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

The Polymerization of Gaseous Hydrogen and Deuterium Fluorides

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Simons and Hildebrand[1] showed that their measurements of the density of saturated hydrogen fluoride vapor, together with the density measurements of Thorpe and Hambly,[2] the only others then available, could be reproduced within the limits of accuracy by assuming the presence of only two molecular species, HF and $(HF)_6$. Subsequently, however, Fredenhagen[3] obtained data which indicated the presence of one or more higher polymers at high pressures and one or more lower polymers at low pressures. Additional uncertainty was injected by the failure of Bauer, Beach and Simons[4] to find evidence from electron diffraction of a benzene-like structure that would seem to be required to make a hexamer more stable than other polymers. This situation made it desirable to obtain independent and accurate measurements of the gas density. The measurements by Simons and Hildebrand[1] showed considerable fluctuation and those by Fredenhagen,[3] while smooth for any one temperature, showed a most improbable temperature coefficient.

In order to throw new light upon the problem we attacked it by a different method, which was to isolate a quantity of the gas in a constant-volume container and to make simultaneous measurements of pressure and temperature. If hydrogen fluoride were unpolymerized and obeyed the perfect gas law, one would expect the ratio of pressure to temperature to remain constant.

It was found by Thorpe and Hambly[2] and again by Fredenhagen[3] that above 80° and approximately atmospheric pressure the polymerization of gaseous hydrogen fluoride is very small. At higher temperatures, then, hydrogen fluoride will be expected to obey the perfect gas laws fairly closely. At lower temperatures, however, polymerization will cause large deviations from perfect-gas behavior. The number of moles of gas present, n, is given by $P/T = nR/V$, although n is variable. At a temperature sufficiently high to dissociate all of the complex molecules into single molecules of HF, P/T becomes constant, except for the small thermal expansion of the vessel and we may write $P_1/T_1 = n_1R/V_1$, n_1 having become constant. The volumes of the vessel at T and T_1 are $V = V_0 \cdot (1 + \alpha t)$ and $V_1 = V_0(1 + \alpha t_1)$ where α is the cubical coefficient of expansion of silver. We can combine these four equations to get the "association factor," $z = n_1/n$

$$z = \frac{(P_1/T_1)(1 + \alpha t_1)}{(P/T)(1 + \alpha t)}$$

Apparatus and Manipulation.—Notwithstanding the interesting properties of hydrogen fluoride, it has not been widely studied because of difficulty in manipulation. Simons[5] has outlined materials suitable for manipulating hydrogen fluoride. The strongly hygroscopic nature of anhydrous hydrogen fluoride makes necessary the exclusion of absolutely all moisture from the liquid or gas.

Anhydrous hydrogen and deuterium fluorides were prepared by the reduction of silver fluoride similar to the method used by Claussen and Hildebrand.[5a] The fluorine used to produce the silver fluoride was prepared essentially as described by Claussen.[6] In addition, the molten potassium bifluoride was stirred mechanically while electrolyzing to remove the last traces of water before using any of the fluorine. This precaution was to make sure that no oxygen was given off at the anode along with the fluorine. The preliminary electrolysis was carried on for at least two hours after the first fluorine was observed at the anode. The entire fluorine generation apparatus of copper was silver soldered into one unit so that there would be no danger of moisture of air leaking into the tubes carrying the fluorine. The fluorine was passed through a copper trap immersed in liquid oxygen to remove hydrogen fluoride and carbon fluorides.

The details of the rest of the manipulation may be understood by referring to Fig. 1 which is a diagrammatic representation not drawn to scale. The fluorine entered the silver reaction chamber G by the monel metal valve F and left through the valve I. Valves K, H, and Y were always closed while producing silver fluoride. The temperature of the reaction vessel G was ordinarily below 100° and the heat of the reaction was usually sufficient to keep it warm. Under these conditions AgF_2 was probably produced.[7] The reaction vessel G was packed with silver foil cut into very narrow strips. The total surface of silver exposed to fluorine was in the order of magnitude of 150 sq. cm. The fluorine reacted with the silver for about one and one-half to two hours and produced enough silver fluoride to prepare roughly a 1000-cc. sample of hydrogen fluoride at room temperature and atmospheric pressure. Nitrogen was

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(1) J. H. Simons and J. H. Hildebrand, THIS JOURNAL, **46**, 2138 (1924).

