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NOBLE-GAS COMPOUNDS

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NOBLE-GAS COMPOUNDS

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ABSTRACT

The noble-gas elements are not of equal reactivity. The heavier elements (Rn, Xe, Kr) are able to share some or all of their valence electrons with electronegative atoms or groups (ligands), to form compounds. The range of known compounds and their physical and chemical properties can be accounted for by allowing that compound formation derives from the transfer of electron from the noble-gas atom to the ligands, such that each species (noble-gas atom and ligand) possesses a shared valence electron octet. The bonding model retains the 'octet' bonding criterion but, where necessary, abandons the 'electron-pair-bond' concept.

INTRODUCTION

This year marks the tenth anniversary of the preparation of the first true compounds of noble-gas elements. Our view of the range of attainable compounds and of the bonding is now more clearly defined than at the time of the first ENDEAVOUR article [1]. Indeed it is now possible, using a simple bonding model, to account for the observed stabilities of the known compounds, and realistically appraise the bonding possibilities for compounds yet unknown. Since the nature of the bonding in noble-gas compounds has remained the major concern of the non-specialist, this review will emphasize that aspect.

THE RANGE OF KNOWN COMPOUNDS [2]

There has, over the past ten years, been much work towards extending the range of noble-gas chemistry: yet the range illustrated in Table I remains limited. The constraints may be readily discerned from an appraisal of the known compounds, which have in common two features: (i) the noble-gas atom is a heavier (more readily oxidizable) atom (Rn, Xe, Kr) and (ii) the atoms or groups (ligands) attached to the noble-gas atom are always highly electronegative. Both of these features indicate that the removal of electron density from the noble-gas atom to the ligands is essential to effective bonding.

A sampling of the known chemistry will illustrate the previous remarks. In keeping with its lower ionization potential (10.6 eV), radon is more readily oxidized than xenon (I = 12.1 eV). The former interacts spontaneously at ordinary temperatures with fluorine or halogen fluorides (except IF_5) to give a radon fluoride (probably RnF_2), whereas the latter must be thermally or photo-excited in order to interact with fluorine.

(By suitably controlling the fluorination conditions for xenon, however, XeF_2 or XeF_4 or XeF_6 may be prepared) In contrast with radon, xenon is not oxidized by ClF_3 or BrF_3, although it is oxidizable by iodine heptafluoride at 200°:

$$Xe + IF_7 \rightarrow XeF_2 + IF_5 \quad .$$

The oxidation of krypton (I = 14.0 eV) is much more demanding and high energy, low-temperature, syntheses are used to prepare the difluoride. Krypton difluoride is thermodynamically unstable (in contrast to XeF_2) and since $\Delta H_{at}(KrF_2(g) \rightarrow Kr(g) + 2F(g)) = +23$ kcal mole^{-1}, whereas $\Delta H_{at}(F_2(g) \rightarrow 2F(g)) = +37$ kcal mole^{-1}, KrF_2 is a better fluorine atom source than molecular fluorine. All efforts to prepare a fluoride of argon (I = 15.8 eV) have failed so far.

Since chlorine is an electronegative ligand it might have been expected that chlorides of radon and xenon would be sufficiently well bound to be stable at ordinary temperatures. Such has not proved to be the case (at least for xenon). However, microscopic quantities of the dichloride have been prepared by electric discharge of xenon-chlorine mixtures, followed by rapid entrapment in inert matrices at 20° K. The dichloride, dibromide and tetrachloride have also been detected via Mossbauer studies in which the xenon halides were derived from the β decay of their ^{129}I relatives e.g.:

$$^{129}IBr_2^- \xrightarrow{-\beta} XeBr_2 \quad .$$

These halides decompose at temperatures well below -100°C and have not been obtained in macroscopic quantities.

Since the oxygen atom is highly electronegative and is comparable in size to the fluorine atom, noble-gas oxyfluorides and oxides were to be expected. Oxyfluorides $XeOF_4$, XeO_2F_2, XeO_2F_4 and XeO_3F_2 have been prepared, directly or indirectly, from XeF_6. Like the oxyfluorides, the only oxides to be prepared are those of xenon and these are limited to the trioxide and tetroxide. Both oxides are endothermic and are dangerously explosive. They have been derived (the latter indirectly) from the thermodynamically stable fluorides. It is of interest that XeO and XeO_2 have not been prepared as laboratory chemicals (an XeO species has been detected in xenon/oxygen discharges) although the fluoro-relatives XeF_2 and XeF_4 are both readily preparable.

A noteworthy feature of the xenon oxide system is the disproportionation behaviour of the lower oxidation states. Hydrolysis of xenon tetrafluoride does not yield a dioxide but proceeds according to the equation

$$3XeF_4 + 6H_2O \rightarrow XeO_3 + 2Xe + 1.5O_2 + 12HF \quad .$$

Furthermore, certain alkaline solutions of Xe(VI) disproportionate to yield perxenate:

$$HXeO_4^- + 2OH^- \rightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O$$

although the perxenate is prepared in better yield by passing ozone through a dilute solution of Xe(VI) in base. Perxenate is the source for the tetroxide:

$$Ba_2XeO_6 + 2H_2SO_4 \rightarrow 2BaSO_4 + XeO_4$$

Although XeO_4 is known and well characterized all attempts to synthesize the octafluoride have failed. There is some evidence [3], however, for the Xe(VIII) oxyfluorides XeO_3F_2 and XeO_2F_4.

