[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Density and Surface Tension of Liquid Fluorine between 66 and 80°K.[1]

BY DAVID WHITE, JIH-HENG HU AND HERRICK L. JOHNSTON

RECEIVED NOVEMBER 2, 1953

The density of liquid fluorine between 66.03 and 77.22°K. is a linear function of temperature, given by the relationship: $d = 1.5127 + 0.00635(T_B - T)$, where d is the density in g./cm.^{3} at temperature T, and T_B is 85.02°K., the normal boiling point of fluorine. The uncertainty in the density is estimated at ±0.1%. The results on the surface tension, in the temperature region 66.21 to 79.90°K., can be represented by the MacLeod equation: $\gamma^{1/4}/(d - d') = C$, where γ is the surface tension in dyne cm.$^{-1}$, d the density of the liquid, d' the density of the gas and C a constant equal to 1.276 ± 0.002. Estimated experimental uncertainty in the surface tension determinations is ±1%.

Introduction

The density of liquid fluorine between 57.40 and 83.21°K. has been measured by Kanda,[2] who obtained values that ranged from 1.204 g./cm.^{3} at the lowest temperature to 1.113 g./cm.^{3} at the highest. There appears to be a discontinuity in these data at approximately 66°K. Kanda's results are in agreement with the earlier work of Moissan[3] and of Drugmann and Ramsay[4] who reported values of 1.14 g./cm.^{3} at −200° and 1.108 g./cm.^{3} at −187°, respectively.

Recently, Kilner, Randolph and Gillespie[5] reported a value of 1.54 ± 0.02 g./cm.^{3} for the density of liquid fluorine at −196° (the boiling point of nitrogen), which is much higher than the earlier reports. The higher value was confirmed, in this Laboratory, by two independent sets of preliminary measurements; the first by Doyle,[6] who used a direct weighing method and obtained a value of 1.604 g./cm.^{3}, at the nitrogen boiling point, for commercial fluorine that contained 2.72% N_2 and 0.16% O_2; the second by Hu, White and Johnston,[7] who obtained a value of 1.6 g./cm.^{3} on very pure fluorine in some crude experiments, which were made in conjunction with calorimetric determinations.

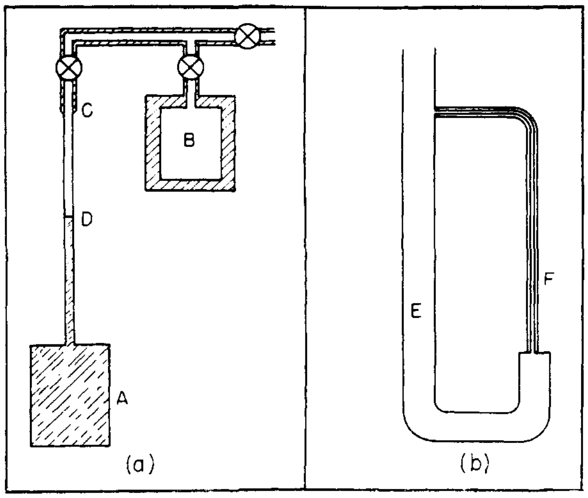

Fig. 1.—Apparatus for the density and surface tension determinations.

Since fluorine of very high purity was available it appeared worthwhile to us to measure the density with more accuracy, over a range of temperature It also seemed worthwhile to us to make measurements of the surface tension, since the only measurements in the literature are those by Kanda[8] who had obtained such low values for the density.

