

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dielectric Polarization and Molecular Association of Hydrogen Fluoride Vapor<sup>1</sup>

BY RICHARD A. ORIANI AND CHARLES P. SMYTH

The polymerization or molecular association of hydrogen fluoride has been known for a long time. Simons and Hildebrand<sup>2</sup> analyzed the data<sup>3</sup> of Thorpe and Hambly on its vapor density and concluded that the gaseous substance was composed mainly of cyclic hexamers (HF)<sub>6</sub>. A very careful redetermination of vapor densities led Long, Hildebrand and Morrell<sup>4</sup> also to the conclusion that the data could be represented by an equilibrium existing between the monomer and the cyclic hexamer, except at low pressures, where there was some indication of lower polymers. Fredenhagen<sup>5</sup> also made vapor density measurements, and concluded that forms other than H<sub>2</sub>F<sub>2</sub> existed and also that the theory that only HF and (HF)<sub>6</sub> existed was untenable. His data were further analyzed by Briegleb,<sup>6,7</sup> who assumed an equilibrium distribution of polymers according to the equation  $HF + (HF)_n \rightleftharpoons (HF)_{n+1}$ , and calculated that the dimer had the largest energy of association, but that values of  $n$  up to 8 were significant. Briegleb considered the configurations of the polymers to be chains in which adjacent HF units were anti-parallel to one another (Fig. 1B). The electron diffraction data of Bauer, Beach and Simons<sup>8</sup> indicated that under the conditions obtaining in their experiments at least, the principal configuration existing in gaseous hydrogen fluoride was a chain-like arrangement in which the fluorines occupied the corners of a zig-zag structure, with the hydrogens lying on a line connecting two consecutive fluorines and with a chain angle of about 140° as in Fig. 1C. The same structure with a chain angle of 135° was indicated by the X-ray analysis of solid hydrogen fluoride.<sup>9</sup> On the other hand, Pauling<sup>10</sup> calculated that, for a degree of polymerization of 6 or more, the cyclic polymer would be more stable than its chain analog by virtue of the additional bond, that the partial covalent character of the hydrogen bonds tended to stabilize bond angles of about 110 or 120° for fluorine, and that as a consequence the cyclic hexamer was somewhat more stable than other polymers.

Because of the large difference in dipole moment to be expected between a cyclic structure and a

zig-zag chain, it has been considered advisable to investigate the molecular association of hydrogen fluoride by measurement of the dielectric polarization of the vapor as a function of temperature and pressure. A preliminary note describing work along these lines has already been published.<sup>11</sup>

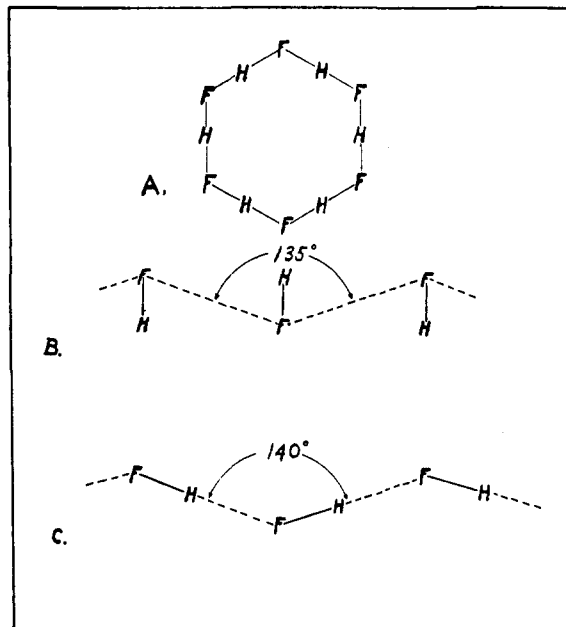


Fig. 1.—A, cyclic hexamer with zero dipole moment; B, linear model with consecutively antiparallel HF molecules; dipole moment either zero or 1.91; C, linear model deduced from electron diffraction data; dipole moment increases with chain length.