(2) Thorpe and Hambly, *J. Chem. Soc.*, **55**, 163 (1889).

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

(4) S. H. Bauer, J. Y. Beach and J. H. Simons, THIS JOURNAL, **61**, 19 (1939).

(5) J. H. Simons, *Ind. Eng. Chem.*, **32**, 178 (1940).

(5a) W. Claussen and J. H. Hildebrand, THIS JOURNAL, **56**, 1820 (1934).

(6) W. Claussen, *ibid.*, **56**, 614 (1934).

(7) Ruff and Giese, *Z. anorg. allgem. Chem.*, **219**, 143 (1934).

passed through G along with the fluorine in order that no moisture or oxygen could diffuse back through I when it was open to the air during the passing of fluorine through the vessel G. In order to remove small amounts of oxygen from the tank nitrogen, it was led over a long train of hot copper gauze in a thick Pyrex tube heated approximately within 50° of its softening point. The nitrogen then passed through a drying trap immersed in liquid air. A 25-cm. section of this trap was packed with glass beads to dry and impede the flow of nitrogen. A needle valve and manometer controlled the flow of nitrogen into the fluorine-generation apparatus. At the end of the reaction the excess fluorine was flushed out with nitrogen, F and I closed, H opened, and the nitrogen pumped out until a high vacuum was obtained in G while it was being heated to 110°. Heating and evacuation usually continued for ten or more hours.

No moisture may come into contact with the silver fluoride because the hydrates of silver fluoride decompose when heated under high vacuum[8] into some silver oxyfluoride along with the anhydrous silver fluoride. Hydrogen would probably react with silver oxyfluoride to give water and hydrogen fluoride.

Hydrogen fluoride was prepared by allowing hydrogen from the storage bulb D to pass through the drying trap E and the valve H into the reaction vessel G which was heated to 110°. The hydrogen fluoride was frozen out as soon as it diffused into the trap J which was immersed in liquid air. As the hydrogen was used up more was admitted through H until the manometer Z showed that sufficient hydrogen had reacted to give the desired quantity of hydrogen fluoride. The trap E was similar to the nitrogen drying trap mentioned previously. It was necessary to dry the hydrogen quite thoroughly because the method of its production often permitted water to come into the storage chamber D. After the reaction between the hydrogen and the silver was nearly complete, G was allowed to cool with J in liquid air continuously. The excess hydrogen was then pumped out through H by means of the high vacuum line. H was closed and G again heated and any hydrogen in the form of a complex with the silver fluoride was distilled into J. After this distillation, H was opened and G and J again thoroughly evacuated. H was then closed and the hydrogen fluoride distilled through K and V into the previously-evacuated constant-volume container M which had a small dewar of liquid air placed around the trap N. G had to be heated during this distillation in order to prevent the complex of hydrogen fluoride and silver fluoride from forming. With the hydrogen fluoride frozen in N the entire system was again evacuated. V was next closed and the trap N permitted to warm. As the pressure in M increased during the vaporization of the hydrogen fluoride from the trap N, it was balanced on the opposite side of the diaphragm gage by the needle valve Q. The amount of hydrogen fluoride in M was adjusted after it had vaporized by distilling any excess from M back into the trap J. The container M had a volume together with the connecting tubing and the gage of 329.0 cc.

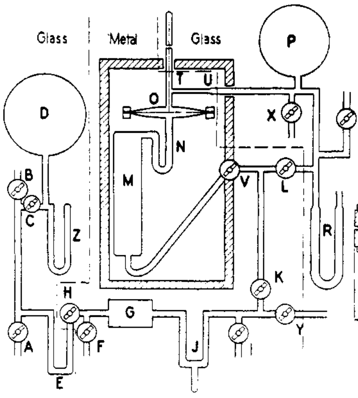

Fig. 1.—Apparatus.

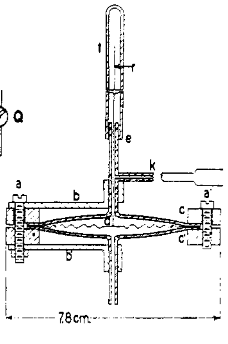

Fig. 2.—Diaphragm gage.

