

at the same wave lengths as for the binary complexes, but with intermediate intensity, *i.e.*, the mixed complex spectra would be expected to follow the median lines shown in Figs. 3, 4 and 5.

A glance at the actual mixed complex spectra shows that neither hypothesis adequately explains the data. The intense peak of mercuric iodide at 210 $m\mu$ is indeed shifted to shorter wave lengths (inaccessible to the present measurements) for HgClI and HgBrI, implying interaction of the ligands for this peak. On the other hand, HgClI has a peak at 265 $m\mu$, whose intensity is slightly less than half that of mercuric iodide. Therefore, the 265 $m\mu$ peak seems characteristic of iodide alone. The species HgBrI also absorbs at 265 $m\mu$ with an

intensity close to the median line, but, in addition, it shows some enhancement of absorption in the 230–250 $m\mu$ region which might be due to interaction of the ligands. A peak intermediate between those of mercuric chloride and mercuric bromide appears for HgClBr, but the overlap of the absorption bands is large, and the spectrum has been measured only in the region of maximum $\Delta\epsilon$ so that the interaction of the ligands is difficult to assess.

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The Preparation and Some Properties of Platinum Hexafluoride^{1,2}

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Platinum hexafluoride is the first simple hexavalent platinum compound that has been prepared. This was achieved by burning a platinum wire in a fluorine atmosphere adjacent to a cold surface with yields of up to 70%. The formula has been established by chemical analyses and vapor density. A solid transition occurs at 3.0°, 32.5 mm. pressure and the fusion point is 61.3°, 586 mm. The heat of transition is 2140 cal. mole⁻¹ and the heat of fusion is 1080 cal. mole⁻¹. The vapor pressure equations are: orthorhombic solid, $\log P$ (mm.) = $-3147.6/T - 6.09 \log T + 27.7758$; cubic solid, $\log P$ (mm.) = $2528.7/T - 4.080 \log T + 20.6280$; liquid, $\log P$ (mm.) = $-5685.8/T - 27.485 \log T + 89.14962$. The boiling point is 69.14°, which is the highest boiling point of the known hexafluorides. The heat of vaporization at the boiling point is 7060 cal. mole⁻¹. The liquid density is 3.826 g. cc.⁻¹ at 64.3°. The density of the low temperature solid varies between 6.0–5.0 g. cc.⁻¹ in the range 77–254°K. The vapor and liquid are red in color and the solids appear black. The molecule does not rotate freely in any of the condensed phases. Platinum hexafluoride is the least stable and most reactive of the known hexafluorides. The use of PtF₆ as a fluorinating agent at room temperature to form BrF₆, NpF₆ and PuF₆ is described.

Introduction

Platinum hexafluoride represents the first hexavalent compound of platinum that has been formed with a monovalent element and definitely establishes the valence of six for platinum. Other hexavalent compounds of platinum have been previously reported but in all cases involve a polyvalent element. These compounds include the trioxide,⁵ triselenide,⁶ diphosphide⁷ and diarsenide.⁸ Owing to the multiple valency of the anion involved, it has been suggested that the valence of platinum in these compounds might be lower than the formula implies.⁹ However, the synthesis of PtF₆ removes any question as to the existence of a hexavalent state for platinum.

The initial preparation and identification of PtF₆ has been reported.¹⁰ This synthesis completed the 5d transition series of hexafluorides that had already included WF₆, ReF₆, OsF₆ and IrF₆. The

present paper describes the original work in more detail as well as some subsequent studies that have been made with PtF₆.

Experimental

Materials.—Platinum metal wire obtained from the Baker Platinum Division of Engelhard Industries was used in the preparations. Within the limits of spectrographic analysis this material was found to be free of impurities. The fluorine gas used in the syntheses was obtained from the Pennsalt Chemicals Corporation. Its analysis showed greater than 99% fluorine by volume. The fluorine contained a small amount of hydrogen fluoride which was removed by condensation with liquid nitrogen.

Preparation.—The apparatus previously described¹⁰ that was used for the first preparation of platinum hexafluoride is shown schematically in Fig. 1. This reactor was constructed chiefly of Pyrex glass and contained 10 g. of 0.030 inch diameter platinum wire in the form of a spiral filament that was attached to electrically insulated nickel leads that were brought out of the apparatus through a Stupakoff seal. The filament was located directly below the surface of a spherical well which was kept full of liquid nitrogen during the course of the reaction.

Prior to admitting fluorine the system was evacuated to a pressure of about 10⁻⁶ mm. and was flamed while pumping to remove absorbed water. During the reaction a reservoir of liquid fluorine at the temperature of boiling nitrogen served to keep the fluorine pressure constant at about 300 mm. An electric current was passed through the platinum wire to initiate the reaction which then continued without external heating until the platinum was substantially consumed. The heat produced in this exothermic reaction caused the burning wire to remain incandescent at a steady state temperature that was estimated visually to be in the neighborhood of 1000°. The burning platinum filament viewed through the dark red vapors of PtF₆ was a strikingly awesome sight. Ultimately the outer wall of the Pyrex

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) The final draft of the paper was written at the Scientific Laboratory of the Ford Motor Company.

(3) Scientific Laboratory, Ford Motor Company, Dearborn, Michigan.

(4) On leave from Wabash College, Crawfordsville, Indiana.

(5) L. Wohler and F. Martin, *Ber.*, **42**, 3326 (1909).

(6) A. Minozzi, *Atti accad. naz. Lincei*, **18**, ii, 150 (1909).

(7) F. W. Clarke and O. T. Joslin, *Am. Chem. J.*, **5**, 231 (1883).

(8) L. Wohler, *Z. anorg. u. allgem. Chem.*, **186**, 324 (1930).

(9) N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford University Press, Oxford, 1950, pp. 1625.

(10) B. Weinstock, H. H. Claassen and J. G. Malm, *J. Am. Chem. Soc.*, **79**, 5832 (1957).

