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THE CHEMISTRY OF KRYPTON, XENON AND RADON

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The Chemistry of Krypton, Xenon and Radon

1. General Features of Noble-Gas Chemistry

1.1 Historical Introduction

When xenon compounds were reported\(^1,2,3\) in 1962, most chemists were greatly surprised, yet, for more than thirty years there had been clear indications\(^4\), from the chemistry of iodine and the other halogens, that the heavier noble-gases might well form compounds, with the more electronegative ligands. However, the most promising previous attempts to prepare chemical compounds had failed. This and the key role that the noble-gas valence electron configurations assumed in the electronic theories of valence, resulted (at least by the 1960's) in an unquestioning confidence in the chemical inertness of the gases.

The discovery of argon (1894), by Rayleigh and Ramsay, was unexpected and was received with much skepticism, even by the great Mendelev.\(^5\) Of course, once the gases were established as a new group in the Periodic Classification, all chemists recognized that this new group beautifully completed Mendelev's Table. The inert elements fitted perfectly into the scheme, between the electronegative elements (the halogens) and the electropositive elements (the alkali metals).

It is a mark of Ramsay's sure chemical awareness that he saw to it that his friend Moissan (see ref. 5, p. 146), the discoverer of fluorine, was promptly supplied with 100 cc of the gas, in order that he should attempt to prepare a fluoride. Moissan was unsuccessful and concluded his account\(^6\) of his experiments (reported in 1895): "A la temperature ordinaire ou sous l'action d'une étincelle d'induction un mélange de fluor et d'argon n'entre pas en combinaison."
Undoubtedly Ramsay, rightly, considered this the ultimate test for chemical activity and this presumably led to his disagreement with the suggestion of Oddo, that krypton and xenon halides should be preparable.

The Bohr model of the atom (1913) quickly brought the noble gases to an established key position in the electronic theory of valence, particularly as first propounded by Lewis (1916) and Kossel (1916). The Lewis and Kossel theories had immediate impact, in rationalizing much of the chemical behaviour of the elements. The noble-gas valence-electron configuration was clearly defined as the configuration to which other elements tended in their chemical bonding. As with all very successful theories, the exceptions and awkward cases tended, as time passed, to be ignored. A few chemists persisted nevertheless in attempts to bring the heavier gases into chemical combination. Ruff and Menzel (1937) again studied the argon/fluorine system and also krypton/fluorine; von Antropoff (1932-33) examined krypton/chlorine or bromine mixtures. No lasting evidence for compounds was found. Of all the post-electronic-theory-of-valence predictions of compounds of the gases, that of Pauling was the most accurate. He suggested in 1933, from considerations of ionic radii, that $\text{XeF}_6$, $\text{KrF}_6$ and perxenates should be preparable and at his suggestion an attempt was made to synthesize a xenon fluoride. The attempt failed. Ironically a similar experiment, carried out thirty years later but replacing the electric discharge of the early experiment with sunlight, provided a convenient preparative method for xenon difluoride!

No doubt, if xenon had been as abundant as argon we should not have had to wait more than sixty years for noble gas chemistry -- it is conceivable that Moissan would have prepared the xenon fluorides in the
last years of the 19th Century, but surely Ruff (the first to synthesize iodine heptafluoride) would have succeeded if Moissan had failed!

The Oxidation of Xenon, 1962. The key to the eventual recognition that the noble-gas octet, in the heavier gases, is not chemically inviolate lay in the long known ionization potentials of the gases: \( I(E,g) \): He, 24.58; Ne, 21.56; Ar, 15.76; Kr, 14.00; Xe, 12.13; Rn, 10.75 ev. Bartlett and Lohmann had discovered an oxyfluoride of platinum which proved to be the salt \( O_2^+[\text{PtF}_6]^- \). This formulation implied that platinum hexafluoride was capable of oxidizing molecular oxygen, \( O_2(g) + \text{PtF}_6(g) \rightleftharpoons O_2[\text{PtF}_6]^-(c) \), and indicated that the hitherto little investigated hexafluoride of platinum was an oxidizer of unprecedented power (with an electron affinity in excess of -160 kcal mole\(^{-1}\)). Since the first ionization potentials of Rn and Xe were less than, or comparable to, the first ionization potential of molecular oxygen (12.2 ev), it was apparent that the heavier gases should be susceptible to oxidation (i.e., should depart from their octet-valence-electron configurations) in interaction with the strongly electron attracting PtF\(_6\) molecule. As predicted, platinum hexafluoride vapour (deep red) spontaneously oxidized xenon gas (colourless), at ordinary temperatures, in a visually dramatic, fast, reaction, which deposited a yellow-orange, quinquevalent, platinum complex fluoride\(^1, 14\). This and the subsequent discovery of the xenon fluorides\(^2, 3\) initiated the surge of activity, the essence of which is reported in this section.
1.2 The Relationship of Noble-Gas Compounds to Compounds of the Other Elements

1.2.1 The Extent of Noble-Gas Chemistry

So far (1970), the experimental evidence suggests that only the heavier noble gases (Kr, Xe, Rn) can form chemical compounds. The favoured oxidation states are in harmony with the pattern of usual oxidation states of the other non-transition elements, obeying the general rule that the group number \((8)\), or group number minus \(2n\) \((n = 0, 1, 2, 3)\), oxidation states, are preferred. The compounds of xenon illustrate this pattern well, with the established positive oxidation states, \(+8\) \((\text{e.g. } \text{Xe}O_4)\), \(+6\) \((\text{e.g. } \text{XeF}_6)\), \(+4\) \((\text{e.g. } \text{XeF}_4)\) and \(+2\) \((\text{e.g. } \text{XeF}_2)\).

The noble-gases are brought into chemical combination only by the most powerfully oxidizing ligands and the known compounds all involve the association of a heavier (more readily oxidizable) noble-gas atom \((\text{Rn, Xe or Kr})\) with electronegative ligands \((\text{e.g. } \text{F, O, O}_2\text{S}_2\text{F, etc.})\). Here we see the drive of the electronegative ligand towards the light noble-gas configurations (particularly that of \(\text{Ne}\)). Clearly the drive of the fluorine atom to attain the \(\text{Ne}\) configuration exceeds the capability of the heavy noble gases to maintain their configurations. Of course, the ligands which provide stable noble-gas compounds are also ligands which promote unusually high oxidation states in other elements. There is a particularly close relationship of noble-gas compounds to non-transition-element Group VII and Group VI compounds involving the same ligand. Thus, the fluorides of xenon and krypton show a familial resemblance to the fluorides of iodine, bromine and even tellurium, and the oxides and oxy-salts of xenon conform to the pattern of antimony, tellurium and iodine behaviour.
1.2.2 Structural Features

The simple noble-gas compounds are closely related structurally to analogous compounds of Groups VII and VI. Since each of the noble gas cations is isoelectronic with its neighbouring halogen atom, it was to be expected that the monofluoro-noble-gas cations (e.g. XeF\(^+\), KrF\(^+\)) would show a close relationship to the corresponding halogen monofluoride. Iodine monofluoride and XeF\(^+\) are compared in Table 1.2.1.

Table 1.2.1
Comparison of XeF\(^+\) and IF

<table>
<thead>
<tr>
<th></th>
<th>XeF(^+)</th>
<th>IF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond Length(Å)</td>
<td>1.84(^{(a)})</td>
<td>1.906(^{(c)})</td>
</tr>
<tr>
<td>(v(\text{cm}^{-1}))</td>
<td>621(^{(b)})</td>
<td>610 (^{(d)})</td>
</tr>
<tr>
<td>Force constant(md/Å)</td>
<td>3.7(^{(b)})</td>
<td>3.6 (^{(e)})</td>
</tr>
</tbody>
</table>


Of course, the chemical binding must be similar in these related species and it is appropriate to think of the bonding in terms of a classical electron-pair-bond, each element achieving an octet configuration.
The bonding of two fluorine atoms to a neutral noble-gas atom, as in the generation of XeF\textsubscript{2} or KrF\textsubscript{2}, must be very like the bonding of two fluorine atoms to the halogen atom of halogen monofluoride: (Cl(Br,I)F + 2F → Cl(Br,I)F\textsubscript{3}). Certainly the approximately linear part of the T shaped BrF\textsubscript{3} molecule resembles the KrF\textsubscript{2} molecule as Table 1.2.2 shows.