## Apparatus and Method of Measurement

While the electrical measuring circuit has been previously described,<sup>12</sup> no account has been published of the cell and vacuum system, which were identical, except for some minor modifications, with the apparatus employed by Hannay and Smyth<sup>13</sup> in the determination of the dipole moment of unassociated hydrogen fluoride. The cell was constructed of three concentric nickel cylinders, of which the outer and the inner were silver-soldered to the same nickel disc, while the middle one was insulated from the other two by a gasket of "Teflon."<sup>14</sup> Electrical contact was made to the middle cylinder by a nickel rod passing through a bushing tightly packed with "Teflon." The capacitance of the empty cell was 250 micromicro-

(1) Presented before the Physical and Inorganic Division at the 112th meeting of the American Chemical Society, New York City, N. Y., September 16-19, 1947.

(2) Simons and Hildebrand, *THIS JOURNAL*, **46**, 2183 (1924).

(3) Thorpe and Hambly, *J. Chem. Soc.*, **55**, 103 (1889).

(4) Long, Hildebrand and Morrell, *THIS JOURNAL*, **65**, 182 (1943).

(5) Fredenhagen, *Z. anorg. allgem. Chem.*, **218**, 161 (1934).

(6) Briegleb, *Z. physik. Chem.*, **51B**, 9 (1941).

(7) Briegleb, *Naturwissenschaften*, **29**, 420 (1941).

(8) Bauer, Beach and Simons, *THIS JOURNAL*, **61**, 19 (1939).

(9) Geunther, Holm and Strunz, *Z. physik. Chem.*, **B43**, 229 (1939).

(10) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 298.

(11) Benesi and Smyth, *J. Chem. Phys.*, **15**, 337 (1947).

(12) Hurdis and Smyth, *THIS JOURNAL*, **64**, 2829 (1942).

(13) Hannay and Smyth, *ibid.*, **68**, 171 (1946).

(14) Renfrew and Lewis, *Ind. Eng. Chem.*, **38**, 870 (1946).

farads, exclusive of lead capacitance; this latter was determined separately and was checked by measurements of the dielectric constant of air. The apparatus for handling the hydrogen fluoride was constructed of copper tubing and nickel with silver-soldered joints, except for the "Kerotest" valves, the brass bodies of which gave some trouble because of jamming due to corrosion. Two valved containers were provided for the purification of the hydrogen fluoride by distillation from one to the other, and for the storage of the purified material. A Bourdon gage, calibrated with air against a mercury manometer and readable to 1 mm., was used to measure the pressure. A commercial tank of hydrogen fluoride from the Matheson Company, East Rutherford, N. J., was permanently connected to the system, as was also a tank of fluorine. The leads to the cell were suitably shielded, and the cell was immersed in a thermostated oil-bath able to hold the temperature constant within  $0.02^\circ$ . The temperature was read by a calibrated platinum resistance thermometer immersed in the bath. The gas system was connected to an oil vacuum pump through a long tube filled with soda-lime. In order to prevent the occurrence of corrosion during the course of a measurement, the system was given a prolonged exposure to fluorine from the attached cylinder, and the fluorination was repeated whenever the inside of the system had been exposed to the atmosphere. The importance of this operation may be gaged by the observation that, when the system was inadequately conditioned, a gas pressure slightly larger than one atmosphere was developed over a period of time apparently by reaction of hydrogen fluoride with the metal.

In order to purify the hydrogen fluoride, a quantity was distilled from the commercial tank into a reservoir by chilling the latter (b. p. of hydrogen fluoride,  $19.4^\circ$ ). This material was then distilled back and forth from one reservoir to the other by alternately chilling and warming the containers. After each distillation the apparatus was evacuated, while the condensate was chilled with liquid nitrogen. At least one of these distillations was performed through an atmosphere of fluorine to aid in the removal of moisture. The procedure was repeated until the vapor pressure of the hydrogen fluoride at  $0^\circ$  was close to the literature value of 357 mm.<sup>15</sup> (358.2 mm.<sup>16</sup>). In these purifications, the vapor pressure at  $0^\circ$  always decreased as the purification proceeded to assume values from 354 to 356 mm. Another criterion of purity was the consistency and reproducibility of the dielectric measurements in the low pressure regions at all the temperatures studied, and their agreement with the results of Hannay and Smyth.<sup>13</sup>

In order to carry out a determination of polarization, the system was evacuated of the fluorine

(15) "International Critical Tables." McGraw-Hill Book Company, Inc., New York, N. Y., 1926.

