

"Noble-Gas Chemistry and The Periodic System of Mendeleev"

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The Stable Noble-Gas Electron Configuration

When, in 1962, chemists were informed that a compound of a noble-gas had been prepared¹, there was much expression of surprise and initially even disbelief.

Faith in the chemical inertness of the noble gases had been fostered in part by previous failures to prepare compounds. The greatest prejudice, however, derived from the electronic theories of the chemical bond, which stressed the noble-gas electron arrangement as the ideal to which all other atoms tended.

When the noble gases were discovered², in the last years of the 19th Century, they were quickly recognized as a new Group of elements of Mendeleev's Table of The Elements. This new Group of elements fitted naturally into the "Table", each noble-gas being located between a halogen and an alkali metal. Since the Halogens included the most strongly oxidizing elements, whereas the Alkali Metals were the most strongly reducing elements of the Periodic Table, it was appropriate, for the intervening group of elements, to exhibit neither oxidizing nor reducing properties, i.e. to be chemically unreactive. All efforts to oxidize or reduce helium and argon (i.e. to bring them into chemical combination with other elements) failed², perhaps the most significant failure being Moissan's attempt in 1895 to prepare an argon fluoride³. The rarer noble gases were not subjected to the same intensive chemical investigation, and no claim for chemical activity of the gases was sustained prior to 1962.

When the electronic theories of chemical bonding were developed it was natural that the chemical inertness of the noble gases should be expressed in the theory. In their pioneering papers of 1916, both W. Kossel⁴ and G. N. Lewis⁵ emphasized the ideality of the noble-gas configuration. An atom of an element other than a noble-gas was represented as gaining or losing electrons until its electron arrangement resembled that of a neighbouring noble-gas atom.

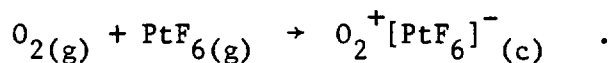
The Kossel and Lewis theories unified and correlated much of what was then known of the bonding capabilities of the chemical elements. The theories quickly had wide appeal. Since the electron arrangements of the noble gases were evidently the ideal arrangements, to which all other atoms aspired, the chemical inertness of the gases was self evident, at least at a superficial level of inspection. Unfortunately in the inevitable shorthand of convenient description, the noble-gas electron arrangements were usually represented by the group term "octet", this being (except in helium, which possesses a "duet") the outermost set of electrons of the noble-gas atom. This "octet" concept helped to foster the illusion that all noble-gas electron configurations are essentially the same and of the same stability. They are not.

Discovery of The First True Chemical Compounds of The Noble Gases

From trends based upon the Periodic Table several chemists had predicted chemical activity for the heavier noble gases. Thus Kossel, in harmony with his emphases of complete electron transfer as the key to

chemical bonding, pointed out⁴ that the ionization potentials of the noble-gases decreased with atomic weight and that fluorides of xenon or even krypton might therefore be possible. On the basis of a survey of the chemical trends evident in the Periodic Table at that time, L. C. Pauling in 1933 suggested⁶ that xenon and krypton compounds should be preparable. (He predicted that XeF_6 , KrF_6 should exist and that XeF_8 might exist). Pauling obtained a sample of Xenon⁷ for his colleague D. M. Yost to attempt the synthesis of a xenon fluoride. That attempt failed.⁸ This failure, along with the success of the simple electronic theories of valence (which emphasized the importance of the stability of the noble-gas electron configuration), contributed to a general acceptance of the complete chemical inertness of the gases.

Of prime importance to the discovery of the chemical activity of the heavier noble gases was the discovery⁹ by Bartlett and Lohmann of the remarkable oxidizing properties of the gaseous compound platinum hexafluoride. In 1962 they had established that a red solid, prepared by burning platinum or platinum compounds in fluorine in glass apparatus was the salt, dioxygenyl hexafluoroplatinate, $\text{O}_2^+[\text{PtF}_6]^-$. This salt was especially noteworthy for its cation, O_2^+ . The salt formulation implied that the free hexafluoride (which had previously been reported, in 1957, by Weinstock, et al.¹⁰ of The Argonne National Laboratory) should be capable of spontaneously oxidizing molecular oxygen. This subsequently proved to be so:



The two gases combined immediately to provide the now familiar salt $O_2^+[PtF_6]^-$. Although the salt formulation had seemed appropriate much earlier in the investigation, it had posed the difficulty that in order for the oxidation of molecular oxygen to proceed spontaneously, the electron affinity for the platinum hexafluoride,

$$E = -\Delta H(PtF_6(g) + e \rightarrow PtF_6(g)^-)$$

needed to be much greater¹² than $160 \text{ kcal/mole}^{-1}$ (that is, approximately twice the value for atomic fluorine or atomic chlorine). With the spontaneous oxidation of oxygen and the salt formulation proved, it was clear that platinum hexafluoride was the most powerful oxidizer that had been discovered. At this point, Bartlett (who was not aware of Kossel's earlier related observation) noted that the ionization potentials of the noble gases decreased markedly, with increasing atomic number as shown in Table I.

It was evident that the heavier gases should be more easily oxidizable than the lighter.¹³ Most importantly, the ionization potentials of xenon (12.2 eV) and radon (10.7 eV) were as low as, or lower than, molecular oxygen (12.2 eV). Radon being difficult to handle as a consequence of the short life and α -particle activity of all of its isotopes, the oxidation of xenon appeared to be the easiest noble-gas oxidation to carry out.