The valve V was arranged with a long stem so that it could be opened or closed from the outside of the thermostat, yet the entire quantity of gas trapped in the constant-volume container and connecting tubing was within the thermostat. This valve was water-cooled in order that the heat from the thermostat would not melt the grease. Each of the needle valves was made of monel metal and had a cup-like arrangement on the top that held a non-reactive grease. This grease served as a packing for the stem of the valve. Each time a valve was turned the surface of the grease was immediately melted around the stem in order that no leakage could take place. Valve V was water cooled in order that the heat from the thermostat would not melt the grease.

All the apparatus that came into contact with hydrogen fluoride was constructed of copper, silver, gold or monel metal. The gage O was of gold; however, the constant-volume container M and the connecting tubes to the valve V were of silver. As mentioned previously, the reaction vessel G and the trap J were also of silver. The other connecting tubes were made of copper. The entire apparatus was welded into one unit with silver solder.

Diaphragm Gage.—The details of the null-point gage O, may be seen from the cross-sectional scale drawing (Fig. 2). The main case consisted of two parts pressed out of solid gold about 1 or 1.5 mm. thick. Five radial corrugations on each case half increased its rigidity. The soft-glass tube t which protruded through the top of the air thermostat was sealed to the gage by means of a platinum-tubing connection. The platinum tube had a small bore which served to guide the pointer r. The pointer r which consisted of a light-weight, blue-grass rod or fiber cut off square on the top, rested on the diaphragm; and its movement was observed through the glass tube t by means of a measuring microscope.

The steel rings c and c' held the diaphragm firmly in place between the two halves of the gold case by means of 19 screws, a and a'. The softness of the gold made possible a vacuum tight seal with the gold-plated brass diaphragm. Extreme tightening on the screws had to be avoided to prevent distortion of the diaphragm d. The surfaces of the case halves that held the diaphragm were ground perfectly smooth with ground glass or pumice and then polished carefully with rouge. The grinding and polishing had to be done in the absence of coarse particles that might scratch the smooth, soft surface of the gold. When using grinding agents such as ground glass or pumice, it was found to be best to remove the coarse particles and obtain

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[8] E. Fremy, *Ann. chim. phys.*, **47**, 39 (1856).

powder of various degrees of fineness by means of a flotation method. After assembling the gage each time, it was filled with hydrogen under moderate pressure, immersed in water and tested for leaks. After the gage had been made free of leaks, it was then coated with bakelite lacquer and baked at 135°. The bakelite treatment was used merely to lessen the likelihood of leaks arising when the gage was in use over a large temperature range. The inlet tube k for the balancing pressure was sealed to the glass line by means of a copper-glass seal.

The case for the diaphragm gage was designed for the most part by the senior author and Dr. W. E. Morrell.[9] Two braces b and b′ were installed to give added strength to the case so that collapsing could be prevented and the movement of the case with pressure changes would be slight.

Diaphragms.—Many materials were tried in the search for a good diaphragm. Gold-plated brass proved to be an ideal diaphragm material. Carefully selected pieces of ordinary shim brass 0.001 of an inch thick were used in this research. Corrugations were pressed in and the diaphragm given several coats of thin gold plating. The surface was buffed between each plating. A diaphragm made in this manner showed no appreciable corrosion after it had been exposed to anhydrous hydrogen fluoride over a period of several months.

The null-point of the diaphragm, as determined with respect to the fixed point on t, varied with the temperature. This variation was quite reproducible, and with a temperature calibration this gage could be depended upon to give an accuracy of greater than 0.1 mm. of mercury in pressure difference. Pressure differences greater than 2 cm. of mercury on either side of the diaphragm would distort the diaphragm somewhat and make a new calibration desirable. The diaphragm could be subjected to pressure differences in the order of magnitude of 15 cm. of mercury without rupture, but such severe treatment caused the null-point to shift greatly and thus make a new calibration necessary. The temperature calibrations were easily made, for the calibration curves were usually parallel to one another, showing that the null point had shifted from its former position with respect to the fixed point on the glass tube t but that the change with the temperature was the same as before the diaphragm was strained. An unusually severe shock was needed in order to change the pressure measurements by more than 0.1 mm. If this gage were used at a single temperature only, pressure differences as small as 0.02 mm. probably could be measured. The variation of the null-point with pressure proved to be so small that no pressure calibration was needed to read to within 0.1 mm. A temperature calibration, however, was usually made before each run. When the gage was not in use and the hydrogen fluoride had been removed from M, it was protected from pressure strains by equalizing the pressure on either side of the diaphragm by closing K and opening V and L.

