

Noble-gas compounds

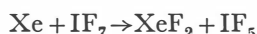
Neil Bartlett

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 since the author first wrote on the subject in this journal eight years ago. 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.

The range of known noble-gas compounds

Over the past ten years, much work has been devoted to extending the range of noble-gas chemistry, the existence of noble-gas compounds having been conclusively established by the author and other workers in 1962. The historical developments leading up to this discovery were described by the author in an earlier article [1]. However, the range of compounds that have so far been produced remains limited, as Table 1 shows [2]. The constraints may be readily discerned from an appraisal of the known compounds, which have two features in common: (1) the noble-gas atom is a heavier (more readily oxidizable) atom (Rn, Xe, Kr) than the atoms of the groups (ligands) attached to it and (2) the ligands are always highly electronegative. Both these features indicate that the removal of electron density from the noble-gas atom to the ligands is essential for effective bonding.

A sampling of the known chemistry will illustrate these remarks. In keeping with its lower ionization potential (10.6 eV), radon is more readily oxidized than xenon ($I=12.1$ eV). Radon interacts spontaneously at ordinary temperatures with fluorine or halogen fluorides (except IF_5) to give a fluoride (probably RnF_2), whereas xenon must be thermally or photo-excited in order to interact with fluorine. However, by suitably controlling the fluorination conditions for xenon, XeF_2 , XeF_4 , or XeF_6 may be prepared. Unlike radon, xenon is not oxidized by ClF_3 or BrF_3 , although it is oxidizable by iodine heptafluoride at 200°:



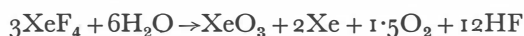
The oxidation of krypton ($I=14.0$ eV) is much more demanding, and high-energy, low-temperature methods are used to prepare the difluoride. Krypton difluoride is thermodynamically unstable (in contrast to XeF_2) and since $\Delta H_{\text{at}}(\text{KrF}_2(\text{g}) \rightarrow \text{Kr}(\text{g}) + 2\text{F}(\text{g})) = +23$ kcal mole⁻¹, whereas $\Delta H_{\text{at}}(\text{F}_2(\text{g}) \rightarrow 2\text{F}(\text{g})) = +37$ 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 we might expect 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 through Mössbauer studies in which the xenon halides were derived from the β -decay of their ^{129}I relatives thus: $^{129}\text{IBr}_2^- \xrightarrow{\beta} \text{XeBr}_2$. 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 that of fluorine, 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 tetroxide 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



Furthermore, certain alkaline solutions of $\text{Xe}(\text{vi})$ disproportionate to yield perxenate:



although the perxenate is prepared in better yield by

Table 1
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
	+4	XeF_4			$\text{Xe}(\text{OR})_2$
	+6	XeF_6	XeOF_4 XeO_2F_2 XeO_2F_4 XeO_3F_2	XeO_3	$\text{F}_3\text{XeOR}'$ $\text{F}_5\text{XeOR}'$
	+8			XeO_4	
Rn +2(?)		RnF_2			

* Available in macroscopic quantities.

† The molecular structure of FXeOSO_2F is illustrated in Figure 1.
‡ —OR includes —OTeF_5 , $\text{—OSO}_2\text{F}$, —OCIO_3 , O_2CCF_3 and OSO_2CF_3 , $\text{—OR}' = \text{—OSO}_2\text{F}$.

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Was born in 1932 and received his training in chemistry at King's College Newcastle-upon-Tyne. In 1966 he was appointed a Professor of Chemistry at Princeton University where he stayed 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 interest is in inorganic fluorine chemistry and he was the first to prepare compounds of the noble gases.