Xenon gas proved to be as easy to oxidize as molecular oxygen. An orange-yellow solid formed rapidly in the spontaneous gas-gas reaction as described in Figure 1. The product was designated xenon hexafluoroplatinate $Xe^+[PtF_6]^-$. Subsequent work¹⁴ showed that the $Xe + PtF_6$ interaction is more complicated. The compound $XePtF_6$ is obtained in high purity only when a

large excess of xenon is employed.¹⁵ When xenon has an opportunity to interact with excess PtF_6 the overall reaction is: $\text{Xe} + 2\text{PtF}_6 \rightarrow \text{XeF}^+\text{PtF}_6^- + \text{PtF}_5$.

When the report of the oxidation of xenon by platinum hexafluoride appeared the reaction was immediately repeated at the Argonne National Laboratory where PtF_6 and its relatives had first been prepared and studied. There, the PtF_6 oxidation of xenon was repeated and extended to the related hexafluorides ruthenium hexafluoride and plutonium hexafluoride.¹⁶ The ruthenium hexafluoride-xenon study proved to be highly revealing. It was clear from the appearance of the characteristic green color of ruthenium pentafluoride that the red hexafluoride was losing fluorine. It could only be lost to the xenon. Xenon fluorides, it was reasoned, ought to exist.

The first xenon fluoride to be reported¹⁷ was the tetrafluoride prepared by Claassen, Selig and Malm of the Argonne National Laboratory. Ironically, Bartlett and Jha soon discovered¹⁸ that the pyrolysis of $\text{Xe}(\text{PtF}_6)_x$ ($1 < x < 2$) at 165° also yielded XeF_4 . More recently¹⁴ this has been shown to derive from the decomposition of $\text{XeF}^+\text{PtF}_6^-$ according to the equation: $2 \text{XeFPtF}_6 \rightarrow \text{XeF}_4 + \text{XePt}_2\text{F}_{10}$ (the last compound being a diamagnetic Pt(IV) compound: $(\text{XeF})_n^+[\text{Pt}_2\text{F}_9]_n^-$). Independently of the work at the Argonne National Laboratory, study of the xenon-fluorine system by Hoppe and his coworkers¹⁹ in Giessen, Germany, led to the isolation of a difluoride. Within a few weeks the fluorides XeF_2 , XeF_4 , XeF_6 and the

oxyfluoride XeOF_4 were known. Within nine months of the first report of XePtF_6 the first conference on Noble-Gas Chemistry was called and met at The Argonne National Laboratory. More than fifty papers were contributed in the two day meeting and the proceedings subsequently appeared as a 400 page volume.¹⁸

The Extent of Noble-Gas Chemistry

In the twenty years which have elapsed since the first synthesis of a chemically bonded noble-gas compound the possible range of noble-gas chemistry has become well defined. The known oxidation states and representative ligands are illustrated in Table 2. The requirements for noble-gas compound formation are: (1) the noble-gas atom must be a larger (more easily oxidizable) atom (Rn, Xe, Kr) and (2) each atom attached to a noble-gas atom must be highly electronegative, either intrinsically or as a result of electronegative groups linked to it.

It is clear that chemical bonding of the noble gases depends upon a larger more oxidizable noble-gas atom yielding valence shell electrons to ligands which are themselves striving for a valence electron octet. The small highly electronegative fluorine ligand is the most effective ligand. Evidently the great stability of the Ne electron configuration induces a sharing of the Kr, Xe or Rn valence-shell electrons with the F ligand, which thus attains that configuration. The oxygen ligand is inferior in electronegativity to the F ligand, but it does have the capacity to accept two electrons to meet the Ne electron configuration. Thus oxygen can and does form stronger bonds to xenon than fluorine.

The O ligand's inferior electronegativity and the great strength of the O₂ bond (ΔH° atomization = 119 kcal mole⁻¹) relative to that of F₂ (ΔH° atomization = 38 kcal mole⁻¹), however, render oxides less stable thermodynamically than fluorides.²⁰ Indeed it is the extraordinary weakness of the F₂ bond, in combination with the small size and high electronegativity of the F ligand, which result in its being the most thermodynamically favorable ligand for binding to any atom.

The substituted O, N and C ligands are only effective when the substituents are highly electronegative. In effect the substituted O, N and C mimic the small electronegative F ligand.

The lower electronegativity and greater size of the halogens heavier than fluorine contribute to their inferiority to F as ligands. Noble-gas compounds derived from the heavier halogens, even the chlorides, are stable only at temperatures well below room temperature.

Only the highly electronegative OTeF₅ ligand has so far revealed²¹ a range of chemistry (for Xe) comparable with that excited by the F ligand. Even it is inferior to F however and it is now apparent that the compound forming ability of F ligand (at least as far as the noble gases are concerned) is unlikely ever to be surpassed. On this basis it is possible to say that neutral compounds of argon or the lighter gases are unlikely to be made at ordinary temperatures and pressures. Similarly higher oxidation states than +2 are unlikely to be attained with krypton. Even other Kr(II) compounds will severely test synthetic expertise since the

difluoride is itself thermodynamically unstable,²² with the weakest bond known for any fluoride available in macroscopic quantities.

A greater range of ligands can be anticipated for radon than is presently known. A fluoride described as RnF_2 has long been known.¹⁸ A possible tetrafluoride and an oxide believed to be RnO_3 have recently been described.²³ Ligands which are effective for xenon should also be suitable for radon. The radioactivity of all isotopes imposes great experimental difficulties however.

To give a more quantitative evaluation of the range and limitations of noble-gas chemistry it is of value to consider some simple bonding models and energetics.

Bonding in Noble-Gas Compounds

As we have seen the phenomenological evidence in Table 2 implies that bonding of noble-gas atoms, N, to other atoms is associated with the removal of electrons from N. Mössbauer²⁴ and ESCA²⁵ studies have established high bond polarity in the xenon and krypton compounds. Since N^+ is a pseudo-halogen atom, $(\text{N-L})^+$ is expected to resemble its isoelectronic halogen relative. Thus XeF^+ ought to resemble IF . Similarly XeF_2 ought to resemble IF_2^- and have a generic relationship to such well known species as ICl_2 and I_3^- .

