1st NORANDA LECTURE

Unusual Oxidation States of the Noble Elements

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WITHIN the past six years the fluorine chemistry of the noble metals has been revised and considerably extended. Weinstock and his co-workers at the Argonne National Laboratory have contributed significantly to the changes (1). They have reported four new hexafluorides (PtF_6 (2), TcF_6 (3), RuF_6 (4), RhF_6 (5)) and have shown (6) the fluoride previously considered to be osmium octafluoride to be the hexafluoride. In addition, rhenium heptafluoride has been prepared and characterized (7).

The known highest oxides and fluorides of the second and third transition series elements are listed in Table 1. An interesting feature of this comparison is that although rhodium hexafluoride exists the trioxide is unknown, but the highest fluoride of ruthenium is the hexafluoride despite the existence of a tetroxide. Osmium is similarly restricted to a hexafluoride despite the existence of a tetroxide. The absence of an octafluoride or at least a heptafluoride of osmium is all the more surprising in view of the existence of rhenium heptafluoride. The nature of the compounds produced with varying proportions of oxygen and fluorine, as shown in Figure 1, is revealing. The attainable formal oxidation state decreases as the proportion of fluorine in the oxidizing gases increases. In all, the trends point to the hexafluoride being the highest fluoride attainable. We may suppose that this limit is imposed by a maximum coordination of six for the osmium but this would not exclude osmium dioxide tetrafluoride, of which no trace has yet been found. If, on the other hand, the *real* oxidation state in osmium tetroxide is the same as that in osmium hexafluoride then the electron withdrawing power of the oxygen ligand would be set at 1.5 times that of the fluorine. This would result in osmium in osmium dioxide tetrafluoride being in the same oxidation state as in osmium heptafluoride, which is also unknown.

Osmium oxide pentafluoride (8), which as is shown in Table 2, resembles the related rhenium compound (9), is of especial interest in that it is the first simple osmium compound in which the formal oxidation state is + 7. Osmium in this oxidation state possesses a d^1 electron configuration and in accord with this the compound is paramagnetic. Since the oxygen ligand is similar in size to fluorine and since the non-bonding electron should show no steric activity the molecule is expected to be similar in size and shape to osmium hexafluoride. In fact the oxyfluoride and hexafluoride both crystallize in the orthorhombic system, the unit cells being similar in size. The molecular shape of the oxyfluoride, as determined by X-ray single crystal methods is shown in Figure 2. The distortions from regular octahedral shape can be interpreted in terms of distortions due to the slightly larger size of the oxygen ligand, superimposed upon a trigonal compression of the molecule. The latter distortion may arise from lattice interactions.

The iodine and technetium analogues of osmium oxide pentafluoride presumably can exist. Even ruthenium oxide pentafluoride may be preparable although the thermal stability may be low. A higher fluoride of ruthenium than the hexafluoride appears to be unlikely in view of the thermal instability of this fluoride.

The data for the second and third transition series hexafluorides given in Table 3, show the fusion point and boiling point rising with increasing atomic number along each series as the effective molecular volume decreases. These trends indicate a significant increase in the intermolecular attraction with atomic number in each series. Thermal stability falls with atomic number in each series also and there is apparently a correlation between thermal stability and effective molecular volume, platinum hexafluoride being comparable, in stability and molecular volume, with ruthenium hexafluoride, and rhodium hexafluoride with the smallest molecular volume being the least thermally stable hexafluoride and the most difficult one to make. Despite some effort in this direction, it has not proved possible to prepare palladium hexafluoride (5).

In the first reports of platinum (2), ruthenium (4) and rhodium (5) hexafluorides their spontaneous liberation of fluorine at ordinary temperatures was mentioned. Clearly

TABLE 1. — HIGHEST FLUORIDES AND OXIDES OF THE 2ND AND 3RD TRANSITION SERIES

Fluorides	MoF_6	TcF_6	RuF_6	RhF_6	PdF_3	AgF_2
Oxides	MoO_3	Tc_2O_7	RuO_4	RhO_2	Pd_2O_3	AgO
Fluorides	WF_6	ReF_7	OsF_6	IrF_6	PtF_6	AuF_3
Oxides	WO_3	Re_2O_7	OsO_4	IrO_3	PtO_3	Au_2O_3

TABLE 2. — COMPARISON OF MOF_5 AND MF_6 COMPOUNDS

	ReF_6 $^{(a)}$	$ReOF_5$ $^{(b)}$	OsF_6 $^{(a)}$	$OsOF_5$ $^{(\;)}$
m.p. (°C)	18.7	34.5	34.4	59.8
b.p.	33.8	55	47.5	~90.0
Eff. mol. vol. (Å³)	106.6 (orth) $^{(d)}$	—	105.7 (orth) $^{(d)}$	103.8 (orth) $^{(\;)}$

(a) Cady and Hargreaves, *J. Chem. Soc.*, 1961, 1565.
(b) Aynsley, Peacock and Robinson, *Ibid*, 1950, 1623.
(c) Bartlett, Jha and Trotter, *Proc. Chem. Soc.*, 1962, 277.
(d) Siegel and Northrop, Personal communication.

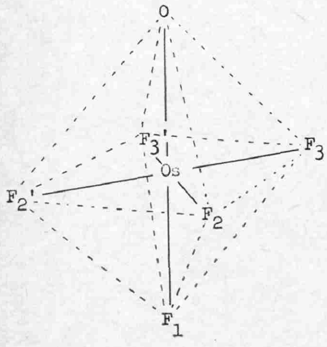
$$
\begin{aligned}
&Os + 3F_2 &&\rightarrow OsF_6\,^{(a)}\\
&Os + 2^1/_2F_2 + {}^1/_2O_2 &&\rightarrow OsOF_5\,^{(b)}\\
&Os + F_2 + {}^3/_2O_3 &&\rightarrow OsO_3F_2\ (\text{m.p. } 172 \text{ b.p. } 200^\circ)\,^{(c)}\\
&Os + 4O_2 &&\rightarrow OsO_4\ (\text{m.p. } 40.1 \text{ b.p. } 129^\circ)\,^{(d)}
\end{aligned}
$$

(a) Weinstock and Malm, *J. Amer. Chem. Soc.*, 1958, *80*, 4466.
(b) Bartlett, Jha and Trotter, *Proc. Chem. Soc.*, 1962, 277.
(c) Hepworth and Robinson, *J. Inorg. Nuclear Chem.*, 1957, *4*, 24.
(d) Wartenberg, *Ann.* 1924, *440*, 97.