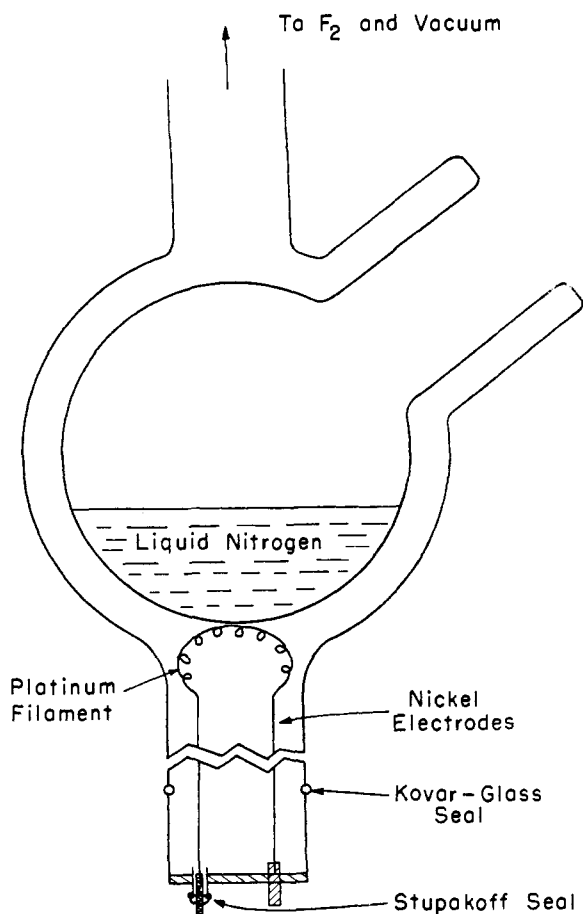


Fig. 1.—Glass reactor used for the first preparation of platinum hexafluoride.

flask was coated with an adherent nonvolatile yellowish-brown deposit, presumably platinum tetrafluoride, which was the major product of the reaction. The platinum hexafluoride that was condensed on the liquid nitrogen cooled surface was distilled into a nickel and monel system and purified by a series of U-tube to U-tube distillations using solid carbon dioxide as refrigerant and a procedure that has been described previously.¹¹ The total yield of PtF_6 after purification was 1.4 g. or 8.8% of the reacted platinum.

An improved reactor for the preparation of PtF_6 is shown in Fig. 2. The Pyrex reaction vessel has been replaced by a brass container. The liquid nitrogen well has been omitted and the walls of the reactor, cooled directly with liquid nitrogen, now serve as the condenser for the PtF_6 that is formed. The procedure used with this system was similar to that described above. The reaction was initiated as before by electrical heating, but the conclusion of the reaction was indicated by the cessation of fluorine uptake. In a typical experiment with this reactor, 14.9 g. of 0.030 inch diameter platinum wire produced 15.0 g. of purified PtF_6 . In this experiment 1.6 g. of platinum was unreacted and the product corresponded to a 71% conversion of the reacted platinum into the hexafluoride.

Chemical Analysis.—Weighed samples of PtF_6 sealed off in Pyrex flasks were hydrolyzed with a threefold excess of concentrated NaOH solution that was admitted through a break seal. The fluoride was first separated from the platinum by distillation from a solution acidified with sulfuric acid and to which Fe^{++} had been added¹² and then titrated spectrophotometrically with thorium nitrate using sodium alizarin sulfonate as the indicator. The residual

(11) B. Weinstock and J. G. Malm, *J. Inorg. Nuclear Chem.*, **2**, 380 (1956).

(12) H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

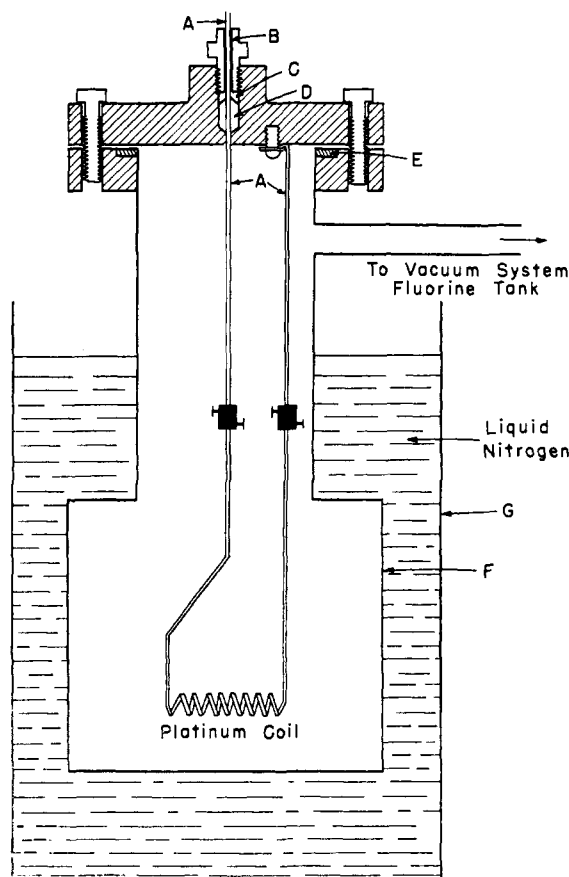


Fig. 2.—Brass reactor for the preparation of platinum hexafluoride: (A) 0.094" copper leads; (B) packing nut with insulating sleeve; (C) packing washer; (D) Teflon packing; (E) Teflon gasket; (F) brass vessel; (G) glass Dewar.

solution containing the platinum was treated with H_2S to precipitate the sulfide which was filtered, dissolved in aqua regia and converted to a chloride system. The platinum was finally precipitated as the metal by reduction with formic acid, filtered, ignited and weighed.

Chemistry of the Hydrolysis.—Different results were obtained upon hydrolysis of PtF_6 dependent upon the size of the sample being hydrolyzed. With samples smaller than 200 mg. the hydrolysis proceeded smoothly to give a clear yellow solution; for sample amounts of one gram or larger the hydrolysis was more vigorous and the platinum, for the most part, precipitated as a finely divided black solid. In all cases a gas was liberated in the hydrolysis and its composition and quantity have been determined for two samples. In these determinations a weighed sample of PtF_6 sealed off in a 100 ml. Pyrex flask provided with a breakseal was hydrolyzed with a degassed NaOH solution and the gas evolved was collected with a Toepler pump after drying by passage through a liquid nitrogen cooled U-tube. The quantity of gas collected was measured with a buret and its composition analyzed with a mass spectrometer.