The simple molecular orbital representation^{26,27} for NL_2 uses the scheme set out in Figure 2. Since the non-bonding molecular orbital has no component from the noble-gas atom the pair of electrons in that orbital reside entirely on the ligands. The bonding of the two ligands

derives from the two electrons in the bonding orbital. This model is therefore equivalent to the single-electron bond model²⁸ and to representation²⁹ as the resonance hybrid of the canonical forms $\{(L-N)^+L^-; L^-(N-L)^+\}$. An advantage of the last bonding model is that it allows a rough estimation of the thermodynamic stability of NL_2 to be made. Examples of such evaluations are illustrated in Table 3, where the enthalpy of atomization (i.e. total bond energy) of NL_2 species is related to the first ionization potential of N, the energetics of $(N-L)^+$ bond formation³⁰, the energy of formation of the ion pair $(L-N)^+L^-$, the resonance energy, and the electron affinity of L. With the known total bond energy of XeF_2 used to fix the value for the resonance energy for each of the fluorides, the total bond energy of KrF_2 is calculated to be 22 kcal mole⁻¹. This is in excellent agreement with experiment. A similar evaluation for ArF_2 shows that it cannot be bound with respect to ground state atoms. The major cause of ArF_2 instability is the high ionization potential of argon. Since the first ionization potential of radon is 248 kcal mole⁻¹ (i.e. 32 kcal mole⁻¹ less than that of xenon) it is probable that the total bond energy of RnF_2 will be correspondingly greater than that of XeF_2 .

From such an evaluation it is evident that large anions are less favorable than small because of the adverse impact which the greater charge separation has upon the electrostatic energy of ion-pair formation. A high electron affinity is also necessary. For such reasons the larger halogen atoms, and all but the least oxidizable complex species, are unsatisfactory ligands for the formation of bonds to noble-gas atoms.

The small size, high electronegativity and electron-pair accepting capability of the oxygen atom, combine to make it a satisfactory ligand for the xenon atom in high oxidation states. The same may also be true for radon.²³ From the data in Table 4, a simple electrostatic evaluation provides a satisfactory accounting for the observed trends in stability of the xenon oxides. This assumes that each oxygen-atom ligand accepts a share in one xenon valence-electron pair, i.e. $\text{Xe:} \rightarrow \text{O}$. Indeed, ESCA studies²⁵ indicate that the negative charge on O ligand in XeOF_4 is approximately twice that of the F ligands. The shorter bond length³¹ and greater force constant³² for the XeO bonds in XeO_3 (Xe-O = 1.76 Å, fr = 5.66 m dyn Å⁻¹) relative to those³³ for the Xe-F bonds in XeF_6 (Xe-F = 1.89 Å, fr = 3.3 m dyn Å⁻¹) fit the representation of Xe-O as an electron pair bond, if the Xe-F bond is a single electron bond. However, the mean thermochemical bond energies for XeF_6 and XeO_3 are respectively^{20,34} 31 and ≤ 21 kcal. Mean thermochemical bond energies are defined with respect to molecules and atoms in ground states. A more appropriate valence state for an oxygen atom to accept an electron pair from xenon, (i.e. $\text{Xe:} \rightarrow \text{O}$) would be $^1\text{D}(\text{O})$. Since ^1D oxygen atom is 45 kcal mole⁻¹ more energetic³⁵ than $^3\text{P}(\text{O})$, we therefore evaluate the intrinsic bond energy per Xe-O linkage, formed from ground-state Xe and $^1\text{D}(\text{O})$ to be ≤ 66 kcal mole⁻¹. This is in much more satisfactory accord with the value of 31 kcal mole⁻¹ for the Xe-F linkage.

The Group Relationships of Noble-Gas Compounds

In the highly selective and brief review which follows, of the compounds of noble-gases and their reactions, the emphasis will be on trends and relationships within the Group and across Periods of the Periodic Table. For fuller information on which this sketch is based the reader is referred to more detailed reviews. Work to 1971 was reviewed by Bartlett and Sladky.³⁶ The comprehensive review by Legasov and Chaivanov³⁷ is more up to date. Stein³⁸ has recently made a detailed assessment of radon chemistry to early 1981.

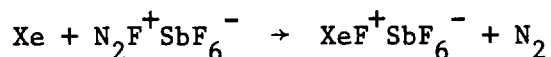
The ease of oxidation of the noble gases follows that indicated by the ionization potentials (Table 1). The trend is the same as for the oxidative chemistry of the halogens with which, as we shall see, the chemistry of the noble-gases has much in common. Radon³⁸ is the easiest of the noble-gases to oxidize and reacts spontaneously with gaseous fluorine at room temperature and even with liquid fluorine at -195° (activation energy coming from the intense α - radiation). It also interacts spontaneously at 20° with solids containing the moderate oxidizers IF_6^+ , ClF_2^+ , or BrF_2^+ . The reactions are assumed to form RnF^+ salts, e.g.:



Such solids do not oxidize the lighter noble gases. Indeed XeF^+ salts oxidize iodine pentafluoride according to the equation:³⁹



Reagents which oxidize xenon, also oxidize radon but by using the moderate oxidizers (IF_6^+ etc.) in an initial scrubbing of mixed gases, the radon alone can be oxidized. Stronger oxidants such as $\text{O}_2^+\text{SbF}_6^-$ or $\text{N}_2\text{F}^+\text{SbF}_6^-$ can then be used⁴⁰ to oxidize the xenon:



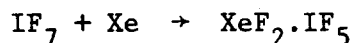
Thus separation of Rn, Xe and Kr ternary mixtures can be achieved by successive oxidation of radon and xenon. To oxidize krypton it is essential to have a source of atomic fluorine and efficient quenching of products to low temperatures.

