3. The dielectric constant of each compound, pure and in benzene solution, has been measured. From these data the electric moments of the compounds have been determined.

4. These moments are compared with those of aliphatic ethers and with mono-substituted and di-substituted aliphatic halides.

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

The Vapor Pressure of Fluorine

BY WILLIAM H. CLAUSSEN

Introduction

The vapor pressure of liquid fluorine has been measured before in this Laboratory by Cady and Hildebrand.[1] We decided to repeat this work because several possibilities for increased accuracy seemed to exist. In the first place, the different runs in the earlier investigation were all made upon one sample of fluorine and it seemed desirable to have some check upon purity. Second, the inclusion of glass parts in the system suggests the possibility of contamination that could be avoided by an all metal apparatus. Third, the use of a diaphragm gage in place of the constant level mercury manometer, and the use of the vapor pressure of pure oxygen as the thermometer in place of the thermocouple used earlier appeared to offer prospects for more accurate work.

Experimental

The fluorine used was generated by the electrolysis of fused potassium bifluoride in the generator used by Cady and Hildebrand.[1] Electrolysis was carried out for several hours before collecting any fluorine to decompose any water present in the electrolyte. The additional precaution was taken of keeping the electrolyte at 150° between runs to prevent water from condensing on the salt. The fluorine was passed through a copper trap cooled with liquid oxygen to remove hydrogen fluoride, carbon tetrafluoride, and oxygen fluoride. The fluorine was always passed through the apparatus for one hour to drive out the air. The volume of fluorine passed through was approximately 60 times the volume of the apparatus. The apparatus was then closed by means of a Monel metal needle valve and cooled with liquid air to condense the gas being generated at the rate of about five grams per hour. After collecting from 10 to 15 g. of liquid, the apparatus was closed off from the generator by means of another Monel metal needle valve.

The fluorine was contained in an annular cell of thin Monel metal in the center of which was a second cell for liquid oxygen that was condensed there at the same time fluorine was condensed in the outer cell. About 8 g. of electrolytic distilled oxygen was used. This fluorine–oxygen cell was surrounded by a calorimeter block of the design used by Giauque and Wiebe.[2] The whole was then surrounded by a Monel metal can which could be filled with pure hydrogen at a pressure of about 10 mm. during condensation of the liquids and subsequent cooling by evaporation of the liquid air under 5 cm. pressure. The apparatus was contained in a 90 cm. Dewar vessel fitted with a vacuum-tight top through which all tubes from the apparatus passed. After cooling to about 68°K. the hydrogen was pumped down to a pressure of 10^{-5} mm. The temperature was obtained by reading the vapor pressure of the liquid oxygen on a mercury manometer and using the Leiden equation for the vapor pressure.[3] The temperature rose about 0.2° per hour because of the heat leak through the Monel metal tubes leading to the cell, the calorimeter block being kept 0.1 to 0.5° above the cell temperature by means of a constantan heating coil to prevent distillation. The temperature difference was measured with a copper–constantan differential thermocouple and a type K potentiometer.

The fluorine vapor pressure was taken as the air pressure needed to balance a metal null instrument that was constructed of a thin (0.12 mm.) hard German silver diaphragm 7.6 cm. in diameter fitted with an ordinary lever arrangement and a mirror from which was reflected a spot of light that fell on a scale one meter away. The instrument was sensitive to a difference of pressure of 0.1 mm. The pressures of the oxygen and fluorine

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[1] Cady and Hildebrand, THIS JOURNAL, **52**, 3839 (1930).

[2] Giauque and Wiebe, *ibid.*, **50**, 101 (1928).

[3] Cath, *Comm. Phys. Lab. Univ. Leiden*, **152d** (1918). The equation is $\log_{10} P(\text{atm.}) = -419.31/T + 5.2365 - 0.00648\,T$.

were read simultaneously on the two manometers. The readings were reduced to 0°.

The apparatus was constructed entirely of copper and Monel metal with the exception of the diaphragm, which was of hard German silver. All joints were silver soldered.