Molecular Weight Determination.—The molecular weight of PtF_6 was calculated from the weight of a quantity of gas collected under conditions of known pressure, volume and temperature. The container for the PtF_6 was a thin walled nickel bulb of all welded construction and fitted with a miniature Hoke brass valve. The volume of the bulb was determined to be 124.63 cc. by weighing it empty and full of water. Preliminary to its use with PtF_6 this bulb was degassed by flaming under high vacuum, reduced with hydrogen gas at about 400°, treated with fluorine gas at about the same temperature and finally seasoned by several exposures to PtF_6 . Three weighings were made with the bulb for each vapor density measurement: an initial evacuated weighing,

a weighing when filled with hexafluoride and a final evacuated weighing. These weighings were made relative to a similar evacuated nickel bulb used as a tare with an accuracy of ± 0.2 mg. The bulb was immersed in a thermostated water bath controlled to $\pm 0.1^\circ$ during the filling. The pressure of the hexafluoride used in the filling was measured with an accuracy of ± 0.1 mm. with the gauge to be described in the vapor pressure section.

Triple Point Determinations.—The triple points were measured with a 2.5 g. sample condensed in a 12 mm. o.d. Pyrex tube by the method of thermal arrest. A 4 junction copper-constantan thermocouple was used for following the temperature. It was located in a 6 cm. long and 3 mm. o.d. central well that was immersed to a depth of 1 cm. in the condensed hexafluoride. The triple point tube was surrounded by a clear Pyrex Dewar in which the amount of gas in the vacuum space could be varied so that a desirable rate of cooling could be obtained. The rate of cooling was followed by means of a Brown recorder with a chart speed of 51 cm. per hour. When the thermal arrest occurred a more accurate measurement of the thermal e.m.f. was made with a Rubicon Type B potentiometer.

Density of the Condensed Phases.—The density of liquid PtF_6 was measured directly in a pycnometer that consisted of a Pyrex bulb with a graduated neck connected through a Kovar-glass seal to a miniature Hoke brass valve. The neck of the bulb was made from a 1 cc. measuring pipet with 0.01 cc. graduations. The volume of the bulb up to a fiducial mark on its neck was determined to be 1.507 cc. by weighing it empty and full of water prior to sealing it to the valve; the volume of the density bulb up to its valve was 6.16 cc. The bulb was carefully seasoned before distilling in the 5.8097 g. of PtF_6 used for the liquid density measurement.

An attempt was made to measure the approximate density of the two solid phases of PtF_6 at several temperatures by a gas displacement method. The volume of a pycnometer bulb was determined both when empty and when containing solid by measurement of the change of pressure obtained when a gas of known pressure and volume was expanded into this bulb. The volume of the solid PtF_6 was taken as the difference between these two measurements. These measurements were made at a variety of temperatures ranging from room temperature to the boiling point of nitrogen for both the empty and loaded pycnometer. The measurements with the cubic solid phase above 3° were too unreliable to be reported due to a partial saturation of the inert gas with PtF_6 . The measurements with the orthorhombic solid phase below 3° were made at temperatures where the vapor pressure of PtF_6 was sufficiently low to make this uncertainty due to saturation less important. Two sets of measurements are reported, one made with the bulb that was used for the liquid density measurements and the other made with the bulb replaced by a length of 5 mm. i.d. Pyrex tubing. These will be referred to in Table IV as Bulb A and Bulb B, respectively. For Bulb A a PtF_6 sample weighing 4.18 g. was used and the bulb was immersed in the bath up to the graduated neck (volume immersed 1.5 cc.). For Bulb B the weight of PtF_6 was 5.066 g., the volume immersed was 0.93 cc. and the total volume 3.20 cc.

All of the modifications of PtF_6 observed in these measurements were deeply colored; the vapor is a deep red resembling bromine; the liquid is dark red; both solid phases appear black.

Vapor Pressure Measurements.—The vapor pressures were measured in an all nickel and Monel apparatus by a null method. The pressure of PtF_6 was transmitted through a thin Monel bellows which was restored to its initial extension by adjustment of an external pressure of nitrogen. The position of balance was determined with a linear variable differential transformer.¹³ The core of the linear differential transformer was connected to the Monel bellows through a 13 cm. length of 0.3 cm. Monel rod. The position of the core was adjusted so that minimum output voltage corresponded approximately to zero pressure difference across the bellows. The tension on a compression spring was adjusted so that the bellows was under tension in its "null" position. The input voltage for the transformer was taken from a 6.3 v. filament transformer connected directly to the 60 cycle line. The output was put through a Hewlett-Packard Model 450

A amplifier set at 40 DB which gave an amplification of 100-fold and a Krohn-Hite Variable Band Pass Filter to improve the wave form. A Hewlett-Packard Vacuum Tube Voltmeter No. 400 D was used to measure the output signal.

The shape of the output voltage *versus* pressure difference curve at the minimum was sharpened by the use of the Band Pass Filter but was too broad to give the desired reproducibility of ± 0.05 mm. The method of calibration that was used consisted of the determination of the pressure difference across the bellows that gave a 100 mv. output on each side of the output voltage minimum. These measurements were made at a variety of pressures in range 0–1150 mm. For the vapor pressure measurements two similar determinations of the balancing pressure to give a 100 mv. output were made for each point and corrected to the true null pressure with the above calibration. A correction also was applied for the temperature coefficient of the device which corresponded to 0.011 mg. per degree C.

A major uncertainty in the device was the hysteresis that was observed for the zero position when excess pressure was applied in either sense across the bellows. This was remedied by successive application of 50–100 mm. pressure differences across the bellows in the sense opposite to the straining pressure and by vigorous tapping of the gauge. When the gauge returned to its usual zero, further tapping or small pressure differences did not produce a zero shift.