Because of greater ease of oxidation of radon relative to xenon, Stein has pointed out that an extensive chemistry could be expected.³⁸ The compounds RnF_4 , RnF_6 , RnCl_2 , RnCl_4 , RnO , RnO_2 , RnO_3 and RnOF_4 all appear to be possible. Until recently it seemed that this was not to be, but Avronin and his coworkers²³ have found that a higher fluoride than the difluoride exists. It could be either a tetrafluoride or a hexafluoride. The hydrolysis of the new fluoride yields an oxide, which behaves as though it is RnO_3 . Early attempts⁴¹ to prepare a chloride failed but other synthetic approaches should be explored before the non-existence of radon chlorides is accepted.

The weakness of the bonding in KrF_2 results in that fluoride being a more effective source of F ligands than the F_2 molecule itself. It can oxidize xenon to the hexafluoride: $3 \text{KrF}_2 + \text{Xe} \rightarrow \text{XeF}_6 + 3 \text{Kr}$. It should be the most effective reagent for higher fluorides of radon. In

contrast the fluoride of radon, which Stein has persuasively argued³⁸ is RnF_2 , is not reduced by hydrogen until 500° , and at a hydrogen pressure of 800 torr.

The energetics of formation of the cations $(\text{Ar-F})^+$, $(\text{Kr-F})^+$ and $(\text{Xe-F})^+$, given in Table 3, parallel the bond energies³⁰ for Cl-F , Br-F and I-F , as does the oxidizing power. Unfortunately salts of $(\text{Ar-F})^+$ are not known and there is no clear evidence to encourage us to believe that an anion will be found to stabilize the cation. Since there is effectively no bonding in ArF^+ , the electron affinity of $(\text{ArF})^+$ is equal to the ionization potential of Ar , less the energy associated with the process: $\text{Ar}_{(g)}^+ + \text{F}_{(g)} \rightarrow (\text{ArF})_{(g)}^+$. This gives a value for $E(\text{ArF})^+ \approx 325$ kcal mole⁻¹. The electron affinity of $(\text{KrF})^+$ is less (≈ 280) but, even so, salts of this cation are remarkably effective oxidizers and have provided efficient syntheses for BrF_6^+ salts.⁴² KrF^+ also oxidizes³⁹ O_2 to O_2^+ , whereas O_2^+ will oxidize³⁸ Xe to XeF^+ . The XeF^+ cation, as befits its lower electron affinity is much less powerful than KrF^+ , but as has been remarked, it is effective in the synthesis of IF_6^+ . This is in spite of the oxidation of xenon⁴³ by IF_7 at 200° :



Periodic Relationships

Comparison of the XeF_2 bonding with that of $(\text{XeF})^+$ illustrates the difference between single-electron bonding and electron-pair bonding. Similar differences are observed in the molecules ClF_3 and BrF_3 (see

Table 5). Indeed the formation of the trifluorides, by the attachment of two F ligands to the heavy halogen of the monofluoride, is equivalent to the formation of the noble-gas difluorides from the noble-gas atom. In much the same way the pentafluorides are related to XeF_4 . The closest relationships, however, involve isoelectronic species of the same period.

The nearly octahedral hexa-oxospecies of antimony, tellurium, iodine and xenon (see Table 5) reveal the central-atom element in the highest attainable oxidation state (in which all valence electrons are involved in bonding). The general decrease in E-O bond distance from Sb to Xe correlates, as expected, with the increasing nuclear charge of E. The molecular oxide XeO_4 is slightly smaller than IO_4^- , as is XeO_3 compared with IO_3^- . The preferred stability of XeO_4 and XeO_3 over XeO_2 and XeO (Table 4) is strikingly similar to the iodine oxyanion system, where IO_3^- and IO_4^- are also favored.

The EF_5 species shown in Table 5 provide the most precisely described isoelectronic series for the comparison of a noble-gas compound (XeF_5^+) with its relatives. One observes that the more polar bonds (the E-F equatorial are 'single-electron' bonds) show a greater shortening, with increasing nuclear charge of E, than do the E-F axial bonds (in which, as a consequence of the electron pair bond, the polarity is likely to be slight). The most remarkable feature of the geometry is, however, the almost constant bond angle F axial-E-F equatorial. Such similarities have been noted elsewhere.⁴⁴ Thus PF_3 and SF_3^+ have the same bond angle

($97.5 \pm 0.5^\circ$) yet there are significant differences from Period to Period, as the data for ClF_3 , BrF_3 and XeF_3^+ also show. Evidently the orbital hybridization at E does change from Period to Period but very little within a Period. Such observations imply that the s and p valence-orbital energy separations change little across a Period but significantly from Period to Period in such fluorospecies.

The existence of IF_7 raises the possibility of the existence of the molecules XeF_8 and XeOF_6 . There is no convincing evidence for either as long lived species at ordinary temperatures and pressures. Huston has recently pointed⁴⁵ to the evident instability of the latter: $\text{XeOF}_6 \rightarrow \text{XeF}_6 + \frac{1}{2}\text{O}_2$. He has succeeded in synthesizing such xenon (VIII) oxyfluorides as XeO_2F_4 and XeO_3F_2 . It seems that the difficulty with XeF_8 and XeOF_6 is the very unfavorable energy associated with coordination numbers beyond six. The major cause of this must be the limited orbital set (s and p) available for bonding at the central atom. Ligand crowding may also have an impact. Even in IF_7 (as seen in its ability to oxidize Xe) the bond energy is markedly lower than in the iodine fluorides.²⁰ One notes also that XeF_6 , when represented with a sterically active non-bonding valence electron pair is also hepta coordinate. Both XeF_6 and IF_7 are good fluoride ion donors and superior in that respect to their lower fluoride relatives (XeF_4 and IF_5). Indeed the molecules approach ion-pair behavior: XeF_5^+ and IF_6^+F^- . Octahedral coordination is favored by both the Xe(VI) and I(VII).