**Table 1.2.2**

| Structural Comparison of KrF\textsubscript{2} with BrF and BrF\textsubscript{3} |
|---|---|
| F — Kr — F | (distances in Å units) |
| 1.759 | |

The unique bond in BrF\textsubscript{3} is short, like the bond in the Br—F molecule. Undoubtedly, the KrF bond in KrF\textsuperscript{+} like XeF\textsuperscript{+} will be shorter than in KrF\textsubscript{2}, and should resemble the Br—F molecule bond.

The XeF\textsubscript{4} molecule, which is square planar,\textsuperscript{17} is similar to the approximately square IF\textsubscript{4} group in the IF\textsubscript{5} molecule.\textsuperscript{18}

Presumably IF\textsubscript{4}⁻, like BrF\textsubscript{4}⁻, is also of D\textsubscript{4h} geometry. The well characterized isoelectronic species XeF\textsubscript{5}⁺, IF\textsubscript{5} and TeF\textsubscript{5}⁻ are very similar in shape, the bond lengths showing a decrease with increase in the atomic number (nuclear charge) of the central atom. The details are
Table 1.2.3

Comparison of Xenon Compounds with Related Molecules

(Internuclear Distances in Å Units)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Symmetry</th>
<th>( E - F_a )</th>
<th>( E - F_e )</th>
<th>( F_a - E - F_e (°) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{TeF}_5 ) (a)</td>
<td>( \text{IF}_5 ) (c)</td>
<td>( \text{XeF}_5^+ ) (b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E - F_a )</td>
<td>1.84</td>
<td>1.89</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>( E - F_e )</td>
<td>1.94</td>
<td>1.88</td>
<td>79</td>
<td></td>
</tr>
</tbody>
</table>

\( \text{EO}_4 \) (\( T_d \) symmetry)

<table>
<thead>
<tr>
<th>( \text{IO}_4^- ) (d)</th>
<th>( \text{XeO}_4 ) (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E - O )</td>
<td>1.79</td>
</tr>
</tbody>
</table>

\( \text{EO}_3 \) (\( C_3v \) symmetry)

<table>
<thead>
<tr>
<th>( \text{IO}_3^- ) (f)</th>
<th>( \text{XeO}_3 ) (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E - O )</td>
<td>1.82</td>
</tr>
<tr>
<td>( O - E - O (°) )</td>
<td>97</td>
</tr>
</tbody>
</table>

\( \text{EO}_6 \) (\( O_h \) symmetry)

<table>
<thead>
<tr>
<th>( \text{[SbO}_6] ) (h)</th>
<th>( \text{[TeO}_6] ) (i)</th>
<th>( \text{[IO}_6) (j)</th>
<th>( \text{[XeO}_6) (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E - O )</td>
<td>1.97</td>
<td>1.83-1.95</td>
<td>1.93</td>
</tr>
</tbody>
</table>
References Table 1.2.3


given in Table 1.2.3. The same kind of relationship occurs in XeO$_3$ and IO$_3^-$, both of which are pyramidal, and XeO$_4^-$ and IO$_4^-$, both of which are tetrahedral. The perxenates are octahedral, like the paraperiodates and orthotellurates.

Table 1.2.3

Comparison of Xenon Compounds with Related Molecules

1.2.3: Thermochemical Relationships

The structural relationships show that the chemical bonding in each series of related compounds across the Periodic Table cannot change sharply in character and indeed suggests that a common bonding description is appropriate. The thermochemical evidence further supports this view.

As may be seen from the thermochemical cycle, for a gaseous xenon compound, XeL$_y$, formed from xenon atoms and gaseous diatomic molecules L$_2$:

\[
\text{Xe}_v(g) + \frac{y}{2} \text{L}_2(g) \xrightarrow{\Delta H_f(XeL_y, g)} \text{XeL}_y
\]

\[
\Delta H_f(L_g)
\]

\[
yL(g) \quad y \text{x Mean Thermochemical Bond Energy}
\]

the enthalpy of formation of the gaseous compound will be exothermic if the mean thermochemical bond energy (T.B.E.) exceeds the enthalpy of formation of the gaseous ligand atom L. In comparing fluorine, oxygen and chlorine ligands it is evident from inspection of $\Delta H_f(L,g)^{19}$: F, 18.8; O, 59.2; Cl, 29.0 kcal mole$^{-1}$, that fluorine presents an unusually favourable case. Furthermore, the fluorine atom has a higher electronegativity than oxygen and chlorine and is also the smallest. It...
Table 1.2.4
Mean Thermochemical Bond Energies for Chlorides*, and Dissociation Energies of the Diatomic Oxides Of The Xenon Period (values in kcal mole⁻¹)

<table>
<thead>
<tr>
<th>Bond Energies</th>
<th>Dissociation Energies (f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl₂</td>
<td>GeO</td>
</tr>
<tr>
<td>90</td>
<td>158</td>
</tr>
<tr>
<td>SnCl₄</td>
<td>75</td>
</tr>
<tr>
<td>SbCl₅</td>
<td>75</td>
</tr>
<tr>
<td>TeCl₄</td>
<td>56</td>
</tr>
<tr>
<td>TeCl₂</td>
<td></td>
</tr>
<tr>
<td>ICl₃ (e)</td>
<td></td>
</tr>
<tr>
<td>XeCl₂</td>
<td>&lt;32 est.</td>
</tr>
</tbody>
</table>

*Lines connect molecules of related geometry.
(c) K. J. Frederick, and J. H. Hildebrand, J. Amer. Chem. Soc., 60 (1938) 2522.
is anticipated, therefore, that fluorine will form stronger bonds than chlorine, or the other halogens, and that the heavier halides and oxides will be thermodynamically less stable. This is the usual situation and the noble-gas compounds prove to be no exception. Although all of the xenon fluorides are thermodynamically stable, the oxides and chlorides are not. Chlorides have been synthesized under high energy conditions, and also by $^{129}$I decay, (see XeCl$_2$, and XeCl$_4$). Oxides have been obtained from the fluorides by metathetical reactions. This instability conforms with the character of oxides and chlorides of elements close to the heavier noble-gases in the Periodic Table, as may be seen in Table 1.2.4. Although the mean thermochemical bond energies in the xenon oxides ($\leq 21$ kcal mole$^{-1}$) are lower than in the fluorides ($\sim 30$ kcal mole$^{-1}$), structural and spectroscopic evidence suggests that the intrinsic Xe-O bond energy is greater than the Xe-F bond energy. This point is discussed further in 1.3.3.

This may account for the considerable kinetic stability of xenon(VI) and (VIII) oxides.

(\text{Table 1.2.4})

As may be seen from the mean thermochemical bond energies listed in Table 1.2.5, there is, for fluorides, a general, smooth, trend of decreasing mean thermochemical bond energy, from left to right in each period of the Periodic Table. This is also the direction of increasing first ionization potential of the elements and, of course, increasing electronegativity. If the mean thermochemical bond energy is traced across a series of geometrically related species (e.g., the octahedral or pseudo-octahedral set, TeF$_6$, IF$_5$, XeF$_4$, 31 kcal mole$^{-1}$) it is seen to fall sharply as the noble-gas compounds are approached.
### Table 1.2.5

Mean Thermochemical Bond Energies (kcal mole⁻¹) for

Noble-Gas Fluorides and Related Fluorides

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiF₄⁽ᵃ⁾</td>
<td>PF₅⁽ᵃ⁾</td>
<td>SF₆⁽ᵃ⁾</td>
<td>[ClF₇]</td>
<td></td>
</tr>
<tr>
<td>143</td>
<td>110</td>
<td>79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SiF₂⁽ᵃ⁾</td>
<td>PF₃⁽ᵃ⁾</td>
<td>SF₄⁽ᵃ⁾</td>
<td>ClF₅⁽ᵇ⁾</td>
<td>[ArF₆]</td>
</tr>
<tr>
<td>143</td>
<td>120</td>
<td>79</td>
<td>36</td>
<td>&lt; 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ClF₃⁽ᵇ⁾</td>
<td>[ArF₄]</td>
</tr>
<tr>
<td>42</td>
<td></td>
<td></td>
<td></td>
<td>&lt; 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ClF⁽ᵇ⁾</td>
<td>[ArF₂]</td>
<td></td>
</tr>
<tr>
<td>61</td>
<td></td>
<td></td>
<td></td>
<td>&lt; 5 est.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ar</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1.2.5
(Mean Thermochemical Bond Energies (kcal mole\(^{-1}\)) for)