(16) Claussen and Hildebrand, *THIS JOURNAL*, **56**, 1820 (1934).

left in it, and flushed out repeatedly with hydrogen fluoride. After another evacuation, and after the cell had attained temperature equilibrium, simultaneous readings of pressure and capacitance were made after admittance of successive small portions of hydrogen fluoride, and also after successive withdrawals of the vapor by recondensation into the storage container. Enough time had to be allowed before making readings after each admission or withdrawal of hydrogen fluoride to permit adsorption of the vapor to attain equilibrium. Adsorption was evidenced in a lag in the attainment of constant capacitance and pressure readings at the higher pressures when the temperature was not far above the boiling point. Repeated measurements of capacitance and pressure as functions of time showed that, in typical experiments where adsorption was a maximum when the pressure was raised to 700 mm., the adsorbed layer raised the capacitance by about 50 scale divisions while the total increase of capacitance produced by the hydrogen fluoride was about 1600 scale divisions. The maximum error thereby produced in the dipole moment value, which is proportional to the square root of the capacitance, was, therefore, about 1.6%.

It was believed that the treatment of the hydrogen fluoride with fluorine had removed any last traces of moisture. As moisture has been supposed to affect the association of hydrogen fluoride materially, a considerable quantity of water vapor was introduced into the cell after the completion of the measurements reported in Tables I and II. A very slight apparent increase in the dipole moment at low pressures was observed and, at higher pressures, adsorption or condensation of the water so affected the capacity measurement as to render the experiment valueless. Indeed, the slight increase in apparent moment at low pressures was probably the effect of adsorption.

### Experimental Results

The molar polarizations  $P$  were computed from the condenser readings  $C$  by the relation

$$P = \frac{RT}{3p} \cdot \frac{C - C_0}{fC_0} \quad (1)$$

in which  $f$  is a condenser calibration factor,  $C_0$  is the condenser reading at zero pressure,  $C'_0$  is the vacuum capacitance in micromicrofarads,  $R$  is the gas constant per mole,  $T$  is the absolute temperature, and  $p$  is the pressure in mm. The dipole moments were computed by the Debye equation

$$\mu = 0.01281 [(P - MR_D)T]^{1/2} \quad (2)$$

in which  $MR_D$ , the molar refraction, was taken<sup>17</sup> as 2.0.

Table I gives the values of the polarization  $P$  in cu. cm. per mole and of the dipole moments in e.s.u.  $\times$  cm. for the linear portions of the capacitance-pressure isothermal curves, that is, for

(17) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, N. Y., 1931, p. 149.

TABLE I  
POLARIZATION AND DIPOLE MOMENT VALUES OF UN-  
ASSOCIATED HYDROGEN FLUORIDE

$t, ^\circ\text{C.}$	$P$	$\mu (\times 10^{18})$
23.10	76.5	1.90
25.20	77.0	1.91
26.00	74.4	1.89
31.30	77.3	1.93
38.05	75.6	1.93
38.50	74.2	1.91
48.35	72.4	1.92
59.7	68.35	1.91

Mean value of moment =  $1.91 \pm 0.01$

the low pressure ranges where the association of the hydrogen fluoride is negligible and the polarization independent of pressure. The mean value found for the moment is identical with that previously reported.<sup>13</sup> Figure 2 shows the polarization

TABLE II  
DEPENDENCE OF POLARIZATION AND AVERAGE DIPOLE  
MOMENT ON PRESSURE AND TEMPERATURE

Pres- sure	Polarization, cu. cm./mole					
	23.10°	25.20°	31.30°	38.50°	48.35°	59.70°
0	76.0	77.0	77.4	74.1	72.4	68.4
50	77.0	77.6	76.9	74.3	72.4	68.4
100	76.5	77.0	77.6	74.7	72.4	68.4
150	77.8	76.6	77.0	74.1	72.4	68.4
200	80.5	78.5	78.0	74.0	72.4	68.4
250	85.0	80.5	79.5	74.1	72.4	68.4
300	91.1	82.7	81.4	74.2	72.4	68.4
350	97.6	85.7	83.8	76.0	72.4	68.4
400	104.3	90.1	86.4	78.0	72.4	68.4
450	110.6	94.6	89.1	80.2	72.4	68.4
500	117.1	99.6	91.5	82.7	72.4	68.4
550	125.0	104.8	95.9	85.4	73.5	68.4
600	135.7	111.3	98.9	88.2	74.6	68.4
650	149.8	127.8	101.0	91.2	76.0	68.4
700	170.9	150.7	104.6	94.2	77.3	68.4
730	198.0	...	...	...	...	68.4
740	...	163.3	...	96.6	78.2	68.4
750	...	...	107.2	...	...	68.4

