were those involved in the decomposition of [Pt(en)$_2$]^0, *i.e.*, 6 and 7. That this interpretation is correct is shown by the data given in Table II.

TABLE II

EQUIVALENCE RATIOS AMONG AMMONIA-INSOLUBLE PRODUCTS

Ratio	Calcd.	Found
en/Pt	2.00	2.02
H_2/[Pt(en-H)$_2$]^0	1.00	1.01
Water-soluble Pt/elemental Pt	1.00[a]	1.07

[a] Based on the assumption that the rates of reactions 6 and 7 are substantially equal.

In arriving at these calculated ratios, [Pt(en-H)$_2$]^0 was determined separately as soluble platinum, and [Pt(en-H)$_2$]^0 and ethylenediamine were determined together by titration with standard hydriodic acid solution as described in the Experimental section.

It also should be noted that, of the products proposed to explain the reduction of [Pt(en)$_2$]I_2 with ammonia solutions of potassium, [Pt(en-H)$_2$]^0 is the only one not identified by direct analysis and/or X-ray diffraction data. However, the presence of this product was established indirectly by reducing [Pt(en)$_2$]I_2 to an iodine-free ammonia-insoluble product, *i.e.*, [Pt(en)$_2$]^0 by reaction 8, and allowing this product to decompose at room temperature *via* reactions 6 and 7. Removal of ethylenediamine by washing with liquid ammonia left only a mixture of elemental platinum and [Pt(en-H)$_2$]^0. Treatment of this mixture with a solution of ammonium chloride in liquid ammonia was shown to lead to the formation of [Pt(en)$_2$]Cl_2 by a reaction strictly analogous to the previously demonstrated reactions of [Pt(en-H)$_2$]^0 with hydrochloric and/or hydriodic acids in aqueous solution.

It is further of interest to note that [Pt(en-H)(en)]I and [Pt(en-H)$_2$]^0 are formed either by

$$[\mathrm{Pt(en)_2}]^{2+} + \mathrm{NH_2}^- \longrightarrow [\mathrm{Pt(en\text{-}H)(en)}]^+ + \mathrm{NH_3} \quad (10)$$

$$[\mathrm{Pt(en)_2}]^{2+} + 2\mathrm{NH_2}^- \longrightarrow [\mathrm{Pt(en\text{-}H)_2}]^0 + 2\mathrm{NH_3} \quad (11)$$

or by the spontaneous decomposition of [Pt(en)$_2$]I and [Pt(en)$_2$]^0, respectively. These species, as shown above, may be either ionic or neutral. The reactions of these complexes with aqueous or ammonia solutions of acids and with sulfur dioxide suggests that each nitrogen atom in an (en-H) group bears an unshared pair of electrons that is not utilized by the available orbitals of the central platinum ion. On the other hand, [Pt(en)$_2$]^0 is of a low order of stability entirely comparable with the unstable [Pt(NH$_3$)$_4$]^0 whereas both [Pt(en-H)(en)]I and [Pt(en-H)$_2$] exhibit so much greater stability that some strong interaction with the platinum ion must be responsible for the observed difference in stability. Further studies bearing upon this particular aspect of the problem as well as upon the mechanism of the reduction reactions are in progress.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION, ARGONNE NATIONAL LABORATORY]

The Preparation and Properties of Vanadium Pentafluoride[1]

BY L. E. TREVORROW, J. FISCHER AND R. K. STEUNENBERG

RECEIVED MAY 31, 1957

Vanadium pentafluoride was prepared by the reaction of fluorine with vanadium metal at 300°. Measurements of the vapor pressure of the liquid from 24.1 to 85.5° resulted in a normal boiling point of 47.9°. The melting point was 19.0 ± 0.9°. Vapor density measurements indicated that the molecular species present in the vapor phase is VF_5.

Distillation experiments in this Laboratory have suggested that vanadium pentafluoride must be a much more volatile compound than the data of Ruff and Lickfett[2] had indicated. They had erroneously described vanadium pentafluoride as a white solid at room temperature which sublimes at 111.2° (758 mm.), and which melts above 200°.