Apparatus and Experimental Procedure

(a) Density.—In Fig. 1(a), A is a 10-cm.^{3} Pyrex glass bulb, to which is attached a 4-mm. diameter glass tube containing an etched line at point D. Before connecting this system to the metal storage bomb B containing fluorine under pressure, by means of a glass-to-metal seal at point C, the volume was calibrated at 20°. This was done by first filling the system with mercury until a level was reached a few centimeters below the etched mark, D. The position of the mercury relative to the mark D was carefully read with a cathetometer and the apparatus weighed. Small amounts of mercury were then added at intervals until the mercury had risen a few centimeters beyond the mark D, weights and positions of the mercury meniscus being recorded after each addition. Thus the volume of the system was known at various positions above and below the etched line. Since experiments were carried out in the vicinity of the boiling point of liquid nitrogen, corrections to the volume were applied using the coefficient of expansion of Pyrex glass (see results).[9] After connecting the system to the gas storage line at point C, and after evacuating and degassing, the apparatus was immersed in a dewar containing liquid nitrogen, whose temperature could be controlled to within ±0.03° by manually adjusting the vapor pressure to the desired point. The fluorine was then condensed into the glass bulb A and the 4-mm. glass tubing at 77.15°K. until the mark D was reached. The system was then isolated from the storage container by means of a valve. The quantity condensed was determined by weighing the storage container before and after filling. To measure the change in volume with temperature the position of the meniscus relative to the mark D was determined to within ±0.003 cm. by means of a cathetometer at various temperatures varying from 66.03 to 77.22°K.

(b) Surface Tension.—The surface tension apparatus shown in Fig. 1(b) was calibrated by two methods. The diameter of the large tube E was calibrated by means of a Ball gage and micrometer, and was found to be 1.20 ± 0.06 cm. The diameter of the glass capillary F was determined by measuring the length of a column of mercury of known weight at various positions, by means of a comparator; it was found to be 0.0233 ± 0.0002 cm. To check further these results and the uniformity of the tubing, the surface tension of benzene was determined four times at 20°, with different amounts of liquid. The value was found to be 28.89 ± 0.06 dyne cm.$^{-1}$. This is in good agreement with the results of Sugden,[10] who reported a value of 28.85 dyne cm.$^{-1}$.

The apparatus was then attached to a fluorine storage

---

[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] E. Kanda, *Bull. Chem. Soc. Japan*, **12**, 473 (1937).

[3] H. Moissan, *Compt. rend.*, **138**, 928 (1904).

[4] J. Drugmann and W. Ramsay, *J. Chem. Soc.* (*London*), **77**, 1228 (1900).

[5] S. B. Kilner, C. L. Randolph, Jr., and R. W. Gillespie, THIS JOURNAL, **74**, 1086 (1952).

[6] W. L. Doyle (unpublished results).

[7] Jih-Heng Hu, D. White and H. L. Johnston, unpublished results.

[8] E. Kanda, *Bull. Chem. Soc. Japan*, **12**, 469 (1937).

[9] E. Wichers, A. N. Finn and W. S. Cabaugh, *J. Research. Natl. Bur. Standards*, **26**, 539 (1941).

[10] S. Sugden, *J. Chem. Soc.* (*London*), **119**, 1483 (1921).

container at point C (Fig. 1(a)), evacuated and degassed, and completely immersed in the liquid nitrogen dewar. A sample of gaseous fluorine was condensed in the system at 77.15°K. until the liquid level was approximately half way up the capillary. The level E was somewhat lower. The difference in heights between the bottom of the mercury meniscus in E and F was measured by means of a cathetometer to within ±0.003 cm. To observe the change in surface tension with temperature, the temperature of the bath was varied in a series of two experiments, first by increasing the temperature from 66.21 to 79.90°K. and then decreasing it to 70.68°K. (see Table II). To ensure attainment of equilibrium, the system was intentionally disturbed several times at each temperature by gently pumping, and then observed to see whether or not the system returned to its original capillary rise.

Material.—The fluorine used in these experiments was prepared electrolytically, passed over an NaF train to remove the hydrogen fluoride, and then triply distilled to remove any traces of impurities. To avoid contamination, only non-reactive metals such as monel and nickel were used for storage purposes and apparatus construction. All the valves were constructed of monel and packed with teflon. The purity of the fluorine was determined from freezing point measurements and was found to be 99.97%.

Results

(a) **Density of Liquid Fluorine.**—The density of liquid fluorine, calculated from the experimental results, is given in Table I and shown in Fig. 2. Since the apparatus was calibrated at 20°, the volume was corrected, using extrapolated values of the coefficient of thermal expansion of Pyrex glass given by Wichers, Finn and Cabaugh.[9] The total correction to the density as a result of the contraction on cooling amounts to only 0.0025 g./cm.^{3}. A correction was also applied to the weight of liquid fluorine at every temperature. This was due to the fact that the amount of fluorine in the liquid phase varied with temperature due to vaporization into dead space. However, since the dead space was approximately 3 cm.^{3}, this correction was small.

