  $A$  in the Arrhenius equation in terms of  $\Delta S$ , the entropy of activation for viscous flow, *viz.* :

$$A = (Nh/V)e^{-\Delta S/R}$$

where  $V$  is the molar volume. The values of  $-\Delta S$  calculated for the first four members of the cyanide series are 0.28, 1.73, 2.29, and 2.48 cal./mole./deg. respectively. There is thus a more marked difference in  $\Delta S$  between the first two members than between higher members so that the value of  $1/A$  for hydrogen cyanide is high. The treatment proposed by Barrer (*loc. cit.*) provides a physical picture of the origin of these entropy changes. On Barrer's views  $\Delta S$  is regarded as made up of two parts, (a) a positive component which is a function of  $E_{\text{visc.}}$  and arises from the loosening of the liquid structure before flow can occur, and (b) a negative component arising from the need for synchronization or co-operation between inter-molecular rotations or vibrations before flow can occur. In the case of hydrogen cyanide the two terms make approximately equal contributions whereas for the other cyanides the entropy of co-operation term is the greater. The fact that  $\Delta S$  is nearly zero for hydrogen cyanide implies that the flowing molecule is substantially the same as the normal molecule and is in accord with the simple linear structure. This is in contrast to hydroxylic liquids which exhibit large positive  $\Delta S$  values.

The temperature dependence of surface tension is reproduced to within 0.1% by the following equation :

$$\gamma_t = 20.62 - 0.1155t + 7 \times 10^{-5}t^2.$$

Present values are 2—3% higher than those reported by Bredig and Teichmann (*loc. cit.*). The parachor shows an increase with temperature amounting to about 2.5% for the liquid range.

No special significance may be attached to this since the parachor values derived by Jeffery and Vogel (*J.*, 1948, 682) for the other cyanides also display some increase with temperature. The revised parachor proposed by Ferguson and Kennedy (*Trans. Faraday Soc.*, 1936, **32**, 1474; cf. Telang, *J. Amer. Chem. Soc.*, 1949, **71**, 1898) is, however, independent of temperature. As with hydrogen fluoride the ratio of molecular surface energy of hydrogen cyanide to that of water is less than the ratio of their molar latent heat of vaporisation. As Bauer, Beach, and Simons (*loc. cit.*) suggest for hydrogen fluoride it is possible that, the hydrogen cyanide polymers being linear, the transporting of an associated molecule from the body of the liquid to the surface involves no breaking of the hydrogen bonds. In the case of water on the other hand, owing to its three-dimensional structure, some hydrogen bonds must break in order to allow the molecules to orientate themselves in positions on the surface so as to give a minimum surface energy. It is of interest to note that although many of the physical properties of hydrogen fluoride are comparable in magnitude with those of hydrogen cyanide, the surface tension of the former is only a half of that of hydrogen cyanide at the same temperature. Thus the surface tension of hydrogen fluoride at  $-82^{\circ}$  observed by Simons and Bouknight (*J. Amer. Chem. Soc.*, 1932, **54**, 129) is approximately that of hydrogen cyanide at  $25^{\circ}$ . There appears to be no satisfactory explanation of the abnormally low surface tension of hydrogen fluoride.

Grunberg and Nissan (*Trans. Faraday Soc.*, 1949, **45**, 125) have recently discussed the structure of liquids as deduced from relations between their energies of vaporisation, viscosity, and cohesion, the latter being defined as twice the molar surface energy. Calculation of these quantities showed that on the arguments presented by these authors the aliphatic cyanides are associated but that the hydrogen cyanide aggregates are somewhat more stable than those of the other lower cyanides. This agrees with the added hydrogen-bonding nature of the association in the case of hydrogen cyanide in contrast to the dipolar association of the other cyanides.

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