Noble-Gas Fluorides and Related Fluorides*

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Se</th>
<th>Br</th>
<th>Kr</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeF(_4) (c)</td>
<td>AsF(_5) (d)</td>
<td>SeF(_6) (e)</td>
<td>[BrF(_7)]</td>
<td></td>
</tr>
<tr>
<td>112</td>
<td>92</td>
<td>72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeF(_2) (c)</td>
<td>AsF(_3) (e)</td>
<td>SeF(_4) (f)</td>
<td>BrF(_5) (e)</td>
<td>[KrF(_6)]</td>
</tr>
<tr>
<td>113</td>
<td>116</td>
<td>76</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>≲ 9 est.</td>
</tr>
<tr>
<td></td>
<td>[SeF(_2)]</td>
<td></td>
<td>BrF(_3) (e)</td>
<td>[KrF(_4)]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>48</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>≲ 9 est.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Br(_5) (e)</td>
<td>KrF(_2) (k)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
<td>Xe</td>
</tr>
<tr>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>SnF₄(g)</td>
<td>SbF₅(f)</td>
<td>TeF₆(e)</td>
<td>IF₆(a)</td>
<td>[XeF₈]</td>
</tr>
<tr>
<td>98</td>
<td>92</td>
<td>82</td>
<td>55</td>
<td>~21 est.</td>
</tr>
<tr>
<td>SnF₂</td>
<td>SbF₃(e)</td>
<td>TeF₄(f)</td>
<td>IF₅(a)</td>
<td>XeF₆(i)</td>
</tr>
<tr>
<td>105</td>
<td>88</td>
<td>63</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IF₃(h)</td>
<td>XeF₄(i)</td>
<td>65?</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>IF(a)</td>
<td>XeF₂(j)</td>
<td>67</td>
<td>32</td>
</tr>
</tbody>
</table>

*Geometrically related molecular species are cross-linked.*
Table 1.2. 5

References


(d) P. A. G. O'Hare, and W. N. Hubbard, J. Phys. Chem., 69 (1965) 4358.

(e) National Bureau of Standards, Technical Note 270 - 3 (Jan. 1968)


(g) J. L. Margrave, and co-workers, Rice University.


Most importantly, however, in the krypton and xenon periods the bond energy does not fall to zero and indeed the trend in bond energies, already available prior to the discovery of xenon fluorides, was sufficiently clear to have provided the unbiased observer with an indication that xenon fluorides should not only be bound but also thermodynamically stable.

(Table 1.2.5)

The rapid decline in mean thermochemical bond energies in the fluoride sequence Ge → Br presages the thermochemical instability of the krypton fluorides. The difluoride of krypton is the only known binary compound available in macroscopic quantities and its low bond energy of 12 kcal mole\(^{-1}\) indicates that little hope can be held for higher fluorides since, if the usual pattern holds, the higher fluorides will have slightly lower bond energies. Of course, the entropy of formation becomes an ever more unfavorable feature towards thermodynamic stability as the number of atoms in the organized molecular unit increases. Thus for the binary fluorides of xenon the entropy changes\(^{22}\) (cal deg.\(^{-1}\) mole\(^{-1}\)) are:

\[
\begin{array}{ccc}
\text{XeF}_2 & \text{XeF}_4 & \text{XeF}_6 \\
\Delta S_f^{\circ} & -26.5 & -61 & -96
\end{array}
\]

The combination of lower bond energy and less favourable entropy make KrF\(_4\) and KrF\(_6\) markedly less likely than KrF\(_2\). A glance at the bond energy data for the fluorides of the Si → Cl set of elements show that the prospect of obtaining neutral argon fluorides must be very low indeed.

It is striking that for the addition of each pair of fluorine atoms, in the sequence Xe → XeF\(_6\), the enthalpy changes are approximately
constant:

\[ \Delta H_1 (\text{Xe}(g) + 2\text{F}(g) \rightarrow \text{XeF}_2(g)) = -65 \text{ kcal mole}^{-1} \]

\[ \Delta H_2 (\text{XeF}_2(g) + 2\text{F}(g) \rightarrow \text{XeF}_4(g)) = -61 \text{ kcal mole}^{-1} \]

\[ \Delta H_3 (\text{XeF}_4(g) + 2\text{F}(g) \rightarrow \text{XeF}_6(g)) = -55 \text{ kcal mole}^{-1} \]

This is similar to the situation in the chlorine and bromine fluorides. The enthalpy change for addition of each pair of fluorine atoms in the sequence ClF → ClF$_3$ involves approximately the same energy:

\[ \Delta H_1 (\text{ClF}(g) + 2\text{F}(g) \rightarrow \text{ClF}_3(g)) = -64 \text{ kcal mole}^{-1} \]

\[ \Delta H_2 (\text{ClF}_3(g) + 2\text{F}(g) \rightarrow \text{ClF}_5(g)) = -56 \text{ kcal mole}^{-1} \]

this being approximately the same as for a single fluorine atom union with chlorine in ClF:

\[ \Delta H (\text{Cl(f)}(g) + \text{F}(g) \rightarrow \text{ClF}(g)) = -61 \text{ kcal mole}^{-1} \]

The bromine fluoride enthalpy relationships are similar but the BrF molecule bond energy (-60 kcal mole$^{-1}$) is only 50% greater than the enthalpy change (ca. 40 kcal g atom$^{-1}$) for the addition of each fluorine ligand in the sequence BrF → BrF$_5$.

The halogen monofluorides are classical 'electron-pair-bonded' compounds, whereas the higher fluorides must involve either higher valence orbitals of the central atom, or less than electron-pair-bonding, for some of the ligands at least. It is therefore reasonable that the halogen monofluoride T.B.E.'s should be higher. Clearly,
the isoelectronic noble-gas relatives \( \text{XeF}^+ \), \( \text{KrF}^+ \), \( \text{ArF}^+ \) etc., should also show stronger bonding than the neutral fluorides. This is so for \( \text{XeF}^+ \), where the bond energy is \( \text{ca.} \ 47 \text{ kcal mole}^{-1} \) (see 3.2.1.), in contrast to the mean bond energy in \( \text{XeF}_2 \) of 32 kcal mole\(^{-1}\). The \( \text{KrF}^+ \) bond energy must certainly be greater than 12 kcal mole\(^{-1}\) and it is argued that \( \text{ArF}^+ \) should also be a bound species. It should be appreciated, however, that the \( \text{ArF}^+ \) bond is unlikely to be as strong as the bond in its isoelectronic relative \( \text{ClF} \). Unfortunately, the enormous electron affinity of the \( \text{ArF}^+ \) ion, which must exceed -14.0 ev (see 2.2.1.) will demand an unusually oxidatively resistant counter anion, if it is to be stabilized.

The change in bond-energy in the iodine fluorides (T.B.E.: \( \text{IF} \), 67; \( \text{IF}_3 \), 65(est.); \( \text{IF}_5 \), 63 kcal mole\(^{-1}\)) is much less dramatic than in the chlorine and bromine series, but there is a sharp decline with \( \text{IF}_7 \) (T.B.E. 55 kcal mole\(^{-1}\)). This represents an enthalpy change for the process:

\[
\text{IF}_5(\text{g}) + 2\text{F}(\text{g}) \rightarrow \text{IF}_7(\text{g}) = -65 \text{ kcal mole}^{-1}
\]

which contrasts with \( \Delta H \), for each previous fluorine ligand pair addition, of \( \text{ca.} \ 125 \text{ kcal mole}^{-1} \). It may be that this lower enthalpy derives in part from the ligand crowding in molecular \( \text{IF}_7 \). If so, we can be certain that the steric inhibition to \( \text{XeF}_8 \) formation will be even more pronounced. The extrapolated mean bond energy given in Table 1.2.5, may therefore be over-optimistic of \( \text{XeF}_8 \) formation.