Since groups like $-OSO_2F$ and $-OClO_3$ are known to be highly electronegative, it was anticipated that substitution for fluorine could be effected by interactions such as

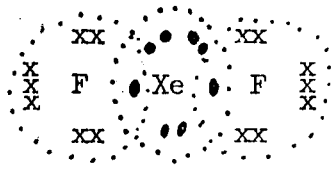
$$XeF_x + yHOSO_2F \rightarrow XeF_{x-y}(OSO_2F)_y + yHF \quad .$$

Preparations of this kind have been indicated for all three binary xenon fluorides and the xenon(II) compounds, particularly the compound $FXeOSO_2F$, shown in Figure 2, have been well characterized. (It should be noted that the F-Xe-O arrangement in $FXeOSO_2F$ is linear; similar geometry is anticipated for all $Xe(OR)_2$ compounds.) All of these $XeF_{x-y}(OR)_y$ compounds are thermally less stable than the corresponding fluorides.

THE NATURE OF THE BONDING IN NOBLE-GAS COMPOUNDS

Since, as we have seen, only the heavier more readily ionizable gases form compounds and only the most electronegative atoms or groups are satisfactory ligands for the noble gases, it is to be expected that there should be appreciable bond polarity in noble-gas compounds: e.g. $Xe^{\delta+}-F_x^{\delta-}$. We shall illustrate the several theoretical models which readily allow for this using the XeF_2 case.

The simplest model to visualize is that proposed by Bilham and Linnett [3]. They suggest that each fluorine atom acquires a share in a xenon valence-shell electron;



each Xe-F bond being a single electron bond. In this representation, each fluorine ligand tends towards the electron configuration of neon; the xenon atom, however, retains a (somewhat imperfect) octet configuration. The acceptability of these postulates is supported by ionization potential data, given in Table 2, showing the xenon electron configuration to be less stable than the neon configuration. (Neglect of this long known information was a prime factor in the prejudice against heavy-noble-gas chemistry.) If the single electron in each Xe-F internuclear region is equally shared between the two atoms, then the net charge distribution in the molecule becomes $^{-\frac{1}{2}}F\text{-}Xe^{+1}\text{-}F^{-\frac{1}{2}}$.

An identical charge distribution is predicted by the Valence-Bond representation advocated by Coulson [4] and by the three-centre molecular orbital approach suggested independently by Pimentel [5] and Rundle [6]. The former model represents XeF_2 as a resonance hybrid of the canonical forms $[(Xe\text{-}F)^+F^-]$ and $[F^-(Xe\text{-}F)^+]$ (Note that $(Xe\text{-}F)^+$ and F^- are both 'classical' octet species). If the positive charge is localised on the xenon atom, the net charge distribution is again $^{-\frac{1}{2}}F\text{-}Xe^{+1}\text{-}F^{-\frac{1}{2}}$.

The simple molecular orbital model, for XeF_2, represents the bonding in terms of three-centre molecular orbitals, derived from a p orbital from each of the participating atoms. Combination of the three atomic orbitals provides three molecular orbitals; one bonding (+F-, -Xe+, +F-); one non-bonding (+F-, -F+); and one anti-bonding (+F-, +Xe-, +F-). The three atom system provides four electrons to populate these orbitals. The lowest

energy orbital, which is the bonding orbital, receives the full quota of two electrons, as does the non-bonding orbital which is of intermediate energy. The highest energy molecular orbital is the anti-bonding orbital and it remains empty; consequently there is net bonding. Since the pair of electrons in the non-bonding orbital reside largely on the fluorine ligands, the charge distribution in the molecule is effectively $^{-\frac{1}{2}}F\text{-}Xe^{+1}\text{-}F^{-\frac{1}{2}}$, the bonding-orbital electron pair being assigned to the internuclear regions. The molecular orbital model, therefore, corresponds closely to the Bilham and Linnett model. All three models are, in effect, equivalent, but each viewpoint has unique advantages. The Coulson Valence-Bond approach is particularly convenient for our discussion.

A wealth of physical data, some of which is presented in Table III, supports appreciable bond polarity $Xe^{\delta+}\text{-}L^{\delta-}$ in XeF_2 and the other xenon compounds. For the XeF_2 case, a polarity of $^{-\frac{1}{2}}F\text{-}Xe^{+1}\text{-}F^{-\frac{1}{2}}$ is consistent with all of the experimental findings, but it is particularly impressive that the enthalpy of sublimation calculated by Rice and his coworkers [8] in 1963, assuming that point charge distribution, is 13.3 kcal mole^{-1}, whereas the experimental value, reported [9] in 1968, is 13.2 kcal mole^{-1}.