Pres- sure	DIPOLE MOMENT ( $\times 10^{18}$ )					
	23.10°	25.20°	31.30°	38.50°	48.35°	59.70°
0	1.90	1.91	1.93	1.91	1.92	1.91
50	1.91	1.91	1.92	1.91	1.92	1.91
100	1.90	1.91	1.93	1.92	1.92	1.91
150	1.92	1.91	1.92	1.91	1.92	1.91
200	1.95	1.93	1.94	1.91	1.92	1.91
250	2.01	1.96	1.96	1.91	1.92	1.91
300	2.09	1.98	1.99	1.91	1.92	1.91
350	2.16	2.02	2.02	1.94	1.92	1.91
400	2.24	2.08	2.05	1.97	1.92	1.91
450	2.30	2.12	2.09	2.00	1.92	1.91
500	2.36	2.18	2.11	2.03	1.92	1.91
550	2.45	2.24	2.16	2.06	1.94	1.91
600	2.54	2.31	2.20	2.10	1.96	1.91
650	2.68	2.48	2.22	2.14	1.98	1.91
700	2.87	2.70	2.26	2.18	2.00	1.91
730	3.08	...	...	...	...	1.91
740	...	2.80	...	2.20	2.01	1.91
750	...	...	2.28	...	...	1.91

isothermals as functions of pressure, the temperature in  $^\circ\text{C.}$  being given beside each curve, and Table II lists the polarization values from which the curves were constructed, as well as the dipole moments calculated by means of equation (2). The values at 26.00 and 38.05° are so close to those at 25.20 and 38.50° that they have been omitted.

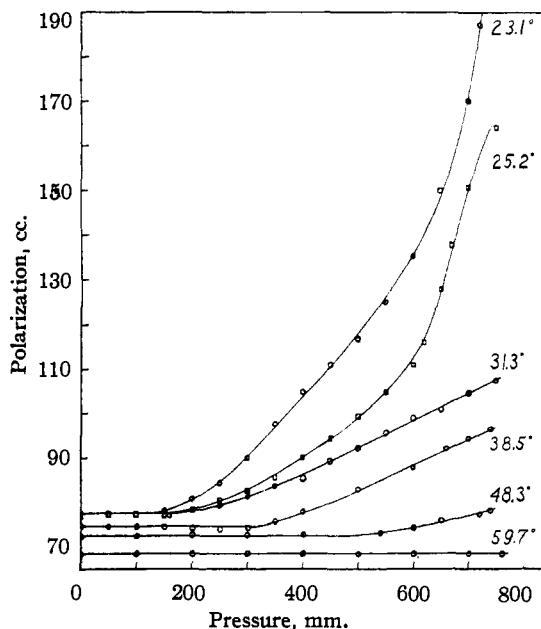


Fig. 2.—Polarization of hydrogen fluoride vapor.

### Discussion of Results

Without close analysis, it is evident that the  $6\text{HF} \rightleftharpoons (\text{HF})_6$  (cyclic) equilibrium postulated by some investigators<sup>2,4</sup> cannot be the whole story; such an equilibrium would predict lower polarizations as the ratio of hexamer to monomer increased with increasing pressure, since the dipole moment of a plane ring (Fig. 1A) or of any ring formed by joining the ends of the chain shown in Fig. 1C would be zero. Also, these results invalidate Briegleb's model (Fig. 1B) of a polymeric chain in which the units are consecutively antiparallel, since this structure would have a moment 0 or 1.91 according as the number of HF units was even or odd.