Since the fluorides are thermodynamically the most favourable compounds of the noble gases, it is evident from Table 1.2.5 that unless remarkable, oxidatively resistant, anion sources can be found
to stabilize cations like ArF\(^+\) and NeF\(^+\), the chemistry of the noble gases will be limited to the heaviest elements, Rn, Xe and Kr.

1.3. **Bonding in Noble-Gas Compounds**

1.3.1 **Introduction**

Bonding in noble-gas compounds has attracted much attention from theorists as well as experimentalists. Unfortunately, there is still no definitive finding to resolve the central controversy, which is concerned with the degree of involvement of 'outer,' valence-shell orbitals of the noble-gas atom in bonding.

Obviously any acceptable theory should account for the following observations: (a) only the heavier, more readily ionizable gases, form compounds (b) only the most electronegative atoms or groups are satisfactory ligands for the noble gases. Clearly, no matter what the nature of the bonding, the noble-gas atom, in a compound, should bear a net positive charge and the ligands should be negatively charged.

From the outset, the majority of bonding models have preferred to involve only s and p valence-shell orbitals of the noble-gas in bonding.\(^ {15,23} \)

Most descriptions use only the p orbitals. All preserve the valence octet as a bonding criterion. The proponents of these models argue that the promotional energy necessary for the involvement of 'outer' noble-gas orbitals in bonding is greater than the possible bond-energy gain. Thus, it has been pointed out that for the xenon atom, the spectroscopic data indicate the \(5p \rightarrow 5d\) promotion energy to be \(~10\) ev. It appears then that the valence-state promotion energy for the pentagonal bipyramidal-valence-state xenon atom, appropriate for XeF\(_6\) formation, would require \(~11\) kcal g atom\(^{-1}\) valence-state promotional energy.\(^ {25*} \)

\(^*\)Valence-state promotion energies of several hundred kcal mole\(^{-1}\) are probably common; thus, the tetrahedral carbon atom requires \(~150\) kcal g atoms\(^{-1}\) in its valence state promotion, but this is more than adequately returned in enhanced bond energy.
Most theorists have been unwilling to accept that this energy expenditure could be provided by the enhanced bond energy. This has not been the unanimous view however, and recent work suggests that outer orbitals may play a major role in the bonding, at least in the higher noble-gas oxidation states.

The electron-pair-bond descriptions of the noble-gas halides, which models either implicitly or explicitly involve 'outer' \( d \) (or \( f \)) orbitals of the noble-gas in bonding, are supported by the phenomenological evidence. Thus, the noble-gas and other non-transition-element compounds exhibit close physical relationships to their transition-element relatives. Furthermore, the very successful Electron-Pair-Repulsion Rules for molecule and ion shape are as effective for noble-gas compounds and their relatives as for classical 'octet' compounds.

1.3.2 A Comparison of Non-Transition-Element with Related Transition-Element Compounds

It is generally accepted that all of the valence-shell orbitals of the transition elements are available for bond formation. Thus, in tungsten hexafluoride, a \( d_{sp^3} \) tungsten atom orbital hybridization (or its equivalent) is assumed for the \( \sigma \) bonds - \( \pi \) bonding, involving the other \( d \) orbitals may also be admitted. Similarly, rhenium heptafluoride is assumed to involve \( d_{sp^3} \) rhenium \( \sigma \) orbital hybridization. Also, osmium tetroxide may be described in terms of four \( \sigma \) orbitals involving osmium \( sp^3 \) hybrids, plus \( \pi \) orbitals, involving at least four osmium \( d \) orbitals.

Now, as may be seen in Table 1.3.1 the analogous non-transition element compounds, \( TeF_6, IF_7 \) and \( XeO_4 \) are geometrically akin to their transition element relatives. It should also be noted that \( OsF_8 \) like \( XeF_8 \) (see 3.5.1.) is unknown; all evidence pointing to both as very unstable species. Similarly, \( OsO_2F_4 \) and \( XeO_2F_4 \) (see 3.5.3.) are unknown and again appear to be very
Table 1.3.1

A Comparison of Some Transition and Non-Transition Element Compounds

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$WF_6$</th>
<th>$TeF_6$</th>
<th>$ReF_7$</th>
<th>$IF_7$</th>
<th>$OsO_4$</th>
<th>$XeO_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry</td>
<td>$O_h$ (a)</td>
<td>$D_{5h} \uparrow C_2\perp, C_s$ (b, c)</td>
<td>$T_d$ (d)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-L (Å units)</td>
<td>1.833(e)</td>
<td>1.83(f)</td>
<td>---</td>
<td>1.825(b)</td>
<td>1.74(g)</td>
<td>1.74(h)</td>
</tr>
<tr>
<td>$f_r$ (mdyn/Å)</td>
<td>5.1(1)</td>
<td>5.01(j)</td>
<td>---</td>
<td>3.4(k)</td>
<td>7.14(d)</td>
<td>5.75(d)</td>
</tr>
<tr>
<td>$v_1$ (cm$^{-1}$)</td>
<td>769(a)</td>
<td>701(a)</td>
<td>736(e)</td>
<td>676(e)</td>
<td>971</td>
<td>906 est</td>
</tr>
<tr>
<td>T.B.E. (kcal mole$^{-1}$)</td>
<td>121(m)</td>
<td>82(n)</td>
<td>100 est</td>
<td>55(o)</td>
<td>127(p)</td>
<td>21(q)</td>
</tr>
</tbody>
</table>
(a) K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*,

(b) R. D. Burbank, and N. Bartlett; *Chem. Commun.*, (1968) 645.

(c) E. W. Kaiser, J. S. Maenter, W. Klemperer, W. E. Falconer, and W. A. Sunder,


(1968) 4001.

(f) Mean of 1.84 and 2.82 Å quoted respectively by L. Pauling, and L. O. Brockway,
Chem.*, (Leipzig) 221 (1933) 297.


558.

(o) JANAF Thermochemical Tables, The Dow Chemical Co., Midland Michigan, Supplement
32 (December 31, 1969).


unstable species, whereas both OsO$_3$$^F_2$ and XeO$_3$$^F_2$ are known (the latter is kinetically stable to decomposition, although, thermodynamically unstable (see 3.5.2.). These admittedly superficial relationships do give the impression that the bonding in the non-transition element compounds should be akin to that in their transition element relatives.

Table 1.3.1
A Comparison of Some Transition and Non-Transition Element Compounds

Since the bond lengths and stretching force constants for WF$_6$ and TeF$_6$ are similar, we can assume that the intrinsic bond energy (which is represented in Figure 1.3.1.) must have approximately the same value in Figure 1.3.1.

The Inter-relationship of Intrinsic Bond Energy, Valence-State Promotion Energy and Mean Thermochemical Bond Energy

\[
\begin{align*}
\text{Valence State} & \quad E'(g)(v.s.) + x L'(g)(v.s.) \\
\text{Valence State Promotion} & \quad \Delta H (E_v.s.) \\
\text{Valence Promotion Energy} & \quad x X \text{ Intrinsic Bond Energy} \\
\text{Ground State} & \quad E(g) \\
& \quad x X \text{T.B.E.} \quad \rightarrow \quad \text{EL}_x(g)
\end{align*}
\]

the two cases. It is a reasonable assumption that a $^2P$ state F atom is already in its valence state, but in any case it is unlikely that the valence state is very different for WF$_6$ and TeF$_6$. Differences in the total valence-state-promotion energy for WF$_6$ and TeF$_6$ can therefore be related to differences in the central-atom valence-state-promotion energy.
Since the I.B.E. for both WF\textsubscript{6} and TeF\textsubscript{6} appear to be similar, the differences in T.B.E. presumably reflect differences in the W and Te valence-state-promotion energies. It would appear then, that the valence-state-promotion energy for the tellurium atom, i.e., \( \Delta H(\text{Te}(g)\text{ (ground-state)} \rightarrow \text{Te}(g)\text{ (valence-state)}) \), exceeds the corresponding tungsten promotion by \( \sim 240 \text{ kcal g atom}^{-1} \). It is not inconceivable that this energy could represent the difference in the valence-state-promotion energies for \( \text{d}^2\text{sp}^3 \text{W} \) and \( \text{sp}^3\text{d}^2 \text{Te} \), each in an octahedral field of six fluorine ligands.