It will be recognized that if a fluoride ion is removed from the XeF_2 molecule:

$$XeF_2 \rightarrow XeF^+ + F^-$$

the resulting cation will be an electron-pair-bond species $(:\ddot{\underset{\cdot\cdot}{Xe}}:\ddot{\underset{\cdot\cdot}{F}}:)^+$. If, therefore, the single-electron bond representations for the XeF_2 molecule are valid, XeF^+ salts should exhibit a shorter Xe-F bond than in XeF_2 itself. Vibrational spectroscopic and crystal structure findings, given in Table IV, show that the removal of a fluoride ion from the XeF_2

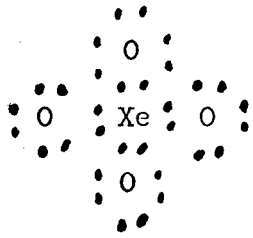
molecule does indeed furnish a bond which is shorter and stronger than in XeF_2. Furthermore, if we accept that the bond length of 2.01 Å reported for XeF_2 represents a bond order of 0.5 (i.e., a one electron bond), then by employing an empirical equation, given by Pauling [10] which relates fractional bond order to bond length, we can predict the bond length for bond order unity. The predicted length for $Xe\text{-}F^+$ of 1.83 Å is very similar to the shorter Xe-F distance in $FXeSb_2F_{11}$, which may, therefore, be formulated as the salt $[FXe]^+[Sb_2F_{11}]^-$.

The single electron bond model applies to all of the noble-gas halides. In valence-bond terms the tetrahalides are representable as the resonance hybrid of the canonical forms $(NL_2)^{2+}(L^-)_2$, e.g., $(XeF_2)^{2+}(F^-)_2$. Similarly, xenon hexafluoride is the resonance hybrid of $(XeF_3)^{3+}(F^-)_3$ canonical forms. Note that the ion species represented in the canonical forms are always classical octet species (i.e., each atom possesses a valence-electron octet). The increase in net positive charge on the xenon atom, as its coordination number grows, accounts adequately for the decrease in bond length and increase in stretching force constant (given in parentheses, in mdynes $Å^{-1}$), in the series of xenon fluorides:

XeF_2, 2.01 Å (2.6); XeF_4, 1.95 Å (3.0); XeF_6, 1.89 Å (3.3)

Comparison of the Xe-O bonds with Xe-F bonds reveals that the oxygen linkage is much stronger than the fluorine linkage. Thus the bond length and the force constant for the Xe-O bond in XeO_3 are 1.76 Å and 5.66 mdynes $Å^{-1}$, respectively; whereas for XeF_6 the corresponding values are 1.89 Å and 3.3 mydnes $Å^{-1}$. In the molecule $XeOF_4$, the bond lengths and force constants are, for XeO, 1.70 Å and 6.6 mdynes $Å^{-1}$ and for Xe-F 1.90 Å and 3.0 mdynes $Å^{-1}$, respectively. It is appropriate to represent the Xe-O

linkage as an electron-pair bond. On this basis the molecule XeO_4 is represented simply as



This implies an appreciable positive charge on the xenon atom, since equal sharing of a xenon electron pair with an oxygen ligand gives a net charge of -1 to that ligand. Evidence for greater polarity of the Xe-O compared with the Xe-F linkage has been obtained from X-ray photoelectron spectroscopy. Analysis of the chemical shift data for molecular XeF_2, XeF_4, XeF_6, and $XeOF_4$ indicates that the oxygen ligand in $XeOF_4$ withdraws approximately twice the electron density from the xenon atom than does each of the fluorine ligands [11]. The findings are consistent with the charge distribution $Xe^{+3}O^{-1}(F^{-\frac{1}{2}})_4$ which the simple bonding model suggests.

The simple bonding model also permits us to assess the stabilities of compounds in a semiquantitative way.

ENERGY CONSIDERATIONS

The marked decrease in ionization potential with increase in atomic number in the helium group is itself suggestive of chemical activity for the heavier elements. We can appreciate that an electronegative ligand, L, interacting with a noble-gas atom, N, is likely to remain bound if the energy required for electron removal from N is compensated for by the electron acquisition by L and the electrostatic attraction energy of $N^{\delta+}$ and $L^{\delta-}$. In order that we may make energy estimates using readily available thermochemical data it is convenient to use the cycle shown in

Table V. We see that for the XeF_2 case, the ionization energy for Xe^+ formation (280 kcal $mole^{-1}$) is appreciably compensated for by the attraction energy between Xe^+ and F^-, (-166 kcal $mole^{-1}$). (This is what one expects, since the electron is not removed far from the xenon atom when it becomes associated with the adjacent, small, fluorine atom.) The attraction energy and the electron affinity of atomic fluorine together (-246 kcal $mole^{-1}$) come close to meeting the requirement; the contributions of an electron-pair bond energy for $Xe\text{-}F^+$ (-48 kcal $mole^{-1}$) and resonance energy for the canonical forms $(Xe\text{-}F)^+F^-$ and $F^-(Xe\text{-}F)^+$ generate a stable molecule for which $\Delta H_{at}(XeF_2(g) \rightarrow Xe(g) + 2F(g)) = 65$ kcal $mole^{-1}$. A similar evaluation for KrF_2 immediately reveals that the greater ionization potential of the noble-gas atom is not recompensed by an increased attraction energy. Assuming the same resonance energy as in the XeF_2 case the heat of atomization of KrF_2 is determined to be +33 kcal $mole^{-1}$: the experimental value is +23 kcal $mole^{-1}$. By similar reasoning we can readily appreciate why ArF_2 has proved to be so difficult to prepare.