The 2-liter container P (Fig. 1) and the needle valve Q made precise regulation of the pressure possible. P was not thermostated but was prevented from undergoing any sudden change in temperature by a thick insulation of rock wool, cotton, and asbestos. The connecting tubes leading to the bulb P and the manometer R were protected by cotton insulation.

The thermostated portions of the apparatus are shown inside the cross-hatched rectangle (Fig. 1). For temperatures up to 50° a manually controlled water thermostat (not shown in Fig. 1) was placed around M. This water thermostat was inside of the larger air thermostat shown in the diagram. The gage and some of the connecting tubing was thermostated by the air only. The volume of hydrogen fluoride not thermostated by water was only about 3% of the total. At temperatures above 50° the water was removed and the air thermostat used alone. At higher temperatures the pressure does not change rapidly with temperature, so several readings at any one point will give a good average value of the P/T ratio. When the water thermostat was used in connection with the air thermostat, the temperature of the air thermostat was adjusted manually until it equalled the temperature of the water thermostat. The drift was slow enough so that temperature and pressure readings could be made with precision and at the same time precise pressure adjustments could be made.

An oil thermostat was found to be quite unsatisfactory. No oil was found which was quite fluid at 0° and would not decompose severely at 170°.

All temperature readings were made with calibrated copper–constantan thermocouples. A thermocouple was placed on each end of M and one on the gage, O. Calibrations before and after the measurements agreed well.

The hydrogen used in the runs was either tank electrolytic hydrogen of high purity or hydrogen made by the action of water on zinc dust at about 400°. Hydrogen from both sources gave the same results.

The deuterium was made by the action of heavy water on zinc dust by a method similar to that used by Claussen and Hildebrand.[5a] All operations and measurements were carried out in the same manner for deuterium fluoride as for hydrogen fluoride.

Measurements and Data.—The apparatus was tested by measuring the P/T ratio for dry nitrogen over a temperature range of 80°. After the P/T values were corrected for the expansion of the constant-volume container, they were constant as far as the calculations were carried out, *i. e.*, 1 part in 1500.

During the first runs high values for the association factor of hydrogen fluoride as compared to results by other investigators and lack of consistency between various runs showed that something was wrong with the technique. Control experiments showed that some water in the hydrogen fluoride was responsible for the difficulty in the measurements. Hydrogen fluoride and water evidently form a stable gaseous hydrate that is more stable than the polymerized molecule of hydrogen fluoride. Each water molecule is probably surrounded by several hydrogen fluoride molecules.

The implications of these measurements are rather important, indicating that association factors will appear much too high if any water is present. This result explains the deviations in the first runs of this research and possibly also the deviations in the data of other investigators.

Undoubtedly the greatest inaccuracy in this work is the presence of impurities in the hydrogen fluoride. Since the quantity of hydrogen fluoride needed to fill the constant-

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(9) W. E. Morrell, Ph.D. Thesis, Univ. of Calif., 1938.

TABLE I

ISOTHERMS FOR HF AND −LOG *K* FOR EQUILIBRIUM: $6HF = (HF)_6$

$T = 273.15°$			$T = 299°$			$T = 305°$			$T = 311°$		
P	*z*	−log *K*	*P*	*z*	−log *K*	*P*	*z*	−log *K*	*P*	*z*	−log *K*
244.5	3.118	10.78	488.5	1.708	13.90	561.5	1.510	14.45	639	1.354	14.99
230.2	2.953	10.93	460.5	1.614	13.89	528	1.434	14.44	596	1.294	14.95
216.9	2.750	11.02	433	1.508	13.90	492.5	1.347	14.43	551	1.231	14.92
209.7	2.673	11.00	418	1.464	13.89	477	1.315	14.42	528.5	1.207	14.89
200.2	2.597	11.00	418	1.475	13.87	476	1.322	14.41	528.5	1.215	14.87
	$T = 286°$		407	1.415	13.90	462	1.285	14.42	511	1.184	14.88
348	2.297	12.51	404	1.437	13.85	457	1.295	14.37	506	1.193	14.83
328.5	2.162	12.53	401	1.422	13.86	453	1.283	14.38	501	1.184	14.84
311	2.013	12.57	399	1.417	13.86	451	1.285	14.36	498	1.185	14.72
300	1.955	12.55	360	1.323	13.80	402	1.210	14.29	436	1.138	14.68
287.5	1.890	12.53	342.5	1.279	13.78	378.5	1.179	14.24	407	1.118	14.61