The oxides XeO\textsubscript{4} and OsO\textsubscript{4} are also similar. The bond lengths are akin and the bond stretching force constants not too dissimilar. Again, the intrinsic bond energies should be alike. This is in sharp contrast to the impression given by the mean thermochemical bond energies. It is therefore probable that the valence-state-promotion energy for XeO\textsubscript{4} formation, exceeds that for OsO\textsubscript{4} formation by approximately \( 420 \text{ kcal mole}^{-1} \). It is possible that this derives from \( \text{d} \) (or \( \text{f} \)) orbital utilization in the xenon bonding.

It should also be noted that although the bond lengths decrease and the stretching force-constant increases in the sequence XeF\textsubscript{2}, 2.00\text{Å}, 2.8 \text{mdyn/Å}; XeF\textsubscript{4}, 1.95\text{Å}, 302 \text{mdyn/Å}; XeF\textsubscript{6}, 1.89\text{Å}, the T.B.E. shows a slight decrease (see Table 1.2.5). Clearly, the T.B.E. should increase in this sequence. Evidently, some valence-state promotion must be involved in xenon fluoride formation (at least for the higher fluorides).
1.3.3. Bonding Without 'Outer' Noble-Gas Orbitals

There is a considerable weight of expert opinion\textsuperscript{15, 23, 31} that the bonding in noble-gas compounds does not involve outer, or higher valence-shell, orbitals of the noble-gas atom, at least not to an extent which could significantly affect the bond energy. Thus, xenon is considered to use only its $5p$ and possibly $5s$ orbitals in bonding, which is essentially of sigma type. The bonding has usually been discussed in molecular orbital terms, although Coulson has favoured the valence bond scheme for his discussion of the xenon fluorides.\textsuperscript{23} In this model, XeF\textsubscript{2} is represented as primarily involving resonance between $F^{-}\text{Xe}^{+}F^{-}$ and $F^{-}\text{Xe}^{+}F^{+}$. This scheme preserves both classical concepts: the 'octet' and the 'electron-pair-bond.'

Halides. The widely accepted simple m.o. model, proposed independently by Pimentel\textsuperscript{32} and Rundle\textsuperscript{33}, applies well to noble-gas-halides. It is of historical interest that in Pimentel's 1951 paper, which was devoted primarily to bonding in trihalide ions, he discussed the validity of his bonding scheme for noble gas dihalides also. This model is best presented with a brief description of xenon difluoride. The krypton difluoride case can be taken as similar. Three three-centre molecular orbitals (represented in Figure 1.3.2.) generated from the Xe $5p_x$, and a $2p_x$ orbital of each fluorine ligand (molecular axis being taken as $x$), are of most favourable energy, with a co-linear disposition of the atomic orbitals

Figure 1.3.2.

Simplified Representation of the $p_0$ m.o.s. for XeF\textsubscript{2}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1_3_2.png}
\caption{Simplified Representation of the $p_0$ m.o.s. for XeF\textsubscript{2}}
\end{figure}
from which they are derived. The best net bonding for the three atoms occurs when the arrangement is centro-symmetric. The observed $D_{\infty h}$ molecular symmetry of XeF$_2$ (see 3.2.1.) is in harmony with these requirements. Since the noble-gas atom contributes two electrons and each of the fluorine ligands only one electron to this $\pi$ m.o. system, the antibonding m.o. remains empty. In effect the filling of the non-bonding orbital 'restores' the fluorine ligand electron density, since the orbital is largely concentrated on the fluorine ligands. The bonding pair of electrons is, therefore, responsible for the binding together of all three atoms. Obviously, the delocalization of the electron pairs in this orbital must result in a net negative charge on each of the fluorine ligands, thus leaving the xenon atom positively charged. Because of this, the bonding has been termed 'semi-ionic'.$^{15}$ The best calculations place the net charge distribution to be close to the representation $\pm_2$Xe$^{1+}_2$F$^{\pm}_2$. As will be shown (see 3.2.1.) this assignment fits most, if not all, of the physical and chemical properties of the compound. A similar view of the bonding in XeF$_2$ is given by Linnett's representation.$^{34}$

Each fluorine ligand possesses a closed spin quartet, the other quartet being shared with the central xenon atom, which, in effect then, provides the two electron for bonding.

Bonding in the xenon tetrafluoride molecule may be dealt with similarly, by considering two three-centre orbitals at right angles.$^{33}$ The square planar geometry of the molecule is 'predicted' by this
Table 1.3.2.
Comparison of Bond Lengths in XeF⁺, XeF₂⁻ and Bromine Fluorides
(internuclear distances in Å units)

'Electron-Pair-Bond' Species:

<table>
<thead>
<tr>
<th>Species</th>
<th>Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Br-F]<strong>(a)</strong></td>
<td>1.756</td>
</tr>
<tr>
<td>[F-Br-F]<strong>(b)</strong></td>
<td>1.70 +</td>
</tr>
<tr>
<td>[Xe-F]<strong>(c)</strong></td>
<td>1.84 +</td>
</tr>
</tbody>
</table>

'Single-Electron-Bond' Species:

<table>
<thead>
<tr>
<th>Species</th>
<th>Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[F-Br-F]<strong>(d)</strong></td>
<td>1.88</td>
</tr>
<tr>
<td>[F-Xe-F]<strong>(e)</strong></td>
<td>2.00</td>
</tr>
</tbody>
</table>

A Mixed Species:

<table>
<thead>
<tr>
<th>Species</th>
<th>Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[F-Br-F]<strong>(f)</strong></td>
<td>1.81</td>
</tr>
</tbody>
</table>

description as is the approximate charge distribution \( \text{Xe}^{2+} (\text{F}^{-} \frac{1}{2})_{4} \).

A full molecular orbital treatment (see 3.3.1.) is needed to interpret the detailed spectroscopic (electronic) properties, however. The simple three-centre four-electron m.o. approach fails in the case of \( \text{XeF}_{6} \), since it predicts an octahedral symmetry for the monomer. It is necessary to use a full m.o. description (see 3.4.1.) in order to account for the observed non-octahedral geometry, although again, in this description, higher orbitals are not necessarily involved and the bonding may simply amount to one-electron-bonding.

We would expect the one-electron-bonds in the noble-gas halides to be weaker than in related compounds, where electron-pair-bonding must occur. In particular, we would expect the \( \text{Xe} \equiv \text{F} \) bond in \( \text{XeF}_{2} \) to be weaker than in \( \text{XeF}^{+} \). This is supported by the experimental findings (see 3.2.6.), given in Table 1.3.2. As has already been discussed (1.2.2.) the relationship of \( \text{XeF}^{+} \) to \( \text{XeF}_{2} \) is very similar to that of the halogen monofluorides to their higher fluorides. Thus, for bromine fluoride structures, shown in Table 1.3.2., the 'electron-pair-bond'

\[
\begin{array}{c}
\text{(Table 1.3.2.)}
\end{array}
\]

length would be represented as \( 1.68 - 1.76 \AA \) and the 'one-electron-bond' as \( 1.78 - 1.88 \AA \). It is apparent that the 'electron-pair-bonds' are not twice as strong as the 'one-electron-bonds' as the above bonding description implies. Clearly, either the representation of the bonding in terms of assemblies of two-atom and three-atom centres is not adequate, or the total neglect of outer orbital contributions to the bonding is at fault.

The bond shortening in the series of fluorides \( \text{XeF}_{2} (2.00 \AA), \text{XeF}_{4} (1.95 \AA), \text{XeF}_{6} (1.89 \AA) \) (see 3.2.1., 3.3.1. and 3.4.1.) may be accounted
for in terms of the increase in the charge on the xenon atom. The
same feature is seen in the bromine fluorides and the other halogen
fluorides.\textsuperscript{35} There is also the possibility of greater 'outer' orbital
participation of the central atom in bonding, the higher the oxidation
state,\textsuperscript{27} and this participation may contribute to the bond shortening.