The density is found to be a linear function of temperature in the region 66.03 to 77.22°K. and is given by the equation

$$d = 1.5127 + 0.00635(T_B - T) \qquad (1)$$

where d is the density in g./cm.^{3} at temperature T, and T_B is the boiling point which has been found to be 85.02°K.[6] Deviations between the experimental values and values calculated from equation 1 are given in column 3 of Table I.

TABLE I

DENSITY OF LIQUID FLUORINE

Temp., °K.	Density, g./cm.^{3}	Dev. from eq. 1 obsd. − calcd.
66.03	1.633_1	−0.0002
67.98	1.621_3	+ .0004
70.00	1.608_1	.0000
72.55	1.592_0	+ .0001
75.01	1.576_1	− .0002
77.22	1.562_2	.0000

(b) **Surface Tension of Liquid Fluorine.**—The surface tension of liquid fluorine was calculated from the experimentally determined difference in heights, H, of the liquid level in the two arms of the capillarimeter, using the equation

$$\gamma = \frac{H}{\left(\frac{1}{b_1} - \frac{1}{b_2}\right)} [(^1/_2)g(d - d')] \qquad (2)$$

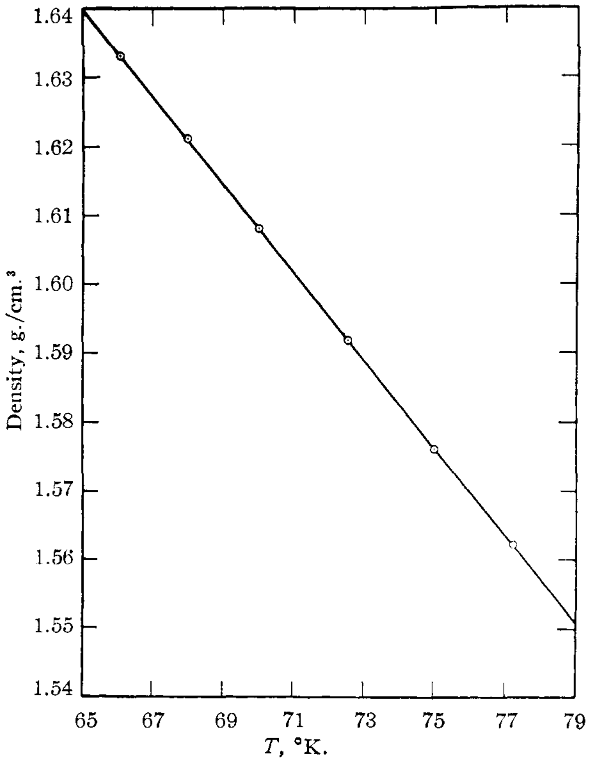

Fig. 2.—The density of liquid fluorine.

where b_1 and b_2 are radii of curvature of the two menisci; d and d', the density of the liquid and gas, respectively; and $g = 980.11$, the acceleration due to gravity. The contact angle was assumed to be zero; some justification for this assumption was found from some measurements attempted during the surface tension experiments. Although the angle could not be accurately determined it was quite small. The radii of curvature were calculated from the radii of the two arms of the capillarimeter (corrected for contraction on cooling) with the aid of tables given by Sugden.[10] The final results for the surface tension are tabulated in Table II and shown in Fig. 3.[11]

The surface tension data over the entire temperature range could be represented by the MacLeod equation

$$\frac{\gamma^{1/4}}{d - d'} = C \qquad (3)$$

where the constant C was equal to 1.276 ± 0.002. The deviations of the experimental results from the ones calculated using equation 3 and the above value for C are given in Table II, column 5. Although the average deviation is only ±0.6%, there still remains an uncertainty of approximately ±1%.

