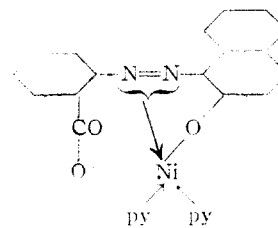


nation number of four or six; it is probable that some coordinated water was lost on drying.

Nickel shows a coordination number of only four in the lake with this dihydroxy compound, as it does in many coordination compounds. As might be expected from the structure of the dye, magnetic measurements indicated the lake to be tetrahedral.

Lakes of 2'-Carboxybenzene-4-azo-1-phenyl-3-methylpyrazol-5-one.—This dye resembles the previous one in having two replaceable hydrogen atoms in groups ortho to the chromophore group. Again, the cobalt was found to be in the cobaltous condition.

Drew and Fairbairn^{3b} isolated the nickel complex of *o*-carboxybenzeneazo- β -naphthol as the dihydrate, and postulated that the nickel and the carboxyl group are not joined. This suggestion was supported by the fact that solution of the dihydrate in pyridine gave a dipyridino compound.



In the nickel and cobalt lakes of 2'-carboxybenzene-4-azo-1-phenyl-3-methylpyrazol-5-one, which has a similar structure, the carboxyl group evidently takes part in lake formation, for these lakes are monohydrates rather than dihydrates.

The authors take pleasure in acknowledging their indebtedness to the General Aniline and Film Corporation for grants which made this work possible, and for generous gifts of the dyes used.

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

Preparation and Physical Properties of Niobium Pentafluoride¹

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Niobium pentafluoride was prepared by fluorinating the metal with elemental fluorine at 300°. The melting point was found to be $78.9 \pm 0.2^\circ$, the boiling point $233.3 \pm 0.5^\circ$, and the heat of fusion was estimated to be 8600 cal./mole. A sample of the compound was distilled in a 20-plate column. The vapor pressure of the middle fraction was measured and may be expressed by equation (1). Using the value of the heat of fusion given above, the vapor pressure over the solid may be expressed by equation (3). The liquid density was measured in the range of 86 to 125° and may be expressed by equation (4). The following thermodynamic quantities for the vaporization process were calculated from the vapor pressure data and corrected for deviation from ideality by the density measurements: $\Delta C_p = -8.5$ cal. deg.⁻¹ mole⁻¹; $\Delta H_v = 16,800 - 8.5 T$; $\Delta S_v = (16,800/T) - 8.5$. The compound was found to be more stable toward hydrolysis than either ruthenium pentafluoride or uranium hexafluoride. There was no evidence of decomposition of niobium pentafluoride at temperatures up to 255°.

Introduction

The chemistry of inorganic fluorides has been a subject of increased interest in recent years partially as a result of the unusual character of many of these compounds but to a greater extent on account of the possible application to new chemical processes. Among the many compounds first studied but incompletely characterized by Ruff and his co-workers^{2,3} was niobium pentafluoride. In view of the reactive nature of this compound, especially with glass, one can well appreciate the difficulties encountered by the early workers; and since the data in the literature were somewhat inconsistent, measurements of the vapor pressure, melting point, liquid density and the calculation of associated thermodynamic properties were undertaken.

Experimental and Results

Preparation and Purification.—Niobium pentafluoride was prepared by direct fluorination of niobium metal in a

nickel reactor at 300°. The powdered metal was placed in one leg of the L shaped reactor tube before the segments of the L were welded together. After fabrication the system was warmed and pumped to remove air and traces of moisture; then, with the outlet of the reactor connected to a vacuum pump and the inlet to a source of fluorine, the leg of the reactor which contained the niobium metal was placed in an electric tube furnace and the other leg was suspended in Dry Ice slush. The temperature of the furnace was increased to 300° and fluorine was admitted into the static system forming the pentafluoride which deposited in the cool leg of the preparation tube.

Since this crystalline white solid niobium fluoride reacts with traces of moisture in the air, transfers of material from the preparation tube to other apparatus were made in an atmosphere which had a dew point of -40° or lower. The composition of the preparation is shown in Table I. The purity is limited by the presence of the order of 0.5 mole % of tantalum in the niobium metal, according to spectrographic analysis.

