bility. This is compatible with the view that at infinite dilution the water molecules in the immediate neighborhood of the cation are more electrostricted than those surrounding the anion. Consequently the change in environment for the cation is less drastic than for the anion when the solvent is subjected to increased electrostriction by increasing the total electrolyte concentration. Since these effects would be more apparent in dilute solutions (when most of the electrostriction occurs) it can be assumed that these differences in environmental change are, in part, responsible for the lack of constancy of the ratios of salt mobilities to ionic mobilities which are observed in the more dilute solutions. As would be anticipated, in the same concentration interval, the ratio $D'/(2D^*_{\mathrm{Na}^+}D^*_{\mathrm{Cl}^-})/(D^*_{\mathrm{Na}^+} + D^*_{\mathrm{Cl}^-})$ is nearly constant (it equals 1.12 ± 2%). At lower concentrations it approaches unity by analogy with the Nernst expression.

Also in Fig. 1, all the Gouy data are plotted for $BaCl_2$ as well as the available electrometric values. The two sets of data are entirely consistent. The not unexpected maximum in the D *vs.* $\sqrt{\bar{c}}$ plot is evident for this system at $\bar{c} \cong 1.4$ molar.

The fact that the Gouy data for $BaCl_2$ so nicely substantiate the electrometric data in dilute solutions leaves still unexplained the anomalous behavior of $CaCl_2$ solutions which have been shown to depart from the Onsager–Fuoss theory much more drastically than either $MgCl_2$ or $BaCl_2$.[3,13]

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NEW HAVEN, CONN.

[CONTRIBUTION FROM THE PENNSYLVANIA SALT MANUFACTURING CO., RESEARCH AND DEVELOPMENT DEPARTMENT. WHITEMARSH RESEARCH LABORATORIES]

The Density of Liquid Fluorine between 67 and 103°K.[1,2]

BY ROGER L. JARRY AND HENRY C. MILLER

RECEIVED NOVEMBER 17, 1955

The density of liquid fluorine has been measured over the temperature range 67 to 103°K. An all metal system was used. The data obtained have been fitted to the equation, $d = 1.907 - 2.201 \times 10^{-3}T - 2.948 \times 10^{-5}T^2$, where d is the density in g./cm.^{3} at temperature T. The uncertainty in the density is estimated to be ±0.1%, and in temperature ±0.05°.

Introduction.—As part of a program at this Laboratory for the determination of the physical properties of fluorine-containing compounds, an all-metal apparatus was devised for measuring the density of liquefied gases. This apparatus was used to extend the temperature range of measurements on liquid fluorine and to prevent possible contamination by reaction with glass.

Apparatus and Experimental Procedure.—A cryostat similar to those in the various low temperature laboratories in this country was used. The nickel pycnometer was enclosed in a copper block which was suspended within a vacuum space. A small monel packless valve was used to close off the pycnometer volume (about 27 cc.). Measurement of temperature was accomplished by means of a capsule type platinum resistance thermometer, which had been compared with the National Bureau of Standards temperature scale.

The mass of fluorine introduced into the pycnometer was measured by means of calibrated volumes in an air thermostat. Pressure of the fluorine in these calibrated volumes was measured by means of a Booth–Cromer nullpoint gage[3] and a mercury manometer.

The determination of the amount of liquid fluorine held in the pycnometer was made in the following manner. To start a series of determinations the pycnometer was filled at a temperature slightly below that chosen for the first point, using an excess of about 2%. Following the condensation filling operation and after temperature equilibrium had been obtained the pycnometer valve was closed and the excess liquid allowed to expand as a gas into an evacuated volume. At the same time heat was applied to the valve and the 1/8" nickel line leading from it. This heat was maintained until the valve and line had reached a temperature well above that needed to prevent condensation in the line and valve. From this initial point each successive determination was made by allowing the liquid to expand with increasing temperature into the line above the valve, obtaining temperature equilibrium, closing the valve and allowing the excess liquid to expand into a calibrated volume. As a check on the mass balance at the end of a run, the entire remaining quantity of liquid fluorine was expanded into the volumes and measured.

Materials.—The fluorine used in this study was production material manufactured by this company and packaged in cylinders as a compressed gas. To purify the fluorine, it was condensed using liquid nitrogen and the middle portion from the revaporization used. The purity of the fluorine used in this study by comparison with analysis of a cylinder of the same lot which was not given any purification step was 99% or better. In view of the agreement with previous data (see Results and Discussion below), and within the limits of precision of the measurements, the fluorine must have been of a purity of at least 99.5%.

Results and Discussion.—The values for the density obtained from the experimental data, for two separate runs, are given in Table I. The estimated uncertainty in the density is ±0.1%. Temperature was known to ±0.05°. In the temperature equilibrium period of approximately 25 minutes, the temperature drift was no more than 0.002° per minute. This order of stability was easily maintained due to the large size of the copper block, approximately 6000 g. Since the pycnometer was calibrated at 30°, the volume was corrected using values of the coefficient of thermal ex-

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(1) Presented before the Symposium on Fluorine Chemistry, Division of Industrial and Engineering Chemistry, 128th meeting of the American Chemical Society, September, 1955.