Oxides. The only noble-gas oxides established so far are the trioxides
and tetroxides of xenon. Although the \(\text{Xe-O}\) bonds are shorter (\(\text{XeO}_3\), 1.76;
\(\text{XeO}_4\), 1.74\(\text{Å}\), see 3.4.4. and 3.5.4.) than \(\text{Xe-F}\) bonds and the \(\text{Xe-O}\) stretching
force constants, e.g. \(f_r(\text{XeO}_3) = 5.66 \text{ mdyne Å}^{-1}\) (3.4.4.), are greater
than for \(\text{Xe-F}\), e.g. \(f_r(\text{XeF}_4) = 3.02 \text{ mdyne Å}^{-1}\) (3.3.1.), the mean
thermochemical bond energy for \(\text{XeO}\) is \(<21 \text{ kcal mole}^{-1}\), which contrasts
with the \(\text{Xe-F}\) value of \(31 \text{ kcal mole}^{-1}\). Evidently, some oxygen or
xenon valence-state excitation is involved in the oxygen-ligand bonding.

Again, it is commonly assumed that higher orbitals (e.g. \(\text{Xe}^{4f}\) and \(5d\))
play an insignificant role. Since the oxygen atom can receive two
electrons, the simplest representation for the \(\text{Xe-O}\) bond is as an
'electron-pair-bond,' both electrons, in effect, being provided by the
xenon atom, i.e., a classical semi-ionic linkage \(\text{Xe} : \equiv \text{O}\). Of course,
the appropriate valence-state of the oxygen atom for such a bond would
be \(1\text{D}\), which is 45.1 kcal mole\(^{-1}\) above the ground \(3\text{P}\) state.\textsuperscript{36} On this
basis, then, the intrinsic \(\text{Xe-O}\) bond energy would be the mean thermo-
chemical-bond-energy (\(<21 \text{ kcal mole}^{-1}\)), plus the oxygen valence-state
promotion energy (\(\sim 45 \text{ kcal mole}^{-1}\), i.e., 65 kcal mole\(^{-1}\), which is more
in keeping with the vibrational spectroscopic data. Now the \(\text{Xe-O}\) bond
must have considerable polarity, since any oxygen ligand share of the
bonding-electron pair will contribute net negative charge to that ligand
and corresponding positive charge to the xenon atom. For an ideally shared electron-pair, the charge distribution should amount to $\text{Xe}^{1+} - \text{O}^{1-}$.

Valence-state promotional enhancement of the bonding in the oxides may well account for the kinetic stability of $\text{XeO}_3$ and $\text{XeO}_4$.

### 1.3.4 Electron-Pair Repulsion Theory

Although, as has been remarked, there has been considerable reluctance on the part of those providing bonding models for noble-gas compounds to admit the involvement of 'outer' noble-gas orbitals in bonding, it is striking that the theory which, almost without exception, has correctly predicted the geometrical features of the noble-gas compounds, has been the Electron-Pair Repulsion Theory. This theory implies 'outer' orbital involvement in the bonding.

Electron-Pair Repulsion Theory, which was first formulated independently by Tsuchida\(^{37}\) and Powell and Sidwick\(^{38}\), gained widespread appeal when it was rendered much more quantitative by Gillespie and Nyholm.\(^{29}\) The theory assumes that each halogen-ligand bond to the central atom involves an electron-pair, and also usually assumes that the binding of a unidentate oxygen ligand involves four electrons (a double bond). Furthermore, all non-bonding valence electrons are assumed to have steric effect (i.e., be in directional orbitals). A basic tenet of the Gillespie-Nyholm rules is that the non-bonding electron pairs repel other electron pairs more than do bonding electron pairs (although the two 'pairs' of an oxygen-ligand bond have approximately the same repulsive effect as a non-bonding 'pair').

Shortly after the first reports of the noble-gas compounds, Gillespie\(^{39}\) used the theory to predict the shape of a number of then unknown species.
Table 1.3.3.

Some Molecule and Ion Shapes Predicted by Electron-Pair Repulsion Theory
(Internuclear distances are in Å units)

<table>
<thead>
<tr>
<th>Species</th>
<th>Central Atom Coordination</th>
<th>Predicted Geometry</th>
<th>Observed Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>XeF₂</td>
<td>5 - trigonal bipyramid</td>
<td>F—Xe—F</td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>(3 n-b e.p.; 2 b.e.p.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(D₆h)</td>
<td></td>
</tr>
<tr>
<td>XeF₄</td>
<td>6 - pseudo octahedron</td>
<td>F—Xe—F</td>
<td>(b)</td>
</tr>
<tr>
<td></td>
<td>(2 n-b. e.p.; 4b.e.p.)</td>
<td></td>
<td>1.95 F—Xe—F</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(D₄h)</td>
<td></td>
</tr>
<tr>
<td>XeF₆</td>
<td>Either:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7 - pseudo pentagonal</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>bipyramid (1 n-b. e.p.; 6 b.e.p.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>or:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7 - face occupied octahedron</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1 n-b. e.p.; 6 b.e.p.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(C₃ᵥ)</td>
<td></td>
</tr>
</tbody>
</table>

XeF₆ monomer is not octahedral. XeF₆(g) undergoes rapid intramolecular rearrangement through C₃ᵥ, Cᵥ and C₃ symmetry species. (d) The cubic crystalline phase contains tetrarers and hexamers which are essentially XeF₅⁺ F⁻ clusters. (e)
<table>
<thead>
<tr>
<th>Species</th>
<th>Central Atom Coordination</th>
<th>Predicted Geometry</th>
<th>Observed Structure</th>
</tr>
</thead>
</table>
| XeF$_3^+$ | 5 - pseudo trigonal bi-pyramid (2 n-b.e.p.; 3 b.e.p.) | $\begin{array}{c}
\text{Fa} \\
\text{F} \\
\text{Xe} \\
\text{Fe} \\
\text{Fa}
\end{array}$ | $\begin{array}{c}
\text{Fa} < 90^\circ \\
\text{F} \\
\text{Xe} \\
\text{Fe} \\
\text{F}
\end{array}$ | unknown |
| $\begin{array}{c}
\text{Xe-Fa} > \text{Xe-Fe}
\end{array}$ |
| XeF$_5^+$ | 6 - pseudo octahedron (1 n-b. e.p.; 5 b.e.p.) | $\begin{array}{c}
\text{Fa} \\
\text{F} \\
\text{Xe} \\
\text{Fe} \\
\text{F}
\end{array}$ | $\begin{array}{c}
\text{Fa} < 90^\circ \\
\text{F} \\
\text{Xe} \\
\text{Fe} \\
\text{F}
\end{array}$ | 1.81 $\begin{array}{c}
\text{F} \\
\text{Xe} \\
\text{F}
\end{array}$ $\text{79}^\circ$ (f) |
| $\begin{array}{c}
\text{Xe - Fa} < \text{Xe - Fe}
\end{array}$ |
| OXeF$_4$ | 6 - pseudo octahedron (1,4 - e.b.; 1 n-b. e. p.; 4 b. e. p.) | $\begin{array}{c}
\text{O} \\
\text{F} \\
\text{Xe} \\
\text{F}
\end{array}$ | $\begin{array}{c}
\text{O} \sim 90^\circ \\
\text{F} \\
\text{Xe} \\
\text{F}
\end{array}$ | 1.70 $\begin{array}{c}
\text{O} \sim 91^\circ \\
\text{F} \\
\text{Xe}
\end{array}$ (g) |
| $\begin{array}{c}
\text{C}_{4v}
\end{array}$ | $\begin{array}{c}
\text{C}_{4v}
\end{array}$ |
| $\begin{array}{c}
\text{O}_2\text{XeF}_2
\end{array}$ | 5 - pseudo trigonal bi-pyramid (2, 4 - e.b.; 1 n-b. e. p.) | $\begin{array}{c}
\text{O} \\
\text{F} \\
\text{Xe} \\
\text{F}
\end{array}$ | $\begin{array}{c}
\text{O} \sim 90^\circ \\
\text{F} \\
\text{Xe}
\end{array}$ | $\begin{array}{c}
\text{O} \sim 180^\circ \\
\text{F}
\end{array}$ (h) |
| $\begin{array}{c}
\text{C}_{2v}
\end{array}$ | $\begin{array}{c}
\text{C}_{2v}
\end{array}$ |
<table>
<thead>
<tr>
<th>Species</th>
<th>Central Atom Coordination</th>
<th>Predicted Geometry</th>
<th>Observed Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{XeF}_2$</td>
<td>5'- trigonal bipyramidal (3, 4 - e.b.; 2 b.e.p.)</td>
<td>$\text{F} \quad \text{Xe} \quad \text{F}$</td>
<td>Molecular Geometry Unknown</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\left( \text{D}_{3h} \right)$</td>
<td></td>
</tr>
<tr>
<td>$\text{XeO}_3$</td>
<td>4 - pseudo tetrahedral (1 n-b.e.p.; 3, 4 - e.b.)</td>
<td>$\text{Xe} \quad \text{O}$</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\left( \text{C}_{3v} \right)$</td>
<td>$103^\circ$</td>
</tr>
<tr>
<td>$\text{XeO}_4$</td>
<td>4 - tetrahedral (4, 4 - e.b.)</td>
<td>$\text{Xe} \quad \text{O}$</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\left( \text{T}_{d} \right)$</td>
<td>$109.28^\circ$</td>
</tr>
<tr>
<td>$\text{XeO}_2\text{F}_4$</td>
<td>6 - pseudo octahedral (2, 4 - e.b.; 4 e.p.b.)</td>
<td>$\text{F} \quad \text{Xe} \quad \text{F}$</td>
<td>Compound Unknown</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\left( \text{D}_{4h} \right)$</td>
<td></td>
</tr>
<tr>
<td>Species</td>
<td>Central Atom Coordination</td>
<td>Predicted Geometry</td>
<td>Observed Structure</td>
</tr>
<tr>
<td>---------</td>
<td>---------------------------</td>
<td>--------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>XeOF$_5^+$</td>
<td>6 - pseudo octahedral</td>
<td>![Predicted Geometry Diagram]</td>
<td>(ion unknown)</td>
</tr>
<tr>
<td></td>
<td>(1, 4-e.b.; 5 b.e.p.)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- e., electron; p., pair; n - b, non-bonding; 4 - e, four electron. The ground state geometry is the geometry which provides the largest solid angle for the non-bonding electron pairs or multiple bonding pairs. Non-bonding electron pairs and multiple bonding pairs usually have maximum separation.
Those that are now known conform with his predictions. Some predicted and established geometries are compared in Table 1.3.3.