Pure vanadium pentafluoride was prepared from the elements, and the vapor pressure of the liquid was measured as a function of temperature. Melting point and vapor density determinations were also made.

Experimental

Materials.—Vanadium metal with a purity analysis of 99.5% was obtained from the Vanadium Corporation of America. Commercial fluorine of high purity was used. It was analyzed by the method of Aoyana and Kanda,[3] employing the quantitative reaction of mercury with fluorine, and found to be at least 99% fluorine by volume. It was also shown to contain less than 0.5% impurities by its quantitative reaction with bromine[4] and by various physical measurements.

Apparatus.—The equipment used in this work was constructed of nickel and Monel. The components were joined by welding or by flare connectors with Teflon gaskets. Preliminary work had shown that vanadium pentafluoride reacts with silver solder, and to a lesser degree with Fluorothene (poly-chlorotrifluoroethylene). These materials were avoided in the apparatus used for the final purification of the vanadium pentafluoride and for the determinations of its physical properties. The various portions of the apparatus were joined to a manifold which was provided with liquid nitrogen-cooled traps and sources of vacuum, helium and fluorine. Monel diaphragm and Teflon-seated bellows valves were employed.

That portion of the apparatus in which the vapor pressure and vapor density measurements were made was housed in a constant-temperature air bath. Care was taken to ensure that no portion of the apparatus was at a lower temperature than the liquid when the vapor pressure measurements were made.

The temperature was measured to the nearest 0.1° with a copper–constantan thermocouple which had been calibrated previously against a standard platinum resistance thermometer using a Leeds and Northrup G-2 Mueller

---

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) O. Ruff and H. Lickfett, *Ber.*, **44**, 2539 (1911).

(3) A. Aoyana and E. Kanda, *Bull. Chem. Soc. Japan*, **12**, 409 (1937).

(4) J. Fischer, J. Bingle and R. C. Vogel, THIS JOURNAL, **78**, 902 (1956).

bridge. In the vapor pressure measurements the temperatures were determined with a Rubicon Type B potentiometer. For the melting point a Brown multi-point recording potentiometer was used to obtain time–temperature curves.

Pressures were observed by means of a mercury manometer used in conjunction with a Booth–Cromer pressure transmitter and self-balancing relay.[5] This arrangement allowed the manometer to be isolated from the fluoride system. The pressure transmitter was located in the constant temperature air-bath. Pressures were measured to the nearest 0.1 mm.

The method of thermal analysis was used for the melting point determination. The vanadium pentafluoride sample was contained in a $^{3}/_{4}$-inch nickel tube 6 inches in length. The tube was provided with a well in the bottom, into which the copper–constantan thermocouple was inserted.

The vapor density measurements employed a nickel vessel with a volume of 892.6 ml. The vessel was fitted with a Hoke No. 1103 bellows valve and a $^{3}/_{8}$-inch flare connection by which it could be attached to the manifold. The vapor density was determined by weighing to 0.1 mg. a known pressure of the vapor in this vessel at a known temperature.

Procedure.—The vanadium pentafluoride was prepared by passing elemental fluorine over granulated vanadium metal in a $^{3}/_{4}$-inch nickel reaction tube at 300°. Chemical analyses of the product indicated 34.2% vanadium and 66.5% fluorine. The corresponding theoretical values for vanadium pentafluoride are 34.9 and 65.1%. Since vanadium pentafluoride is very hygroscopic, vacuum distillation techniques were used in the manipulations to avoid contact with the atmosphere.

An approximately 15-ml. portion of the vanadium pentafluoride was distilled into the $^{3}/_{4}$-inch nickel tube fitted with a thermocouple well. Its total capacity was 25 ml. The melting point determinations and the vapor pressure measurements were both made in this tube. In order to remove residual traces of hydrogen fluoride and fluorine from the sample, the material was frozen with Dry Ice and the tube was evacuated. The vanadium pentafluoride was allowed to melt, frozen again, and the tube was re-evacuated. This cycle was repeated several times. Fractions were then distilled from the sample until it showed a constant vapor pressure at a fixed temperature.

