2.   The conclusion is drawn that upon absorption of light between 2145 and 2240 Å., cyanogen dissociates (predissociation) into either two normal CN radicals or one normal and one excited.

3.   No cyanogen fluorescence was obtained.

4.   The quantitative absorption of light by cyanogen in the region 2145 to 2140 Å. was determined.

5.   The quantum efficiency for the photochemical reaction $(CN)_2 \longrightarrow$ paracyanogen was determined to be three moles per einstein.

6.   A brief discussion of the mechanism, together with a discussion of the results of other investigators on the polymerization of cyanogen, concludes the work.

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THE DENSITY AND SURFACE TENSION OF LIQUID HYDROGEN FLUORIDE

BY J. H. SIMONS AND J. W. BOUKNIGHT

Hydrogen fluoride is a substance of considerable interest because of its unusual properties.[1]   The vapor has been shown to consist of an equilibrium between HF and H_6F_6.[2]   There are, however, very few available data about the anhydrous liquid upon which one may even make assumptions as to the molecular condition in the liquid state.   This is of particular interest because the heat of vaporization as calculated from the vapor pressure curve[3] is constant over a wide temperature range.   The heat of vaporization calculated in this manner is for one mole of the gas independent of the weight of the molecules.   As the apparent molecular weight of the gas changes considerably with temperature and the heat of polymerization[2] is fairly high, one may be led to assume that the liquid has the same apparent molecular weight as the gas.   Kolosovskii[4] has assumed this at the boiling point, because the liquid obeys Trouton's rule.   This would seem to be a peculiar behavior.   The material presented in this paper represents the beginning of an attack upon this problem.

The anhydrous liquid was prepared in the manner described by Simons[3] and was condensed directly into the apparatus in which it was to be used

The Density.—The apparatus used to make the density determinations is shown in Fig. 1.   This consisted of a cylindrical vessel of copper 2.5 cm.

[1] For a review of this subject see "Hydrogen Fluoride and Its Solutions," Simons, *Chem. Reviews*, **8**, 213 (1931).

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

[3] Simons, *ibid.*, **46**, 2179 (1924).   In this paper an error is made in calculating ΔH, which should be 6025 calories per mole.

[4] Kolosovskii, *Bull. soc. chim.*, **41**, 422 (1927).

in diameter and 20 cm. long.   Six copper trays which fitted into the upper part of the cylinder were provided on which to place chemicals to prevent hydrogen fluoride vapor from escaping or water from entering.   All joints were made with silver solder.   A copper bob which was immersed in the liquid was suspended from the arm of a balance by a number 40 copper wire.   This wire extended through the 2-mm. holes provided in the trays and their cover.   The lower three trays were filled with pulverized sodium fluoride and the upper three with pulverized anhydrous calcium chloride.
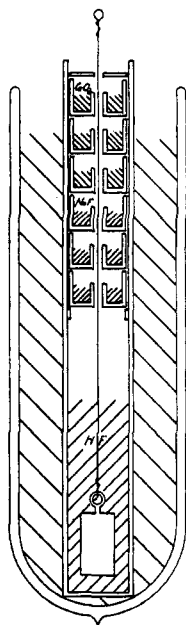

Fig. 1.—Density apparatus for hydrogen fluoride.

The liquid hydrogen fluoride was condensed into the cylinder from the generator using an ice–salt cooling bath. The bob was placed in it, and then the trays containing the chemicals were carefully slid into place with the wire from the bob extending through them.   The apparatus was then placed in a Dewar vessel containing solid carbon dioxide and either acetone or ether.   The Dewar was placed in a balance, and the bob suspended from the beam.   The bob was repeatedly weighed in this manner as the temperature slowly rose.   The temperature was determined by means of a calibrated toluene thermometer. A calibrated set of weights was used, and the frost collecting on the wire was carefully removed before each determination.   Free swinging of the balance indicated when the wire was not in contact with the walls of the trays. The weight of the bob in air and immersed in water enabled the calculations to be made in the usual manner. Corrections were made for the thermal expansion of copper.