It should be realized that the shape-predicting quantities of Rundle's three-centre four-electron m.o. approach are as successful as the E.P.R. approach for less than six coordination. Thus, $\text{XeF}_3$ is predicted to be a T shaped species, the 'linear' $\text{F-Xe-F}$ array being three-centre four-electron bonded (hence long, weaker, $\text{Xe-F}$ bonds), the unique $\text{XeF}$ bond being an electron pair bond (hence short). However, as we have seen, Rundle's approach fails for $\text{XeF}_6$ and $\text{IF}_7$.

Of course, it can be argued that the electron repulsion rules would be appropriate for bonds containing less than one electron pair. Thus, $\text{IF}_7$ could be represented as involving 7 single-electron bonds (see Linnett, loc. cit.) and $\text{XeF}_6$ as 6 single-electron bonds and a non-bonding electron pair. However, the similarity of the IF bonds in IF and $\text{IF}_5$ (see 1.2.3) should be borne in mind.

1.3.5. Covalent Radii of The Noble-Gases

Covalent radii for the noble gases have been given by several authors, their estimates, usually being extrapolations from Pauling values for the neighbouring elements or otherwise dependent on them. Sanderson has taken a somewhat different approach, his values being based on his electronegativity equalization principle and related concepts -- his value for xenon is similar to that given by other authors. Values from the various authors are given in Table 1.3.4.

1.3.6 Electronegativity Coefficients of the Noble Gases

Most authors are agreed that the chemically reactive noble-gases are of high electronegativity. Fung has derived electronegativity
coefficients via a variant of the original Pauling method. Other
estimates given by Rundle were from the Mulliken formula. The various
values are given in Table 1.3.4.

Table 1.3.4
Covalent Radii of The Noble-Gas Atoms

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
<th>Rn</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.4-0.6</td>
<td>0.70</td>
<td>0.94</td>
<td>1.09</td>
<td>1.30</td>
<td>1.4-1.5</td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>0.95</td>
<td>1.11</td>
<td>1.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.31</td>
<td>2.12</td>
<td>(c)</td>
<td></td>
</tr>
</tbody>
</table>

Electronegativity Coefficients of The Noble-Gases

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
<th>Rn</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.5-3.0</td>
<td>4.4</td>
<td>3.5</td>
<td>3.0</td>
<td>2.6</td>
<td>2.3-2.5</td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>4.0</td>
<td>2.9</td>
<td>2.6</td>
<td>2.25</td>
<td>2.00</td>
<td>(d)</td>
</tr>
</tbody>
</table>

(a) Bing-Man Fung, J. Phys. Chem. 64, 596 (1965).
(b) R. J. Gillespie, "Noble-Gas Compounds," H. H. Hyman, Ed., The
(c) R. T. Sanderson, Inorg. Chem. 2 (1963) 660; R. T. Sanderson,
1.4 Adsorption, Enclathration and Encapsulation of The Noble-Gases

The heavier noble-gas atoms are bigger than the lighter. The packing diameters derived for the gases in their crystal lattices and the diameters derived from viscosity measurements are in rough agreement, as may be seen from the data in Table 1.4.1, and show a smooth increase with atomic number. Of course, the size of the atom is a rough measure of the size of the outer-most shell of electrons, which is the valence shell. Clearly, the valence electrons of the larger-atom noble-gases, being further from the nucleus, are less firmly held. We have seen, earlier, that the heavier gases are active chemically. They are also the more polarizable. The static atomic polarizability, $\alpha$, for each of the noble-gas atoms is given in Table 1.4.1. The linear relationship of the heat of adsorption

Table 1.4.1

<table>
<thead>
<tr>
<th>Noble-Gas Atom diameters, ionization potentials, static polarizabilities and heat of adsorption on activated charcoal.</th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic lattice diameter (Å)</td>
<td>3.2</td>
<td>3.84</td>
<td>3.96</td>
<td>4.36</td>
<td></td>
</tr>
<tr>
<td>Viscosity diameter (Å)</td>
<td>2.7</td>
<td>2.8</td>
<td>3.42</td>
<td>3.6</td>
<td>4.05</td>
</tr>
<tr>
<td>1st ionization potential (eV)</td>
<td>24.586</td>
<td>21.563</td>
<td>15.759</td>
<td>13.999</td>
<td>12.129</td>
</tr>
<tr>
<td>Static polarizability $(\alpha \text{Å}^3)$</td>
<td>0.204</td>
<td>0.392</td>
<td>1.63</td>
<td>2.465</td>
<td>4.01</td>
</tr>
<tr>
<td>Heat of adsorption on activated charcoal (kcal/g-atom) at temp($^\circ$C)</td>
<td>0.54($^{\text{very low}}$)</td>
<td>1.13(-182)</td>
<td>3.93(-105)</td>
<td>5.32(-50)</td>
<td>8.74(-25)</td>
</tr>
</tbody>
</table>


(b) Ref (a) p. 237.

(c) Ref (a) pp. 150-152.

(d) Ref (a) p. 224. The gas pressures were in the range 0.02-0.04 mm Hg.
### Table 1.4.2.

