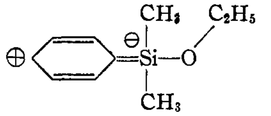

The value of -0.33 D for the moment of the Si–C_{arom} bond is not altogether improbable in the light of discussions of previous compounds, since there is evidence to indicate that this bond has a value of at least -0.14 D, with the negative end toward silicon, in the compound ethoxytriphenylsilane. The presence of a highly electronegative element such as oxygen, attached to the central silicon atom, seemingly should promote such structures. It would seem, however, that the chloromethyl group attached to silicon should also promote "reverse halogen" structures. Yet use of the value $+0.42$ D, with the negative end of the dipole toward the ring carbon, permitted, in the case of chloromethyldimethylphenylsilane, calculation of a value very close to the observed value.[1] That replacement of the chloromethyl group by the ethoxy group, leaving the dimethylphenylsilyl residue unchanged could result in a change of the Si–C_{arom} bond moment from $+0.42$ to -0.33 D, a total change of 0.75 D, is difficult to understand.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, K-25 PLANT, CARBIDE AND CARBON CHEMICALS COMPANY, UNION CARBIDE AND CARBON CORPORATION]

The Vapor Pressure and Critical Constants of Uranium Hexafluoride[1]

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Vapor pressure measurements were made on uranium hexafluoride from 0° to the critical point. The vapor pressure of the solid is represented by the equation: $\log_{10}P_{mm} = 6.38363 + 0.0075377t - 942.76/(t + 183.416)$. Pressure data on the liquid from 64 to 116° are represented by equation (2): $\log_{10}P_{mm} = 6.99464 - 1126.288/(t + 221.963)$, and above 116° by equation (3): $\log_{10}P_{mm} = 7.69069 - 1683.165/(t + 302.148)$. Critical constants determined from experimental data are: t_c, 230.2 ± 0.2° and P_c, 45.5 ± 0.5 atm. Calculated ΔH_v at the triple point, 64.02 ± 0.05°, was 6.82 kcal./mole. Calculated deviations from ideality were 0.0062 at 25° and 0.043 at 64.02°.

Since the early vapor pressure data of Ruff and Heinzelmann, in 1911, many measurements on uranium hexafluoride have been made by various methods in the low pressure range. However, there is only one report of an attempt to measure the vapor pressure above four atmospheres. Most of these data are summarized along with other properties of uranium hexafluoride in reference 3. Uncertainties in the published data, which were due indirectly to the reactivity of the compound, have been essentially eliminated in the present work by an ebulliometric method of measurement.

Several values for the critical temperature and pressure of this compound have been estimated from related physical properties.[3] Since these values vary as much as 30° and 20 atm., respectively, it was considered worthwhile to publish experimental values for these constants.

Experimental

Material.—Two samples of uranium hexafluoride were used in the present investigation over the entire liquid range. The purity of these samples was estimated to be 99.75 mole per cent. by mass spectra analysis that showed 0.01% fluorocarbon and 0.24% other volatiles, and emission spectra that showed 0.005% non-volatile impurities. The vapor pressure of a third sample was measured over the solid range and up to 2500 mm. of the liquid range. Volatile impurities were removed from this sample by repeatedly pumping the equilibrated vapors from the sample, held at room temperature, until only one-fourth of the original material remained. Then, the residue was treated with anhydrous potassium fluoride for 68 hours. The purity of the final material was 99.985 mole per cent., as determined by a calorimetric fractional melting point method. The data indicated that a final elimination of volatile impurities, *e.g.*, hydrogen fluoride, was accomplished in the boiler of the vapor pressure apparatus.

Apparatus and Procedure.—Both the ebulliometric and static apparatuses were used to measure the vapor pressure of the solid, while only ebulliometric measurements were made on the liquid. Primary equipment employed in the static measurements on the solid state consisted of the manometer and platinum resistance thermometer for the ebulliometric apparatus, a refrigerated 20-gallon bath, and a null-point pressure transmitter. The transmitter was connected between the manometer system containing helium and a nickel cylinder containing 15 g. of uranium hexafluoride. The cylinder and thermometer were mounted adjacently in a copper block which was suspended in the bath. Temperature of the bath was regulated to ±0.005°. Measurements of the vapor pressure were verified by pumping off the vapor above the valve on the sample cylinder and remeasuring the pressure of new charges of vapor until reproducible pressures were obtained.