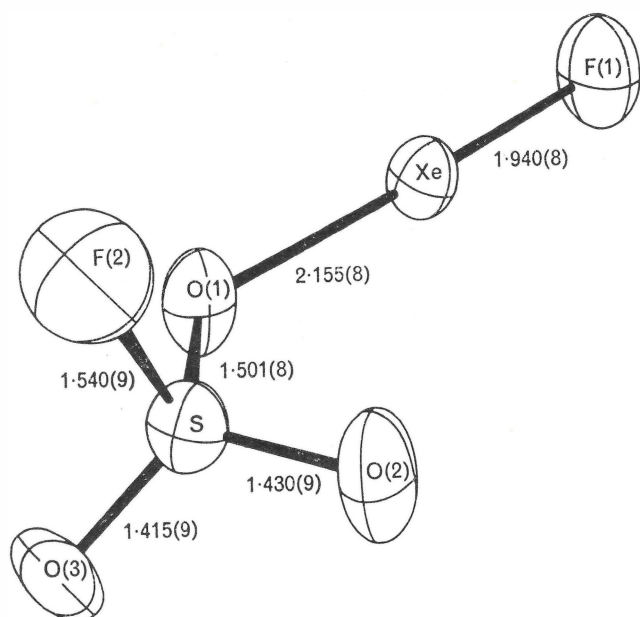
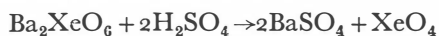


Figure 1 The molecular structure of FXeOSO_2F [2].

passing ozone through a dilute solution of $\text{Xe}(\text{VI})$ in base. Perxenate is the source for the tetroxide:



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

Since groups like $-\text{OSO}_2\text{F}$ and $-\text{OCIO}_3$ are known to be highly electronegative, it was anticipated that substitution for fluorine could be effected by interactions such as

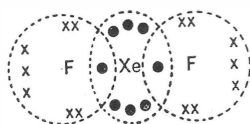


Preparations of this kind have been indicated for all three binary xenon fluorides and the xenon(II) compounds, particularly the compound FXeOSO_2F , shown in figure 1, have been well characterized. (It should be noted that the F-Xe-O arrangement in FXeOSO_2F is linear; similar geometry is anticipated for all $\text{Xe}(\text{OR})_2$ compounds.) All of these $\text{XeF}_{x-y}(\text{OR})_y$ 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, appreciable bond polarity is to be expected in noble-gas compounds: $\text{Xe}^{\delta+}-\text{F}_x^{\delta-}$ for example. 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 J. Bilham and J. W. 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, how-

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

ever, retains a (somewhat imperfect) octet configuration. The acceptability of these postulates is supported by ionization potential data, given in Table II, showing the xenon electron configuration to be less stable than the neon configuration. Neglect of this long known information was a primary reason for the slow progress of 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 $-\frac{1}{2}\text{F}-\text{Xe}^{+1}-\text{F}-\frac{1}{2}$.

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

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 ($+\text{F}-, -\text{Xe}+, +\text{F}-$); one non-bonding ($+\text{F}-, -\text{F}+$); and one anti-bonding ($+\text{F}-, +\text{Xe}-, +\text{F}-$). 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 resides largely on the fluorine ligands, the charge distribution in the molecule is effectively $-\frac{1}{2}\text{F}-\text{Xe}^{+1}-\text{F}-\frac{1}{2}$, 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 are presented

Table III

Mössbauer data for the xenon halides.* [7]

Halide	Splitting (mm/sec)	e^2qQ_{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.

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

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



the resulting cation will be an electron-pair-bond species ($:\ddot{\text{Xe}}:\ddot{\text{F}}:$) $^+$. 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 \AA reported for XeF_2 represents a bond order of 0.5 (that is, a one-electron bond), then by employing an empirical equation, given by Linus Pauling [10] which relates fractional bond order to bond length, we can predict the bond length for bond order unity. The predicted

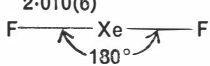
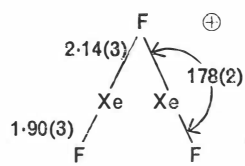
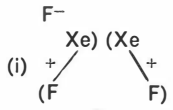
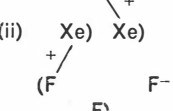
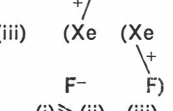
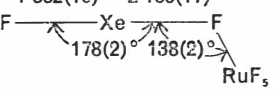
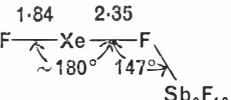
length for Xe-F^+ of 1.83 \AA is very similar to the shorter Xe-F distance in $\text{FXeSb}_2\text{F}_{11}$, which may, therefore, be formulated as the salt $[\text{FXe}]^+[\text{Sb}_2\text{F}_{11}]^-$.