TABLE I
ANALYSIS OF NIOBIUM PENTAFLUORIDE

	Found	Theoretical (NbF ₅)
Niobium, %	49.7 \pm 1.0	49.5
Fluorine, %	50.2 \pm 0.6	50.5

A sample of niobium pentafluoride prepared in the manner just described was used without further purification for the determination of the melting point and estimation of the heat of fusion. Material employed in the determination of the vapor pressure was purified by distillation in a nickel fractionating column whose efficiency had been found by the

(1) (a) 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. (b) The information in this document was presented at the Fluorine Chemistry Symposium, American Chemical Society, New York Meeting, September 4, 1951.

(2) Otto Ruff and Emil Schiller, *Z. anorg. Chem.*, **72**, 329 (1911).

(3) Otto Ruff and Julian Zedner, *Ber.*, **42**, 492 (1909).

method of Willingham and Rossini⁴ to be 20 theoretical plates. The desired cut of the fluoride distillate was discharged into the product receiver by means of a reflux splitter which was energized by an electromagnet located outside the column.

Determination of the Melting Point and Heat of Fusion.—The melting point was determined and the heat of fusion estimated by analysis of warming and cooling curves. The apparatus consisted of a platinum sample container and nickel reference shield suspended in a heavy copper heating block inside a metal dewar which was insulated with asbestos. A length of nickel tubing was welded to the top of the sample container, and a flare connection was provided at the top of the tubing through which the sample could be introduced in the gas phase. A non-inductively wound auxiliary heater, actuated by an electronic controller and thermocouples located at the top and bottom of the tube, respectively, maintained a temperature at the top of the tube equal to the temperature at the bottom. Hence, temperature uniformity was maintained in the sample zone. A typical warming curve is shown in Fig. 1. The melting temperature was obtained by extrapolating the warming curve to a 100% melted condition. The heat of fusion was estimated by the graphical method from Area A, where the calorific value represented by each unit area had been determined using benzoic acid as a standard. Niobium pentafluoride has, according to this method, a melting point of $78.9 \pm 0.2^\circ$. The limits of precision expressed are based upon the precision to which the thermopiles were calibrated. The heat of fusion estimated from the area is 8600 (± 500) cal. mole⁻¹ and the corresponding entropy of fusion 24 cal. deg.⁻¹ mole⁻¹.

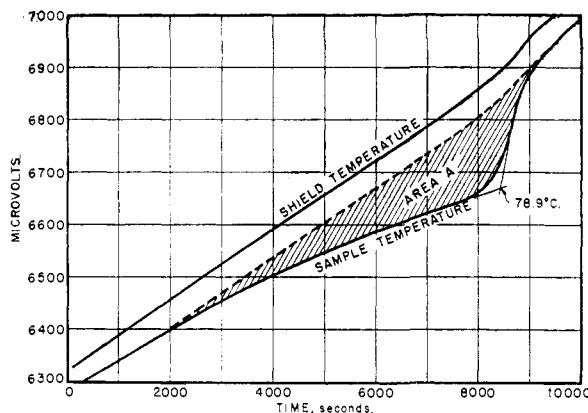


Fig. 1.—Heating curve for niobium pentafluoride.

Measurement of the Vapor Pressure.—The vapor pressure was measured in a static, all nickel, diaphragm type pressure transmitter, which was mounted in a 5-inch electric tube furnace. The transmitter was a modification of a design by K. O. Johnson to be published. The observation was started with the system cool and both the inert and active sides of the apparatus evacuated, the vapor pressure of niobium pentafluoride at room temperature being negligible. As the system is heated, the vapor pressure of the fluoride moves the diaphragm causing it to touch an electrical contactor. This contactor is connected to an electronic self-balancing relay valve which maintains an air pressure on the inert side of the diaphragm equal to the vapor pressure of the fluoride on the active side, plus or minus a small calibration correction. During operation, the inert side of the transmitter is pumped through a closely throttled needle valve. As the pressure decreases the diaphragm touches the contactor rod actuating the relay valve and admitting air into the system. When the air balancing pressure reaches the null-point the transmitter contacts open. This de-energizes the relay coil allowing the valve to close. The cycle is the order of $1/2$ second long. Pressure readings at the contact point were reproducible to ± 0.2 mm. In the statistical treatment of the data, the variance of a value of $\log p$ was ± 0.0058 or $\pm 1.0\%$ of the pressure. Temperatures

were measured with a White double potentiometer and a platinum-rhodium thermocouple calibrated to yield an accuracy of $\pm 0.1\%$ of the centigrade reading.