Two ebulliometers were used to measure the vapor pressure of the liquid and a portion of the sublimation pressures. The low pressure apparatus has been described briefly,[4] and both are described in detail in a pending publication.[5] Briefly, the high pressure apparatus consisted of two monel boiling point tubes connected through traps to a common pressure system containing helium as a buffer. A certified platinum resistance thermometer measured the boiling temperatures of the material in each tube. The pressure in the system was determined by measuring the boiling temperature of water in one boiling point tube and obtaining the corresponding pressure from steam tables.[6] Temperatures were measured absolutely to within ±0.01° but the accuracy of the pressure readings was no better than that of the steam tables.

To determine the critical temperature and pressure, the system was brought to equilibrium at a temperature and pressure below the critical point of uranium hexafluoride. The heat input to the system was maintained practically

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(1) This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Company, Union Carbide and Carbon Corporation, Oak Ridge, Tennessee.

(2) Monsanto Chemical Co., Texas City, Texas.

(3) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," Part I, National Nuclear Energy Series, Division VIII, Volume 5, McGraw-Hill Book Co., Inc., 1951, p. 404.

(4) G. D. Oliver and J. W. Grisard, THIS JOURNAL, **73**, 1688 (1951).

(5) G. D. Oliver and J. W. Grisard, *Rev. Sci. Instruments*, in press.

(6) N. A. Osborne and C. H. Meyers, *J. Research Natl. Bur. Standards*, **13**, 1 (1934).

constant while the pressure was increased by two to five pound increments until the critical pressure was exceeded. Since the heat of vaporization is small in this region and diminishes to zero at the critical point, this procedure was practical even though it was difficult to prevent superheating. By plotting the pressure–temperature data as they were obtained, the critical temperature and pressure were readily estimated from the break in the curve at the critical point.

Results and Discussion

The vapor pressure of uranium hexafluoride was measured from 0° to the triple point, 64.02°, by the static and ebulliometric methods and from 64° to the critical temperature by the ebulliometric method. Data on the solid are given in the first part of Table I; the second part includes those data measured in the low pressure apparatus having a single boiling point tube, and the third part of Table I presents the measurements made in the double boiling point tubes. Even though the method of measuring the pressure was different, the data are consistent within experimental error.

TABLE I

VAPOR PRESSURE OF URANIUM HEXAFLUORIDE

$t_{\text{obsd.}}$, °C.	$P_{\text{obsd.}}$, mm.	$P_{\text{obsd.}} - P_{\text{calcd.}}$	$t_{\text{obsd.}}$, °C.	$P_{\text{obsd.}}$, mm.	$P_{\text{obsd.}} - P_{\text{calcd.}}$
		Solid			
0.00	17.57[a]	0.05	31.30	169.36	0.04
4.92	26.05	.10	33.94	200.54	.08
5.32	26.83[a]	.01	35.86	226.32	.10
9.40	36.72	−.01	37.58	251.78	.13
9.49	36.99[a]	.01	41.89	327.18	−.16
17.92	68.58[a]	.01	47.01	443.13	−.02
18.12	69.60[a]	.02	50.00	526.26	−.29
21.40	87.57	.06	54.91	694.35	−.18
22.92	97.02[a]	−.11	59.84	910.4	.04
25.41	114.95	.01	63.88	1129.5	.10
		Liquid			
64.20	1145.2	0.0	99.94	3131.1	−.4
65.99	1211.4	−.1	108.07	3818.4	−.9
66.18	1218.8	.0	116.03	4596.8	.9
67.06	1252.2	−.1	124.17	5512.3	−15.4
68.59	1313.1	.1	133.19	6669.7	−3.7
69.55	1352.2	.1	141.44	7888.6	13.5
70.79	1404.3	.1	149.50	9226.0	22.0
71.86	1450.4	.0	157.83	10773	22.0
72.82	1492.3	−.1	170.64	13528	16.0
74.11	1550.7	−.1	180.57	15986	−4.0
74.75	1580.3	−.1	188.85	18294	−14.0
76.52	1164.2	−.3	196.02	20477	−33
78.25	1750.1	.0	199.85	21735	−30
80.19	1849.2	.2	207.32	24329	−45
82.08	1951.2	.0	213.82	26779	−46
83.87	2050.8	.0	218.74	28773	−24
85.54	2147.8	.0	220.52	29468	−69
86.63	2212.8	.2	224.76	31409	57
87.20	2247.0	.1	225.14	31611	92
88.84	2348.7	.0	225.57	31781	73
90.35	2445.3	−.2	227.93	32908	145
91.35	2511.1	0.0	228.38	33260	294
91.88	2546.5	.1	229.11	33740	441

