2. The freezing point was found to be —83°C.

3. The vapor-pressure curve was established from the melting point, 192°K., to 320°K. and a pressure of 25 atmospheres.

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THE DENSITY AND MOLECULAR COMPLEXITY OF GASEOUS HYDROGEN FLUORIDE

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The Density of Hydrogen Fluoride Vapor Below its Boiling Point

Thorpe and Hambly[1] have shown that the apparent molecular weight of hydrogen fluoride vapor is 51.18 at 26.4° and 745 mm. This corresponds to a higher polymerization than the H_2F_2 often stated in the textbooks, and indicated to us the desirability of pushing the measurements to lower temperatures in order to determine the degree of complexity which this interesting substance may be capable of assuming.

The "dynamic" method of measuring vapor density was adopted with the following procedure. Nitrogen gas, freed from oxygen by passage through a cuprous ammonia reducing tower and thoroughly dried, was bubbled through anhydrous liquid hydrofluoric acid. It was then passed through copper tubes containing dry sodium fluoride, which absorbed the hydrogen fluoride, the quantity of which could be ascertained by weighing the tubes. Knowing the vapor pressure of the liquid from the data in the preceding paper and the weight of the acid carried off by a known quantity of nitrogen, the density and apparent molecular weight of the gas can be calculated from the perfect gas law.

A diagram of the apparatus is shown in Fig. 1.

The volume of the nitrogen was obtained by weighing the 2-liter bottle in which it was contained, displacing the gas with water and weighing again. The water contained a small amount of ferrous sulfate in solution to prevent its containing oxygen. The reason for the precautions to remove oxygen is that it would oxidize the copper vessel in which the acid was contained and so contaminate it. The nitrogen was passed through sulfuric acid and phosphorus pentoxide to dry it and then into the copper vessel containing the acid; twice in its passage it was forced to bubble through the liquid. It then passed through the train of sodium fluoride tubes which removed the hydrogen fluoride. The vessel was made of thin-walled copper tubing, silver soldered throughout. It was inserted in a Dewar vessel in which was placed the constant-temperature bath. The connections of the copper part of the gas train that had to be broken between every two runs were made of tightly fitting sleeves of copper tubing covered with pure gum rubber tubing. Two small auxiliary cells, containing mercury at the bottom and to which small glass tubes were connected with outer sleeves to aid in sealing, served

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[1] Thorpe and Hambly, *J. Chem. Soc.*, **55**, 163 (1889).

both to determine the pressure during the run and to seal the anhydrous liquid between runs by adding sufficient mercury to cover the ends of the entry tubes.

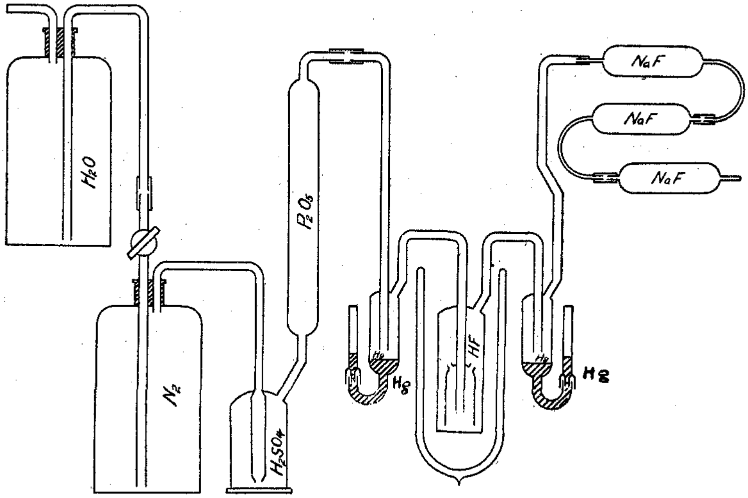

Fig. 1.—Low temperature vapor-density apparatus.