It should now be evident that there is no qualitative difference between the bonding in noble-gas compounds and that observed in other high

oxidation state compounds of the non-transition elements. More surprisingly perhaps there also appears to be little difference from related compounds of the transition elements.

Compounds of the transition elements and the non-transition elements of the same group number are most alike in the highest oxidation states and least alike in the lowest oxidation states. Similarities of XeO_4 with OsO_4 and XeF_6 with OsF_6 may be seen from the data given in Table 6, where similarities of ReF_7 with IF_7 and TeF_6 with WF_6 can also be seen. This suggests that in the high oxidation states the involvement of d orbitals (outer d for the non-transition elements and inner d for the transition elements) in the molecular orbitals, may be approximately the same. Presumably the orbital-contracting influence of the highly electronegative ligands in the high oxidation states is sufficient to bring the 5 d orbitals into an effective bonding role in XeO_4 or XeF_6 , whereas in OsF_6 and OsO_4 , those same influences are rendering the 5 d orbitals less effective in bonding than they are in lower oxidation states.

Future Possibilities for Noble-Gas Chemistry

As we have seen, an extension of noble-gas chemistry to other elements than Rn, Xe and Kr is only possible with Ar in Ar-F^+ salts. New oxidation states and a greater range of ligands than those presently known for xenon might occur for radon. It remains to be seen if the +1 oxidation state of that element is a favorable one, as has been argued by Pitzer⁴⁶ on the basis of relativistic effects which should be important for such a heavy atom.

Otherwise the extension of the chemical compounds of the noble-gases is likely to be confined to extension (with other electronegative ligands) in the known oxidation states of xenon and krypton. Because of the stronger bond in $(N-L)^+$ relative to NL_2 , salts of $(XeL)^+$ and $(KrL)^+$ might be preparable, even though the NL_2 relatives may never be made. As usual L will need to be an electronegative ligand, although the high proton affinities of the heavier noble gases⁴⁷ ($Xe \geq 6$; $Kr \geq 4$ eV) also raises the possibility of $(XeH)^+$ and $(KrH)^+$ salts being preparable. Compared with their NL_2 relatives, the NL^+ salts are not only more stable but are also more reactive (as a result of their high electrophilicity). It is in the exploitation of noble-gas compounds as reagents that we are likely to witness the greatest extension of noble-gas chemistry.

Although the very weak bond present in $(NL)^\cdot$ radicals is of importance to the efficiency of the laser emission from excited states,⁴⁸ for most chemical purposes this bond can be ignored. The $(NL)^\cdot$ radical behaves essentially as the L^\cdot radical, although N atom can also serve to carry off energy (generated in the interaction of $(NL)^\cdot$ with a substrate) as kinetic energy. Of course the NL_x compounds (particularly for $X = 2$) can be used as a route to oxidative reagents which do not contain a noble gas atom. An instance of this is the generation of the high purity peroxide $S_2O_6F_2$ (which is a source of SO_3F radicals)⁴⁹ by the sequence of reactions:⁵⁰ $XeF_2 + 2HSO_3F \rightarrow Xe(SO_3F)_2 + 2HF$; $Xe(SO_3F)_2 \rightarrow Xe + S_2O_6F_2$. An illustration of the direct application of an NL_2 compound as an L source is in the substitution of F ligands (from XeF_2)

into aromatic hydrocarbons:⁵¹ $\text{XeF}_2 + \text{C}_6\text{H}_6 \rightarrow \text{Xe} + \text{C}_6\text{H}_5\text{F} + \text{HF}$.

The most valuable reagents are likely to be the $(\text{NL})^+$ salts. In effect they act as suppliers of L^+ . The synthesis of BrF_6^+ salts is a spectacular instance⁴² of the application of such a salt (KrF^+). No doubt interaction of NL^+ with an electron-rich substrate will sometimes result in its electron-oxidation: $(\text{NL})^+ + \text{Sub} \rightarrow (\text{NL})^\cdot + \text{Sub}^+$. With salts of cations⁵² such as Xe_2^+ this may be an excellent route to novel salts ($\text{Xe}_2^+ + \text{Sub} \rightarrow 2\text{Xe} + \text{Sub}^+$) but in other cases the $(\text{NL})^\cdot$ radical will pass the L^\cdot radical to the cation: $\text{NL}^\cdot + \text{Sub}^+ \rightarrow (\text{SubL})^+ + \text{N}$. The bonding and the energetics of some noble-gas compounds mean that in certain cases (e.g. the oxides) the ligands can be provided (for interaction with substrates) in what amounts to excited states. Thus the use⁵³ of XeF_2 in aqueous solution as the oxidative reagent for conversion of bromate to perbromate, suggests the possibility of $^1\text{D}(0)$ availability, perhaps via a $[\text{XeO}]$ intermediate: $(\text{BrO}_3^- + [\text{XeO}] \rightarrow \text{BrO}_4^- + \text{Xe})$. It is possible that the xenon oxides, xenates and perxenates could be similarly exploited. Their application in oxidations as clean sources of oxygen is in any case assured.

The greatest utility of the noble-gas compounds will surely derive from the weakness of their bonds and the near-inertness of the reduction product--the noble-gas atom.