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 $(\text{NL}_2)^{2+}(\text{L}^-)_2$, for example, $(\text{XeF}_2)^{2+}(\text{F}^-)_2$. Similarly, xenon hexafluoride is the resonance hybrid of $(\text{XeF}_3)^{3+}(\text{F}^-)_3$ canonical forms. Note that the ion species represented in the canonical forms are always classical octet species (that is, 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 mdyn \AA^{-1} or 10^{-16} N/m), in the series of xenon fluorides:

XeF_2 , 2.01 \AA (2.6); XeF_4 , 1.95 \AA (3.0); XeF_6 , 1.89 \AA (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 \AA and $5.66 \text{ mdyn \AA}^{-1}$, respectively; whereas for XeF_6 the corresponding values are 1.89 \AA and $3.3 \text{ mdyn \AA}^{-1}$. In the molecule XeOF_4 , the bond lengths and force constants are, for XeO, 1.70 \AA and $6.6 \text{ mdyn \AA}^{-1}$ and for

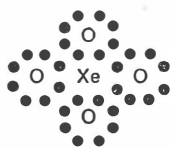
Table IV
Bond length and bond order in XeF_2 and its complexes with F $^-$ -acceptors

Molecule	Possible contributing Canonical forms	Bond length (\AA)	Bond order*	$\nu(\text{cm}^{-1})$
$2.010(6)$ 	$(\text{F-Xe})^+\text{F}^-$; $\text{F}^-(\text{Xe-F})^+$	2.01	0.5†	497
	(i)  (ii)  (iii)  (i) \gg (ii) = (iii)	1.90 2.14	0.7 ₆ 0.3	588 —
$1.882(16)$ $2.186(17)$ 	$(\text{F-Xe})^+(\text{RuF}_6)^-$; plus possibly, $\text{F}^-(\text{Xe-F})^+ \cdot \text{RuF}_6$	1.88 2.2	0.8 ₃ 0.2	604 —
1.84 2.35 	$(\text{F-Xe})^+(\text{Sb}_2\text{F}_{11})^-$; plus possibly, $\text{F}^-(\text{Xe-F})^+ \cdot \text{Sb}_2\text{F}_{10}$	1.84 2.35	0.9 ₆ 0.1 ₃	621 —
XeF^+		1.83	1.0	

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

† Assumed value.

Xe-F 1.90 Å and 3.0 mdyne Å⁻¹, respectively. It is appropriate to represent the Xe-O linkage as an electron-pair bond. On this basis the molecule XeO₄ 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 XeF₂, XeF₄, XeF₆, and XeOF₄ indicates that the oxygen ligand in XeOF₄ 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⁺³O⁻¹(F⁻¹)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^{δ+} and L^{δ-}. 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 XeF₂ 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-F⁺ (-48 kcal mole⁻¹) and resonance energy for the canonical forms (Xe-F)⁺F⁻ and F⁻(Xe-F)⁺ generate a stable molecule for which $\Delta H_{at}(\text{XeF}_2(\text{g}) \rightarrow \text{Xe}(\text{g}) + 2\text{F}(\text{g})) = 65$ kcal mole⁻¹. A similar evaluation for KrF₂ 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 XeF₂ case, the heat of atomization of KrF₂ is determined to be $+33$ kcal mole⁻¹, the experimental value being $+23$ kcal mole⁻¹. By similar reasoning we can readily appreciate why ArF₂ 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-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 (for example, I-F=67 where I-Cl=58 kcal mole⁻¹). We can also ascribe the low thermal stability of the fluorosulphates and perchlorates to the large ligand size (the electron affinities of $-\text{OSO}_2\text{F}$ and $-\text{OClO}_3$ 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 been observed only as short-lived species in discharges. The geometries of XeO₄ and XeO₃ being known, the electrostatic point charge