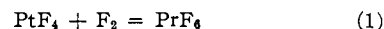
The balancing pressure was read on a mercury manometer made with 19 mm. i.d. precision bore tubing and read with a Wild cathetometer with a precision of ± 0.01 mm. The vapor pressure bulb was constructed from a 4 inch length of $\frac{3}{8}$ inch o.d. by $\frac{1}{8}$ inch wall Monel tubing. The lower two inches were drilled out to give a $\frac{1}{32}$ inch wall and had a welded bottom. The vapor pressure bulb was connected to the Monel bellows and to a high pressure Monel valve with $\frac{3}{8}$ inch Monel high pressure tubing and fittings.

The temperature of the vapor pressure bath was measured for some of the points with a 10-junction copper-constantan thermopile and for the rest with a single junction copper-constantan thermocouple. Both of these were calibrated with a platinum resistance thermometer. For the measurements above 0° a regulated water-bath was used which was kept constant to $\pm 0.01^\circ$. For the measurements below 0° , an ethylene glycol bath was used. For the measurements below room temperature the bellows was kept at 30° ; for the measurements above room temperature the bellows was at 95° .

Prior to admitting platinum hexafluoride to the system the apparatus was treated first with hydrogen and then with fluorine at elevated temperatures. Although this treatment had been adequate for seasoning similar equipment used in studies with other hexafluorides, it proved inadequate for PtF_6 . When the system was first exposed to PtF_6 at room temperature a rapid reaction took place that continued for many days before the system stabilized.

Results and Discussion

Preparation.—The method developed for the preparation of PtF_6 was based on the presumption that this compound would be quite unstable with respect to dissociation into fluorine and a lower platinum fluoride. It was felt that ΔH for the reaction



would be positive and in accordance with the van't Hoff relation

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^0}{RT^2} \quad (2)$$

the formation of PtF_6 would be more favorable at relatively higher temperatures. In the reactor that proved successful for the preparation of PtF_6 , the platinum wire reached a steady state temperature in the neighborhood of 1000° ; preliminary experiments with other reactors at lower temperatures had been unsuccessful. (Since the completion of this research Bartlett and Lohmann¹⁴ have reported the preparation of the tetrafluoride and pen-

(13) K. M. Sancier and W. Richeson, *Rev. Sci. Instr.*, **27**, 134 (1956).

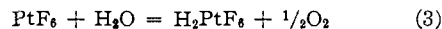
(14) N. Bartlett and D. H. Lohmann, *Proc. Chem. Soc.*, 14 (1960).

taffluoride of platinum at temperatures of less than 200° and of about 350°, respectively, in agreement with the presumption that lower temperatures would favor the formation of lower platinum fluorides.) A positive value for ΔH^0 of reaction 1 is not inconsistent with a negative heat of formation for PtF_6 since the heat of formation of PtF_4 could be negative and of greater magnitude than ΔH^0 for reaction 1. The large amount of heat evolved by the burning platinum wire and the observed instability of PtF_6 are consistent with this view.

Although PtF_6 is relatively more stable at the reaction temperature than at lower temperatures, it is still unstable and must be cooled very rapidly, as it is formed to prevent its dissociation into fluorine and a lower platinum fluoride. By maintaining the walls of the reactor at the temperature of boiling nitrogen, a temperature gradient of about 1200° per inch between the wall and the burning filament is produced. The resulting convection currents provided a mechanism for quenching the reaction product rapidly and the relatively high yields of 70% resulted. The importance of the quenching efficiency for the success of the preparation is apparent from the much smaller yield of 8.8% obtained initially with the glass reactor. In the glass system the volatile product had a relatively small solid angle subtended by a liquid nitrogen cooled surface and the yield was accordingly an order of magnitude poorer.

Chemical Analysis.—Three samples were analyzed with the results: 0.4086 mmole PtF_6 , 2.439 mmole F^- found (2.452 calcd.); 2.591 mmole PtF_6 , 2.574 mmole Pt found (2.591 calcd.); 3.071 mmole PtF_6 , 18.4 mmole F^- found (18.4 calcd.), 3.06 mmole Pt found (3.07 calcd.). The calculated values are based on the formula PtF_6 , and agree with the measurements to better than 0.7%.

Chemistry of the Hydrolysis.—This investigation was undertaken to determine whether PtF_6 like OsF_6 and IrF_6 would oxidize water to liberate oxygen and to measure the change in oxidation number of the platinum in this process. Mass spectrometer analysis showed the gas liberated to be chiefly oxygen, molar composition: $\text{O}_2 = 95.8\%$, $\text{N}_2 = 0.2\%$, and $\text{H}_2\text{O} = 4\%$. The quantitative results are: 2.591 mmole PtF_6 hydrolyzed, 1.39 mmole O_2 liberated, molar ratio O_2 to PtF_6 , 0.536; 0.420 mmole PtF_6 hydrolyzed, 0.213 mmole O_2 liberated, molar ratio O_2 to PtF_6 , 0.507. These results can be summarized by the stoichiometric relation



for which the molar ratio of oxygen liberated to platinum hexafluoride hydrolyzed is 0.5. The molar ratio of oxygen liberated to platinum hexafluoride hydrolyzed is significantly greater than 0.5 for the larger sample and corresponds to some of the platinum being reduced by the water below the tetravalent state in a more vigorous hydrolysis.

It is interesting to compare the relative simplicity of this hydrolysis with the very complicated chemistry encountered in the hydrolysis of OsF_6 .¹⁵ In that work, 20% of the hexafluoride disproportionated

(15) B. Weinstock and J. G. Malm, *J. Am. Chem. Soc.*, **80**, 4466 (1958).

into tetravalent and octavalent osmium and the remaining 80% was reduced by the water to the tetravalent state. The tetravalent osmium also was found to be complexed so strongly by the fluoride present that it was converted to an analyzable form only with great difficulty.