Figure 1—Oxides, Oxyfluorides and Fluorides of Osmium.

any species which will liberate fluorine is a powerful oxidizing agent.Their oxidizing potential, however, remained largely unexplored.

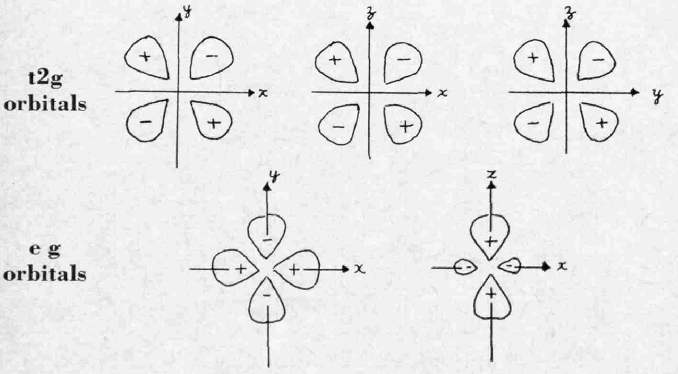
Orthorhombic unit cell (23° ± 2): a = 9.540 ± 0.004, b = 8.669 ± 0.004, c = 5.019 ± 0.004 Å; V = 415.1 Å³; Z = 4. Space group Pnma (D_{2h}^{16}, No. 62).



	Å		
Os-O	**1.74**	**O-Os-F_2**	**87°**
Os-F_1	**1.73**	**O-Os-F_3**	**97**
Os-F_2	**1.82**	**F_2-Os-F_3**	**90**
Os-F_3	**1.75**	**F_2-Os-F_2'**	**87**
O-F_2	**2.44**	**F_3-Os-F_3'**	**93**
O-F_1	**2.61**	**F_1-Os-F_2**	**91**
F_2-F_3	**2.52**	**F_1-Os-F_3**	**86**
F_2-F_2'	**2.51**		
F_3-F_3'	**2.51**		
F_1-F_2	**2.52**		
F_1-F_3	**2.36**		

(a) **Bartlett and Trotter, Unpublished results.**

Figure 2 — Molecular structure of osmium oxide pentafluoride $OsOF_5$(a).



d^0	d^1	d^2	d^3	d^4	d^5	d^6
MoF_6	**TeF_6**	**RuF_6**	**RhF_6**			
WF_6	**ReF_6**	**OsF_6**	**IrF_6**	**PtF_6**		
NbF_6^-	**MoF_6^-**	**TcF_6^-**	**RuF_6^-**	**RhF_6^-**		
TaF_6^-	**WF_6^-**	**ReF_6^-**	**OsF_6^-**	**IrF_6^-**	**PtF_6^-**	

Figure 3—d-electron configurations for 2nd and 3rd trans. series hexafluorides.

The dissociation of some of the hexafluoride molecules implies that in these molcules the noble metal atom has a sufficiently high electron attracting power to withdraw a bonding electron from a fluorine ligand. That this tendency should increase with atomic number in each series may be seen by reference to the non-bonding valence electron configurations for the various hexafluorides, which are given in Figure 3. Tungsten and molybdenum use all of their valence electrons in the hexafluorides but with technetium and rhenium and the later elements, non-binding d electrons remain and are located in the lower lying t_{2g} orbitals, in which situation they do not effectively screen the ligands from the nuclear charge, which increases with atomic number. The fluorine ligands in platinum hexafluoride, with a $d^4{}_{t_{2g}}$ configuration for the platinum, are evidently exposed to a strongly electron attracting central atom. Since gold hexafluoride would be a $d^5{}_{t_{2g}}$ system then the polarizing power of the gold would be greater than that of platinum in platinum hexafluoride and in consequence the stability should be lower. Nevertheless this does not mean that gold hexafluoride can not exist. It may be no more unstable than rhodium hexafluoride.

TABLE 3. — 2ND AND 3RD TRANSITION SERIES HEXAFLUORIDES

	MoF_6(1)	TcF_6(b,d)	RuF_6(b)	RhF_6(b)
m.p. (°C)	17.4	37.0	54	70
vap. press. 15°C.	361	135	58	38
ΔH_{fus}(kcal.mole^{-1})	0.92	–	–	–
ΔH_{vap}(kcal.mole^{-1})	6.94	–	–	–
Eff. mol. vol. (Å³)(e)	106.6	104.8	101.0	99.5

	WF_6(a)	ReF_6(a)	OsF_6(a)	IrF_6(a)	PtF_6(c)
m.p. (°C)	2.0	18.7	33.4	43.8	61.3
b.p. (°C)	17.1	33.8	47.5	53.6	69.14
ΔH_{fus}(kcal.mole^{-1})	0.42	1.107	1.76	1.19	1.08
ΔH_{vap}(kcal.mole^{-1})	6.33	6.867	6.72	7.38	7.06
Eff. moi. vol. (Å³)(e)	108.5	106.6	105.7	105.4	104.6

(a) Cady and Hargreaves, J. Chem. Soc., 1961, 1565.
(b) Chernick, Claassen and Weinstock, J. Amer. Chem. Soc., 1961, *83*, 3165.
(c) Weinstock, Malm and Weaver, *Ibid*, 1961, *83*, 4310.
(d) Selig, Chernick and Malm, *J. Inorg. Nuclear. Chem.*, 1961, *19*, 377.
(e) Siegel and Northrop, Personal Communication.