It is also easy to understand why the other halides should be so much less stable than the fluorides. The atoms of chlorine and the other halogens are much bigger than the fluorine atom. The attraction energy, for the $(LN)^+L^-$ ion pair, is therefore significantly less (being estimated at 138 kcal $mole^{-1}$ for $(Cl\text{-}Xe)^+Cl^-$). Also, the electron pair energies for $XeCl^+$ and the other species must be less than for XeF^+ since fluoride bond energies are well known [10] to be stronger than those of the other halides, (e.g., I-F = 67 where I-Cl = 58 kcal $mole^{-1}$). We can also ascribe the low thermal stability of the fluorosulfates and perchlorates to the large ligand size (the electron affinities of $-OSO_2F$

and $OClO_3$ are much more favourable than for F.)

The case of the xenon oxides is of particular interest, since the tetroxide and trioxide are known whereas the dioxide and monoxide have only been observed as short lived species in discharges. The geometries of XeO_4 and XeO_3 being known, the electrostatic point charge energies for the $Xe^{x+}(O^-)_x$ configuration may be readily determined. From Table VI, it can be seen that the ionization energy is largely compensated for by the electrostatic attraction term, although the oxygen atom electron affinity also contributes. In order to estimate the heat of formation from the atoms it is, however, necessary to know the energy to be associated with the electron-pair-bond formation, i.e.,

$$\Delta H(Xe^{x+}(O^-)_x \rightarrow Xe^{x+}{:}O^-{}_x)$$

In the case of XeO_4 the observed heat of atomization requires that this term be -152 kcal mole^{-1}; the derived average electron pair bond energy (-38 kcal mole^{-1}) when applied to the other oxides allows us to determine the heat of atomization, $\Delta H_{at}(XeO_x \rightarrow Xe + xO)$. The value of -38 kcal mole^{-1} for the Xe:O electron-pair bond is compatible with the experimental value [13] of -47 kcal mole^{-1} for $Xe{:}F^+$. As may be seen from Table VI, the calculated $\Delta H_{at}(XeO_3)$ agrees with the observed value within the experimental error. The dioxide is predicted to be very weakly bound and the monoxide unbound to the extent of +33 kcal mole^{-1}.

It is of interest that spectroscopic studies [12] indicate that Xe-O is bound with respect to an unspecified singlet oxygen species, the reported dissociation energy being 8 kcal mole^{-1}. If the singlet species were $^1D(O)$ this would imply that XeO should be unbound by 35 kcal mole^{-1} with respect to $^3P(O)$, providing remarkable agreement with

the simple calculations. In any case, the failure to prepare macroscopic quantities of XeO or XeO_2 is accounted for.

Although these simple evaluations ignore many difficult points, there is a comforting fit of observed behaviour with theoretical expectation.

FLUORIDE ION DONOR PROPERTIES OF THE KRYPTON AND XENON FLUORIDES

The single-electron bond model for the halides indicates that donation of a halide ion, e.g.,

$$XeF_x \rightarrow XeF_{x-1}^{+} + F^{-} \quad \text{or} \quad 2XeF_x \rightarrow Xe_2F_{2x-1} + F^{-}$$

should be assisted by formation of one electron-pair bond in the cation. Examples are known for all of the xenon fluorides and KrF_2 Raman spectra show that the complex $KrF_2 \cdot 2SbF_5$ is very much like its xenon relative and is best represented as the salt $[KrF]^{+}[Sb_2F_{11}]^{-}$. Now consideration of the thermodynamic cycle (values in kcal mole^{-1}):

$$\begin{array}{ccc} Kr^{+} + F & \xrightarrow{\sim -38} & KrF^{+} \\ 315 \uparrow & & \downarrow E(KrF^{+}) \\ Kr + F & \xleftarrow[\leq 12]{} & KrF \end{array}$$

shows that the electron affinity of the cation is equal to the ionization potential of krypton, less the difference in the bond energies of KrF^{+} and KrF, which is unlikely to be greater than 40 kcal mole^{-1}. The electron affinity of KrF^{+} is therefore, at least 275 kcal mole^{-1}. The spontaneous oxidation of iodine pentafluoride is in keeping with this value:

$$KrF^{+}Sb_2F_{11}^{-} + IF_5 \rightarrow IF_6^{+}Sb_2F_{11}^{-} + Kr$$

The increasing effective positive charge on the Xe atom in the series XeF_2, XeF_4, and XeF_6, suggests that the ease of fluoride ion donation should decrease from XeF_2 to XeF_6. The difluoride is a superior donor to XeF_4, but surprisingly XeF_6 is the best donor of the three fluorides.