[a] Static measurements.

Observed data were used to calculate the constants of the Antoine equation by a method of least squares.[7] It was necessary to use the modified Antoine equation[8] to obtain equation (1) which would satisfactorily represent the vapor pressure of the solid.

$$\log_{10} P_{\text{mm}} = 6.38363 + 0.0075377t - 942.76/(t + 183.416) \quad (1)$$

Uncertainty of the equation, based on confidence limits at the 0.95 level, is estimated to be ±0.05% of the pressure. The observed data on solid uranium hexafluoride were not corrected for the 38 cm. column of vapor in the ebulliometer as were the data represented by equation (2).

The second part of Table I contains a portion of the observed data measured on three different samples of uranium hexafluoride. A comparison of the vapor pressure data of several investigators[3] in this range showed a variation of as much as ±2%. Consequently, it seemed desirable to obtain precise data on materials whose impurities had been estimated quantitatively and identified sufficiently so that the volatile impurities could be eliminated effectively from the test sample. Constants of equation (2) were determined from the data between 64.20 and 91.88°. Confidence limits at the 0.95 level ranged from 0.06 mm. at 64° to 0.13 mm. at 92°, and the uncertainty of the equation is estimated as ±0.03% of the pressure.

$$\log_{10} P_{\text{mm}} = 6.99464 - 1126.288/(t + 221.963) \quad (2)$$

The data of part three of Table I were measured several months after equation (2) had been calculated. Therefore, since equation (2) represented the data up to 116.03° within its stated precision, equation (2) was not recalculated to include the additional data and equation (3) was fitted to the remaining data above 116.03°.[9] In fitting the data to the Antoine equation, one of the first iterations showed that the three highest points deviated from the calculated values considerably more than the remaining points. Moreover, it was found by further iteration that if these points were omitted, an equation could be developed that would represent the remaining data much better. These points were not used in calculating the equation

$$\log_{10} P_{\text{mm}} = 7.69069 - 1683.165/(t + 302.148) \quad (3)$$

Even though its range was also decreased on the low pressure end, the above equation does not represent the data better than 0.3% of the pressure at high pressures.

Critical Constants.—When the pressure and temperature data were plotted as shown in Fig. 1, the slope of the resulting line increased rapidly in the critical region. As previously found in experiments on water and hexadecafluoroheptane in this Laboratory, changes in pressure above the critical point did not change the temperature. This experimental fact is in agreement with theory on phase relationship since the liquid–vapor state no longer exists as such, and the heat of vaporization has diminished toward zero. Consequently, one may readily estimate the critical pressure from the

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[7] C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D Rossini, *ibid.*, **35**, 219 (1945).

[8] A. Weissberger, "Physical Methods of Organic Chemistry," Part I, Interscience Publishers, Inc., New York, N. Y., 1949, p. 208.