Results

The data are represented by the equation

$$\log_{10} P \text{ (cm.)} = -462.66/T + 8.7202 - 0.01656\,T$$

This equation was calculated by the "method of averages" from the one-hundred and forty points observed with three different samples of fluorine. No point deviates more than 0.15°, while three-fourths of them lie within 0.10° of the equation. Differentiation of this equation with respect to T and then equating to $\Delta H/RT^2$ of the Clausius–Clapeyron equation gives 1560 calories as the heat of vaporization at 85.21°K. the calculated boiling point. The entropy of vaporization is therefore approximately 18.3 entropy units. We believe the error in the boiling point is 0.1° or less.

The results of the earlier work on the vapor pressure of fluorine give 84.93°K. as the boiling point and 1600 calories as the heat of vaporization.[1] Moissan and Dewar[4] gave 85.1°K. as the boiling point of fluorine when recalculated, in close agreement with our figure.

If log P is plotted against log T for our data a curve is obtained that has exactly the same slope at equal volumes of vapor, as a similar plot for oxygen. This shows that fluorine obeys Hildebrand's rule[5] regarding the entropy of vaporization. From this criterion, fluorine is a normal liquid.

The author wishes to express his appreciation to Professor Hildebrand, who suggested this research, and under whose guidance it was carried out, and to Professor Giauque, who suggested the experimental technique at the low temperatures.

Summary

1. The vapor pressure of liquid fluorine has been measured from 6.3 to 75.2 cm. The vapor pressure is given by the equation

$$\log_{10} P \text{ (cm.)} = -462.66/T + 8.7202 - 0.01656\,T$$

2. The boiling point is calculated to be 85.21°K., a value correct within 0.1°.

3. The heat of vaporization is calculated to be 1560 calories per mole from the Clausius–Clapeyron equation and $\Delta S = 18.3$.

4. Fluorine obeys Hildebrand's rule regarding the entropy of vaporization.

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[4] Moissan and Dewar, *Compt. rend.*, **125**, 505 (1897).

[5] Hildebrand, THIS JOURNAL, **37**, 970 (1915).

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Atomic Weights of Iodine, Carbon and Sodium. The Ratio of Iodine Pentoxide to Sodium Carbonate

BY GREGORY PAUL BAXTER AND ARTHUR HAYS HALE

In three investigations in this Laboratory iodine pentoxide has been compared with silver,[1] with iodine by thermal decomposition[2] and with arsenic trichloride.[3] Since the results of these three comparisons are not wholly consistent, we have carried out a fourth comparison, with sodium carbonate by neutralization.

The Preparation of Iodine Pentoxide

Iodic acid remaining from the investigation of Baxter and Butler[2] was further purified by continuing the fractional crystallization to which it had already been subjected. This iodic acid had been prepared from iodine, which had already been freed from other halogens and organic matter, through potassium and barium iodates by treatment of the latter with sulfuric acid. Crystallization was carried out in platinum dishes except that some of the less pure fractions were temporarily stored in quartz. For the present work the material was handled wholly in platinum. The chief evidence of purity was obtained by carefully dehydrating and decomposing at as low a temperature as possible 25 g. of pentoxide, slightly less pure than the poorest used in the actual analyses, in a current of pure air while contained in a weighed platinum boat inside a quartz tube. The weight of the residue was 0.07 mg. and this was not altered by further heating to dull redness. Another 5-g. portion gave no weighable residue. The apparent percentage of impurity, 0.0003%, is too small to be of significance.

To prepare iodine pentoxide from iodic acid the procedure used by Baxter and Tilley[1] was employed. Iodic acid crystals were pulverized in an agate mortar and were

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[1] Baxter and Tilley, THIS JOURNAL, **31**, 203 (1909).

[2] Baxter and Butler, *ibid.*, **53**, 970 (1931).

[3] Baxter and Shaefer, *ibid.*, **55**, 1957 (1933).