For associated hydrogen fluoride, the polarization is the sum of the contributions from the molecules of each of the several species present, so that the Debye equation becomes

$$P = \frac{4\pi}{3} \sum_{i=1}^n N_i \alpha_i = \frac{4\pi}{3} \left( \sum_{i=1}^n N_i \alpha_{0i} + \sum_{i=1}^n N_i \frac{\mu_i^2}{3kT} \right) \quad (3)$$

in which  $\alpha_i$ ,  $\alpha_{0i}$  and  $\mu_i$  are, respectively, the total polarizability, distortion polarizability and dipole moment of the  $i^{\text{th}}$  species;  $N_i$  is the number of molecules of the  $i^{\text{th}}$  species, and  $\sum_{i=1}^n N_i = N_A$ , the Avogadro number. The index  $i$  has integral val-

ues from 1 to  $n$  corresponding to monomer, dimer, etc., to the  $n^{\text{th}}$ -mer. The application of equation (2) to the polarization data gives an average dipole moment, which, in terms of the quantities used in equation (3) is

$$\mu = \left( \frac{1}{N_A} \sum_{i=1}^n N_i \mu_i^2 \right)^{1/2} \quad (4)$$

Similarly, the average distortion polarizability is

$$\alpha_0 = \left( \frac{1}{N_A} \sum_{i=1}^n i N_i \right) \alpha_{0i} \quad (5)$$

Although the distortion polarizabilities of the polymers are larger than that of the monomer, the value 2.0 has been used for  $MRD$  throughout since, in the range of these measurements, the molar refraction should never increase above 2.0 by more than 2, an amount negligible in its effect upon the calculations.

The dipole moments given in Table II are the average values represented by equation (4). In order to obtain values of the degree of association from these average dipole moments, a molecular model is necessary. The most probable structure would seem to be the chain with bond angles of  $140^\circ$  (see Fig. 1C), as indicated by X-ray<sup>9</sup> and electron diffraction<sup>8</sup> studies. As a basis for calculation, it may be assumed, as an approximation, that the moment of each monomeric unit remains unchanged at 1.91 when it forms part of a polymeric chain, and that each such unit is free to rotate with respect to the HF unit to which it is linked by a hydrogen bond, the bond angle being maintained at  $140^\circ$ . Such a polymeric chain would have a dipole moment dependent upon the degree of association, the relationship being obtainable from an equation<sup>18</sup> which, for this particular case, assumes the form

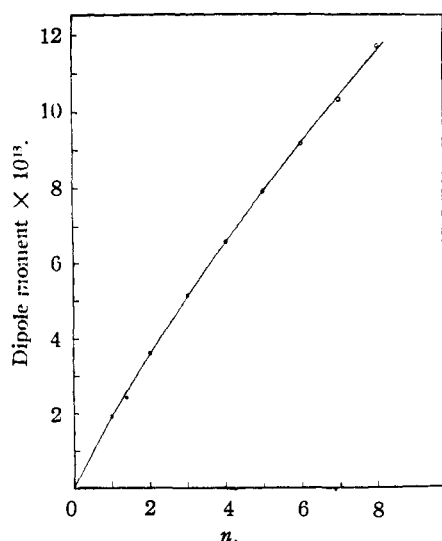


Fig. 3.—Calculated moment of polymeric chain of  $n$  units.

(18) Eyring, *Phys. Rev.*, **39**, 746 (1932).

$$\mu = \mu_1 (n + 2[(n-1) \cos 40^\circ + (n-2) \cos^2 40^\circ + \dots + (n-(n-1)) \cos^{n-1} 40^\circ])^{1/2} \quad (6)$$

in which  $n$  is the degree of association, and  $\mu_1$  is the moment of one HF, 1.91. In Fig. 3, a smooth curve is drawn through the values of  $\mu$  calculated for  $n = 1, 2, 3, \dots, 8$  by means of equation (6). For a mixture of monomer and dimer, dimer and trimer, or any pair of successive polymers, the value of  $\mu$  calculated from equations (2) and (3) could be used to calculate an average value of  $n$  by means of equation (6). This average value of  $n$  is a special case of the association factor,  $z$ , which may be defined as the ratio of the total number of HF units to the total number of molecules. In view of the small departure of the curve in Fig. 3 from linearity, its abscissas may be treated as giving the approximate values of an association factor,  $z_m$ , for the polar molecules of average moment  $\mu$ .