Determinations were made using the following constant-temperature baths; melting mercury, sodium chloride-ice eutectic, sodium thiosulfate-ice eutectic and melting ice. Duplicate runs were made in these cases. The average rate of passage of the gas was 30 bubbles per minute. Trebling the rate did not affect the results, showing that equilibrium was established. Four single determinations were then run at temperatures between 0° and the boiling point, but due to the high vapor pressure of the liquid at these temperatures no great accuracy can be claimed.

The experimental data are given in Table I. They show a polymerization of hydrogen fluoride far above the ordinarily assumed H_2F_2. In the following section these results will be coördinated with other experiments and the degree of polymerization determined.

TABLE I

MOLECULAR WEIGHT OF HYDROGEN FLUORIDE AT LOW TEMPERATURES

Wt. H_2O displacing N_2 G.	Room temp. °C.	Bar. pressure Mm. of Hg	Temp. of HF °K.	Wt. of HF G.	Vapor pressure HF Mm. of Hg	Molecular weight HF	Av. value at each temp.
2538	18	750	234	0.743	56.2	89.4	
2499	17	748	234	0.743	56.2	90.3	
2575	17	748	234	0.735	56.2	86.8	
2480	15	752	234	0.713	56.2	86.6	
2547	17	752	234	0.715	56.2	85.4	
2506	16	758	234	0.712	56.2	86.0	87.4
1198	16.5	752	252	0.944	144	81.5	
1269	17	752	252	1.014	144	82.9	
1192	18	751	252	0.934	144	81.5	81.6

TABLE I (*Concluded*)

Wt. H_2O displacing N_2 G.	Room temp. °C.	Bar. pressure Mm. of Hg	Temp. of HF °K.	Wt. of HF G.	Vapor pressure HF Mm. of Hg	Molecular weight HF	Av. value at each temp.
835	18.5	752	263	1.134	234	74.3	
916	19	753	263	1.241	234	74.3	74.3
2571	17.5	758	273	6.666	364	68.6	
609	15	759	273	1.511	364	64.9	
645	16	758	273	1.649	364	67.0	
587	16.5	758	273	1.498	364	67.2	
432	16.5	758	273	1.100	364	67.0	67.6
547	16	755	278.3	2.135	436	69.3	69.3
611	16	755	281.6	3.016	491	64.3	64.3
486	16	754	285	4.503	576	69.5	69.5
378	15	754	289	5.285	661	47.7	47.7

The Molecular Complexity of Gaseous Hydrogen Fluoride

In the preceding section evidence has been given for a molecular species of hydrogen fluoride with a higher molecular weight than 80, that is, for molecules with a higher degree of association than $(HF)_4$. Thorpe and Hambly in an investigation previously referred to measured the density of the gas by direct weighing in a platinum vessel. Their measurements cover a range of temperature at constant pressure and a range of pressure at constant temperature. We will now proceed to correlate our data with those of Thorpe and Hambly by assuming a definite type and degree of association.

It is conceivable that the simple molecules of HF, of which the gas consists almost wholly above 90°C. according to Thorpe and Hambly, may form several polymers, in which case a quantitative treatment would be very difficult, or it may form a single polymer $(HF)_n$. We have assumed that the latter is the case, with very striking success as follows. The equation of equilibrium in this case is $n\text{HF} = (\text{HF})_n$, and if the partial pressures are respectively p and p_n we can write

$$K = \frac{p_n}{p^n} \tag{1}$$

The experimental data have been expressed in terms of apparent molecular weight of the mixture, m, which has been calculated by the relation

$$PV = \frac{20}{m}RT \tag{2}$$

If 1 mole of HF gives x moles of $(HF)_n$ there would be left $1-nx$ moles of HF and a total of $1-nx+x$ moles in the mixture. We can therefore write $PV = (1-nx+x)RT$, whence we see that

$$1 - nx + x = \frac{20}{m} = \frac{1}{z}, \tag{3}$$

where z expresses the degree of polymerization.