volume container was quite small, small quantities of impurities could produce comparatively large percentage contamination of the hydrogen fluoride. Much care was taken to remove all sources for the entrance of water. All parts of the copper portion of the apparatus were heated to a red heat several times while passing hydrogen through in order to remove any copper oxide that may have been present on the walls of the tubing. One of the chief disadvantages of using copper as the material for hydrogen fluoride apparatus is that in welding the parts of the apparatus together considerable oxide is produced and must be removed by reduction. Copper also reacts slowly with hydrogen fluoride to form copper fluoride which has a stable hydrate. This means that all moisture must be kept from contact with copper apparatus that has been in previous contact with hydrogen fluoride. This hydrate of copper fluoride would probably contaminate any anhydrous hydrogen fluoride that would pass over it. In spite of tedious and time-consuming precautions to prevent impurities from entering the hydrogen fluoride, the only proof that such contamination did not exist appreciably was the reproducibility of the results with different preparations of hydrogen fluoride.

Experimental Results[10]

Runs were made with ten different fillings of hydrogen fluoride and eight of deuterium fluoride. A total of 106 points were observed for the former and 76 for the latter. In view of the space that would be required for tabulating all of these original observations, it has been decided to report only the isotherms calculated from them. The original data will be gladly furnished to anyone who cares to calculate from them.

Table I gives a series of isotherms obtained by plotting *P* and (P/T) $(1 + \alpha t)$ against temperature and interpolating graphically. Table II gives isotherms for DF. Both sets are plotted in Fig. 3 along with the results of Fredenhagen.

TABLE II

ISOTHERMS FOR DF

P	*z*	*P*	*z*
$T = 273.15°$		$T = 305°$	
215.3	3.025	515	1.493
203.5	2.881	500	1.470
191.1	2.720	472	1.385
$T = 286°$		441	1.313
317	2.289	440	1.322
307	2.219	439	1.312
292	2.102	406	1.257
275	1.969	354	1.182
$T = 299°$		$T = 311°$	
447	1.690	586	1.340
433.5	1.656	567	1.305
412	1.529	531	1.253
387	1.474	492	1.205
386	1.472	491	1.207
386	1.465	489	1.203
358.5	1.392	447	1.163
320	1.285	382	1.118

Interpretation of Results

The association factors obtained in this research agree rather well with those of Fredenhagen at $T = 305°$, but are rather higher at 299 and 311°. In view of the sensitivity of *z* to temperature, the difference could be accounted for by small constant differences in the actual temperatures such as might have arisen from unrecognized cooling in the dynamic method used by Fredenhagen. The spacing of the three curves obtained by Fredenhagen can hardly be correct because, although the association factor must change more rapidly at lower temperatures, pressure constant, the spacing of Fredenhagen's curves below about 500 mm. is greater between 32 and 38° than it is between 26 and 32°. The only other way of accounting for this that we can think of might be the presence of traces of water whose effects we have discovered to be so pronounced. The earlier measurements of Thorpe and Hambly[2] are more scattered but agree within their own limit of accuracy with those here reported.

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(10) The results reported were all obtained by Robert W. Long; however, the pioneering work of William E. Morrell contributed greatly to the final success of the investigation.