Molecular Weight Determination.—Two measurements of the molecular weight of the vapor were made and the results are summarized in Table I. The first column gives the filling pressures which are too low to expect any effect arising from non-ideal behavior. The weight of gas given in column 2 was calculated using the evacuated weight of the container after exposure to the PtF_6 sample. The molecular weights using this value are given in the fifth column. For the second sample the increase in weight of the container due to PtF_6 decomposition was obtained and is given in column 3. The weight of PtF_6 is increased by this amount over the value given in column 2 if the assumption is made that no decomposition of PtF_6 occurs prior to closing the bulb valve. The molecular weight calculated on this assumption is given in column 4. The average of the three values is 305.2 ± 3.5 g. in satisfactory agreement with the formula weight for the hexafluoride of 309.09 g. The estimated uncertainties of the weighings, pressure measurement, temperature measurement and volume determination give rise to an uncertainty of ± 1.1 g. A likely explanation for the low value obtained for the molecular weight is a slight decomposition of PtF_6 with the liberation of fluorine prior to closing the bulb valve.

TABLE I
MOLECULAR WEIGHT OF PtF_6
(Formula weight 309.09)

Pressure, mm.	Weight of gas, g.	Increase in bulb weight, g.	Molecular weight	
			Initial bulb weight used, g.	Final bulb weight used, g.
68.81	0.1418	308.4
58.17	0.1167	0.0028	307.2	300.0

The chemical analysis and molecular weight determination establish the formula as PtF_6 . Corroborative evidence already has been reported from infrared studies.¹⁶

Triple Point Determinations.—Platinum hexafluoride was found to have two triple points, one corresponding to a solid transformation at $3.0 \pm 0.1^\circ$ and the other to fusion at $61.3 \pm 0.3^\circ$. The estimated uncertainty represents the average deviation of the potentiometer readings taken during the constant temperature interval. It could be concluded from the thermal arrest behavior that the heat of fusion is much smaller than the heat of the solid transition. Liquid PtF_6 reacted with the Pyrex to form a soluble decomposition product; after two remeltings the fusion temperature had fallen to 61.0° .

Density Measurements.—The liquid density was determined to be 3.826 ± 0.008 g. cc.⁻¹ at 64.3° . The uncertainty was estimated from the amount of decomposition of the PtF_6 . The correction for the holdup of material in the vapor phase was 0.0444 g.

(16) B. Weinstock, H. H. Claassen and J. G. Malm, *J. Chem. Phys.*, **32**, 181 (1960).

The results of the density determinations for the low temperature solid phase are given in Table II. A comparison of the data obtained with the two bulbs indicates differences as large as 10%. For Bulb B a major uncertainty arises due to the difficulty in exactly reproducing the position of the bath during calibration and measurement. For Bulb A the position of the cold bath was of much less importance because of its long narrow neck. On the other hand the ratio of sample volume to dead volume for the measurements with Bulb A was much less favorable than with Bulb B. Actually this method for determining the solid density should have given more reliable results. The unexpected poor quality of the data may be a result of the decomposition of PtF₆.

The low temperature form of solid PtF₆, OsF₆ and IrF₆ are similar to the UF₆ solid structure,¹⁷ orthorhombic holohedral symmetry, space group D_{2h}¹⁶-P_{nma}.¹⁸ For UF₆ Hoard and Stroupe concluded that the U-F distance in the solid was greater than that obtained by electron diffraction measurement in the vapor phase. If this increase in U-F distance results from intermolecular librations, then it might be possible for the U-F distance in solid UF₆ to approach the value for the vapor at very low temperatures. In this idealized form the orthorhombic solid would be represented as a group of parallel planes of double hexagonally close packed (ABAC) fluorine atoms with the metal atoms in appropriate interplanar positions. The intermolecular fluorine to fluorine distance would be equal to the intramolecular F-F distance, and the molecule would be a regular octahedron. The metal to fluorine distance, which determines the fluorine to fluorine distance as well as the spacing of the planes, is the only parameter needed to calculate the density.

TABLE II
DENSITY OF ORTHORHOMBIC PtF₆

Temp., °K.	Density, g. cc. ⁻¹		Eq. 4
	Bulb A	Bulb B	
0	7.0
77.3	5.9	5.9	6.5
194.5	5.5	6.0	5.6
		6.0	
224.2	5.8	5.4	5.4
252.2	..	5.1	5.2
253.7	5.0	..	5.2
276.2	5.1

The idealized density for orthorhombic PtF₆ has been calculated to be 7.0 g. cc.⁻¹ on this model. The Pt-F distance used was 1.83 Å. which is the value obtained from electron diffraction measurements for all of the metal to fluorine distances in gaseous WF₆, OsF₆ and IrF₆.¹⁹ For the purpose of comparison with the experimental measurements, the relation (4) was used to represent the change of

$$\rho = 7.0 - 0.007 T \text{ g. cc.}^{-1} \quad (4)$$

(17) S. Siegel, ANL Memorandum.

(18) J. L. Hoard and J. D. Stroupe, X-Ray Crystal Structure of UF₆, Cornell Report A-1296 (1944); "Chemistry of Uranium, Collected Papers," TID-5290, U.S.A.E.C. Technical Information Service Extension, Oak Ridge, Tennessee, Book 1, pp. 325-350.

(19) V. Schomaker, M. Kimura, D. W. Smith and B. Weinstock, unpublished results.

density ρ with absolute temperature T and the calculated results are given in column 4 of Table II. The experimental measurements are not sufficiently accurate to decide whether PtF₆ approaches the idealized density at low temperatures. Taken without qualification the experimental results suggest that solid PtF₆ at liquid nitrogen temperatures, similarly to UF₆ at room temperature, has a much smaller density than the idealized structure.

Preliminary X-ray measurements with the higher temperature form of solid PtF₆ show the platinum atoms to be located at the body center and corners of a cube.¹⁷ The value a_0 , for the cube edge, is 6.209 Å. at room temperature and corresponds to a density of 4.29 g. cc.⁻¹. If we consider the six Pt-F bonds to be pointed along the rectangular axis of this cubic structure, a minimum value for the F⁻ or van der Waals radius in these molecules can be calculated. Using 1.83 Å. for the Pt-F distance and subtracting this from $a_0/2$, the minimum value of 1.27 Å. is obtained for the F⁻ radius. The van der Waals radius for F⁻ is 1.35 Å. and the ionic radius 1.36 Å. These values are much greater than 1.27 Å. and suggest that the Pt-F bonds are tilted to some degree from the axes of the cube. A quantitative estimate cannot be made of the orientation of the fluorine bonds in the crystal from these considerations because the van der Waals radii are not believed to be more accurate than 0.05-0.10 Å.,²⁰ the fluorine bonds have a partial covalent character which reduces the F⁻ radius, and the high positive charge of the platinum also reduces the F⁻ radius.²¹