(2) This paper represents the results of one phase of research carried out under Contract #18(600)-(761) sponsored by the Air Force Research and Development Command.

(3) S. Cromer, USAEC Declassified Report, MDDC-803.

pansion for pure nickel furnished by A. S. Friedman[4] of the National Bureau of Standards. The largest correction to the volume as the result of contraction of the pycnometer on cooling was 0.1911 cm.,[3] or 0.7% of its volume at 30°.

TABLE I

DENSITY OF LIQUID FLUORINE

T, °K.	Density, g./cm.[3]	Dev. from eq. 1 Obsd. − calcd.	T, °K.	Density, g./cm.[3]	Dev. from eq. 1 Obsd. − calcd.
65.78[a]	1.638	+0.004	86.91	1.496	+0.003
71.76	1.594	− .003	88.26[a]	1.481	− .002
74.93	1.578	+ .002	88.50	1.484	+ .002
78.59[a]	1.550	− .002	90.08	1.472	+ .002
78.62	1.553	+ .001	91.55[a]	1.458	− .001
81.72	1.532	+ .002	91.75	1.460	+ .003
81.73[a]	1.528	− .002	94.73[a]	1.434	.000
84.34	1.514	+ .003	97.56[a]	1.412	.000
85.05[a]	1.505	− .002	100.21[a]	1.391	.000
85.67	1.505	+ .003	102.75[a]	1.370	.000

[a] Indicates a separate run.

TABLE II

VALUES OF THE DENSITY OF LIQUID FLUORINE FROM VARIOUS SOURCES

Source	Temperature, °K. 66.00	77.16	85.02
Kanda[5]	1.173	1.130	...
Kilner, Randolph and Gillespie[6]	...	1.54	...
Elverum and Doescher[7]	1.636	1.567	1.510
White, Hu and Johnston[8]	1.634	1.563	1.513
This research	1.634	1.561	1.507

A comparison, at several temperatures, of the values for the density obtained in this study and those of various other sources are given in Table II. We agree well with White, Hu and Johnston[8] over the range duplicated and deviate only on extrapolation of their data to the boiling point of fluorine, 85.02°K.[9] Comparing with the data of Elverum and Doescher[7] we tend to parallel their data with their values being 0.2–0.3% higher.

The data of Table I have been fitted to the equation

$$d = 1.907 - 2.201 \times 10^{-3}T - 2.948 \times 10^{-5}T^2 \quad (1)$$

where d is the density in g./cm.[3] at the absolute temperature T. Deviation between the experimental and values calculated from equation 1 are given in column 3 of Table I.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AT THE UNIVERSITY OF WASHINGTON AND THE UNIVERSITY OF NEW ENGLAND]

Pentafluorosulfur Hypofluorite and Thionyl Tetrafluoride

BY F. B. DUDLEY,[1] G. H. CADY AND D. F. EGGERS, JR.

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The silver difluoride "catalytic" fluorination of thionyl fluoride at 200° results in the formation of thionyl tetrafluoride, SOF_4, and a sulfur-hypofluorite-type molecule with the formula $SF_5{\cdot}OF$. The structure of each of these compounds has been confirmed by chemical reactions and by infrared spectra. In the vapor state, thionyl tetrafluoride absorbs strongly at 1383, 928, 821, 752, 637 and 567 cm.$^{-1}$, while the pentafluorosulfur hypofluorite absorption bands occur at 935, 888, 614 and 585 cm.$^{-1}$. Both substances are gases. Thionyl tetrafluoride condenses to give a colorless liquid boiling at −49.0° and freezing at −99.6°. Pentafluorosulfur hypofluorite condenses to form a faintly yellow liquid which freezes at −86.0° and boils at −35.1°. This substance is a highly reactive oxidizing agent with an odor like that of oxygen difluoride.

Introduction

The successful addition of fluorine to sulfur trioxide across a sulfur–oxygen double bond to form fluorine fluorosulfonate[2] suggested the possibility of forming other sulfur-hypofluorite-type molecules by allowing fluorine to react with molecules such as sulfur dioxide and thionyl fluoride. As expected, the predominant product of the reaction between fluorine and sulfur dioxide was sulfuryl fluoride, but a small amount of a highly reactive material of high molecular weight, and possessing the typical hypofluorite odor, indicated that a compound such as $SF_4(OF)_2$ or $SF_5(OF)$ was being formed. To test the first possibility, sulfuryl fluoride was passed through the silver difluoride "catalytic" reactor[3] with excess fluorine, but the sulfuryl fluoride was unchanged. If the reactive substance being sought had the structure SF_5OF, then the obvious preparative method would be the fluorination of thionyl fluoride. However, thionyl fluoride was known to react with fluorine on a platinum spiral at 150° to form thionyl tetrafluoride, SOF_4.[4] As a result of

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