The xenon hexafluoride molecule has been extensively studied but we still do not know the ground state geometry. In the vapour phase the molecule is evidently fluxional (a 'jelly-fish' like molecule): while electron diffraction data indicate that it is much distorted from octahedral symmetry [14], molecular beam studies [15] indicate that any dipole moment must be less than 0.03 Debye. Crystalline XeF_6 is best represented as the salt $XeF_5^+F^-$ [16]. The XeF_5^+ species seen in crystalline XeF_6 is similar in size and shape to that in the salt $XeF_5^+RuF_6^-$, whose structure [17] is illustrated in Figure 2. Crystal structure studies give convincing evidence that the non-bonding Xenon(VI) electron pair occupies the sixth position of the pseudo-octahedral XeF_5^+ species. It is probable that the tendency of the non-bonding 'pair' to steric activity in molecular XeF_6 is hindered by the ligand crowding and manifests itself not only in the fluxional behaviour but also in aiding the release of fluoride ion.

RELATIONSHIP OF NOBLE-GAS COMPOUNDS TO COMPOUNDS OF THE PRECEEDING GROUPS

It should be recognized that the noble-gas compounds are close relatives of compounds of preceeding elements in the periodic table [1]. The perxenates (XeO_6^{4-}) are isoelectronic with the paraperiodates and the orthotellurates; and XeO_3 with IO_3^-. Furthermore, XeF_2 can be simply correlated with IF_3 and TeF_4; KrF_2 with BrF_3 and SeF_4; XeF_4 with IF_5 and TeF_6; and XeF_6 with IF_7. As expected, the bonding models, which

work so well for the noble-gas compounds, account in a very satisfactory manner for the properties of these relatives also.

APPLICATIONS AND FUTURE DIRECTIONS FOR RESEARCH

The ability of radon, xenon and krypton to form compounds [2] may well prove to be of value to the nuclear energy program. Radon is a health hazard in uranium mines. It is now feasible to scrub the air of such mines with suitable oxidizers to remove the radon. Xenon and krypton are gaseous fission products. The krypton is dangerously radioactive and presents a considerable handling and storage problem. Compound formation could provide for convenient separation and storage.

Perhaps the largest potential for noble-gas compounds lies in their exploitation as clean oxidative or substitutive reagents. The exceptional oxidizing properties of KrF_2 have already been remarked upon. Even Xe(II) is an unusual oxidizer as the ready generation of the SO_3F radical indicates:

$$XeF_2 + 2HSO_3F \rightarrow Xe\uparrow + 2HF + 2SO_3F \leftrightarrows S_2O_6F_2$$

Since the reduction product is a 'relatively inert' gas the noble-gas compounds behave almost as ligand radical sources and the noble-gas leaves the reaction system:

$$N\text{-}L_x + \text{Reactant} \rightarrow \text{Reactant } L + N\uparrow$$

or

$$2N\text{-}L_x + xHA \rightarrow xAL + xHL + 2N\uparrow$$

The interaction of XeF_2 with aromatic hydrocarbons [18] promises to be a convenient source of aromatic fluorocarbons, e.g.,

$$XeF_2 + C_6H_6 \rightarrow Xe\uparrow + C_6H_5F + HF$$

Of course, the noble-gas, expelled from the reaction may be collected and recycled.

Perhaps the greatest scope for new compounds lies in the preparation of NL^+ salts. Thus it is possible that ArF^+ salts could be prepared (the cation is bound [16]) but a major difficulty is presented in finding a counter-anion which will withstand the enormous electron affinity of the cation. It is probable that a variety of XeL^+ species (with L ranging from aromatic hydrocarbons to inorganic radicals like $-SF_5$) can be prepared. Such species would be powerful electrophilic reagents and one can anticipate that ingenious chemists will respond to the challenge of their synthesis.

ACKNOWLEDGMENT

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Was born in 1932 and received his training in chemistry at King's College, Newcastle-upon-Tyne. After a year as senior chemistry master at the Duke's School, Alnwick, Northumberland, he joined the faculty of The University of British Columbia. In 1966 he was appointed a Professor of Chemistry at Princeton University where he served until 1969 when he accepted his present appointments as Professor of Chemistry in The University of California at Berkeley and Principal Investigator in The Inorganic Materials Research Division of The Lawrence Berkeley Laboratory. His prime research interests are in inorganic fluorine chemistry, particularly the relationship between structure and bonding.

TABLE I: A selection of Noble-Gas compounds* to illustrate known oxidation states and ligands. [2]

Noble-Gas and Oxidation State	Ligands			
	Fluorides	Oxyfluorides	Oxides	Other
Kr +2	KrF_2			
Xe +2	XeF_2			$FXeOR^{\dagger}$ $Xe(OR)_2$
+4	XeF_4			F_3XeOR'
+6	XeF_6	$XeOF_4$ XeO_2F_2	XeO_3	F_5XeOR'
+8		XeO_2F_4 XeO_3F_2	XeO_4	
Rn +2(?)	RnF_2			

* Available in macroscopic quantities.