Vapor Pressure Results.—PtF₆ is the least volatile of the 5 d transition series hexafluorides. The measurements of the vapor pressures of the two solid phases of PtF₆ and of the liquid phase are given in Table III. For the absolute temperatures given in the first column the ice point was taken as 273.15°K.; the vapor pressures recorded in the second column are in mm. corrected to 0° and the standard gravity. These data are represented by the equations

Orthorhombic solid (250.22°K. - 276.15°K.)

$$\log P \text{ (mm.)} = -\frac{3147.6}{T} - 6.09 \log T + 27.7758 \quad (5)$$

Cubic solid (276.15°K. - 334.45°K.)

$$\log P \text{ (mm.)} = -\frac{2528.7}{T} - 4.080 \log T + 20.6280 \quad (6)$$

Liquid (334.45°K. - 354.93°K.)

$$\log P \text{ (mm.)} = -\frac{5685.8}{T} - 27.485 \log T + 89.14962 \quad (7)$$

The boiling point of PtF₆ calculated from equation 7 is 69.14°, which is the highest boiling point of all the known hexafluorides. These equations were derived by the method of least squares with each point being weighted by the observed vapor pressure at that point. This procedure corresponds to minimizing the sums of the squares of the deviations of the observed pressures. Such a choice was made because the major uncertainty in the measurements was the observed pressure.

(20) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, pp. 260.

(21) W. H. Zachariasen, *Z. Kristallographie*, **80**, 137 (1931).

TABLE III
 VAPOR PRESSURE OF PtF₆

Temp., °K.	Obsd. press., mm.	P _{obsd.} - P _{calcd.} , mm.	Temp., °K.	Obsd. press., mm.	P _{obsd.} - P _{calcd.} , mm.
Orthorhombic solid			Cubic solid		
250.22	3.86	-0.04	293.74	88.30	-0.84
264.64	13.59	.16	296.45	103.41	.49
269.29	19.21	-.17	297.65	109.49	-.39
271.27	22.26	-.29	297.65	109.59	.01
273.15	26.20	.21	305.04	159.39	.13
273.15	26.26	.27	307.75	181.66	-.07
274.48	28.66	-.04	311.40	214.71	-1.48
274.75	29.16	-.11	317.91	291.42	0.04
275.30	30.45	-.03	319.87	318.09	.18
			325.36	403.89	.67
			330.53	500.69	.45
Cubic solid			Liquid		
276.27	32.72	0.03			
276.82	33.99	.18			
277.09	34.55	.18			
277.31	35.04	.20			
278.32	37.24	.20	336.62	622.0	-9.4
279.27	39.45	.23	339.92	692.9	-11.4
279.63	40.18	.10	340.17	713.0	3.0
281.54	44.21	-.69	344.58	820.9	5.2
381.85	45.97	.25	345.34	840.5	5.9
284.18	53.01	.64	348.35	920.0	7.8
284.74	53.44	-.65	349.83	943.3	-8.6
285.01	55.11	.17	350.85	988.0	8.0
286.80	61.43	.60	350.90	973.0	-8.5
287.42	62.33	-.67	352.65	1023.5	-6.7
288.05	65.32	.05	353.83	1063.0	0.0
290.48	74.15	-.54	354.31	1077.7	0.3
291.41	79.10	.51	354.93	1099.2	3.9

It was also felt desirable for the intersections of the vapor pressure equations to reproduce the directly measured values of the two triple points. To accomplish this the solution of the least squares problem for the data with the cubic solid, equation 6, was first derived with an IBM 704 computer. From this equation the vapor pressures at the solid-solid triple point and solid-liquid triple point were calculated using the triple point temperatures obtained by the thermal arrest method. These values are: solid transition, 276.15°K., 32.47 mm.; fusion, 334.45°K., 586.0 mm. It then remained to obtain the least squares solution for the constants of the equation

$$\log P = -A/T + B \log T + C \quad (8)$$

that also satisfied the relation

$$\log P_0 = -A/T_0 + B \log T_0 + C \quad (9)$$

where P_0 and T_0 are the triple point pressure and temperature, respectively. Subtracting equation 9 from 8 to eliminate C and weighting by the pressure reduced the problem to finding the values of A and B for which the sum of the squares of the deviations, δ_i , is a minimum, where

$$\delta_i = P_i (\log P_i - \log P_0) +$$

$$P_i \left(\frac{1}{T_i} - \frac{1}{T_0} \right) A - P_i (\log T_i - \log T_0) B \quad (10)$$

The value of the constant C was evaluated from equation 9, using the triple point data and the values obtained for A and B in the least squares solution of equation 10. Equation 5 for the vapor pressure of the orthorhombic solid and equation 7

for the vapor pressure of the liquid were each separately obtained in this way.

The differences between the observed vapor pressures and those calculated from the equations are given in the third column of Table III. The standard deviations of the observed vapor pressures from their respective equations are: for the orthorhombic solid ± 0.17 mm., for the cubic solid ± 0.50 mm., and for the liquid ± 7.1 mm. The pressure measurements were reproducible to ± 0.05 mm. and the temperatures to $\pm 0.005^\circ$. The standard deviations of the data are much greater than can be explained from the uncertainties of the measurements and are in all probability a consequence of the continual corrosive attack of the PtF₆ on the apparatus. This difficulty increased with rising temperature and became most severe for the liquid phase.

Thermodynamic Calculations.—The heat of sublimation of the orthorhombic and the cubic solid and the heat of vaporization of the liquid have been calculated from the Clapeyron relation using the corresponding vapor pressure equation. The gas volume was computed from the equation of state

$$PV = RT + bP/T^2 \quad (11)$$

The value of -1.13×10^8 cm.³ deg.² mole⁻¹ for the second virial coefficient, b , that was found for UF₆²² was used in these calculations. The values used for the solid and liquid densities were those reported in this paper. The results of these calculations as well as some other physical properties are summarized in Table IV.