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13. Although the greater sizes of the more easily ionizable gas are somewhat disadvantageous to bond formation, this adverse size effect is much less significant than the lower ionization potentials.
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15. XePtF_6 is paramagnetic unlike XePdF_6 which is diamagnetic.¹⁴ The latter is prepared from XeF_2 and PdF_4 , whereas interaction of XeF_2 and PtF_4 under comparable conditions gives $\text{XeF}^+\text{PtF}_6^-$ (with Xe evolution). The formulation $\text{Xe}^+\text{PtF}_6^-$ is the most probable one for XePtF_6 whereas XePdF_6 is almost certainly $\text{XeF}^+\text{PdF}_5^-$ (the anion being polymeric).
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Figure 1: The Xe + PtF₆ Experiment

The first experiment was carried out in dry glass and quartz apparatus.

A small sample of PtF₆ was transferred to the quartz sickle gauge, and was allowed to vaporize in the gauge, closed by the metal valve 1. Following pressure measurement it was transferred to (b) via the break-seal by-pass which was then sealed at X. Xenon was admitted to the gauge to the same pressure as the PtF₆ sample. The sample of Xe from the gauge was condensed in (a) at -196°C and valves 2 and 1 closed to ensure a small volume. Both the Xe and PtF₆ were vaporized, then the break-seal separating them was broken with nickel balls, moved within the system by means of an external magnet. The interaction of the gases, to produce an orange solid, was immediate and the gauge showed that the residual pressure in the system was low.

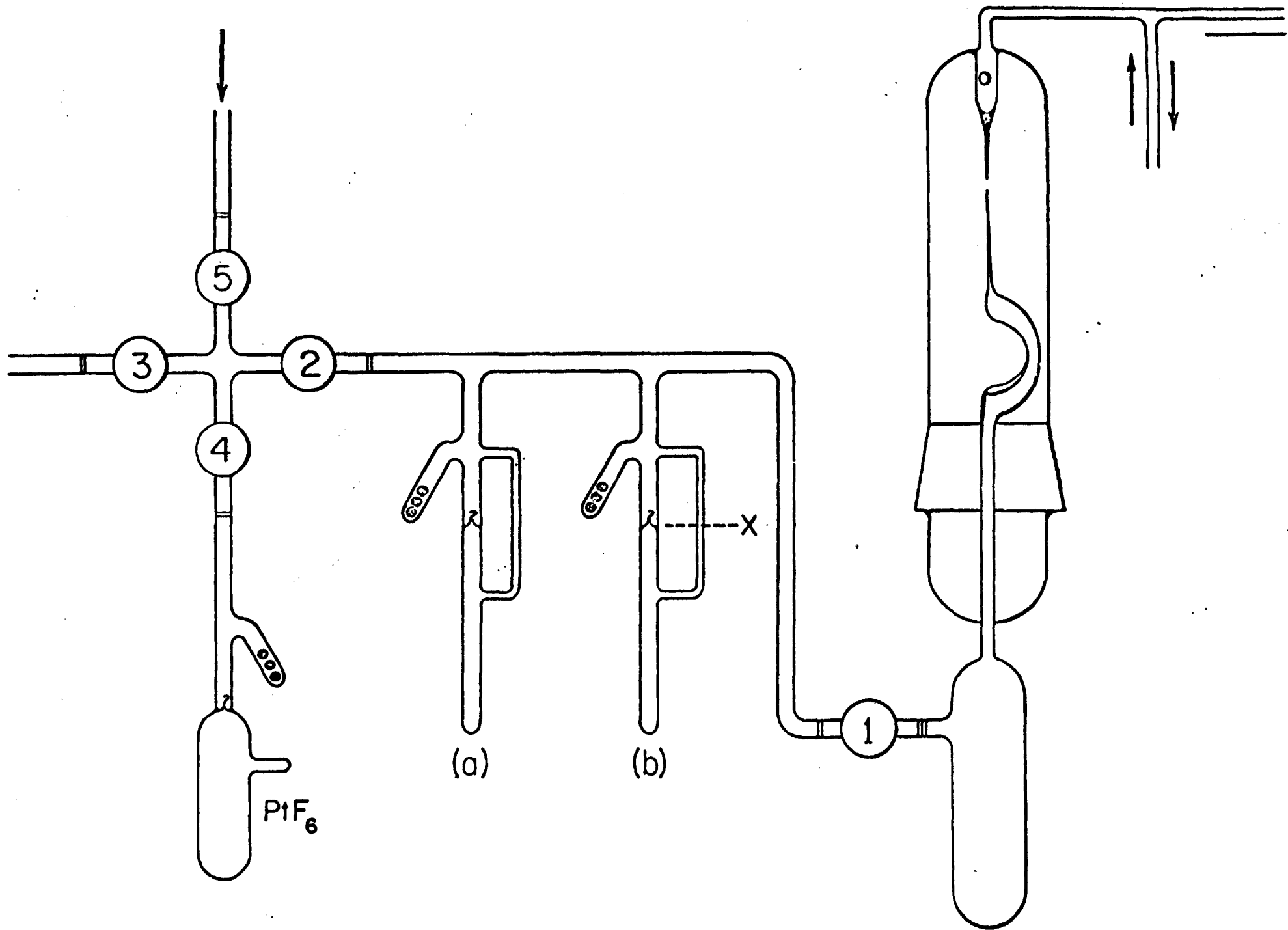


Figure 2. Simplified representation of the $p\sigma$ m.o.s. for XeF_2 .