Table III gives the values of the association factor  $z_m$  estimated by means of the curve in Fig. 3 from the average dipole moment values, and Fig. 4 represents  $z_m$  as a function of pressure at the indicated temperatures.

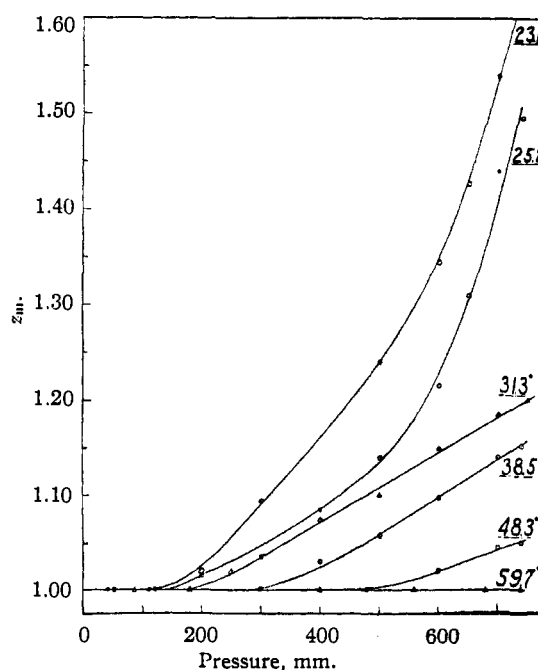


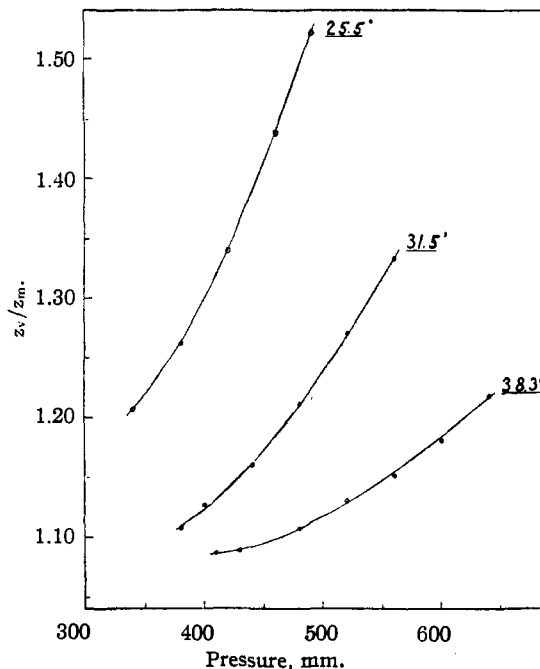
Fig. 4.—Variation of association factor,  $z_m$ , with pressure.

It must be kept in mind that since equation (6) postulates random orientation of the units of the chain because of complete freedom of rotation around the bonds, this method of evaluating the degree of association will give low results if any ring formation occurs and slightly high results if the chain is an extended, rigid structure. It will also tend to give high results if the hydrogen bonding raises the hydrogen-fluorine moment above that found for the monomer and assumed to be unchanged in the polymer. On the other hand,

TABLE III

Pressure	VALUES OF ASSOCIATION FACTOR, $z_m$					
	23.10°	25.20°	31.30°	38.50°	48.35°	59.70°
0	1.00	1.00	1.00	1.00	1.00	1.00
50	1.00	1.00	1.00	1.00	1.00	1.00
100	1.00	1.00	1.00	1.00	1.00	1.00
150	1.00	1.00	1.00	1.00	1.00	1.00
200	1.02	1.02	1.01	1.00	1.00	1.00
250	1.05	1.03	1.02	1.00	1.00	1.00
300	1.10	1.04	1.04	1.00	1.00	1.00
350	1.13	1.06	1.06	1.01	1.00	1.00
400	1.18	1.09	1.08	1.03	1.00	1.00
450	1.21	1.11	1.09	1.05	1.00	1.00
500	1.24	1.14	1.01	1.06	1.00	1.00
550	1.29	1.18	1.13	1.08	1.01	1.00
600	1.35	1.22	1.15	1.10	1.02	1.00
650	1.43	1.31	1.17	1.12	1.03	1.00
700	1.54	1.44	1.19	1.14	1.04	1.00
730	1.67	..	..	..	..	1.00
740	..	1.50	..	1.15	1.05	1.00
750	..	..	1.20	..	..	1.00