‡ -OR includes $-OTeF_5$, $-OSO_2F$, $-OClO_3$, O_2CCF_3 and OSO_2CF_3. -OR' = $-OSO_2F$

† The molecular structure of $FXe-OSO_2F$ is illustrated in Figure 1.

TABLE II: Atomic radius and first ionization potential for each Noble-Gas [2]

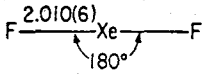
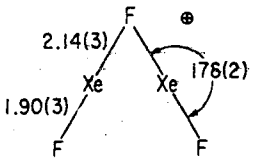
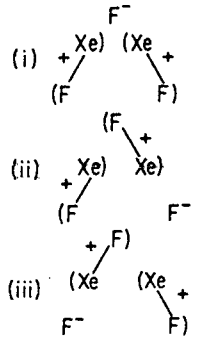
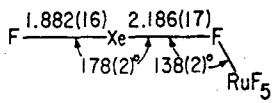
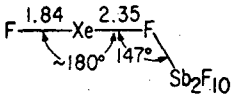
Noble-Gas	He	Ne	Ar	Kr	Xe	Rn
Radius (Å)	1.3	1.6	1.92	1.98	2.18	--
First Ionization Potential (eV)	24.586	21.563	15.759	13.999	12.129	10.747

TABLE III: Mössbauer data for the xenon halides.* [7]

Halide	Splitting (mm/sec.)	$e^2 q Q_{exc}$ (MHz)	5p Electron transfer	Electron transfer per bond
XeF_4	41.04 ± 0.07	2620	3.00	0.75
XeF_2	39.0 ± 0.1	2490	1.43	0.72
$XeCl_4$	25.6 ± 0.1	1640	1.88	0.47
$XeCl_2$	28.2 ± 0.1	1800	1.03	0.52
$XeBr_2$	22.2 ± 0.4	1415	0.81	0.41

* The bonding model assumes that the only Xe orbitals participating in the bonding are the Xe 5p orbitals.

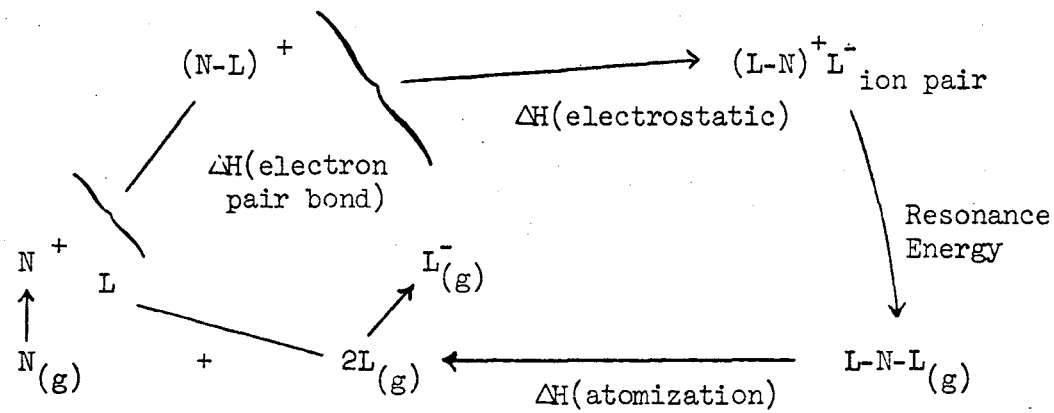
TABLE IV: Bond length and bond order in XeF_2 and its complexes with F^- acceptors.

Molecule	Possible Contributing Canonical Forms	Bond Length (Å)	Bond Order*	$\nu(cm^{-1})$
	$(F-Xe)^+F^-$; $F^-(Xe-F)^+$	2.01	0.5‡	497
	 (i) >> (ii) = (iii)	1.90 2.14	0.76 0.3	588 —
	$(F-Xe)^+(RuF_6)^-$; plus possibly, $F^-(Xe-F)^+$. RuF_5	1.88 2.2	0.83 0.2	604 —
	$(F-Xe)^+(Sb_2F_{11})^-$; plus possibly, $F^-(Xe-F)^+$. Sb_2F_{10}	1.84 2.35	0.96 0.13	621 —
XeF^+		1.83	1.0	

*From the Pauling equation $r(n/2) = r(1) - 0.60 \log n/2$. [10]

‡Assumed value.