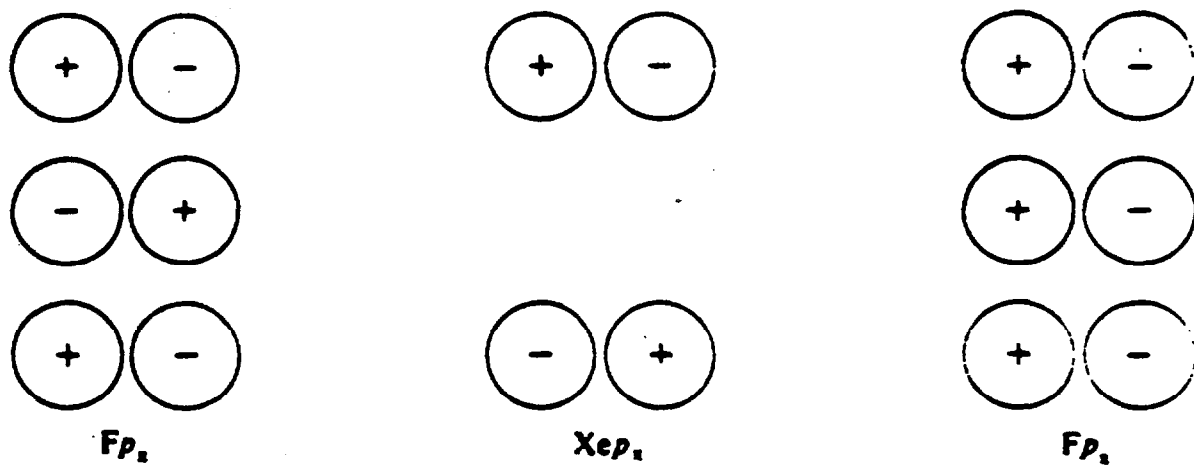


Table 1: Atomic radius and first ionization potential
for each Noble Gas ^a

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

^a G. A. Cook, ed., Argon, Helium and the Rare Gases, 2 vols., Interscience,
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Table 2: A selection of Noble-Gas Compounds* to illustrate known oxidation states and ligands.

Noble-Gas and Oxidation State	Ligands			
	Fluorides	Oxyfluorides	Oxides	Other [±]
Kr +2	KrF ₂ ^a			
Xe +2	XeF ₂ ^b			FXeOR ⁿ FXeN(SO ₂ F) ₂ ₅ ^o Xe(OR) ₂ ⁿ Xe(CF ₃) ₂ ^p Xe[N(SO ₂ F) ₂] ₂ ^o XeOR ⁺ q
+4	XeF ₄ ^c	XeOF ₂ ^g		F ₃ XeOR ^r
+6	XeF ₆ ^d	XeOF ₄ ^h XeO ₂ F ₂ ⁱ	XeO ₃ ^l	F ₅ XeOR ^r XeF _{6-x} (OR') _x ^r (x = 1 → 6)
+8		XeO ₂ F ₄ ^k XeO ₃ F ₂ ^k	XeO ₄ ^m	
Rn +2(?)	RnF ₂ ^e			
+4	RnF ₄ ^f			
or	or			
+6	RnF ₆		RnO ₃ ^f	

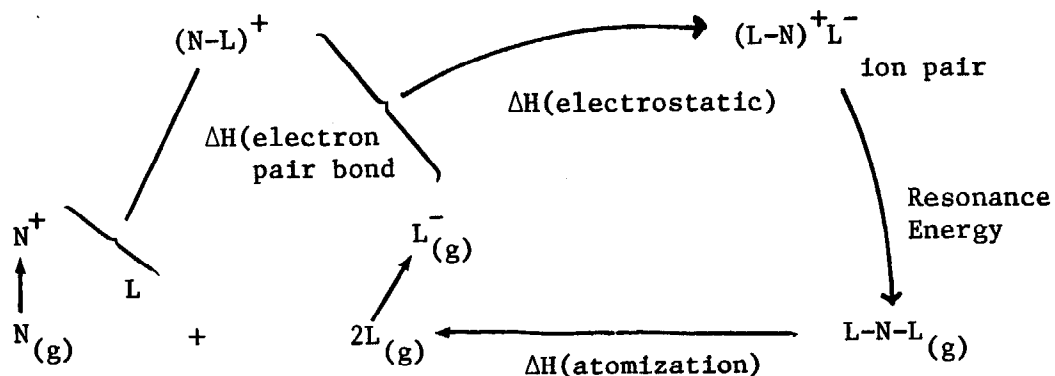
* Available in macroscopic quantities.

± -OR includes -OTeF₅, -OSO₂F, -OC1O₃, O₂CCF₃ and OSO₂CF₃. -OR' = -OTeF₅

Table 2 References

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TABLE 3: Estimation of the heat of atomization of a noble-gas dihalide, NL_2 (Values in kcal mole⁻¹)



Molecule	← Experimental Quantities →				$\Delta H(\text{electrostatic})^a$	Resonance energy assumed constant ^d	$\Delta H(\text{atomization})$	
	I(N)	$\Delta H(L + e \rightarrow L^-)$	$\Delta H(N^+ + L \rightarrow (N-L)^+)$	from cycle			observed	
XeF ₂	280	-80	-47 ^c	-166	-52	65 assumed	65	
KrF ₂	323	-80	-37 ^c	-176	-52	22	23	
ArF ₂	365	-80	-38 ^c	-195	-52	0	Molecule not known	
XeCl ₂	280	-83	-40(est.)	-138	-52	32	b	