Table V
Estimation of the heat of atomization of a noble-gas dihalide, NL₂ (values in kcal mole⁻¹)

Experimental Quantities				$\Delta H(\text{electrostatic})^*$	Resonance energy assumed constant	$\Delta H(\text{atomization})$ [2]	
Molecule	I(N)	$\Delta H(\text{L} + e \rightarrow \text{L}^-)$	$\Delta H(\text{N}^+ + \text{L} \rightarrow (\text{N-L})^+)$ [13]			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 $\Delta H(\text{electrostatic})$ is estimated as the attraction energy ($E = -e^2/\text{estimated or observed N-L distance}$).

† The bond stretching force constant for XeCl₂=1.3 and that for XeF₂ 2.6 mdyne Å⁻¹.

energies for the $\text{Xe}^{x+}(\text{O}^-)_x$ configuration may be readily determined. Table vi shows that the ionization energy is largely compensated for by the electrostatic attraction term, although the oxygen atom electron affinity also contributes. 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, that is,

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

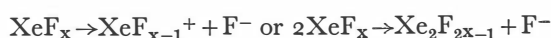
In the case of XeO_4 the observed heat of atomization requires that this term be $-152 \text{ kcal mole}^{-1}$; the derived average electron-pair bond energy ($-38 \text{ kcal mole}^{-1}$) when applied to the other oxides allows us to determine the heat of atomization, $\Delta H_{\text{at}}(\text{XeO}_x \rightarrow \text{Xe} + x\text{O})$. The value of $-38 \text{ kcal mole}^{-1}$ for the $\text{Xe}:\text{O}$ electron-pair bond is compatible with the experimental value [13] of $-48 \text{ kcal mole}^{-1}$ for $\text{Xe}:\text{F}^+$. As may be seen from Table vi, the calculated $\Delta H_{\text{at}}(\text{XeO}_3)$ agrees with the observed value within experimental error. The dioxide is predicted to be very weakly bound and the monoxide unbound to the extent of $+33 \text{ kcal mole}^{-1}$.

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

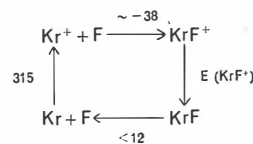
Fluoride ion donor properties of krypton and xenon fluorides

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

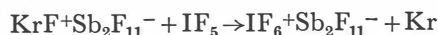


should be assisted by formation of one electron-pair bond in the cation. Examples are known for all of the xenon

fluorides, and KrF_2 Raman spectra show that the complex $\text{KrF}_2 \cdot 2\text{SbF}_5$ is very much like its xenon relative and is best represented as the salt $[\text{KrF}]^+[\text{Sb}_2\text{F}_{11}]^-$. Now consideration of the thermodynamic cycle (values in kcal mole^{-1}):



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 exceed $40 \text{ kcal mole}^{-1}$. The electron affinity of KrF^+ is, therefore, at least $275 \text{ kcal mole}^{-1}$. The spontaneous oxidation of iodine pentafluoride is in keeping with this value:



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 its ground-state geometry. In the vapour phase the molecule is evidently fluxional (a 'jellyfish'-like molecule): whereas electron diffraction data show 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 $\text{XeF}_5^+\text{RuF}_6^-$, 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

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

Molecule	$\Sigma I_{\text{F} \rightarrow \text{X}}$	$\Delta H(\text{xO}^-)$	$\Delta H(\text{electrostatic})^*$	Electron-pair - bond energy† $x(\text{Xe}:\text{O})$	ΔH (atomization) Cycle	
					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 $\text{Xe}:\text{O}$ bond was obtained from the cycle for the XeO_4 case and the unit energy ($-38 \text{ kcal mole}^{-1}$) then used for all other cases.