The results are given in Table I and represented graphically in Fig. 2.   Gore[5] gives three values (0.9885 at 13.6°, 0.9875 at 12.8° and 0.9922 at 11.1°) which do not lie on the curve, but Hill and Sirkar[6] report a value (1.0005 at 0°) with which we

TABLE I

THE DENSITY OF LIQUID HYDROGEN FLUORIDE

Temperature, °C.	Density, g./cc.	Temperature, °C.	Density, g./cc.
−73.9	1.1828	−72.9	1.1828
−72.9	1.1828	−71.0	1.1792
−71.5	1.1773	−67.0	1.1708
−68.0	1.1705	−63.0	1.1617
−66.0	1.1659	−55.1	1.1364
−52.1	1.1299	−49.1	1.1222

5 Gore, *J. Chem. Soc.*, **22**, 368 (1869).

6 Hill and Sirkar, *Proc. Roy. Soc.* (London), **A83**, 130 (1909).

TABLE I   (*Concluded*)

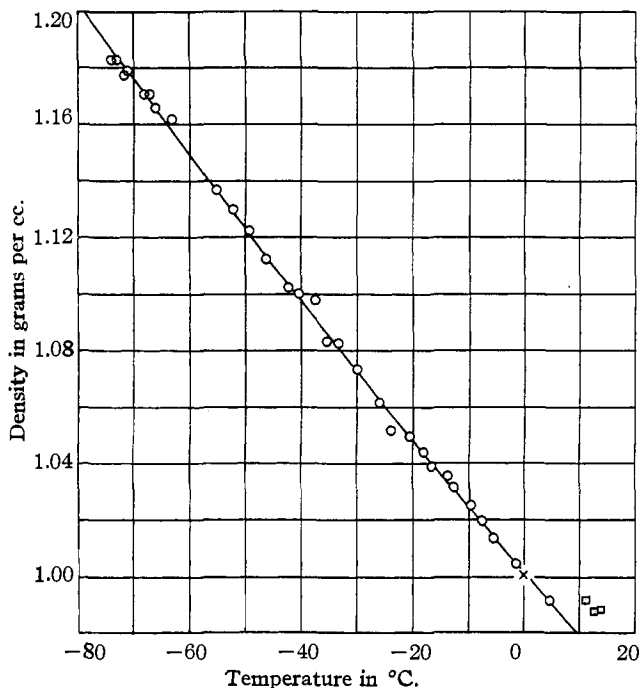| Temperature, °C.	Density, g./cc.	Temperature, °C.	Density, g./cc.
−40.2	1.1000	−46.1	1.1121
−35.2	1.0831	−42.2	1.1022
−23.8	1.0519	−37.2	1.0979
−20.3	1.0493	−33.2	1.0827
−16.4	1.0389	−29.8	1.0731
−12.4	1.0316	−25.8	1.0616
− 7.4	1.0199	−17.8	1.0440
		−13.4	1.0354
		− 9.4	1.0252
		− 5.4	1.0136
		− 1.4	1.0047
		+ 4.2	0.9918

Fig. 2.—The density of liquid hydrogen fluoride. The curve is drawn from the equation given in the text: the circles represent the experimentally determined values, the squares represent the values reported by Gore, and the cross represents the value reported by Hill and Sirkar.

are in very good agreement. The values of Gore can be accounted for by assuming that his liquid contained 1% water. The equation for the curve which falls through the points is

$$d = 1.0020 - 0.0022625t + 0.000003125t^2$$

in which d is the density in grams per cubic centimeter and t is the temperature in degrees centigrade. The probable error is estimated at $\pm 0.1\%$ and the maximum error at $\pm 0.2\%$.

The complete density curve for hydrogen fluoride–water mixtures is given by Hill and Sirkar.[6] From their work it is seen that the determination of density is an excellent method for estimating the amount of water in almost anhydrous hydrogen fluoride. The density changes more than 16% for the first 9% of water.