TABLE 4. — ANALYTICAL DATA FOR PtO_2F_6

	Found
Pyrohydrolysis: (solid + H_2O vapor — followed by steam → HF	F, 32.4%
(residue ignited in H_2	Pt, 57.5
Sodium fusion: Fluoride precipitated as lead chlorofluoride	F, 32.7
Bromine trifluoride: Oxygen evolved measured with gas burette	O, 10.4
PtO_2F_6 requires F, 33.4; O, 9.4; Pt, 57.2%	

Prior to the first report of platinum hexafluoride (2), we had observed that when platinum or platinum salts were fluorinated in silica apparatus a deep red solid was produced. This solid sublimed in a good vacuum, below 100°. It was evidently an oxyfluoride, the oxygen being derived from interaction of fluorine with the silica: $SiO_2 + 2F_2 \rightarrow SiF_4 + O_2$, since fluorination of platinum in nickel apparatus did not give it.

The analysis of this most interesting material (10), which was largely the concern of my collaborator D. H. Lohmann, proved to be difficult. The solid reacted violently with water or alkaline solution to give a mixture of products among which ozone, platinum, hydrated platinous oxide and platinic oxide and the hexafluoroplatinate (IV) ion were identified. It is probable that oxygen difluoride was also produced in such reactions since fluorine analyses employing aqueous solution techniques always gave low results. Only when the hydrolysis was carried out with water vapor were consistent analytical data obtained. The data are given in Table 4. They indicated that the red solid was a compound of empirical formula PtO_2F_6.

Of course several formulations are possible for the compound. Fortuntely the solid gave a simple X-ray powder diffraction photograph which was indexed on the basis of a cubic unit cell, a = 10.032Å. The compound was apparently structurally similar to potassium hexafluoroantimonate (V) the structure of which had been given by Bode and Voss (11). Furthermore we found that nitrosyl hexafluoro-osmate (V) and nitrosyl hexafluoro-antimonate (V) were also isomorphous with the compound. Figure 4 shows the close resemblance of the X-ray powder photographs. Good agreement was obtained between the line intensities calculated on the basis of the ionic structure, O_2^+ $[PtF_6]^-$, represented in Figure 5, and those observed. The structure reveals that the PtF_6 octahedra are compressed along the three fold rotation axis along which the dioxygenyl ions lie. Each O_2^+ ion has 12 fluorine neighbours, six in a puckered ring and almost coplanar with the ion, the other six in sets of three, one above and one below the plane. Apart from the non-spherical nature of the cation, the structure is almost identical with that proposed for potasium hexafluoroantimonate (V).

The other properties of the compound were consistent with the dioxygenyl hexafluoroplatinate(V) formulation. In its chemical reactions which are shown in Figure 6, it behaves as a powerful oxidizing agent and as a derivative of platinum (V).

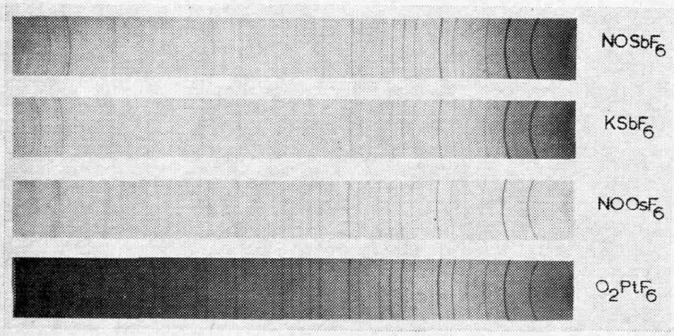


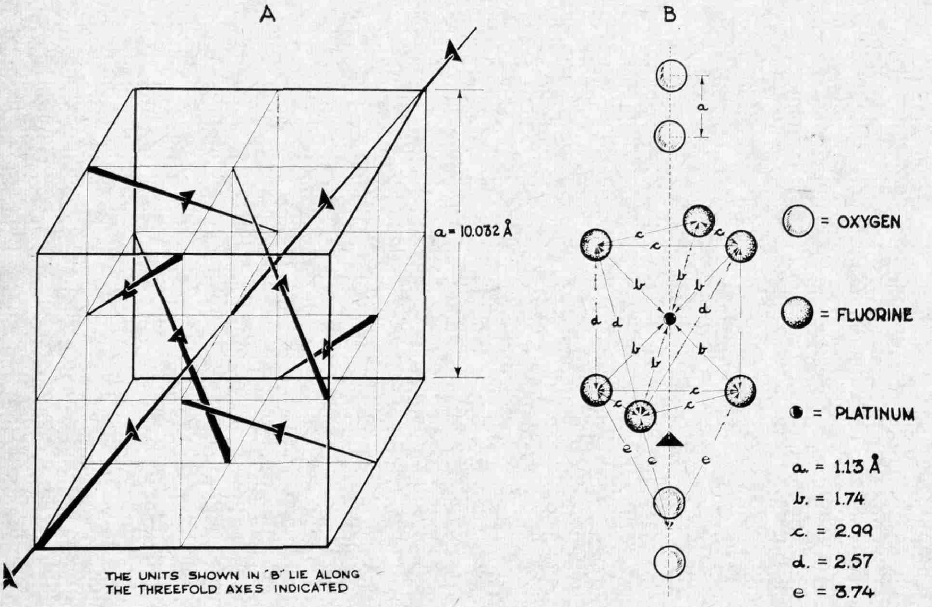
Figure 4—X-ray powder photographs of some ABF_6 complexes.

The magnetic behavior of the compound is unusual for a complex of an element of the third transition series in that the susceptibility obeys the Curie Weiss Law, $\chi_M \propto 1/(T + \theta)$, where $\theta = +45°$. This and the magnitude of the magnetic moment (μeff 2.57 B.M) are compatible with the effect of the d^5_{t2g} configuration of the Pt^{5+} and the unpaired electron associated with the dioxygenyl ion. Since for the third transition series, the spin-orbit interaction is great, the magnetic moment associated with the d^1_{t2g}-configuration is almost temperature-independent (12), over the range used for the magnetic study, and is 1.73 B.M. It is also to be expected that the magnetic behavior of the dioxygenyl ion will resemble that of nitric oxide with which it is isoelectronic. Magnetic moment values computed for a nitric oxide hexafluoroplatinate (V) ion combination are similar to those observed for the salt. Representative values are given in Table 5.