The partial pressures in Equation 1 are equal to the total pressure times the respective mole-fractions, that is,

$$p_n = P\frac{x}{1 - nx + x}, \text{ and } p = P\frac{1 - nx}{1 - nx + x} \tag{4}$$

Substituting these values in Equation 1 and substituting z for x by Equation 3, we get finally

$$KP^{(n-1)} = \frac{(1-n)^{(n-1)}(1-z)}{(z-n)^n} \tag{5}$$

This equation can be used to express the experimental data in terms of the total pressure and n, provided the polymerization is of the single type assumed. An algebraic solution would be very complicated, for higher values of n, so we have adopted a graphic method. The logarithm of the right-hand member of the equation was plotted against a series of arbitrary values of m (which equals $20z$). This gives $KP^{(n-1)}$ as a function of m for any set of data for a given value of n. The value of K necessary to give the relation between the experimental values of P and m could then be easily selected.

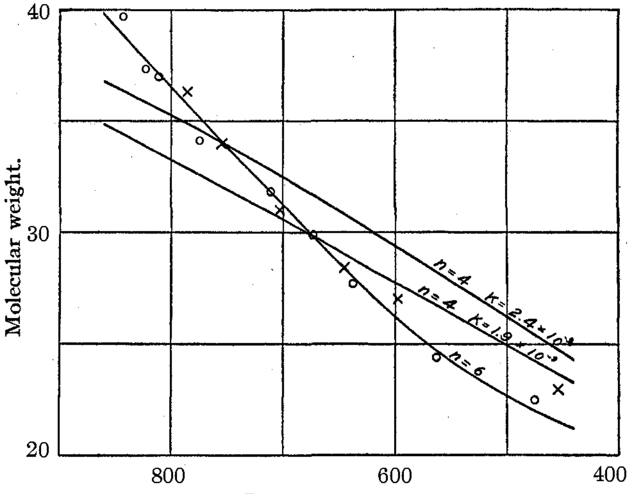

Fig. 2.—Variation of molecular weight with pressure at 305°K.

Thorpe and Hambly give values showing the variation of m with P at two different temperatures, 305°K., and 315.3°K., the former in two series, one obtained by reducing the pressure by exhaustion only, here reproduced in Table II, the other by dilution with air, given in Table III. (The values have been corrected for the slight temperature variations, using Equation 6 below.) We have calculated this relation between m and P from Equation 5, assuming $n = 6$ and $K = 2.91 \times 10^{-15}$ at 305°K., and $K = 1.91 \times 10^{-9}$ at 315.3°K. It will be seen from Tables II and III that the corrected experimental values for the lower temperature, given in the fourth column of each table, agree excellently with those in the last columns. Fig. 2 shows this agreement in an even more striking manner. The crosses denote the experimental values in Table II, the circles those in Table III, the curves the calculated values.

TABLE II

VARIATION OF MOLECULAR WEIGHT WITH PRESSURE AT 305°K.

(Pressure of hydrogen fluoride reduced by reducing total pressure)

		Observed		Calculated			
				for $n = 4$ $K = 2.40 \times 10^{-9}$		for $n = 6$ $K = 2.91 \times 10^{-15}$	
Partial pressure Mm. of Hg	Temp. °K.	m Exptl.	m, corr. to 305.0°	log KP^3	m	log KP^5	m
743	305.1	39.74	40.0	−0.01	36.3	−0.20	38.8
686	305.3	35.78	36.3	− .11	34.9	−0.37	35.8
655	304.9	33.98	34.0	− .17	34.0	−0.47	34.1
603	305.1	30.82	31.0	− .28	32.5	−0.65	31.4
545	305.6	27.78	28.5	− .41	30.8	−0.87	28.4
498	305.4	26.54	27.0	− .53	29.2	−1.07	26.1
354	305.0	23.00	23.0	− .97	24.7	−1.80	21.5
353	305.4	22.78	23.0	− .98	24.6	−1.81	21.4

TABLE III

VARIATION OF MOLECULAR WEIGHT WITH PRESSURE AT 305°K.