TABLE V: Estimation of the heat of atomization of a noble-gas dihalide, NL_2 (Values in kcal $mole^{-1}$

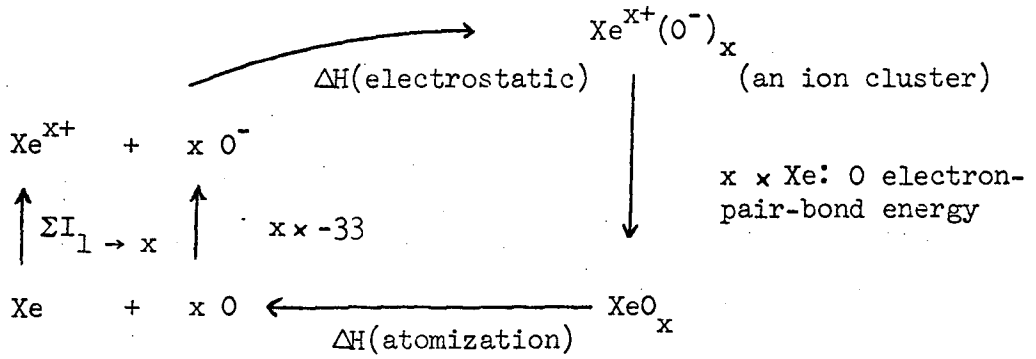


← Experimental Quantities →					Resonance energy assumed constant	ΔH(atomization)[2]	
Molecule	I(N)	$\Delta H(L + e \rightarrow L^-)$	$\Delta H(N^+ + L \rightarrow (N\text{-}L)^+)$[13]	ΔH(electrostatic)*		from cycle	observed
XeF_2	280	-80	-47	-166	-52	65 assumed	65
KrF_2	312	-80	-37	-176	-52	33	23
ArF_2	342	-80	-38	-195	-52	23	Molecule not known
$XeCl_2$	289	-83	-40(est.)	-138	-52	32	†

* The ΔH(electrostatic) is estimated as the attraction energy ($E = -e^2$/estimated or observed N-L distance).

† The bond stretching force constant for $XeCl_2$ = 1.3 and that for XeF_2 2.6 mdynes $Å^{-1}$.

TABLE VI: An estimate of the relative stabilities of the xenon oxides (values in kcal $mole^{-1}$)



Molecule	$\Sigma I_{1 \to x}$	$\Delta H(xO^-)$	ΔH(electrostatic)*	Electron-pair† -bond energy x(Xe:O)	ΔH atomization Cycle	ΔH atomization Observed[2]
XeO_4	2520	-132	-2320	-152	=obs.	-84
XeO_3	1507	- 99	-1339	-114	- 45	≈ -50
XeO_2	768	- 66	- 634	- 76	- 8	——
XeO	280	- 33	- 176	- 38	+ 33	——

* Estimated as the point charge attraction energy using observed (or where necessary) estimated interatomic distances.

† The electron-pair-bond energy for the Xe:O bond was obtained from the cycle for the XeO_4 case and the unit energy (-38 kcal $mole^{-1}$) then used for all other cases.