association factors calculated from vapor density measurements are unaffected by the configuration of the polymers. Consequently, a comparison of the values estimated from the dipole moments with those obtained from vapor density data should make possible a rough estimate of the relative proportion of cyclic structures among the polymers. In Fig. 5 the ratios of the values of the association factor  $z_v$  obtained from vapor density measurements<sup>4</sup> to those of  $z_m$  are plotted against pressure at different temperatures for the whole range within which the two sets of data overlap. This graph shows that, as association increases,  $z_v$  becomes increasingly larger than  $z_m$ , by an amount greater than one would expect to be occasioned by any difference in the two methods of averaging. Actual computations for many equilibria assumed between two or more linear molecular species show that the discrepancy between  $z_v$  and  $z_m$  should be small. That these two association factors are different must then be attributable to the presence of cyclic structures which contribute to  $z_v$  but not to  $z_m$ . Stabilization of coiled-chain structures in which the dipole moments would largely cancel one another and give small resultant moment to the molecule as a whole would give the same effect as the presence of cyclic structures. Since, however, these coiled-chain structures do not possess the stabilizing factor of the extra bond possessed by the cyclic structures, there appears to be no reason to expect a proportion of coiled-chain structures greater than that corresponding to the random distribution assumed in the calculation of  $z_m$ . Contributory evidence along these lines is obtained from the work of Briegleb,<sup>7</sup> who, by assuming that only monomer and dimer were present at low pressures and that successively larger polymers made their appearances at successively higher pressures used vapor density data<sup>5</sup> to calculate the dependence

Fig. 5.—Variation of  $z_v/z_m$  with pressure.

of the concentrations of the individual polymers upon pressure at 28 and at 38°. The average dipole moments calculated by means of equation (6) from these extremely approximate concentrations are considerably higher than those in Table II, just as the values of  $z_v$  are higher than those of  $z_m$ . The presence of cyclic structures without dipole moment accounts for one discrepancy as well as for the other.

If the angle of 140° in the zig-zag chain indicated by electron diffraction were larger than the actual value, the error introduced in equation (6) would result in too low values for  $z_m$ . However, lowering of the angle to 90°, thereby replacing 40° by 90° in equation (6), still leaves the  $z_m$  values well below those of  $z_v$ .

### Conclusions

The dielectric constant measurements and dipole moment calculations established the fact that hydrogen fluoride forms polar and, therefore, more or less linear polymers as indicated by X-ray and electron diffraction measurements. The discrepancy between the association factor calculated from dipole moment and that calculated from vapor density indicates the presence of cyclic polymers, the relative proportion of which increases with increasing association. The adsorption of hydrogen fluoride molecules on the metal surface of the condenser produces no significant error and the dielectric behavior of the adsorbed layer evidences the freedom of molecular orientation found in a liquid. The dipole moment results are consistent with the successive equilibria  $\text{HF} + (\text{HF})_n \rightleftharpoons (\text{HF})_{n+1}$  postulated by Briegleb<sup>6,7</sup> in the interpretation of the vapor densities, but show the incor-

rectness of the linear model with anti-parallel units which he adopted for the polymer structure. The existence of but one equilibrium,  $6\text{HF} \rightleftharpoons (\text{HF})_6$ , with the hexamer a ring, which was found<sup>4</sup> capable of representing the vapor density data, is quite inconsistent with the dipole moment results. The infinitely extended zig-zag chain shown by X-ray analysis<sup>9</sup> to exist in the crystal would, of course, be broken into fragments in the vapor. In the molecular beam indicated by electron diffraction<sup>8</sup> as consisting of these fragments, an appreciable proportion of cyclic structures might have escaped detection and the proportion may actually have been much lower than that existing under the conditions of the dielectric measurements. It is interesting to note that the zig-zag structure indicated for the polymeric chain as compared to a rectilinear structure involves an attractive force between the proton of one hydrogen fluoride unit and negative charge localized as by an orbital in the fluorine of the adjacent hydrogen fluoride unit. In other words, the hydrogen bonding, in this case, though electrostatic, is not merely the undirected electrostatic attraction between the charges of a proton and an anion, as often implied in hydrogen bonding. The existence of both linear and cyclic structures in hydrogen fluoride is consistent with the belief of Bernal and Fowler<sup>19</sup> that both should exist in the liquid and with the conclusion of Pauling<sup>10</sup> that the additional bond obtained by ring formation should

(19) Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

increase the stabilities of ring structures over open-chain structures when the degree of polymerization is greater than 5.

