[Contribution from the Chemical Laboratory of the University of California]

THE VAPOR PRESSURE AND CRITICAL TEMPERATURE OF FLUORINE

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The vapor pressure of liquid fluorine has heretofore been known at only one point, the boiling point being given by Moissan and Dewar as approximately −187°.[1] It seemed worth while, therefore, to utilize the equipment and experience available in this Laboratory to determine the vapor pressure of this element over a range of temperatures.

Experimental

Fluorine was generated by the electrolysis of fused potassium bifluoride in an apparatus of the type designed by Argo, Mathers, Humiston and Anderson[2] as modified by Simons.[3] The generator now in use has been further modified by increasing its capacity to 2.4 liters and by casting the vessel with a disk attached to the top rim of the cylinder sufficiently wide to cover the electrical heating coils and their insulating packing. The outer edge of the disk was further provided with a vertical rim. It had been found in working with the older form of generator that the electrolyte gradually crept over the rim of the containing vessel and worked down to the heating circuit. The present arrangement successfully prevents this difficulty.

Fluorine from the generator was passed through the copper trap, A (see Fig. 1), which was kept at a temperature of about 86°K. by a bath of liquid air rich in oxygen. This vessel served to remove impurities less volatile than fluorine, which probably were hydrogen fluoride, evolved from the molten bifluoride, fluorides of carbon, from the graphite anode, oxygen and oxygen fluoride[4] produced from traces of water in the electrolyte. Since neither O_2 nor OF_2 could be completely condensed in A, both having appreciable vapor pressures at 86°K., preliminary electrolysis of the molten salt was carried on for several hours, thereby decomposing the dissolved water. Fluorine, which was generated at a rate of about five grams per hour, was passed through the apparatus for thirty minutes, in order to sweep out the enclosed air. At the end of this time, the glass tube at D was sealed shut and gas was condensed in the cylindrical copper bulb, B, which was constantly maintained at the boiling temperature of the liquefied gas. After the desired quantity of liquid had been collected the tube at E was sealed shut. Pieces

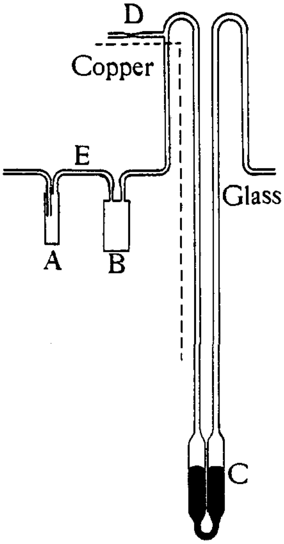

Fig. 1.—Apparatus for measuring the vapor pressure of fluorine.

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[1] H. Moissan and J. Dewar, *Compt. rend.*, **125**, 505 (1897).

[2] Argo, Mathers, Humiston and Anderson, *Trans. Am. Electrochem. Soc.*, **35**, 335 (1919).

[3] Simons, This Journal, **46**, 2175 (1924).

[4] P. Lebeau and A. Damiens, *Compt. rend.*, **188**, 1253 (1929).

of small German silver tubing were inserted in the line immediately above B to diminish the heat leak to the liquid fluorine.

C is a glass equalizing mercury manometer of about 1.5 cm. diameter attached to the copper tubing by a copper to glass seal. Since fluorine reacts with mercury, forming a thin skin of mercury fluoride which adheres to the walls of the tube, it was not possible to observe both mercury levels accurately when balancing the air pressure upon the right-hand column against the fluorine pressure on the left. The vapor pressure was, therefore, taken as equal to the air pressure required to bring the mercury surface, in contact with the air, to the position of balance at the start of the experiment. The error in pressure readings, caused by the consumption of mercury during a run, was found to be not more than a millimeter of mercury. Temperatures were read with a copper-constantan thermocouple made from wire kindly furnished us by Professor W. F. Giauque. Since samples of wire from the same spools had been carefully calibrated,[5] we were able to use a thermocouple correct to within 0.05°K. The junction of the thermocouple was soldered to the outside of the bulb, B, at a point near the surface of the fluorine inside.

A Leeds and Northrup type K potentiometer was used to measure the e. m. f. of the thermocouple. Results were reproducible to about one millionth of a volt, which corresponds on the temperature scale to about 0.05°.

The bulb, B, was immersed in a liquid-air bath. Various temperatures could be obtained either by changing the composition of the liquid or by lowering the pressure of the gas phase. Constant temperatures could be maintained for sufficient time for the attainment of vapor pressure equilibrium.