TABLE 5. — SOME CALCULATED AND OBSERVED MAGNETIC MOMENTS FOR $O_2^+[PtF_6]^-$

Temp. (°K)	113	178	300°
μ calc. (B.M.)	2.31	2.40	2.56
μ obs. (B.M.)	2.12	2.28	2.34

It was clear that if the formulation O_2^+ $[PtF_6]^-$ were true, then platinum hexafluoride should oxidize molecular oxygen. A sample of platinum hexafluoride was therefore prepared, and since it has a vapor pressure of ~ 80 mm. at room temperature, the interaction with molecular oxygen was followed tensimetrically. The deep red (bromine colored) platinum hexafluoride vapor reacted instantly with the oxygen in a 1:1 molar ratio to give the familiar red compound. Interestingly, the solid made by this method at low temperatures, is isomorphous and almost isodimensional with rhombohedral potassium hexafluoroplatinate(V). At higher temperatures transition to the cubic phase occurs.



THE UNITS SHOWN IN 'B' LIE ALONG THE THREEFOLD AXES INDICATED

A. UNIT CELL OF $O_2^+[PtF_6]^-$ (Cub.)

B. CONTENTS OF CUBIC PSEUDO UNIT CELL

Figure 5.

A simple lattice energy calculation using Kapustinskiis equations (13) gives $\Delta H = \sim -120$ kcal. mole^{-1} for the process: $[PtF_6]^-_{(g)} + O^+_{2g} \rightarrow O_2^+ [PtF_6]^-_c$. Since the first ionization of molecular oxygen is + 281 kcal. mole^{-1} the required minimum energy for the electron affinity of platinum hexafluoride is − 161 kcal. mole^{-1}. This value, is twice that of atomic fluorine. Platinum hexafluoride was evidently the most powerful oxidising agent known hitherto.

The way in which the oxidizing power of the hexafluorides increases with atomic number in the third transition series is demonstrated by the nature of the reactions with nitric oxide which are summarized in Figure 7. Since the ionization potential of nitric oxide[14] is 62 kcal. mole^{-1} lower than for oxygen it can reduce osmium hexafluoride to the quinquevalent and platinum to the quadrivalent

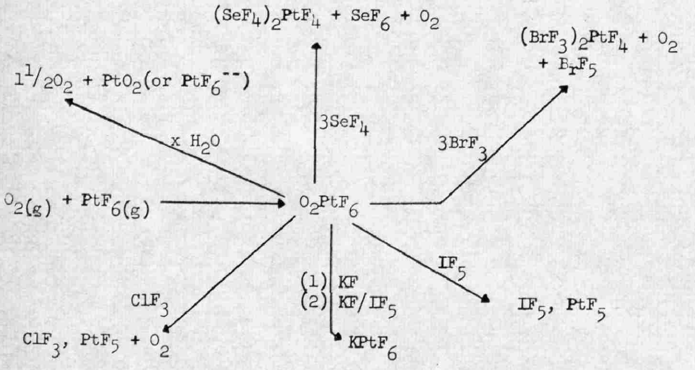


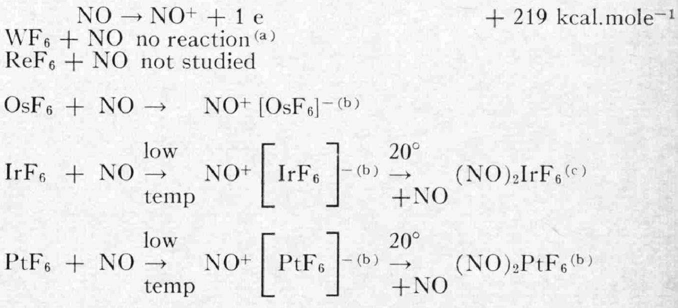
Figure 6—Chemical reactions of O_2^+ $[PtF_6]^-$.

state. Of the third transition series hexafluorides, oxygen will only reduce the platinum fluoride. It is clear however that both rhodium hexafluoride and ruthenium hexafluoride should in view of their thermal instability be close in oxidizing power to platinum hexafluoride and should also interact with oxygen.

It was quickly realized that platinum hexafluoride being capable of oxidizing molecular oxygen would probably also be capable of oxidizing the heavier noble gas elements. In particular xenon, the first ionization potential of which (14) is the same as for molecular oxygen and radon with a first ionization potential of 10.7 e.v. were possibly within range. Although the lattice energy of a salt is inversely proportional to the sum of the ionic radii, in the case of the hexafluoroplatinates it is rather insensitive to cationic radii changes since the complex ion radius is large. A simple calculation made for the oxidized xenon case showed that the lattice energy would be decreased by little more than 10 kcal. mole^{-1} from that of the dioxygenyl salt. The predicted interaction of xenon and platinum hexafluoride was confirmed in a simple and visually dramatic experiment. The deep red platinum hexafluoride vapor of known pressure was mixed, by breaking a glass diaphragm, with the same volume of xenon with pressure greater than that of the hexafluoride. Combination to produce a yellow solid was immediate at room temperature and the quantity of xenon remaining was commensurate, within the limits of error, with a combining ratio of 1:1 (15).

This experiment was quickly confirmed by the workers at the Argonne National Laboratory (16) who went on to study the interaction of xenon with ruthenium hexafluoride. At that time we were without the facilities for preparing the second period hexafluorides. The Argonne workers noted that roughly three molecules of ruthenium hexafluoride were consumed per atom of xenon and that a material resembling ruthenium pentafluoride was a product of the reaction. This suggested that this hexafluoride was, at least in part, acting as a fluorinating agent and that a fluoride or fluorides of xenon must exist. This led to the discovery of the simple fluorides of xenon.