(Pressure of hydrogen fluoride reduced by diluting with air)

		Observed		Calculated			
				for $n = 4$ $K = 1.91 \times 10^{-9}$		for $n = 6$ $K = 2.91 \times 10^{-15}$	
Partial pressure Mm. of Hg	Temp. °K.	m Exptl.	m, corr. to 305.0°	log KP^3	m	log KP^5	m
743	305.1	39.74	40.0	−0.14	34.4	−0.18	38.8
723	304.8	37.80	37.3	− .18	33.9	− .24	37.7
712	304.9	37.24	37.0	− .20	33.6	− .27	37.1
675	305.6	34.10	35.0	− .27	32.6	− .39	35.2
611	304.8	31.82	31.6	− .40	30.9	− .60	32.0
574	304.8	29.88	29.9	− .48	29.9	− .74	29.9
539	304.8	27.92	27.7	− .56	28.9	− .88	28.0
463	304.7	24.64	24.4	− .76	26.7	−1.21	24.7
375	304.6	22.66	22.5	−1.03	24.3	−1.66	22.0

TABLE IV

VARIATION OF MOLECULAR WEIGHT WITH PRESSURE AT 315.3°K.

(Partial pressure reduced by diluting with air)

		Observed		Calculated			
				for $n=4$ $K=2.81 \times 10^{-10}$		for $n = 6$ $K=4.16 \times 10^{-16}$	
Partial pressure Mm. of Hg	Temp. °K.	m Exptl.	m corr. to 315.3°	log KP^3	m	log KP^5	m
741	315.9	26.26	26.9	−0.94	25.0	−1.03	26.4
718	315.2	25.30	25.3	−0.97	24.7	−1.10	25.8
640	315.3	23.48	23.5	−1.13	23.6	−1.35	23.6
631	315.3	23.46	23.5	−1.15	23.4	−1.38	23.4
601	315.1	23.14	23.0	−1.21	23.0	−1.49	22.8
589	315.1	22.64	22.6	−1.24	22.9	−1.53	22.5
434	315.5	21.50	21.5	−1.64	21.3	−2.19	20.6
370	315.6	20.32	20.4	−1.85	20.9	−2.54	20.2

To show the effect of assuming a different value of n we give in these tables and in Fig. 2 two curves for $n = 4$ with different equilibrium constants. It is evident that no value of K that we might assume for $(HF)_4$ could satisfy the data.

The values for the higher temperature are given in Table IV and represented graphically in Fig. 3. It will be seen again that the assumption $n = 6$ holds better than $n = 4$, although the smaller degree of association at this temperature makes the difference less pronounced.

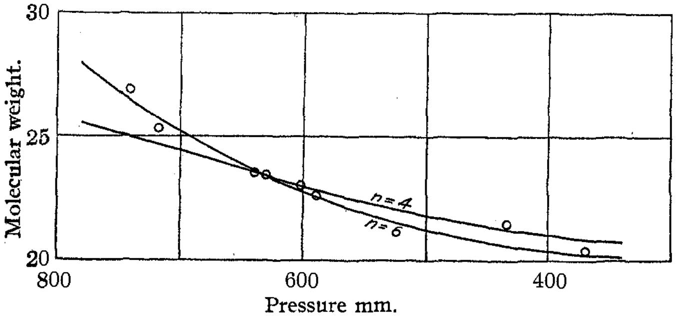

Fig. 3.—Variation of molecular weight with pressure at 315.3 °K.