When glass bulbs were used for A and B, no two samples of fluorine gave the same vapor pressure curve and their boiling points all increased when part of the liquid was allowed to boil away. Boiling points ranged from 83 to 86°K., and one sample would change as much as from 84 to 85.5°K. while boiling away. All attempts at fractionation failed to give pure products. In spite of these results we had reason to believe that the boiling point of fluorine was near to 84.9°K., because the bath about the condensing gas had to be kept within 0.2° of 84.8°K. while the atmospheric pressure was 75 cm.

When the metal apparatus was used, the first sample of fluorine condensed behaved very satisfactorily. It represented the product of four hours of electrolysis with a current of eighteen amperes and probably amounted to about 18 cc. of liquid. No appreciable change in boiling point could be observed when part of it boiled away. Fully half of the specimen must have been set free during such tests, so we were working with either a constant boiling mixture or pure fluorine. The former state of affairs is very improbable, because the water in the electrolyte had been decomposed by preliminary electrolysis. Not more than traces of oxygen and OF_2 could have been in the fluorine, and our constant boiling point indicates that even these were absent.

Vapor Pressure of Fluorine.—The results are given in Table I. The first column gives the observed temperature in degrees absolute; the second, the observed pressure in centimeters; the third, the pressure calculated by substituting the observed temperatures in the equation given below.

The data are represented by the empirical equation

$$\log_{10}P = 7.3317 - \frac{406.8}{T} - 0.007785T$$

where P is in cm. of mercury and T in degrees Kelvin. No observed point

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[5] Giauque, Buffington and Schulze, THIS JOURNAL, 49, 2343 (1927).

TABLE I

VAPOR PRESSURE OF FLUORINE

T, °K. (obs.)	P, cm. (obs.)	P, calcd.	T, °K. (obs.)	P, cm. (obs.)	P, calcd.
72.53	14.54	14.41	80.98	48.23	47.59
72.53	14.57	14.41	81.19	49.32	48.85
75.18	21.53	21.65	81.20	49.34	48.92
75.18	21.54	21.65	81.22	49.53	49.04
75.18	21.53	21.65	83.09	61.53	61.55
75.18	21.50	21.65	83.11	61.57	61.67
75.45	22.25	22.50	83.45	64.24	64.20
75.53	22.53	22.78	83.48	64.48	64.38
75.59	22.69	22.99	84.13	68.64	69.35
75.88	23.83	23.99	84.65	73.40	73.50
75.93	24.01	24.16	84.68	74.18	73.78
76.70	27.10	26.97	84.68	73.93	73.78
76.72	27.20	27.03	84.73	74.02	74.19
76.72	26.90	27.03	84.77	73.84	74.55
76.74	27.09	27.11	84.81	74.14	74.85
78.96	36.68	36.76	85.28	78.02	78.95
79.01	36.78	36.99	85.25	78.55	78.62
79.02	36.87	37.01	85.27	79.40	78.85
79.18	37.88	37.80	85.32	79.36	79.35
79.18	37.87	37.80	85.40	79.77	79.87
80.09	43.00	42.58	85.81	84.11	83.56
80.09	43.00	42.58	85.99	85.50	85.20
80.96	48.03	47.48			

departs from this equation by more than 0.1°. The data are plotted in Fig. 2, and the line represents the equation.

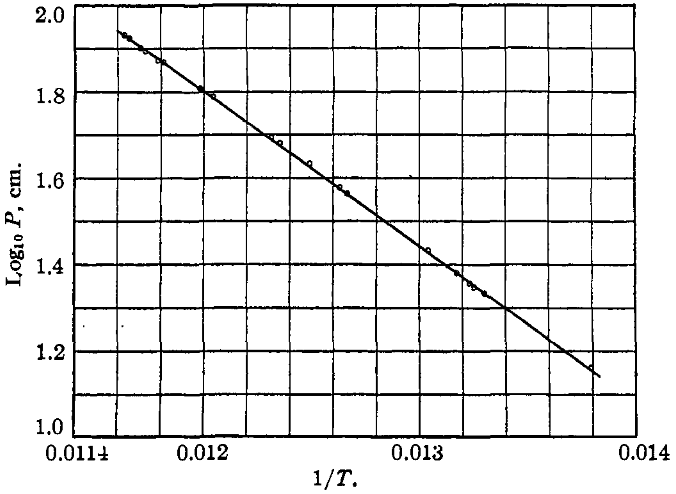

Fig. 2.—Vapor pressure of fluorine.

The boiling point of fluorine is calculated from this equation to be 84.93°K. Taking into account not only the experimental error in our vapor pressure measurements but also the chance that our temperature scale might have been wrong by a few hundredths of a degree, this value is probably correct within 0.1°.