Meanwhile at the University of British Columbia we discovered that the xenon-platinum hexafluoride reaction was not as simple as the first experiments had indicated. The reaction was repeated numerous times in a variety of containers and never with a consistent series of results. Occasionally, as the results given in Table 6 indicate, a 1:1 stoichiometry is obtained but usually between one and two molecules of platinum hexafluoride are consumed per atom of xenon. Unfortunately the 1:1 adduct does not give a powder diffraction pattern and attempts to grow single crystal of the material have met with no success. Since, however, material of composition $XePtF_6$ and that approximating to $Xe(PtF_6)_2$ both interact with alkali fluorides in the non oxidizing medium, iodine pentafluoride: $XePtF_6 + RbF \xrightarrow{IF_5} RbPtF_6$; $Xe(PtF_6)_2 + 2CsF \rightarrow 2CsPtF_6$, to give hexafluoroplatinates (V) it is evident that the platinum is in the quinquevalent state no matter what the composition of the adduct. The most satisfactory explanation for the observations at this time is that two reactions occur simultaneously the first forming the 1:1 adduct presumably $Xe^+ [PtF_6]^-$ and the second producing platinum pentafluoride and a xenon fluoride: $Xe + 2PtF_6 \rightarrow XeF_2 + 2PtF_5$. The rather scanty spectroscopic evidence, shown in Table 7, gives some support to these conclusions. Although the xenon-platinum hexafluoride adduct decomposes at 160° to liberate xenon tetrafluoride, approximately half of the xenon remains to form a diamagnetic material of empirical formula $XePt_2F_{10}$.



$$NO \rightarrow NO^+ + 1\,e \qquad + 219\ \text{kcal.mole}^{-1}$$

$$WF_6 + NO\ \text{no reaction}^{(a)}$$

$$ReF_6 + NO\ \text{not studied}$$

$$OsF_6 + NO \rightarrow NO^+[OsF_6]^{-(b)}$$

$$IrF_6 + NO \xrightarrow[\text{temp}]{\text{low}} NO^+\left[IrF_6\right]^{-(b)} \xrightarrow[+NO]{20^\circ} (NO)_2IrF_6^{(c)}$$

$$PtF_6 + NO \xrightarrow[\text{temp}]{\text{low}} NO^+\left[PtF_6\right]^{-(b)} \xrightarrow[+NO]{20^\circ} (NO)_2PtF_6^{(b)}$$

(a) Geichmann, Smith, Trond and Ogle, *Inorg. Chem.*, 1962, *1*, 661.
(b) Bartlett and Jha.
(c) Robinson and Westland, *J. Chem. Soc.*, 1956, 4481.

Figure 7—The reactions of third transition series hexafluorides with nitric oxide.

TABLE 6. — SOME RESULTS FOR THE XENON + PLATINUM HEXAFLUORIDE REACTION

Tensimetric results for gas + gas reaction in a glass bulb

	(1)	(2)
Pressure of PtF_6 mm.	95.0	70.0
Initial pressure of Xe mm.	156.5	72.0
Residual pressure of Xe mm.	82.0	23.0
Combining ratio Xe: PtF_6	1:1.27	1:1.42

Tensimetric results for PtF_6 (solid + gas) + Xe (gas) in a glass bulb

	(1)	(2)	(3)
Initial pressure of PtF_6mm.	93.0	56.0	117.5
Residual pressure of PtF_6mm.	0	12.0	0
Initial pressure of Xe mm.	108.0	27.5	117.5
Residual pressure of Xe mm.	17.0	0	59.0
combining ratio Xe:PtF_6	1:1.02	1:1.60	1:2.0

TABLE 7

	$KPtF_6$	$\overset{+}{O_2}[PtF_6]^-$	$Xe(PtF_6)$
I.R. (cm^{-1})	640 (v.s) 590 (s)	631 (v.s)	652 (v.s) 550 (s)
vis. and U. V. (Å)	—	3500	3825

TABLE 8. — XENON — RHODIUM HEXAFLUORIDE
RhF_6 (solid + gas) + Xe (gas) in a nickel weighing can

	(1)	(2)
Wt. of xenon consumed g.	0.0050	0.0120
Wt. of adduct	0.0139	0.0337
Combining ratio Xe:RhF_6	1:1.05	1:1.10

Rhodium hexafluoride also reacts with xenon and the reacting ratio was, in the two experiments performed, close to 1:1 (Table 8). Presumably the adduct is $Xe^+ [RhF_6]^-$ but again no X-ray patterns were secured. Since rhodium hexafluoride was considered, because of its small size and low thermal stability to be the most powerful oxidizer of

TABLE 9. — AVERAGE BOND ENERGY (IN KCAL) FOR SOME FLUORIDES

SbF^5 90.0 (a)	TeF_6 78.5 (b)	IF_7 54.0 (c)	[XeF_8] [24] (f)
SbF_3 105 (b)	TeF^4 88.1 (a)	IF^5 62.3 (d)	XeF_6 31.5 (e)
			XeF^4 32.0 (e)

$$Xe_{(g)} + {}^{1}/_{2}nF_{2(g)} \rightarrow XeF_2$$

Exothermic when A.B.E. > ΔHf(F) i.e. 18.3 kcal.

(a) Nichols, Ph.D. Thesis, University of Durham 1958.
(b) Rossini, Wagman, Evans, Lavine and Joffe, *Natl. Bur. Standards* (U.S.) Circ. *500* (1952).
(c) Wiebenger, Havinga and Boswijk, "Advances in Inorganic Chemistry and Radiochemistry", Ed. Emeleus and Sharpe, Vol. 3, Academic Press Inc., N.Y., 1961, p. 136.
(d) Woolf, *J. Chem. Soc.*, 1951, 231.
(e) Stein and Plurien, Conference on Noble Gas Compounds, Argonne Natl. Lab., April 1963.
(f) Estimated.

the known hexafluorides it was mixed with gaseous krypton in an attempt to oxidise this gas. The red vapor of the hexafluoride persisted in the presence of a considerable excess of the noble gas. Platinum hexafluoride displayed a similar inability to oxidize krypton.

Within a few weeks of the discovery (17) of xenon tetrafluoride by Claassen, Selig and Malm, they and their collaborators at the Argonne National Laboratory, had also prepared and characterized a difluoride (18, 19) and a hexafluoride (20). These compounds were soon confirmed in a number of other laboratories. All thee fluorides, which are white crystalline solids at room temperature are preparable from fluorine and xenon, the nature of the product depending upon the ratio of the reactants and the temperature, the tetrafluoride being thermally more stable than the hexafluoride (21).