Discussion of Results

The results on the density are in agreement with the recent determination by Kilner, Randolph and

---

[11] During the preparation of this manuscript for publication the results of G. W. Elvrum, Jr., and R. N. Doescher on the Physical Properties of Liquid Fluorine appeared in the *J. Chem. Phys.*, **20**, 1834 (1952). Their experimental data on the density and surface tension of liquid fluorine are in excellent agreement with our data given in Tables I and II.

TABLE II

SURFACE TENSION OF LIQUID FLUORINE

Temp., °K.	*H*, cm.	Surface tension, dyne cm.$^{-1}$	MacLeod constant eq. 3	Dev. from eq. 3 obsd. − calcd.
66.21	1.003[a]	18.85	1.277	+0.06
70.26	0.957[a]	17.70	1.277	+ .07
70.68	.942	17.40	1.275	− .09
72.05	.927	17.02	1.274	− .10
73.35	.923[a]	16.86	1.278	+ .11
75.09	.909	16.49	1.280	+ .20
75.19	.898[a]	16.28	1.277	+ .02
77.15	.875	15.73	1.276	+ .01
79.90	.833[a]	14.81	1.272	− .19

[a] Measured by increasing the temperature starting from 66.21°K.; remaining points measured by decreasing the temperature from 77.15°K.

Gillespie,[5] the latter being approximately 1.5% lower than the present values, at corresponding temperatures. The values reported by Kanda, however, are 25% lower. The reason for this large discrepancy cannot be readily determined, since insufficient information was given by Kanda to determine sources of error.

A similar discrepancy exists between Kanda's data on surface tension and our own (see Fig. 3). That this probably was due to Kanda's erroneous use of density values is indicated by our recalculation of Kanda's data with use of our density values (see Fig. 3). Still better agreement is obtained when the results are further recalculated with use of our equation 2 instead of that given by Kanda.[8] Of course this recalculation is justified only if one assumes that the results of the density are in error while the surface tension measurements are correct. If Kanda's density errors are due to the presence of impurities (which could account for such large discrepancies only if the impurities were of such a nature as to promote considerable chemical change), this correction of his surface tension data is, of course, not valid.

The representation of our surface tension data by the MacLeod equations yields a constant that appears to be independent of temperature (see Table II, column 4). The data also can be fitted to the Eötvös equation

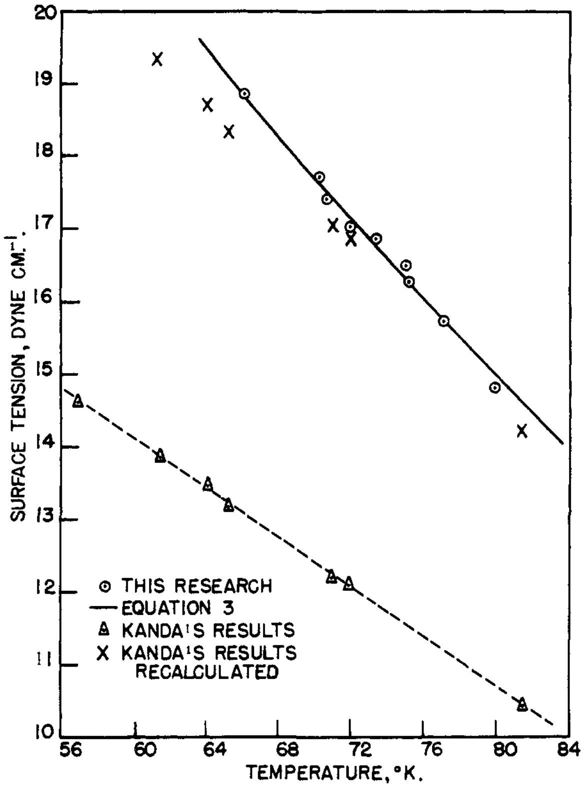

Fig. 3.—Surface tension of fluorine.

$$-\frac{d}{dT}\gamma\left(\frac{M}{d-d'}\right)^{2/3} = k \qquad (4)$$

where k is a constant equal to 2.1 ± 0.1. Since this is the form of expression for a normal liquid, it would appear that liquid fluorine behaves in a normal manner.

COLUMBUS, OHIO