Moissan and Dewar[1] obtained the boiling point by condensing the gas in a glass bulb cooled with liquid oxygen under reduced pressure. They found the minimum reduction of pressure which allowed condensation of fluorine to be 32.5 cm. of mercury and concluded that fluorine boils at −187°C. or 86.1°K. Unfortunately they do not state the atmospheric pressure at the time of this observation, but if we assume that it was 76.0 cm. and employ recent data for the vapor pressure of oxygen,[6] the calculated boiling point is 85.10°K., a figure which is in rather good agreement with our value.

The Critical Temperature of Fluorine.—We have made a few measurements of the critical temperature in a capillary glass tube. Since our previous experience with glass was not very satisfactory, we made no extended efforts to obtain reproducible results. One tube gave 143.3°K., and another, treated more carefully, gave 144.1°K. An approximate value of the critical temperature, is therefore, 144°K.

The critical pressure can be estimated with considerable confidence, since a plot of log P against $1/T$ for related gases shows the critical pressure lying above the vapor pressure line by only about 2 atmospheres.[7] Using our vapor pressure measurements in this way we get $P_c = 55$ atmospheres.

The heat of vaporization of fluorine at the boiling point may be determined, from the slope of the vapor pressure curve given above, to be 1600 cal. per mole. Giauque and Wiebe[8] have found that by substituting the value of P as calculated from Berthelot's equation of state in the equation of Clapeyron, a closer approximation to the calorimetric heat of vaporization of hydrogen chloride is obtained than one gets from the slope of the vapor pressure curve. From our value for the critical temperature and from the density of liquid fluorine as given by Moissan and Dewar[1] we have made a similar calculation. The results at the boiling point are $\Delta H = 1540$ cal. and $\Delta S = 18.1$.

Summary

1. Measurements of the vapor pressure of fluorine have been made between 15 and 86 cm. which are closely given by the equation

$$\log_{10}P(\text{cm.}) = 7.3317 - \frac{406.8}{T} - 0.007785T$$

2. The boiling point is calculated to be 84.93°K.

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[6] Cath, *Comm. Phys. Lab. Univ. Leiden*, No. 152 (1918).

[7] J. H. Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, *1924*, pp. 32–34.

[8] Giauque and Wiebe, This Journal, **50**, 101 (1928).

3. The critical temperature is approximately 144°K. and the critical pressure is about 55 atmospheres.

4. The heat of vaporization at the boiling point is 1600 cal. per mole, as calculated by the Clausius–Clapeyron equation, or, allowing for deviations from the gas laws, 1540 cal.

BERKELEY, CALIFORNIA

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

FREEZING POINTS OF THE SYSTEM WATER-HYDROGEN FLUORIDE

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The highly polar nature of both water and hydrogen fluoride suggested that an especial interest would attach to a determination of the solid compounds they might form with each other. We wished particularly to learn whether any of these might be regarded as resulting from the partial substitution of water in the polymer $(HF)_6$, which Simons and Hildebrand[1] assumed to explain the vapor densities of hydrogen fluoride over a considerable range of pressure and temperature. In spite of the excellent agreement of the assumption with the data, it is quite possible that the association actually involves more numerous molecular species, one of which might be $(HF)_4$, which has been proposed by Berliner and Hann.[2] They point out that the hydrofluorides of amines have the general formula $B\cdot 4HF$ in which B stands for the molecular formula of the base. Other compounds such as $KF\cdot 3HF$ and $MgF_2\cdot 2NaF$ may be regarded as derivatives of the hypothetical acid H_4F_4. If water behaves in a manner similar to the amines, one compound formed should be $H_2O\cdot 4HF$.

Although no complete study of the system $HF–H_2O$ has previously been made, the freezing points of hydrogen fluoride,[3] of the compound $H_2O\cdot HF$,[4] and of dilute hydrofluoric acid solutions in concentrations ranging up to 4.140 molal[5] have been known for several years. Mr. L. Clark, working in this Laboratory during 1928, made a partial investigation of the system, but his work was considered of too preliminary a nature to warrant publication

Experimental Part

The apparatus used is illustrated in Fig. 1. The equilibrium mixture was contained in a gold cup of about 175-cc. capacity. This was surrounded by a taller copper cup

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

[2] J. F. T. Berliner and R. M. Hann, *J. Phys. Chem.*, **32**, 1142–1162 (1928).

[3] Simons, THIS JOURNAL, **46**, 2179 (1924).

[4] R. Metzner, *Compt. rend.*, **119**, 682 (1894).

[5] Paterno and Peratoner, *Atti Accad. Lincei*, **6**, 306 (1890); Kendall, Booge and Andrews. THIS JOURNAL, **39**, 2303 (1917); Anthony and Huddleston, *J. Chem. Soc.*, **127**, 1122 (1925).