The vapor density of vanadium pentafluoride was obtained by weighing samples of the gas at known temperatures and pressures in the calibrated nickel vessel. The same result was obtained, within the experimental error, at temperatures of 24 and 76° and at pressures from 121.5 to 406.0 mm. No change was observed in the vapor density of a sample which had been stored as a liquid in the system for 36 hours at 76°.

In the freezing point determinations, the purified liquid supercooled to such an extent that satisfactory observations could not be made. It was possible, however, to obtain thaw curves using the method of thermal analysis. The vapor pressure of the compound at the melting point is appreciable (about 200 mm.). As a result, the melting point plateaus of the thermal analysis curves were distorted by the heat loss due to vaporization of the material. This effect was repressed by allowing vanadium pentafluoride vapor from another vessel at room temperature to vaporize into the melting point tube during the thawing process.

The reported melting point, which was obtained in this fashion, averaged about one degree higher than that measured in the usual manner.

In the vapor pressure measurements, the equilibrium values were verified by approaching them experimentally from both higher and lower temperatures.

Results and Discussion

Several measurements of the vapor density gave an average result of 146.1 ± 0.2 g./g.m.v. The formula weight is 145.95 g./mole. It was concluded that the molecular species in the vapor is VF_5 and that it exhibits very nearly ideal behavior.

The melting points of two different vanadium pentafluoride preparations agreed within the experimental uncertainty. The average of several determinations was 19.0 ± 0.9° which is in agreement with another recently observed value of 19.5 ± 0.5°.[6]

TABLE I

VAPOR PRESSURE OF VANADIUM PENTAFLUORIDE

t, °C.	p, mm.	t, °C.	p, mm.
24.6	214.6	64.5	1697.2[a]
25.4	222.1[a]	64.5	1708.1
25.7	225.1[a]	69.9	2158.8
34.6	372.5[a]	70.0	2154.5[a]
34.7	377.3	70.0	2155.0
44.4	633.2[a]	73.7	2523.9[a]
44.6	636.9	74.1	2528.8
50.5	871.5[a]	78.4	2971.1[a]
55.6	1123.9	78.4	2972.1
55.6	1123.9[a]	83.0	3467.6[a]
58.2	1281.4[a]	83.0	3467.6
58.3	1289.8	85.4	3734.5
		85.5	3734.0[a]

[a] Values were approached from a lower temperature. All others were approached from a higher one.

The vapor pressure of vanadium pentafluoride from 24 to 58° is expressed by the equation

$$\log p_{\text{mm}} = 11.7640 - \frac{3.38742 \times 10^{3}}{T} + \frac{1.7191 \times 10^{5}}{T^{2}} \quad (1)$$

and from 58 to 86° by the equation

$$\log p_{\text{mm}} = 1.0020 + \frac{3.65386 \times 10^{3}}{T} - \frac{9.7935 \times 10^{5}}{T^{2}} \quad (2)$$

The experimental values for the vapor pressure agree with values calculated from eq. 1 with an average deviation of ± 0.4%, and with values calculated from eq. 2 with an average deviation of ± 0.5%. The experimental data are listed in Table I. A normal boiling point of 47.9° was obtained from these data, and the heat of vaporization at this temperature is 10.60 kcal./mole. Vapor pressure determinations by Emeleus and Clark[6] up to 45° have resulted in a calculated boiling point of 48.3°, and a heat of vaporization of 10.640 kcal./mole.

The work of Emeleus and Clark was done with quartz apparatus, while the results reported here were obtained with nickel and Monel equipment. It appears that either of these materials may be used satisfactorily in handling vanadium pentafluoride.

Acknowledgment.—The authors wish to acknowledge the assistance of Mr. H. D. Tyler and Mr. W. H. Gunther in the experimental determinations.

LEMONT, ILL.

---

[5] S. Cromer, "The Electronic Pressure Transmitter and Self-Balancing Relay," SAM Laboratories, Columbia University, MDDC-803, 1947.

[6] H. C. Clark and H. J. Emeleus, *J. Chem. Soc.*, 2119 (1957).