The Surface Tension.—The maximum bubble pressure method of determining surface tension was chosen, because it enabled the determinations to be made by making measurements on an inert gas and avoided the necessity of either seeing the corrosive liquid or making measurements directly upon it.
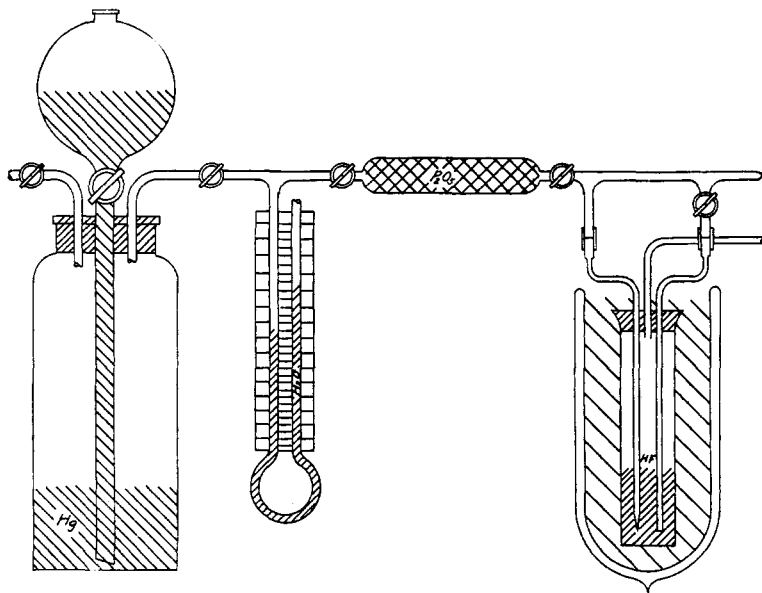

Fig. 3.—Surface tension apparatus for hydrogen fluoride.

A diagram of the apparatus is shown in Fig. 3. Nitrogen from a cylinder was stored in the aspirator using mercury as the impelling liquid. A water manometer was used, and a phosphorus pentoxide tube was located between the manometer and the bubbler to prevent water from reaching the hydrogen fluoride. The bubbler was made entirely of pure silver. A bottle containing a mixture of sodium fluoride and anhydrous calcium chloride into which the exit from the bubbler extended prevented the escape of hydrogen fluoride or the entrance of water. The apparatus was

calibrated with both water and benzene over a range of temperature. The equation given by Sugden[7] was used

$$\gamma = AP \left(1 + 0.69 \, r_2 g \, \frac{D}{P}\right)$$

in which γ is the surface tension in dynes per square centimeter, A is a constant for the apparatus, P is the difference in pressure needed to form bubbles from the small tube and the large tube, in dynes per square centimeter, r_2 is the radius of the large tube in centimeters, g is the acceleration due to gravity, and D is the density of the liquid in grams per cubic centimeter.

The hydrogen fluoride was condensed into the bubbler, the amount being determined by weighing before and after the condensation. The bubbler was then connected to the rest of the apparatus and immersed in a Dewar vessel containing solid carbon dioxide and acetone. A calibrated toluene thermometer was fitted to the bubbler by means of a copper sheath. The measurements were made as the temperature was allowed to rise slowly. Several check series of determinations were taken.

The results are given in Table II and shown graphically in Fig. 4. The equation for the curve which fits the points is given in the usual form

$$\gamma = 40.7 \left(1 - \frac{T}{503.2}\right)^{1.78}$$

where 503.2 is the critical temperature on the absolute scale as determined by Bond and Williams.[8] T is absolute temperature. The estimated error is $\pm 1\%$.

TABLE II

THE SURFACE TENSION OF HYDROGEN FLUORIDE

Temperature, °C.	Surface tension, dynes/sq. cm.	Temperature, °C.	Surface tension, dynes/sq. cm.
−81.8	17.70	−81.8	17.60
−72.4	16.20	−71.9	16.48
−64.0	15.33	−65.0	15.95
−57.0	14.77	−61.0	15.48
−46.1	14.10	−51.4	14.30
−43.7	13.80	−44.6	14.00
−43.2	13.95	−35.2	13.25
−23.2	12.00	−24.8	11.93
−16.3	11.40	−16.3	11.19
− 7.4	10.83	− 2.4	10.43
+ 3.6	9.85	+ 4.6	10.19
+11.3	9.68	+16.0	8.87
+16.0	9.10	+18.5	8.81
+18.2	8.63	+19.2	8.92

[7] Sugden, *J. Chem. Soc.*, **125**, 29 (1924).

[8] Bond and Williams, THIS JOURNAL, **53**, 34 (1931).