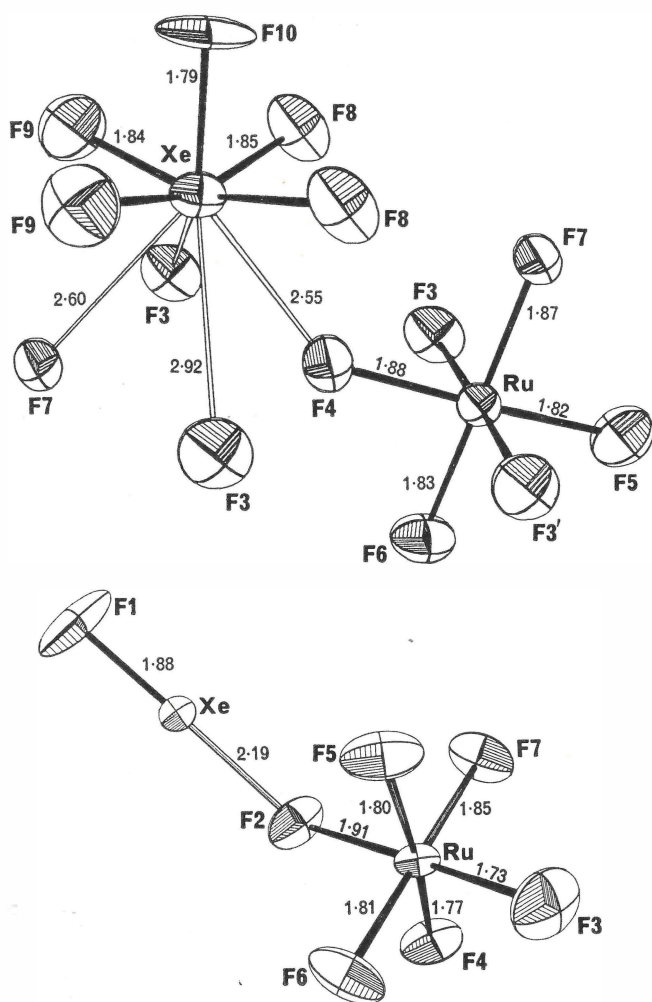


Figure 2 Structural features of FXeFRuF_5 and $\text{XeF}_5^+\text{RuF}_6^-$ [17]. (Attempts to prepare a $\text{XeF}_4\cdot\text{RuF}_5$ complex have failed.)

not only in the fluxional behaviour but in aiding the release of fluoride ion.

Relationship of noble-gas compounds to compounds of the preceding groups

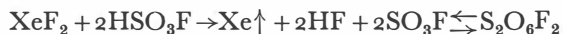
It should be recognized that the noble-gas compounds are close relatives of compounds of preceding elements in the Periodic Table [1]. The perxenates (XeO_6^{4-}) are isoelectronic with the paraperiodates and the orthotellurates; and XeO_3 with IO_3^- . Furthermore, XeF_2 can be simply correlated with 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

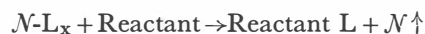
The ability of radon, xenon, and krypton to form compounds [2] may well prove to be of value to the nuclear energy programme. Radon is a health hazard in uranium mines. It is now feasible to scrub the air of such mines with suitable oxidizers to remove the radon. Xenon and krypton are gaseous fission 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:



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:



or



The interaction of XeF_2 with aromatic hydrocarbons [18] promises to be a convenient source of aromatic fluorocarbons, for example,



The noble gas, expelled from the reaction may of course be collected and recycled.

The greatest scope for new compounds may well lie in the preparation of $\mathcal{M}\text{L}^+$ salts. Thus it is possible that ArF^+ salts could be prepared (the cation is bound [13]) but a major difficulty is to find a counter-anion that 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 $-\text{SF}_5$) can be prepared. Such species would be powerful electrophilic reagents and we may expect that ingenious chemists will respond to the challenge of their synthesis.

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