 TABLE IV
 PROPERTIES OF PtF₆

Sublimation and vaporization	Temp., °K.	ΔH , cal. mole ⁻¹	ΔS , cal. deg. ⁻¹ mole ⁻¹	P , mm.
Orthorhombic solid	276.15	11,440	41.4	32.5
Cubic	276.15	9,300	33.7	32.5
Cubic	334.45	8,590	25.7	586.0
Liquid	334.45	7,510	22.5	586.0
Boiling	342.29	7,060	20.6	760.0
Transitions				
Solid transition	276.15	2,140	7.8	32.5
Fusion triple point	334.45	1,080	3.2	586

Rotation in the Condensed Phases.—Pauling²³ suggested that the solid transition in methane, the hydrogen halides and other compounds was a consequence of the onset of free rotation in the solid phase. Subsequently, Timmermans²⁴ called attention to a large number of organic compounds, which he named plastic crystals, that had the common characteristic of a small entropy of fusion and for which rotation in the solid state was also likely. Nuclear magnetic resonance measurements of the second moment for many of these substances²⁵⁻²⁷ have shown that free rotation does not occur at the transition temperatures. These ob-

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(23) L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

(24) J. Timmermans, *J. chim. phys.*, **35**, 331 (1938).

(25) N. L. Alpert, *Phys. Rev.*, **75**, 398 (1949).

(26) H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.*, **18**, 162 (1950).

(27) J. T. Thomas, N. L. Alpert and H. C. Torrey, *ibid.*, **18**, 1511 (1950).

servations were a confirmation of Frenkel's theory²⁸ that interpreted these solid transitions in terms of a change in orientational order. Calorimetric and X-ray measurements on many similar compounds also are in agreement with this view.²⁹ The entropy of transition is given as $R \ln(A/B)$ where A and B are integral symmetry numbers that can be derived from the structure of the solid phases.

Platinum hexafluoride, similarly to the other hexafluorides, has the structure of a regular octahedron in the vapor phase.¹⁶ Such a symmetrical structure is common to Timmermans' globular compounds and like them PtF_6 has a solid transition before melting. This transition is also observed for many of the hexafluorides of lower molecular weight but not for the three heavier ones, UF_6 , NpF_6 and PuF_6 . The entropy change in this transition for PtF_6 derived from the vapor pressure data in $7.75 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ is almost the same as the calorimetric value of $7.72 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ found for the corresponding transition in MoF_6 . This value for the entropy change corresponds to $R \ln 48$. Since the symmetry number for a regular octahedron is 24, it is difficult to see how this large value for the entropy of transition can be explained as a change of configurational order.³⁰

The solid transition in PtF_6 appears to be intermediate in character between that observed in methane, where free rotation occurs, and those cases that can be explained as configurational transitions. At the transition temperature there appears to be an important additional contribution to the configurational entropy in the form of strong librations or hindered rotation. The entropy of fusion for PtF_6 and MoF_6 are 3.23 and 3.65 $\text{cal. mole}^{-1} \text{ deg.}^{-1}$, respectively, which values are in the range observed for the plastic crystals. This small value for the entropy of fusion that is close to the value expected for the communal entropy establishes that the degree of rotation in the liquid is not very different from the rotation in the solid. In neither solid nor liquid does free rotation take place because the sum of the transitional entropies is 11 $\text{cal. mole}^{-1} \text{ deg.}^{-1}$ which is about half the value of 22 $\text{cal. mole}^{-1} \text{ deg.}^{-1}$ for the rotational entropy of these molecules in the vapor phase at these temperatures. The same argument applies to the 5f hexafluorides that do not have the solid transition and for which the entropy of fusion is about 13 $\text{cal. mole}^{-1} \text{ deg.}^{-1}$.

The lack of free rotation for the hexafluorides in the liquid and the likelihood of a more limited cogwheel type of rotation is supported by a consideration of the density and molecular size. If PtF_6 were rotating freely in the liquid, the molecule would sweep out a spherical envelope. The estimated diameter for this sphere could vary from 6.36 Å., derived from the Pt-F distance and the F^- radius, to 6.209 Å. which is a_0 for the cubic solid. The corresponding density of these spheres in a close packed array would vary from 2.82–3.03 g. cc.^{-1} or from 74 to 79% of the observed

density of 3.83 g. cc.^{-1} . From these estimates it seems most likely that the hexafluoride molecules are still arranged in a correlated fashion in the liquid.

Chemical Reactivity.—Platinum hexafluoride is the most reactive and least stable of the known hexafluorides. These qualities undoubtedly bear a major responsibility for this compound remaining unknown until this late date although the four preceding members of its transition series, WF_6 , ReF_6 , OsF_6 and IrF_6 , were already known. Some studies with this extremely reactive compound that characterize its chemical behavior have been made and will be reported here.

The reaction between PtF_6 and BrF_3 was observed in a previously baked out and evacuated quartz tube. Initially a measured quantity of BrF_3 vapor was mixed with a smaller amount of PtF_6 vapor at room temperature and the two vapors were observed to react rapidly. The remaining BrF_3 was then frozen down with liquid nitrogen and an excess of PtF_6 condensed upon it. Upon warming this mixture reacted rapidly with the formation of a viscous black solution. The volatile material was then pumped out and the non-volatile residue analyzed for platinum. The amount of platinum found was 2.26×10^{-3} mole compared with 2.57×10^{-3} mole BrF_3 used. It seems probable from this data that PtF_6 fluorinated BrF_3 to form BrF_6 . The fluorination of BrF_3 by an unstable hexafluoride also had been observed previously with PuF_6 .¹¹

Prior to the preparation of PtF_6 , the least stable known hexafluoride was PuF_6 . It is then a matter of interest to establish the relative stability of PtF_6 and PuF_6 . Because of the radioactivity of plutonium the measurement of the dissociation constant for PuF_6 is relatively easy even though the hexafluoride is present in very small concentration at equilibrium. Since a similar measurement is not as readily performed with platinum hexafluoride, a qualitative approach was tried in which an attempt was made to produce PuF_6 from PuF_4 using PtF_6 as a fluorinating agent.