Discussion

The surface tension is unusually low. As the Eötvös equation has no theoretical foundation and as hydrogen fluoride is known to have a high dielectric constant and to form conducting solutions, we would not be justified in calculating the molecular weight by this means. However, assuming H_6F_6 as the formula for the liquid, the Eötvös constant is 1.52, which is what one might expect for this liquid. Assuming HF, the con-
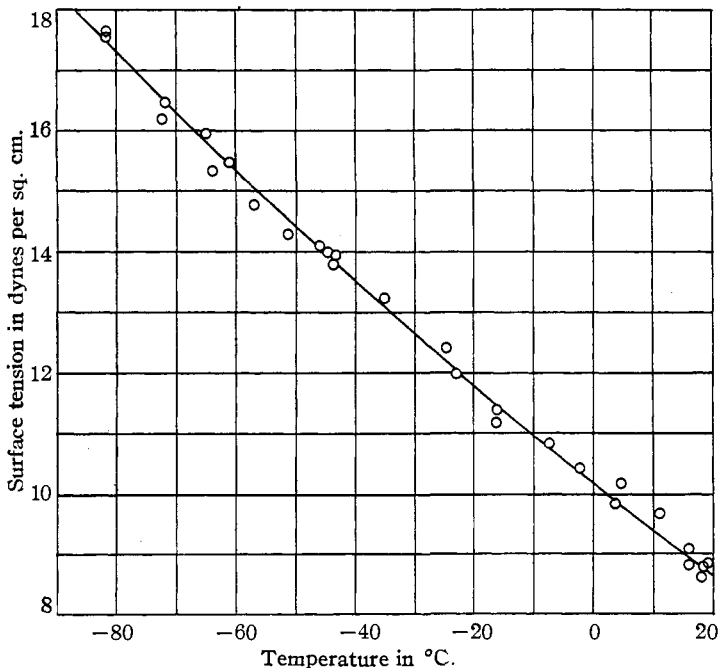

Fig. 4.—The surface tension of hydrogen fluoride. The curve is drawn from the equation given in the text, and the circles represent the experimentally determined values.

stant is 0.46, which is much too low a value. Assuming the Eötvös constant 2.0, the molecular weight becomes 180. There is no apparent change of Eötvös constant with temperature. The application of the Eötvös equation indicates that the liquid is polymerized probably to form H_6F_6.

A comparison of the surface properties of the hydrogen halides is given in Table III. The densities, surface tension, and $(M/D)^{2/3} \gamma$ are compared at the boiling points, this temperature being chosen as it will approximate a corresponding temperature for the different substances. Although the surface tension and total surface energy increase with formula weight in this series there is much greater difference between HF and HCl than there

is between HCl and HBr or HBr and HI. For the Eötvös constant and $(M/D)^{2/3}\gamma$, H_6F_6 seems to fit into the series better than HF.

TABLE III

COMPARISON OF PROPERTIES OF HYDROGEN HALIDES

Compound	Density at boiling point g./cc.	Surface tension at boiling point, dynes/cm.	$(M/D)^{2/3}\gamma$ at boiling point	Eötvös constant	Total surface energy, $\gamma - T(\partial\gamma/\partial T)$
HF	0.9593	8.65	65.5	0.46*	35
H_6F_6			216	1.5	
HCl	1.1957	23.15	226	1.5	61
HBr	2.152	24.9	299	2.0	70
HI	2.796	26.8	344	2.0	72

Different conclusions are arrived at as to the nature of liquid hydrogen fluoride by applying different criteria. Its high dielectric constant and ability to form conducting solutions indicate that it is a polar liquid. Trouton's rule gives a constant 20.6 when calculated in the usual manner and 27 when Hildebrand's modification is used. This fact indicates that the liquid is normal. The value of the Eötvös constant indicates that the liquid is associated; but as it is constant over a wide temperature range, we have a deviation from the usual behavior of associated liquids. This fact may mean that the liquid consists of a single definite polymer. This conclusion is at variance with the conclusion that the liquid has the same molecular species in the same equilibrium as the gas at the same temperature, which might be drawn from the fact that the heat of vaporization per mole is constant over the same temperature range that the Eötvös constant is constant.

Summary

The density of liquid hydrogen fluoride has been determined from −75 to +5°. The values fit the equation

$$d = 1.0020 - 0.0022625t + 0.000003125t^2$$

The surface tension of liquid hydrogen fluoride has been determined from −80° to +19°. The values fit the equation $\gamma = 40.7\,[1 - (T/503.2)]^{1.78}$.

The surface tension and its temperature coefficient indicate that liquid hydrogen fluoride is probably polymerized.

The nature of liquid hydrogen fluoride as indicated by various criteria is discussed.

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