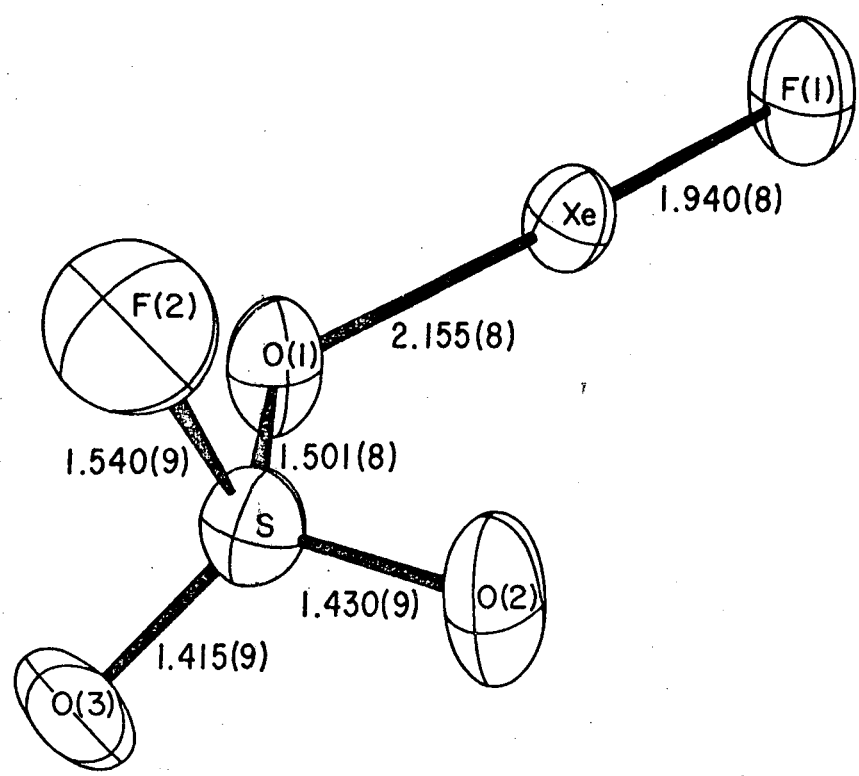


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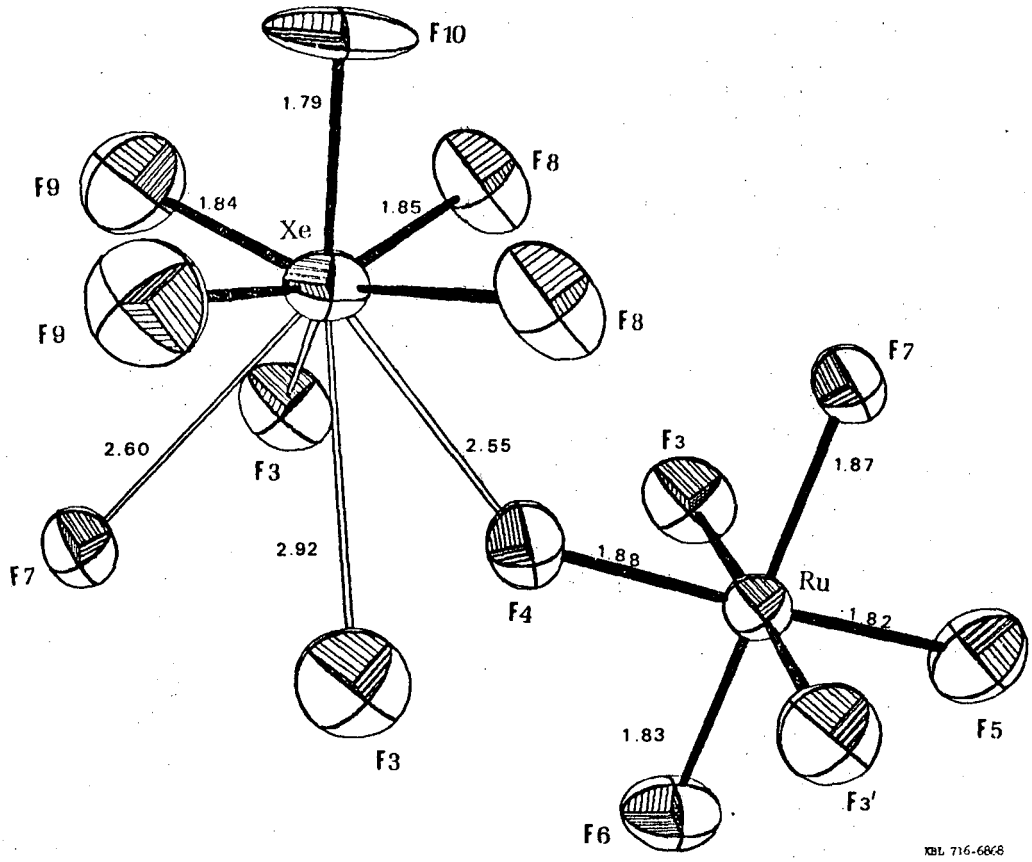
Figure 1: The Molecular Structure of $FXeOSO_2F$ [2]



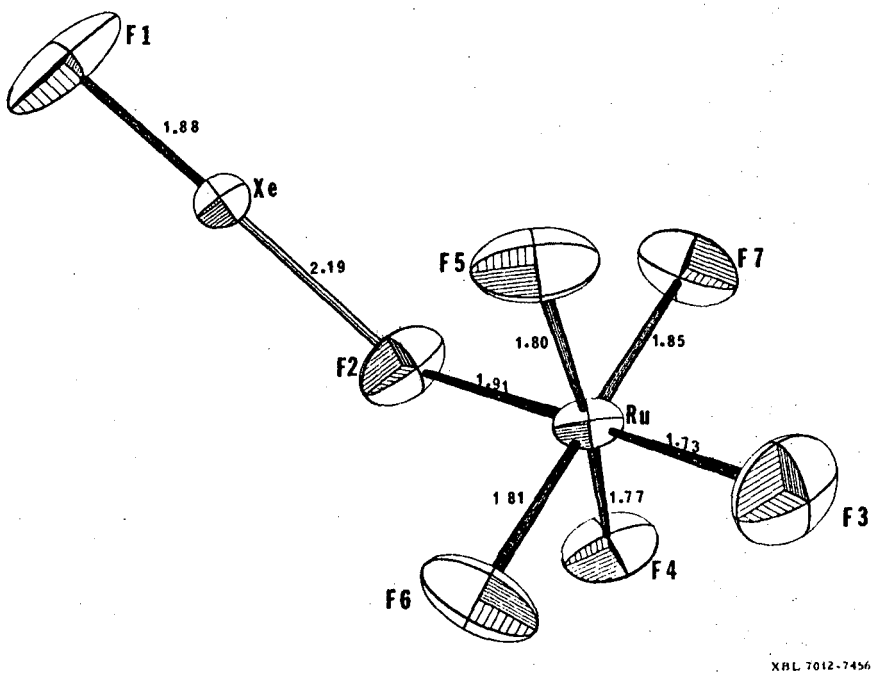


Figure 2 - Structural features of $FXeFRuF_5$ and $XeF_5^+RuF_6^-$ [17].
(Attempts to prepare a $XeF_4 \cdot RuF_5$ complex have failed)

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