Thorpe and Hambly give data for the relation between apparent molecular weight and temperature at approximately constant pressure, here given in Table VI. It is evident that the effect of temperature can be given by the expression

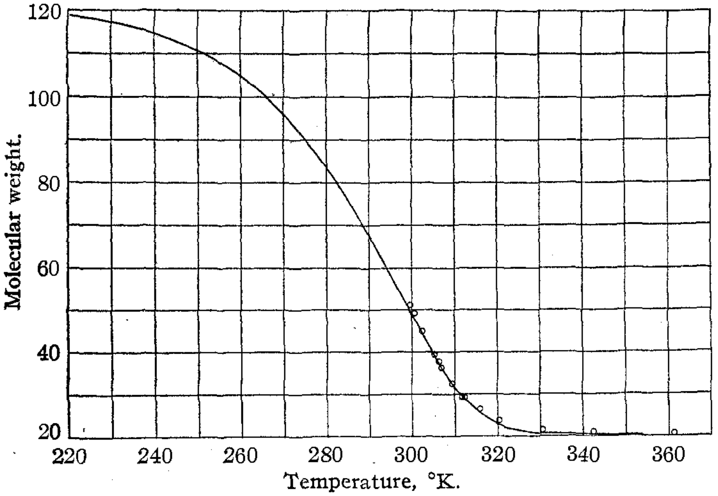

Fig. 4.—Variation of molecular weight with temperature at 745 mm.

$$\log K = \frac{-\Delta H}{4.579\,T} + C. \qquad (6)$$

We have applied this to the data using $\Delta H = -40{,}000$ cals.[2] and $C = -43.145$. The smooth curves for this function at $P = 745$, and when P equals the vapor pressure, have been plotted in Figs. 4 and 5, respectively, from calculated values given in Table V. Table VI gives the experimental data at 745 mm., together with corresponding calculated values of m taken from the curve. The experimental values at this pressure are plotted in Fig. 4.

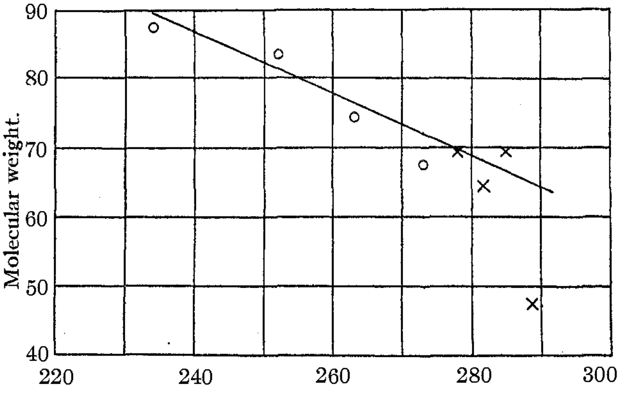

Fig. 5.—Variation of molecular weight with temperature at the saturation pressure.

TABLE V

THE VARIATION OF MOLECULAR WEIGHT WITH TEMPERATURE AT 745 MM. AND AT THE VAPOR PRESSURE

Temp. °K.	Log vapor pressure Mm. of Hg	At 745 mm.		At the vapor pressure	
		Log KP^5	m	Log KP^5	m
227.3	1.590	9.655	117.6	3.245	92.8
232.6	1.712	8.781	116.8	2.981	90.0
238.1	1.844	7.908	115.2	2.768	87.8
243.9	1.977	7.034	113.3	2.559	85.0
250.0	2.111	6.159	110.7	2.354	82.4
256.4	2.242	5.287	107.1	2.137	79.4
263.2	2.373	4.413	102.3	1.918	76.4
270.3	2.505	3.540	95.7	1.705	73.2
277.8	2.637	2.666	86.8	1.491	69.8
285.7	2.770	1.793	74.6	1.283	66.3
294.1	2.900	0.919	59.8	1.059	62.3
303.0	3.032	0.056	43.0	0.856	58.4
312.5	3.160	−0.828	28.8	0.612	53.8
322.6	3.293	−1.702	21.8	0.403	50.3

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[2] A change of 1000 cals. in this value throws the resulting curves obviously away from the experimental data.