The fluorides excited great interest among theoretical chemists and some have undoubtedly felt that an unorthodox form of bonding was necessary. The bonding appears, however, to be little different from that encountered in the halogen fluorides and interhalogens. Average bond energies for the fluorides of the elements antimony to xenon are given in Table 9. They include the recently reported values for the xenon fluorides (22). The smooth reduction in bond strength from antimony to xenon is presumably, in part at least, a consequence of the increase in the coordination number of the central atom. (The average bond energies are derived from the heat of formation from the gaseous atoms and not from the atoms in their valence states.) It is of interest that extrapolation of the average bond energies for the highest fluorides of antimony, tellurium and iodine, shown in Figure 8, gives an average bond energy for xenon octafluoride of 24 kcal., indicating a possible existence for this compound.

On the basis of simple electron pair repulsion theory the difluoride should be linear, with the fluorine atoms at the poles of a trigonal bipyramidal arrangement of electron pairs. The tetrafluoride should be a square planar arrangement of fluorine atoms about the xenon atom, there being a non-bonding electron pair both above and below the plane. The hexafluoride, since it possesses a non-bonding electron pair, should show some deviation from octahedral symmetry. The structural evidence has so far been in accord with all of these expectations. Table 10 contains some of the structural data obtained from X-ray and neutron diffraction studies of the di (23, 24) and tetrafluorides (23, 25, 26). The neutron diffraction data is the more precise. The infra-red spectra of XeF_2 vapor (27) and XeF_4 vapor (28) are consistent with the linear and square planar models.

TABLE 10. — STRUCTURAL DATA FOR XENON FLUORIDES

Xenon Difluoride

Crystal Structure: Body centred tetragonal cell, Z = 2, S.G. 14/m m m

1. S. Siegel and E. Gebert, *J. Amer. Chem. Soc.*, 85, 240 (1963).
2. H. A. Levy and P. A. Agron, *J. Amer. Chem. Soc.*, 85, 241 (1963).

Linear molecule

$$\text{Xe-F} \begin{cases} 1.\ 2.14 \pm 0.14\ \text{Å (X-ray)} \\ 2.\ 2.00 \pm 0.01\ \text{Å (neutron)} \end{cases}$$

Xenon Tetrafluoride

Crystal Structure: Monoclinic unit cell, z = 2, S.G. $P2_1/n$

1. S. Siegel and E. Gebert, *J. Amer. Chem. Soc.*, 85, 240 (1963).
2. J. A. Ibers and W. C. Hamilton, *Science*, 139, 106 (1963).
3. D. H. Templeton, A. Zalkin, J. D. Forrester and S. M. Williamson, *J. Amer. Chem. Soc.*, 85, 242 (1963).
4. J. H. Burns, P. A. Agron and H. A. Levy, *Science*, 139, 1209 (1963).

Molecular symmetry D_{4h}:

$$\text{Xe-F} \begin{cases} 2.\ 1.92 \pm 0.03\ \text{Å} \\ 3.\ 1.93 \pm 0.03\ \text{Å} \\ \quad 1.951 \pm 0.002\ \text{Å} \\ 4.\ 1.954 \pm 0.002\ \text{Å} \end{cases}$$

Molecular species:

Infra red and Raman spectra
H. H. Claassen, C. L. Chernick and J. G. Malm, J. Amer. Chem. Soc., In Press.
Symmetry D_{4h}. Bond length 1.85 ± 0.2 Å (IR)
Maximum puckering from sq. planar config. 0.5° or 0.02 Å Shift for F from plane.

The preparation of the xenon fluorides initiated work on the other noble gases. Radon which would be expected to form compounds more readily than xenon was quickly shown (29) to form a fluoride but at this time its composition is still uncertain. Studies with this noble gas are difficult since its isotopes are short lived and are α emiters. Attempts were made to prepare fluorides of krypton by heating gaseous mixtures but these experiments met with no success. Kirshenbaum and Grosse (30), however, were able to prepare krypton tetrafluoride by passing an electric discharge through krypton, fluorine mixtures at liquid nitrogen temperature. Krypton tetrafluoride which is a transparent colorless solid has a vapor pressure of 115 mm. at 25°C. and is much less stable than its xenon analogue, the decomposition into the elements being rapid at 60°C. The difficulty of formation and thermal instability of this fluoride are consistent with the value of 18 to 19 kcal. obtained for the average bond energy, by extrapolation from the values calculated for the fluorides of arsenic, selenium and bromine. These results are given in Table 11 and Figure 8. In view of the greater bond energy of bromine monofluoride (59.4 kcal.) compared with the values for the trifluoride and pentafluoride (48.3 and 47.7 kcal. respectively) it is possible that the average bond energy for krypton difluoride may be appreciably greater than 19 kcal. making this a thermally much more stable compound than the tetrafluoride. It is of interest that Turner and Pimentel (31), by the matrix isolation technique, have isolated a species which they identify as krypton difluoride. The same authors were unable to prepare an argon fluoride by similar methods. It appears unlikely that argon fluorides can exist.

In view of the ease of formation and thermal stability of the xenon fluorides there was some possibility that oxides and chlorides could also exist. For oxides and chlorides of the noble gases to be formed exothermally, the average bond energy needs to be greater than ~ 30 kcal. (since $\Delta H_f(O) = 59.2$ kcal. mole^{-1} and $\Delta H_f(Cl) = 29.01$ kcal. mole^{-1}). Consideration of the average bond energies, estimated from the available thermodynamic data for the oxides and chlorides of antimony, tellurium and iodine, given in Table 12 and Figure 9, shows however that bond energies for xenon oxides and chlorides are probably smaller than this. Consequently xenon oxides and chlorides should be endothermic compounds. The failure to prepare such compounds from the elements is therefore not surprising. Nevertheless there was some hope that they could be derived from the fluorides. The Argonne workers had noted (18) that the hydrolysis of xenon tetrafluoride was not complete and that a solid, xenon containing, hydrolysis product formed. A study of this reaction at the University of British Columbia showed that a fluorine free solid was produced by the complete hydrolysis of xenon tetrafluoride. Unfortuntely the detonation of a sample of the hydrolysis product brought this investigation to an abrupt halt. Subsequently this material was shown (32) to be xenon trioxide, presumably arising by disproportionation of a xenon (IV) species. The trioxide is best made (33) by the slow and complete hydrolysis of xenon hexafluoride:

$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$. The oxide is non volatile and is dangerously explosive, being comparable in power to T.N.T. There is some indication that it is more unstable in air, with a relative humidity greater than 20% (33). The explosixe nature of the compound is compatible with the high endothermicity ($\Delta Hf = +96$ kcal. mole^{-1}) (34). There is a close resemblance of the crystal structure of xenon trioxide (35), which is represented in Figure 10, with that of iodic acid. The short oxygen-xenon bonds (Xe-O, 1.76 Å) of the trigonal pyramidal molecule indicate appreciable double bond character.