The most reactive form of PuF_4 for this purpose was discovered to be the residues produced in the radiation decomposition of PuF_6 . Such material was found to react with PtF_6 vapor at room temperature to form PuF_6 . In a typical experiment an estimated 3×10^{-3} mole of PuF_4 in a nickel can was treated with 1.6×10^{-3} mole of PtF_6 vapor at 17 mm. pressure. The PuF_4 had been formed during the course of about one year from the radiation decomposition of PuF_6 stored in that can. (In the solid state, PuF_6 is converted into PuF_4 at the rate of 1.5% per day.) After 2 hr. at room temperature the vapor contained 1.1×10^{-3} mole of PtF_6 and 0.16×10^{-3} mole of PuF_6 . No further reaction took place upon additional exposure of the PtF_6 to the plutonium residue even when the temperature was raised to 90° for 2 hr.

This result cannot be used to estimate the relative stability of these two hexafluorides because the system is not at equilibrium. However, it does suggest that PtF_6 is the less stable of the two. Further attempts to prepare very reactive PuF_4 that might react quantitatively with PtF_6 vapor

(28) J. Frenkel, *Acta Physicochim. U.R.S.S.*, **3**, 23 (1935).

(29) G. B. Guthrie and J. P. McCullough, *J. Phys. and Chem. Solids*, **18**, 53 (1961).

(30) B. Weinstock, *ibid.*, **18**, 86 (1961).

at low temperatures were unsuccessful. For example, finely divided plutonium metal was made by the decomposition of plutonium hydride and then slowly fluorinated to the tetrafluoride by reaction with fluorine. After exposure of this material for 25 minutes to PtF_6 , no plutonium was found in the vapor phase.

The reaction at room temperature between PtF_6 and neptunium fluoride residues formed by the radiation decomposition of NpF_6 was quantitative. A short exposure of 100 mg. of PtF_6 vapor to a neptunium fluoride residue in a nickel can resulted in the complete disappearance of PtF_6 from the vapor phase with the formation of 67 mg. of NpF_6 . NpF_6 is a very stable hexafluoride and does not dissociate into fluorine and a lower neptunium fluoride up to 560° .³¹

The ability of PtF_6 vapor to fluorinate materials at room temperature greatly limits the type of apparatus that this material can be handled in. After our early observation of the formation of NpF_6 , all of the studies with PtF_6 were carried out in new systems that had not been used previously in other hexafluoride studies.

Finely divided plutonium metal prepared by the thermal decomposition of plutonium hydride was observed to react rapidly with PtF_6 vapor at room temperature. The solid was brought to red heat by the reaction, and a platinum mirror was deposited on the quartz reaction vessel. No plutonium was found in the excess PtF_6 vapor that was subsequently hydrolyzed and alpha counted. The high temperature of the reaction without the presence of a cold surface to quench any PuF_6 formed

(31) J. G. Malm, B. Weinstock and E. E. Weaver, *J. Phys. Chem.*, **62**, 1506 (1958).

probably was responsible for the failure to find plutonium in the remaining PtF_6 vapor.

Although PtF_6 is quite unstable, the rate of thermal decomposition into fluorine and a lower platinum fluoride is negligible at room temperature. Heating at 90° also produces little thermal decomposition. After 68 minutes at $145\text{--}165^\circ$, 62 mm. of PtF_6 was found to have decomposed slightly with the formation of 1 mm. of fluorine. After 47 minutes at $260\text{--}275^\circ$, 60 mm. of PtF_6 had decomposed to the composition 26 mm. of fluorine and 28 mm. of PtF_6 . The rate of thermal decomposition of PtF_6 in this temperature range is quite similar to that which has been observed with PuF_6 .¹¹

The greater reactivity of PtF_6 compared to all the other hexafluorides is evident in its rapid reaction with Pyrex and quartz. It is possible to degas Pyrex and quartz equipment so that there is no reaction with other hexafluorides, including PuF_6 . With PtF_6 a general attack on the glass is evident immediately. A similar uniqueness for PtF_6 is observed in the corrosion of nickel and Monel equipment. In spite of prior seasoning, exposure of apparatus to PtF_6 at room temperature results in substantial corrosive attack that continues for periods of time extending into weeks. Under comparable conditions where the order of 1 mg. of PuF_6 would be lost due to seasoning, several hundred milligrams of PtF_6 are lost.

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The Chemistry of Ruthenium(IV). I. Ruthenyl and the Nature of Ru(IV) in Perchloric Acid Solutions¹

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Information has been obtained on the nature of Ru(IV) in perchloric acid through solubility studies. The average charge on the aqueous species is 2. Extensive polymerization has been observed in these solutions and the monomer ruthenyl, RuO^{++} , has been identified and isolated as a constituent.

Introduction

Very little previous information has been published on the composition of Ru(IV) in non-complexing media. Wehner and Hindman³ concluded from spectral and transference studies that Ru(IV) in perchloric acid was largely hydrolyzed, and Niedrach and Tevebaugh⁴ proposed two separate species. None of these studies actually succeeded in isolation or identification of any proposed constituents.

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(2) From the Ph.D. thesis of F. P. Gortsema, Purdue University, 1959.

(3) P. Wehner and J. C. Hindman, *J. Am. Chem. Soc.*, **72**, 3911 (1950).

(4) L. W. Niedrach and A. D. Tevebaugh, *ibid.*, **73**, 2835 (1951).

The purpose of this communication is to report the results of solubility and ion-exchange experiments which have fixed the average charge of Ru(IV) species in perchloric acid as +2 and have further identified ruthenyl, RuO^{++} , as a constituent of the system.

Experimental

Materials.—Ruthenium sulfate was prepared from Fisher ruthenium trichloride by treatment of an aqueous slurry of the latter with concentrated sulfuric acid. The resulting mixture was evaporated slowly to fuming and then to semi-dryness on a hotplate at $140\text{--}150^\circ$. More sulfuric acid was added and the process repeated until the product was chloride-free.⁵ Too high a temperature will result in loss of ruthenium by volatilization as RuO_4 .

(5) The presence of chloride was tested by means of the test proposed by Wehner and Hindman (reference 3). A few milliliters of ruthenium solution were treated with a strong oxidizing agent and the