The work described in this paper was carried out as part of a research project supported by the Office of Naval Research.

### Summary

The dielectric polarization of hydrogen fluoride vapor has been measured as a function of pressure at various temperatures above the normal boiling point of 19.4°. The apparatus employed has been described, and the errors due to adsorption of the hydrogen fluoride on the condenser walls have been shown to be unimportant. In the region of temperature and pressure where no molecular association occurs, a dipole moment value identical with that previously found in this laboratory has been obtained. At lower temperatures and higher pressures the experimental results show conclusively that a very considerable fraction of the associated molecules in the vapor state exists in various linear structures of large dipole moment, and that the average degree of association increases rapidly with increasing pressure or decreasing temperature. Further analysis of the data indicates that cyclic structures also exist in equilibrium with the chains, and that the former tend to increase in relative proportion with increase in pressure, and decrease in temperature.

PRINCETON, N. J.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

## Perfluorinated Olefins

BY ALBERT L. HENNE AND THOS. H. NEWBY

The synthesis of perfluorinated ethylene and its polymerization to commercial TEFLON,  $(\text{CF}_2)_n$ , have become industrial processes; efforts are now directed at the synthesis of other fully fluorinated olefins in order to study their polymerization characteristics and their ability to copolymerize with  $\text{CF}_2=\text{CF}_2$ . We report here experiments toward the preparation of  $\text{CF}_3\text{CF}=\text{CF}_2$ ,  $\text{CF}_3\text{CF}=\text{CFCF}_3$ , and  $\text{CF}_3\text{CF}_2\text{CF}=\text{CF}_2$ .

### Synthesis of $\text{CF}_3\text{CF}=\text{CF}_2$

Perfluorinated propylene has been prepared by us before, but by a sequence which has too many steps for industrialization.<sup>1</sup> To simplify, we have subjected the easily available<sup>2</sup>  $\text{CCl}_3\text{CClFCCl}_3$  to fluorination with antimony fluoride in the standard way, and have obtained in one step a 70% yield of  $\text{CF}_2\text{ClCFClCF}_2\text{Cl}$ , from which zinc in alcohol yielded  $\text{CF}_2\text{ClCF}=\text{CF}_2$  almost quantitatively. From this olefin, it was expected that

"allylic" fluorination<sup>3</sup> would easily yield the desired perfluorinated propylene, but this did not appreciably succeed because an allylic rearrangement took place which gave  $\text{CF}_3\text{CF}=\text{CClF}$  instead of the desired product. The course of the rearrangement was evident from the facts that the rearranged olefin differed from the known<sup>3</sup>  $\text{CF}_3\text{CCl}=\text{CF}_2$ , and that its alkaline oxidation<sup>4</sup> yielded nothing but trifluoroacetic acid.

The desired synthesis was, however, completed as follows. The rearranged compound accepted a mole of chlorine to give the known<sup>1</sup>  $\text{CF}_3\text{CFClCFCl}_2$ , which antimony fluoride transformed into the known<sup>1</sup>  $\text{CF}_3\text{CFClCF}_2\text{Cl}$ . Dechlorination with zinc gave the desired perfluorinated propylene. The sequence is thus a simplified laboratory preparation, but is still too complex for industrial application.

The rearrangement reminded us of a similar case which could not be explained at the time. A

(1) Henne and Waalkes, *This Journal*, **68**, 496 (1946).

(2) Henne and Haackl, *ibid.*, **68**, 2692 (1941).

(3) Henne, Whaley and Stevenson, *ibid.*, **68**, 3478 (1941).

(4) Henne, Alderson and Newman, *ibid.*, **67**, 918 (1945).