TABLE 11. — AVERAGE BOND ENERGY (IN KCAL) FOR SOME FLUORIDES

		BrF 59.4[a]	$[KrF_2]$ [~30]
		BrF_3 48.3[a]	KrF_4 [~19]
AsF_3 101.6[c]	SeF_4 75.5[b]	BrF_5 47.7[a]	$[KrF_6]$ [~18]

$$\begin{array}{ccc} (26.1) & (27.8) & (29.7) \end{array}$$
$$Kr_{(g)} + {}^1/_2 nF_2 \rightarrow KrF_{n(g)}$$
$$\text{Exothermic when A.B.E.} > \Delta H_f F_{(g)} = \underline{18.3}\text{kcal}$$

(a) Wiebenger, Havinga and Boswijk, "Advances in Inorganic Chemistry and Radiochemistry", Ed., Emeleus and Sharpe, Vol. 3, Academic Press Inc., New York, 1961, p. 136.
(b) Nichols, Ph.D. Thesis, University of Durham 1958.
(c) Rossini *et al.* N.B.S. circ. *500*.

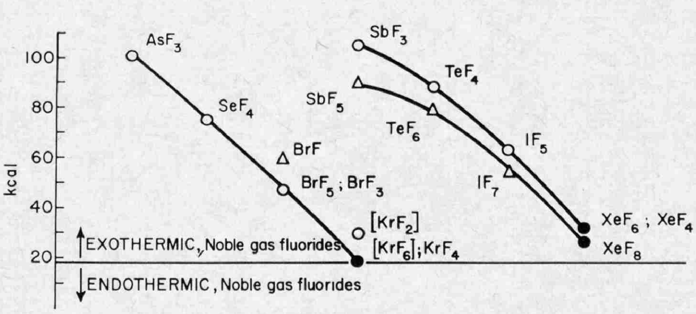


Figure 8 — Average bond energy (in kcal.) for some fluorides.

In view of the instability of the trioxide it is interesting to speculate on the stability of the oxyfluorides. Xenon oxide tetrafluoride should be an exothermic compound since the atomic heat of formation using average bond energies of 32 kcal. and 17 kcal. respectively for Xe-F and Xe-O is −160 kcal. mole^{-1}. The combined heat of atomization of four fluorine atoms (4 x 18.3 kcal.) and one oxygen atom (59.2 kcals.), 132.4 kcal., is less than this. Xenon dioxide difluoride, by such considerations, should be endothermic. It is of interest that xenon oxide tetrafluoride is easily made (35) by controlled hydrolysis of xenon hexafluoride and is a thermally stable entity (m.p. −28) whereas xenon dioxide difluoride has been observed only mass spectrometrically (36).

Although it may prove possible to prepare xenon nitride trifluoride (e.g. by interaction of ammonia with xenon hexafluoride) in all probability, since the heat of atomization of nitrogen is great ($\Delta Hf(N) = 113$ kcal.), it will be an endothermic compound.

It occurred to us that it might be possible to prepare the endothermic chlorides of xenon by interaction of the fluorides with boron trichloride. Figure 11 shows some possible reactions and their estimated enthalpies. Unfortunately, although the reaction has been carried out at −78°C., the last reaction is apparently the only one.

There would appear to be little hope of oxides and chlorides of the noble gases, other than those of xenon and radon, ever being made.

In a prophetic article written some 30 years ago (37) Pauling suggested the existence of XeF_6 and a less stable XeF_8. He also postulated the existence of xenic acid H_4XeO_6 and salts (e.g. Ag_4XeO_6) derivable from this. It was found, at the Argonne Laboratory that hydrolysis of

TABLE 12. — AVERAGE BOND ENERGIES (IN KCAL) FOR SOME OXIDES AND CHLORIDES

Oxides

Sb_2O_3	TeO_2	I_2O_5	XeO_3
74	54	37	[17]

$$\Delta Hf^\circ\ XeO_{3\ (c)} = +95 \text{ kcal. mole}^{-1(a)}$$
$$\therefore \text{Average bond energy} < \frac{3\Delta Hf^\circ(O) - 95}{6} = 14 \text{ kcal.}$$

(a) Gunn and Williamson, Conference on Noble Gas Compounds, Argonne Natl. Lab., April, 1963.

Chlorides

$SnCl_2$	$SbCl_3$	$TeCl_4$	ICl_3	$[XeCl_4]$
92.5	75.1	54.5	<33	[~10]

$$\begin{tikzcd}
2Cl_2 \arrow[d, "116.04 \text{ kcal.}"'] & + Xe \arrow[r, "\Delta Hf^\circ", "\Delta Hf^\circ - 116.04"'] & XeCl_{4\ (g)} \\
4Cl & &
\end{tikzcd}$$

$$\Delta Hf^\circ \sim +116.04 - 40 = +76 \text{ kcal. mole}^{-1}$$

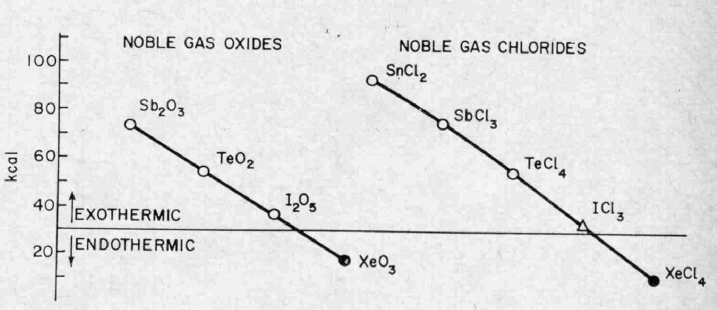


Figure 9—Average bond energies (kcal.) for some oxides and chlorides.