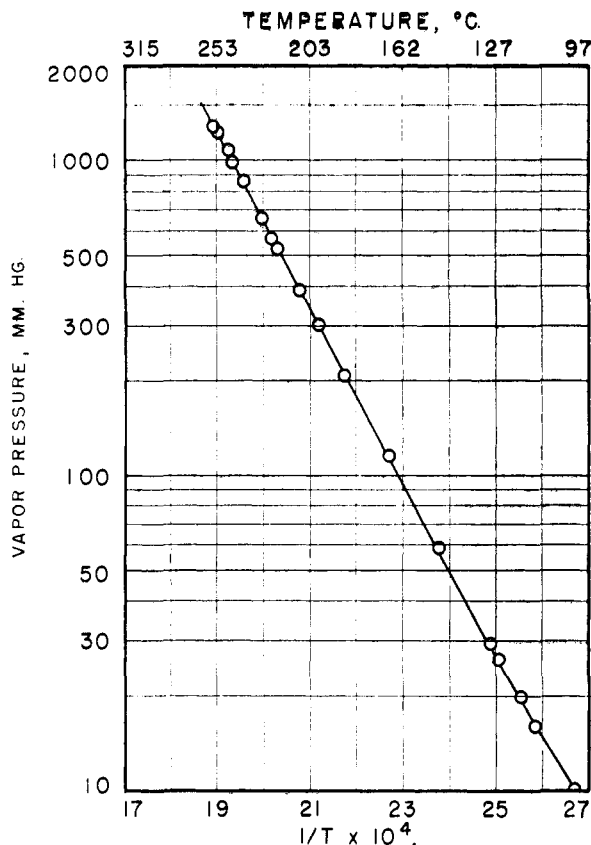


Fig. 2.—Vapor pressure of niobium pentafluoride.

A plot of the vapor pressure versus the reciprocal temperature is shown in Fig. 2. There was possibly present trace amounts of volatile impurities giving the line a slight convex curvature with respect to the $1/T$ axis. The vapor pressure of the liquid over the entire range from 10 to 1286 mm. is best represented by the equation

$$\log_{10} P_{\text{mm.}} = 8.3716 - \frac{2779.3}{T} \quad (1)$$

Above 200 mm. however, a better fit is obtained using a Kirchoff type equation

$$\ln P_{\text{mm.}} = 51.3101 - \frac{8716}{T} - 4.41 \ln T \quad (2)$$

The boiling point from both of these expressions is $233.3 \pm 0.5^\circ$.

The solid-vapor equilibrium pressures were too low to measure with this apparatus; however, since the heat of fusion has been estimated, an expression approximating the values of these pressures may be computed from the vapor pressure at the melting point and the heat of sublimation to be

$$\log_{10} P_{\text{mm.}} = 14.897 - \frac{4900}{T} \quad (3)$$

The vapor pressure at the triple point is 3.0 mm. and the heat of sublimation is calculated to be 22,400 cal./mole.

Determination of the Liquid Density.—The liquid density was determined in order that corrections for deviation from ideality could be applied to the thermodynamic functions, and may be represented by the equation

$$d = 2.8026 - 9.81 \times 10^{-4}t - 6.16 \times 10^{-6}t^2 \quad (4)$$

which covers the range from 86 to 125° . Although the measurements were made in glass, the total contact time was not sufficient to introduce enough impurity to cause serious error in the measurements. The upper temperature at which measurements could be made was limited by the vapor pressure of the fluoride.

(4) C. B. Willingham and F. D. Rossini, "Assembly, Testing, and Operation of Laboratory Distilling Columns of High Efficiency," National Bureau of Standards, December 31, 1945.