TABLE VI

THE VARIATION OF MOLECULAR WEIGHT WITH TEMPERATURE AT 745 MM.

Temp. °K.	Partial pressure Mm. of Hg	Molecular weight Exptl.	Corr. to 745 mm.	Calcd.
299.5	745	51.18	51.2	49.5
300.9	746	49.42	49.2	48.0
302.3	750	45.54	45.0	44.0
305.1	743	39.74	39.4	39.2
306.2	750	38.18	37.7	37.3
306.9	758	36.66	36.1	36.5
309.4	739	32.20	32.5	32.7
311.8	751	29.46	29.2	29.5
312.3	743	28.94	29.1	28.9
315.9	741	26.26	26.5	25.4
320.4	745	23.76	23.8	22.6
330.6	750	21.28	21.3	20.4
342.5	746	20.96	21.0	20.1
361.2	741	20.58	20.6	20.0

The curve shows that the value of m is rising sharply as the temperature is lowered, although the highest value is only 50. It is impossible to follow this curve upwards because the saturation point lies just beyond, at about 292°K. We therefore proceed to the consideration of the data we have obtained for the vapor densities at saturation pressures down to 232°K. and 56 mm. Table VII gives a summary of the data previously given in Table I, together with the values calculated from Equation 6. These are plotted in Fig. 5. The crosses represent single determinations whereas the circles represent the average of a large number, so that the smaller deviations are to be expected. Due to the sensitivity of K, Equation 6 does not give quite the same values that were previously selected to calculate the results at constant temperature. The correction of the values in Tables II to IV to correspond exactly to Equation 6 would not as a matter of fact appreciably alter the position of the smooth curves in Figs. 2 and 3 or the values of m read from them. The apparent sensi-

TABLE VII

VARIATION OF MOLECULAR WEIGHT AT LOW TEMPERATURES AT THE VAPOR PRESSURE

Temp. °K.	Vapor pressure Mm. of Hg	Molecular weight Exptl.	Calcd.
234	56.2	87.4	89.6
252	144	81.6	81.4
263	234	74.3	76.6
273	364	67.6	72.1
278.3	436	69.3[a]	69.7
281.6	491	64.3[a]	68.2
285.0	576	69.5[a]	66.4
289.0	661	47.7[a]	64.8

[a] Single observations.

tiveness of K could have been reduced by the familiar subterfuge of writing it equal to $p_n^{1/n}/p$ instead of p_n/p^n, but this, while making a better showing, would not alter the real state of affairs.

We see from the foregoing that by assuming a single type of polymerized molecule, $(HF)_6$, in equilibrium with molecules of HF, it has been possible, by selecting arbitrary values for the equilibrium constant and the heat of association, to account within the limit of experimental error for a large body of data ranging in temperature from 234°K. to 361°K., and in pressure from 56 mm. to 750 mm. It is interesting to note, further, that the magnitude of the heat of association, 40,000 cals. for 6 moles of HF, or 6670 cals. for the complete polymerization of 1 mole of HF, is very reasonable, as it is of the same order as the heats of vaporization of similar substances. Surprising as is the physical significance of this result, its degree of agreement tends to dissipate the doubt one might feel as to its reality. It is all the more remarkable to arrive at such a conclusion when we consider that it will never be possible to get pure $(HF)_6$ in the vapor state, because the condensation to the liquid phase so limits the pressure possible to impose upon the vapor as to offset the effect of lowering the temperature.

This result suggests some interesting speculations concerning valence and molecular structure, indicating perhaps, a "benzene ring." We plan to investigate the molecular weight when this substance dissolved is in solvents such as benzene.

Summary

1. The vapor density of hydrogen fluoride has been determined at a series of temperatures below its boiling point.

2. The data obtained, together with the extensive data of Thorpe and Hambly at higher temperatures, have been closely calculated by assuming that the vapor contains an equilibrium mixture of HF and $(HF)_6$ with a heat of association of 6670 cals. per mole of HF.

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