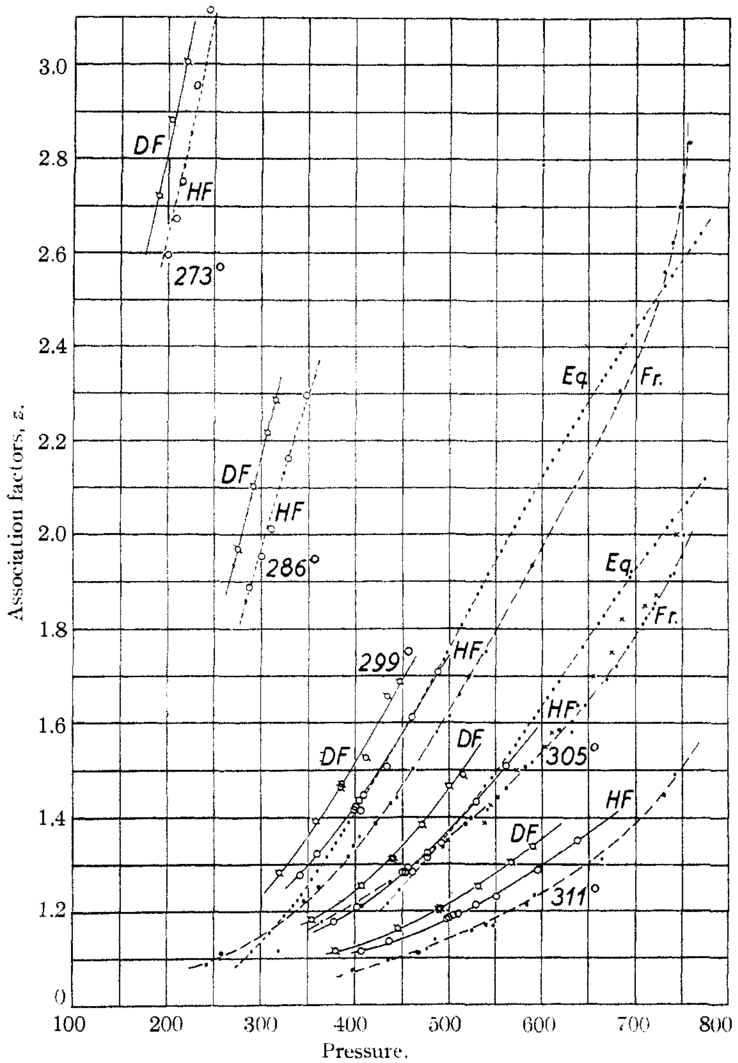

Fig. 3.—Isothermal variation of association factor with pressure for HF and DF. Curves marked "Eq." were calculated for the equilibrium: $6HF = (HF)_6$. The curves marked "Fr" represent data by Fredenhagen. The crosses indicate data by Thorpe and Hambly.

The dotted lines on Fig. 3 correspond to the slopes calculated on the basis of the single equilibrium $6HF = (HF)_6$. If we let p_1 stand for the partial pressure of HF, and p_2 for that of $(HF)_6$, the equilibrium constant is then $K = p_2/p_1^6$. The total pressure is $P = p_1 + p_2$ and the association factor z is the pressure that would exist if $(HF)_6$ were dissociated, *i. e.*, $p_1 + 6p_2$ to the actual pressure P. That is, $z = (p_1 + 6p_2)/P$. From these expressions we can express K in terms of z and p, getting $KP^5 = 5^5(z - 1)(6 - z)^{-6}$.

Table I gives values of log K from which it can be seen how far this single equilibrium is able to account for the data. At $T = 273°$ the data are very slightly steeper, as would be the case if higher polymers were present. At the higher temperatures and corresponding low degrees of associations, 1.3 and less, the data are less steep than the curves, indicating the presence of one or more lower polymers. Dr. V. Schomaker, of the California Institute of Technology, has been analyzing Fredenhagen's figures from the standpoint of successive polymerizations, and we have sent him the data of this paper for similar treatment. It would seem that the single hexamer accounts rather well for the data for all higher values of z but that when the vapor is very dilute one or more lower polymers play an appreciable role. It is obvious that a hexamer would dissociate on dilution far more rapidly than a lower polymer so that the latter might be negligible in a concentrated vapor and the former negligible in a very dilute vapor.

A different method of summarizing the evidence is given in Fig. 4 where we have plotted $-\log K$ against $10^4/T$. The plot shows the points falling very close to a common line except at the upper end, where the values of z are small. It may be added that the association factors reported by Simons and Hildebrand for saturated vapors all the way down to 234°K., although somewhat more scattered, fall close to the line in Fig. 4 when extrapolated downward.

It will be seen that the association factors shown by deuterium fluoride are appreciably higher at each temperature than those for hydrogen fluoride. The values of $-\log K$ for the deuterium fluoride are plotted in Fig. 4 along with those of hydrogen fluoride.