Thermodynamic Functions.—The complete thermodynamics of the vaporization process requires a knowledge of the values of ΔH_v and ΔS_v as functions of the temperature. The heat of vaporization is expressed by the relationship

$$\Delta H_v = \Delta H_0 + \int_0^T \Delta C_p T$$

If it is assumed that the change in the difference between the heat capacities of the two phases is small over the temperature range under consideration, then the influence of the coefficients of the higher order temperature factors $\Delta\beta$, $\Delta\gamma$, $\Delta\delta$... of Kirchhoff's equation becomes small and the following simplified expressions may be written.

$$\Delta H_v = \Delta H_0 + \Delta C_p T \quad (5)$$

$$\Delta S_v = \frac{\Delta H_0}{T} + \Delta C_p \quad (6)$$

By substituting the value for ΔH in the Clausius-Clapeyron equation, one obtains an expression for the liquid-vapor equilibrium.

$$\frac{d \ln P}{d(1/T)} = \frac{-T}{P(V_v - V_l)} (\Delta H_0 + \Delta C_p T) \quad (7)$$

The differentiated experimental equation is similar in form

$$\frac{d \ln P}{d(1/T)} = B - CT \quad (8)$$

By equating the coefficients in equations (7) and (8) expressions for ΔH and ΔC_p are obtained.

$$\Delta H_0 = \frac{-P(V_v - V_l)}{T} B \quad (9)$$

$$\Delta C_p = \frac{P(V_v - V_l)}{T} C \quad (10)$$

Statistical values for B and C are -8716 ± 62 and -4.41 , respectively. The liquid molal volume V_l is taken directly from the liquid density data, and the vapor molal volume V_v may be calculated by the van der Waals equation. By using the rules proposed by Brewer and Searcy⁵ for calculating the values of the van der Waals constants, ΔH_0 and ΔC_p are evaluated

$$\Delta H_0 = 16,800 \pm 120 \text{ cal. mole}^{-1} \quad (11)$$

$$\Delta C_p = -8.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (12)$$

and from equations (5) and (6) expressions for the primary thermodynamic functions are obtained

$$\Delta H_v = (16,800 - 8.5T) \pm 120 \text{ cal. mole}^{-1}$$

$$\Delta S_v = \frac{16,800}{T} - 8.5$$

While these equations are subject to some uncertainty, they do represent the best estimates which can be made from currently available data.

General Comments.—Niobium pentafluoride appears to be more stable to hydrolysis than either uranium hexafluoride or ruthenium pentafluoride. In a dry box with a dew point of -40° the niobium fluoride may be transferred with no appreciable decomposition or fuming, while the ruthenium compound decomposes slowly even at a dew point of -50° . There was no evidence of dissociation of the niobium pentafluoride up to a temperature of 255° .

(5) Leo Brewer and Alan W. Searcy. *J. Chem. Ed.*, **26**, 548 (1949). OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, PURDUE UNIVERSITY]

Chemical Valency Theory and the Electronic Structure of the Methane Molecule¹

BY CHARLES R. MUELLER

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Two principal methods, the atomic and molecular orbital methods, have been used in attacking the problems of chemical valency theory. An alternative method, the semi-localized orbital approach has been developed and includes both of the previous methods as special cases. A semi-localized orbital calculation of the binding energy and electronic structure of methane is made. The bond energy from such a calculation is 160 kcal. greater than that for the atomic orbital method. The latter gives a negative bond energy. The electronic structure of the methane molecule obtained from the semi-localized orbital method is quite different from that of either simpler approach. It is shown that the method gives a natural description of steric effects, resonance, heteropolar binding, inductive effect and has a formal analogy with classical valency theory. This is the first full scale quantum mechanical treatment of the methane molecule as a 10-electron problem.

Introduction

Two principal methods of attacking the problems of chemical valency theory have been utilized. Both of these methods, the atomic and molecular orbital methods, as well as the semi-localized orbital approach used in this paper, postulate that a reasonably good molecular eigenfunction (a good approximate solution of the Schrödinger equation for the molecule) can be formed from a linear combination of all the product of all the one-electron orbitals in the molecule. In all three cases this linear combination must be formed in such a way as to obey the Pauli Exclusion Principle and the Uncertainty

Principle. The individual products differ only in that different electrons are assigned to the orbitals.

The three methods differ in the way the one-electron orbitals are formed. In the atomic orbital method the electrons are assigned to orbitals which are approximate solutions of the Schrödinger wave equation for individual atoms (atomic orbitals). Such a theory gives poor description of heteropolar binding.

There are two variations of the second approach, the molecular orbital method. In one case the one-electron orbitals move over the entire molecule. In the second form, localized molecular orbitals, the one-electron orbitals cover only two atoms which form a chemical bond. Since Lennard-

(1) Presented in part before the Physical-Inorganic Division of the American Chemical Society, Buffalo, N. Y., March, 1952.