xenon hexafluoride in sodium hydroxide solution gave a pale yellow solution which gradually loses color, a stable crystalline salt being slowly precipitated. Addition of potassium iodide to a solution of this salt, followed by acidification, leads to the liberation of eight oxidizing equivalents per xenon. The formula proposed (38) for the salt is $Na_{2n}XeO_{4+n} . y\,{}^{2}O$, with 2 being the most probable value for n. This is the first established compound of Xe(VIII) and represents the maximum oxidation state for the element.

$$XeF_4 + H_2O \rightarrow Xe + XeO_3 + HF + O_2$$
$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

Crystal structure (D. H. Templeton, A. Zalkin, J. D. Forrester and S. M. Williamson, *J. Amer. Chem. Soc.* 85, 817 (1963).

Orthorhombic, a = 6.163 ± 0.008, b = 8.115 ± 0.010, c = 5.234 ± 0.008 Å, Z = 4, S.G. $P2_12_12_1$

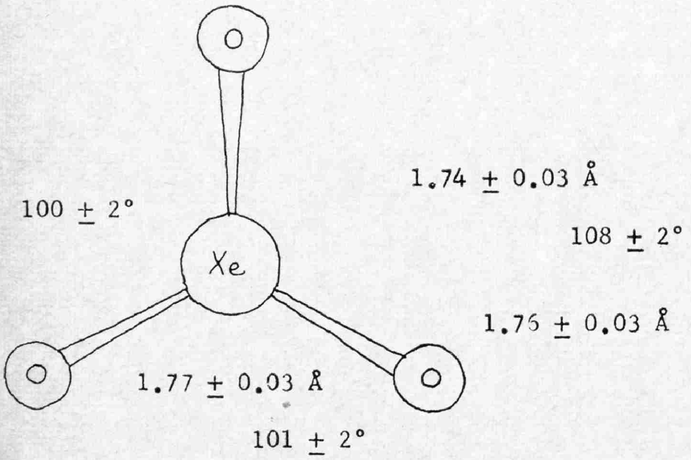


Figure 10—Xenon Trioxide.

Of course it may well prove possible to isolate xenon tetroxide despite its endothermicity and undoubtedly some effort will be made towards this end. The tetroxide should be a regular tetrahedral molecular species and should be volatile.

References

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$$\begin{aligned}
&3\,XeF_{4(g)} + 4\,BCl_{3(g)} && \rightarrow 3\,XeCl_{4(g)} + 4\,BF_{3(g)}\\
&\text{At.}\Delta Hf(\text{kcal}) - 3[4(32)] - 4[3(92.9)] && \rightarrow - 3[4(10)] - 4[3(139.1)]\\
&\Delta H_{\text{reac}}n && = \underline{\sim - 290\ \text{kcal}}\\
&3\,XeF_{4(g)} + 4\,BCl_{3(g)} && \rightarrow 3XeCl_{2(g)} + 3Cl_{2(g)}\\
& && + 4BF_{3(g)} - 3[2(22)]\\
& && - 3[2(29)]\\
&\Delta H_{\text{reac}}n && = \underline{\sim - 476\ \text{kcal}}\\
&3\,XeF_{4(g)} + 4\,BCl_{3(g)} && \rightarrow 3\,Xe_{(g)} + 6\,Cl_{2(g)}\\
& && + 4\,BF_{3(g)} - 6[2(29)]\\
&\Delta H_{\text{reac}}n && = \underline{\sim - 518\ \text{kcal}}
\end{aligned}$$

Figure 11—Possible XeF_4-BCl_3 reactions.

(2) a. Weinstock, Claassen and Malm, J. Amer. Chem. Soc., 1957, **79**, 5832.
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BOOKS IN REVIEW

COMPOUND SEMICONDUCTORS, Volume I, Preparation of III-V Compounds. (Robert K. Willardson, Harvey L. Goering, Editors; Reinhold Publishing Corp., 430 Park Ave., New York 22, N.Y. xxii + 553 pp. $25.00 U.S.) – This compilation on compound preparation comprises 50 chapters written by scientists from all parts of the world. The chapters present the pertinent data from more than 1,000 technical papers plus unpublished work. The authors were selected for each of the chapters on the basis of a bibliography compiled from papers published during the last 10 years. One of the authors is S. C. Liang, Cominco, Trail, B.C.

RADIATION EFFECTS ON ORGANIC MATERIALS. (Robert O. Bolt, James G .Carroll, editors; Academic Press Inc., 111 Fifth Ave., New York 3, N.Y. xv + 576 pp. $13.50 U.S.) – The book is written for Research and Development people so it goes light on fundamentals of physics, chemistry and engineering, but emphasizes background and recent information on radiation effects. After four general chapters, the following chapters on materials are included: polymers, plastics, elastomers, coolants, lubricants, adhesives, textiles, coatings and films, dielectric fluids, fuels and fluid shield materials, and coal, wood and explosives.

CHEMICAL CALCULATIONS – An Introduction to the Use of Mathematics in Chemistry. Second Edition. (Sidney W. Benson; John Wiley & Sons, Inc., 605 3rd Ave., New York 16, N.Y. xii + 254 pp.) – This new edition contains a larger number and variety of problems, with more weight on 'difficult' ones. The sections dealing with acid-base phenomena and complexionic equilibria were completely rewritten.

TOPICS IN ORGANIC CHEMISTRY. (Louis F. and Mary Fieser; Reinhold Publishing Corp., 430 Park Ave., New York 22, N.Y. xii + 668 pp. $10.00 U.S.) – Part one surveys: polynuclear hydrocarbons; aromatic heterocyclic compounds; alkaloids; terpenoids; steroids; vitamins; chemotherapy; synthetic polymers; dyes. Part Two covers the literature of organic chemistry from July 1, 1961 to December 13, 1962, and as such supplements the authors' previous text "Advanced Organic Chemistry".

(See also page 57)