The points in Fig. 4 corresponding to values of z greater than about 1.3 all agree very well with the line drawn through them. This line shows a curvature in the direction corresponding to the fact that the specific heat of the complex is necessarily greater than that of the simple molecules. Neglecting this curvature, we can express all of the data, unless z is too small, by the equations

For HF $\log K = 8910/T - 43.65$
For DF $\log K = 8970/T - 43.65$

This equation for HF agrees well with the one given by Simons and Hildebrand based upon less extensive observations.

These values yield ΔH for forming one mole of hexamer $-40{,}800$ for $(HF)_6$ and $-41{,}100$ for $(DF)_6$.

The heat of association would correspond to 6800 cal. per bond for HF assuming that the polymer contains 6 bonds.

The curves for HF and DF are so nearly parallel and close together that it is hardly possible to conclude from them alone whether the actual difference is mainly one of energy or of entropy.

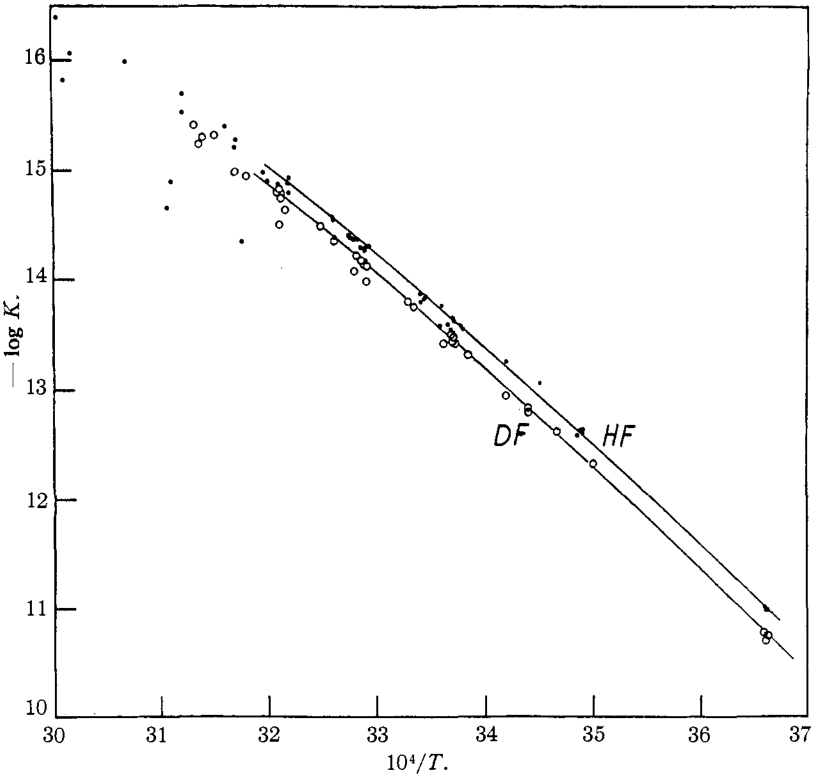

Fig. 4.—Variation of equilibrium constant with temperature.

Summary

The association of gaseous HF and DF to form polymers has been calculated over a range of temperatures and pressures from the deviations from linearity of the ratio of pressure to absolute temperature at constant volume.

At all degrees of association from about 1.2 to 4.5, the highest obtainable, the data conform fairly well to the single equilibrium assumed earlier by Simons and Hildebrand, $6HF = (HF)_6$. There is some indication of lower polymers at low degrees of association. The agreement with the single hexamer equilibrium is not to be regarded as proof of its sufficiency so much as a formal method of accounting for the data.

Neglecting the curvature due to unknown specific heat terms, the data correspond to the equations $\log K = 8910/T - 43.65$ for $(HF)_6$ and to $\log K = 8970/T - 43.65$ for $(DF)_6$.

The corresponding heats of polymerizations are $-40{,}800$ and $-41{,}100$ cal., respectively. If the polymer is a single ring, the hydrogen bond between fluorine atoms has an energy of 6.80 kcal. and the corresponding deuterium bond, 6.85 kcal.

BERKELEY, CALIF. RECEIVED SEPTEMBER 1, 1942