[9] G. W. Thomson, *ibid.*, p. 205.

break in the curve, and the critical temperature from the vertical portion. Apparently, the gross density of the substance in the tube approximated the critical density, else the critical temperature and pressure values determined by this method for water and hexadecafluoroheptane[10] would not check published values determined by other methods. Perhaps the helium in the boiling point tube[5] behaved as an adjustable dimension which permitted the necessary volume changes. A critical temperature of 230.2 ± 0.2° and a critical pressure of 45.5 ± 0.5 atm. were estimated from an enlarged plot of the data. Abelson's value[3] of 232° checked the present critical temperature closer than any other; while the value of 44 atm. estimated by the National Bureau of Standards[3] was the only reasonably close check for the critical pressure.

Latent Heats and Ideality Deviation.—The heat of sublimation, ΔH_s, of uranium hexafluoride was calculated by means of the Clapeyron equation and equation (1) at 25° to be 11.80 kcal./mole, and at 56.54° and 1 atm. to be 11.50 kcal./mole. Molar volume values for the solid were obtained from density data,[3] and similar values for the gas were calculated by means of the Berthelot equation. At the triple point, 64.02 ± 0.05°, where equations (1) and (2) intersect, both the ΔH_s and ΔH_v were calculated by use of the Clapeyron and the respective vapor pressure equations. Molar liquid volumes were obtained from experimental densities,[3] while the gas volumes were calculated by means of the Berthelot equation. The value for ΔH_s was 11.38 kcal./mole and ΔH_v was 6.82 kcal./mole. Since $\Delta H_{\text{fusion}} = \Delta H_s - \Delta H_v$, a value for ΔH_f of 4.56 kcal./mole was obtained which checked to less than 1% the value of 4588 cal./mole determined calorimetrically.[3]

In the course of calculating the molar volumes of the vapor, the amount of deviation of the gas from the ideal gas laws was calculated by using the Berthelot equation and experimental data. The deviation at 25° was 0.0062 and increased to 0.031 at 56.54° where the vapor pressure is 1 atm.; at the triple point, 64.02°, the deviation from ideality was 0.043. Accordingly, uranium hexafluoride gas may be considered ideal at room temperature.

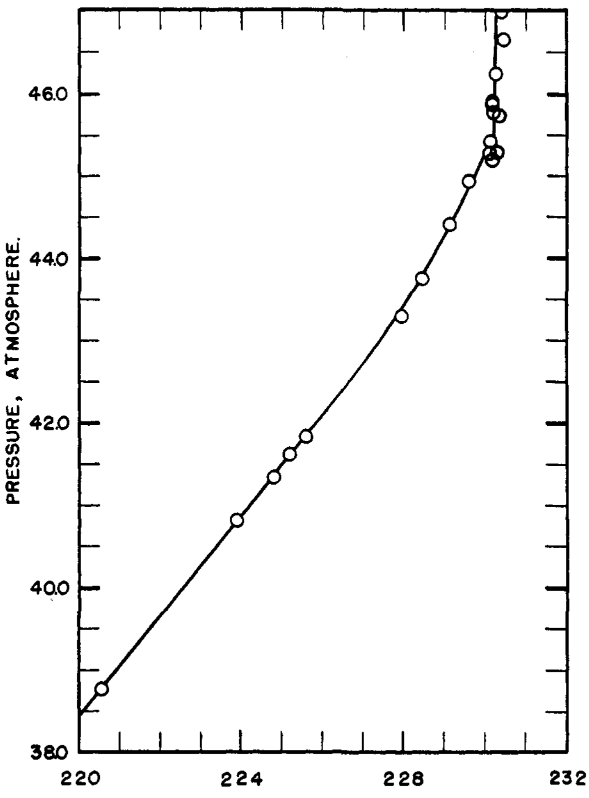

Fig. 1.—Vapor pressure of uranium hexafluoride in the critical region.

Acknowledgment.—The authors are indebted to P. B. Wood for the statistical calculation of the vapor pressure equations.

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[10] G. D. Oliver, S. Blumkin and C. W. Cunningham, THIS JOURNAL, **73**, 5722 (1951); H. T. Milton and G. D. Oliver, *ibid.*, **74**, 3951 (1952).