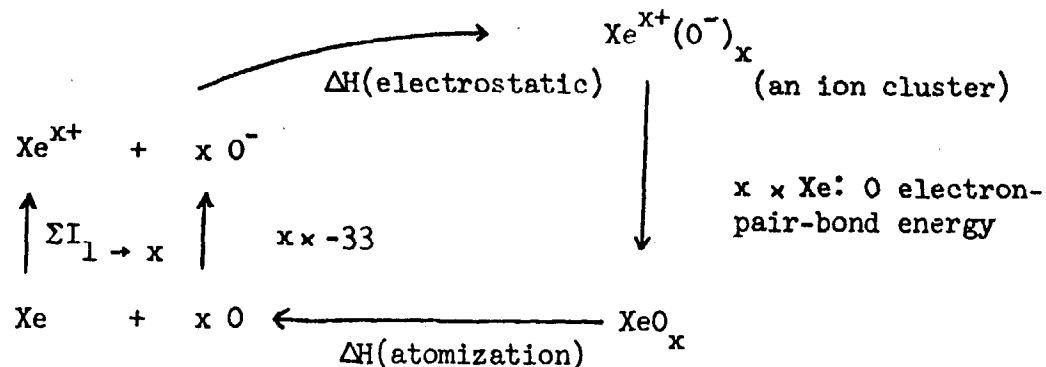
a. The $\Delta H(\text{electrostatic})$ is estimated as the attraction energy ($E = -e^2/\text{estimated or observed N-L distance}$).

b. The bond stretching force constant for XeCl₂ = 1.3 and that for XeF₂ 2-8 mdyn Å⁻¹. L. Y. Nelson and G. C. Pimentel, *Inorg. Chem.* 6, 1758 (1967).

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d. A reasonable assumption since this is an expression of the fact that the electron is delocalized over two F ligands and not localized on one.

TABLE 4: An estimate of the relative stabilities of the xenon oxides (values in kcal mole⁻¹)



Molecule	$\Sigma I_{1 \rightarrow x}^c$	$\Delta H(x\text{O}^{-})^d$	$\Delta H(\text{electrostatic})^*$	Electron-pair [†] -bond energy $x(\text{Xe:O})$	ΔH atomization Cycle	Observed ^a
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 XeO₄ case and the unit energy (-38 kcal mole⁻¹) then used for all other cases.

Table 4 References

- a ref. 34
- b It is of interest that spectroscopic studies (C. D. Cooper, G. C. Cobb, and E. L. Tolnas, J. Molec. Spectrosc., 7, 223 (1961)) indicate that XeO 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 bound by 37 kcal mole⁻¹ with respect to ³P(O), thus providing remarkable agreement with the simple calculations.
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Table 5a

EF ($C_{\infty v}$)

	XeF ⁺	IF
Bond Length(\AA)	1.84(4) ^a	1.906 ^c
$\nu(\text{cm}^{-1})$	621 ^b	610 ^d
force constant($\text{md}/\text{\AA}$)	3.7 ^b	3.6 ^e

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Table 5b

EF₂ ($D_{\infty h}$)

	KrF ₂ (g)	XeF ₂ (g)
E-F (\AA)	1.875(2) ^a	1.977(2) ^b
$\nu_1(\text{cm}^{-1})$	449 ^c	515 ^b
fr($\text{mdynes } \text{\AA}$)	2.46 ^c	2.84 ^b

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c H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, J. Chem. Phys., 42, 1229 (1965).

Table 5c

	EF ₃ (C _{2v})		
	<u>ClF₃</u> ^a	<u>BrF₃</u> ^b	<u>XeF₃⁺</u> ^c
E-F _{equatorial} (Å)	1.598(2)	1.721	1.83(1)
E-F _{axial} (Å)	1.698(2)	1.810	1.88(1), 1.89(1)
F _{ax} E-F _{eq}	87.5°	86.2°	82, 80

a D. F. Smith, J. Chem. Phys., 21, 609 (1953).

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Table 5d

EO₃ (C_{3v} symmetry)

	IO ₃ ^{-a}	XeO ₃ ^b
E-O	1.79(2)	1.76(3)
O-E-O(°)	{ 96 100 102	{ 100 101 108

- a H. Schulz, Acta Cryst., B29, 2285 (1973)
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Table 5e

EO₄ (T_d symmetry)

	IO ₄ ^{-a}	XeO ₄ ^b
E-O	1.775(7)	1.736(3)

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- b G. Gunderson, K. Hedberg, and J. L. Huston, Acta Cryst., A25S1, 124 (1969)

Table 5f

EF₅ (C_{4v} symmetry)

	SbF ₅ ²⁻ ^a	TeF ₅ ⁻ ^b	IF ₅ ^c	XeF ₅ ⁺ ^d
M-F _{ax}	1.916(4)	1.862(4)	1.817(10)	1.813(7)
M-F _{eq}	2.075(3)	1.952(4)	1.873(5)	1.843(8)
F _{ax} ^{-E-F} _{eq}	79.4(1)	78.8(2)	80.9(2)	79.2(4)

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Table 5g

EO₆ (O_h symmetry)

	SbO ₆ ^a	TeO ₆ ^b	IO ₆ ^c	XeO ₆ ^d
E-O	1.97	1.913(3)	1.888(2)	1.864(12)

a Interatomic Distances, L. E. Sutton, Ed., Chem. Soc. Special Publ. No. 11 (1958).

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Table 6

A Comparison of Some Transition and Non-Transition Element Compounds

Molecule	WF ₆	TeF ₆	ReF ₇	IF ₇	OsO ₄	XeO ₄
Symmetry	O_h (a)		$D_{5h} + ?C_{2v}, C_s$ (b,c)		T_d (d)	
E-L (\AA units)	1.833(e)	1.83(f)	---	1.825(b)	1.74(g)	1.74(h)
f_r (mdyn/ \AA)	5.1(i)	5.01(j)	---	3-4 (k)	7.14(d)	5.75(d)
ν_1 (cm^{-1})	769(a)	701(a)	736(e)	676(e)	971	906 est
T.B.E. (kcal mole ⁻¹)	121(m)	82(n)	100 est	55(o)	127(p)	21(q)

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