Some Properties of Noble-Gas Hydrates\(^{(a)}\)

<table>
<thead>
<tr>
<th>Noble-Gas</th>
<th>Decom. Temp. ((°C, 1 \text{ atm press}))</th>
<th>(H_{2}O) Dissocon. Press. ((\text{amt, at } 0°C))</th>
<th>(\Delta H_f^{\circ} (\text{kcal mole}^{-1})) G. 5.75 (H_{2}O)</th>
<th>Cubic unit cell constant(Å)</th>
<th>(\Delta H(G(g) + \text{host lattice})) kcal \text{mole}^{-1}</th>
<th>Decom. Temp. ((°C, 1 \text{ atm press}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>42.3</td>
<td>105</td>
<td>- - -</td>
<td>- - -</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Kr</td>
<td>27.8</td>
<td>14.5</td>
<td>13.9</td>
<td>- - -</td>
<td>6.5</td>
<td>-25.1</td>
</tr>
<tr>
<td>Xe</td>
<td>3.4</td>
<td>1.5</td>
<td>16.7</td>
<td>11.97</td>
<td>9.3</td>
<td>-3.2</td>
</tr>
<tr>
<td>Rn</td>
<td></td>
<td>1</td>
<td>- - -</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^{(a)}\) The values in this table, are taken from G. A. Cook, ref (a) Table 1.4.1, p 164, except for those under \(\Delta H(G(g) + \text{host lattice})\) which were derived from the values in column 4, using Pauling's estimate\(^{45}\) of 0.16 kcal mole\(^{-1}\) for the enthalpy of formation of hydrate cage from ice I.
to the polarizability of the gas atoms was discovered by Chackett and Tuck (see ref (d) Table 1.4.1). There is also abundant evidence that the adsorption of the gases on zeolites and enclathration, in water, hydroquinone, or other host cages, is primarily dependent upon the London dispersion energy. Thus, as discussed by Pauling for the case of the noble-gas hydrates, the energy of the electronic dispersion interaction between two molecules A and B is

\[ W = - \frac{3}{2} \frac{\alpha_A \alpha_B E_A E_B}{r^6 (E_A^1 + E_B^1)} \]

In this equation \( \alpha_A \) and \( \alpha_B \) are the electric polarizabilities of the two molecules, \( E_A \) and \( E_B \) are their effective energies of electronic excitation, and \( r \) is the distance between their centres. The observed enthalpies of sublimation of crystals of the noble gases require that the effective excitation energy be taken as 1.57 times the first ionization energy.

The heat of interaction of each of the noble-gases with the water cage in the 8 G. 46 H₂O hydrates is listed in Table 1.4.2. The values of 6.5 and 9.3 kcal mole⁻¹, for krypton and xenon respectively, are similar to the heats of adsorption for these elements on charcoal.

( Table 1.4.2 )

1.4.1. Noble-Gas Clathrates

Shortly after the discovery of argon, Villard prepared a hydrate of the gas (1898). Hydrates of krypton, xenon and radon were prepared somewhat later. All have the general ideal formula 8 G. 46 H₂O. The gas atoms are held in 'cages' in a pseudo-ice water lattice.
In 1949, Powell and Guter prepared a compound of argon and hydroquinone by crystallizing a solution of the latter in benzene under argon at a pressure of 20 atmospheres. Hydroquinone compounds with krypton or xenon proved to be easier to prepare. These compounds like the hydrates were shown from structural analyses by Powell to be hydrogen bonded networks of the 'host' species (g-hydroquinone) containing cavities, which serve as cages for the 'guest' species i.e., noble-gas atoms, or other suitably sized species, e.g., methane. It is a usual characteristic of these cage-compounds, which were given the name clathrates by Powell, that the lattice of the 'host' shows a structural modification, from that of the pure 'host'. The modified 'host' lattice contains fewer but larger cavities than the more stable, pure, 'host.' This modification is energetically less favourable, but, of course, the energy of interaction with the guest atom (Van der Waals bonding) more than offsets that unfavourable feature.

J. H. van der Waals has used a statistical mechanical theory to account for the noble-gas clathrates, particularly the hydroquinone compounds. From his theory, van der Waals calculates the heat of formation, at constant volume, of the argon-hydroquinone clathrate to be 5.1 kcal g-atom⁻¹ (from solid g-hydroquinone and gaseous argon), compared to a value of 5.4 kcal g-atom⁻¹, derived from experimental findings of Evans and Richards. In this theory, the noble-gas atoms are assumed to be rotating as freely as in liquid argon.

It is not essential for all suitable cavities in the clathrates to be filled to sustain the structure, so long as there is sufficient interaction energy to maintain the 'host' structural form. Accordingly, the clathrates are usually non-stoichiometric.
Apart from their theoretical interest, the clathrates are important as a means of concentrating and holding the heavier noble-gases. The gases may be readily released either by dissolution or thermal decomposition. To illustrate: argon amounts to ~ 8.8 wt % of the argon ε-hydroquinone compound (which has an 'ideal' stoichiometry \([C_6H_4(OH)_2]_3\text{Ar}\)). It may be preserved for several weeks in air at 1 atm. pressure with an argon loss of less than 10%. When it is dissolved in ether, methanol, or other solvents, or heated, the argon is liberated. To achieve the same space concentration of the argon, as in the clathrate, it would be necessary to compress pure argon to 95 atm at room temperature. A ε-hydroquinone clathrate has already proved useful as a carrier for radioactive \(^{85}\text{Kr}\).

**Noble-gas hydrates.** The crystal structures of the simple-noble-gas hydrates were established by Claussen in 1951. Structural features, of the clathrate hydrates generally, have been reviewed by Jeffrey and McMullen. Each noble-gas, except helium and neon, forms a hydrate when mixed with water at ~0°C, under a gas pressure exceeding the invariant decomposition pressure (see Table 1.4.2). Crystallization takes place at the phase boundaries within the water. The hydrates are usually non-stoichiometric.

So called "double hydrates" can be formed if a noble-gas is mixed with another species like acetic acid, chlorine, chloroform or carbon tetrachloride. The noble-gas can also act as a so called "help gas," in enhancing the stability of a clathrate. Thus double hydrates of acetone with Ar, Kr or Xe have been prepared from aqueous solution at -30°C, under gas pressures of 300, 30 and 1 atmosphere respectively.

All noble-gas hydrates contain a common structural feature. This is a pentagonal dodecahedral arrangement of water molecules, shown in
Figure 1.4.1

The 12Å Hydrate-Clathrate Structure (a)


- Sites for pentagonal dodecahedra
- Sites for tetrakaidecahedra

Tetrakaidecahedron
Pentagonal dodecahedron
In these $\text{H}_4\text{O}_{20}$ units, each dodecahedron vertex is an oxygen atom site and each edge represents an O-H-O hydrogen bond. These units are linked differently in the two known, noble-gas-containing, clathrate hydrate structures.

In the simpler structure, which has a cubic unit cell, $a_0 \approx 12\,\text{Å}$, the $\text{H}_4\text{O}_{20}$ units are linked by other water molecules to form a pseudo-body-centered array in which the two $\text{H}_4\text{O}_{20}$ polyhedra at the corner $(0,0,0)$ and body centre $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ of the cubic unit cell ($O^3_h - \text{Pm}3\text{n}$) are linked by six water molecules (two in each face of the cube). The polyhedra at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, are rotated through $90^\circ$ with respect to those at $0,0,0$ sites. Each water molecule is surrounded by four others, with which it forms hydrogen bonds. The O-H-O distance in the dodecahedron is $2.75\,\text{Å}$, which is essentially the same as the value for ordinary ice, which is $2.76\,\text{Å}$. The unit cell contains $46$ water molecules in all and the water structure is approximately $12\%$ less dense than that of ice I. The water structure contains fewer holes than ice I, but the holes are larger. The noble-gas atoms occupy the holes. The holes, or chambers, are of two types: two are defined by the dodecahedra and are smaller than the other six chambers which are defined by 24 water molecules at the corners of a tetrakaidecahedron (shown in Figure 1.4.1). The tetrakaidecahedron has 2 hexagonal and 12 pentagonal faces and there are six tetrakaidecahedra in the unit cell. The hexagonal faces include those water molecules which link the dodecahedra. Pauling has discussed this hydrate structure in detail. He points out that in the crystal $8\text{Xe} \cdot 46 \text{H}_2\text{O}$, two xenon atoms are in pentagonal dodecahedra chambers, and the 20 water molecules are at a distance of $3.85\,\text{Å}$ from the xenon atom. For each of the six xenon atoms
in tetrakaidecahedral chambers, there are 12 water molecules at 4.03\AA
and 12 at 4.46\AA from the xenon atom. Using the dispersion energy
equation given above, and assuming $E_{\text{H}_2\text{O}} \approx E_{\text{Xe}} \approx 1.57 \text{ x the first}
ionization potential of xenon (280 kcal mole}^{-1}$, Pauling derives the
interaction energy for two molecules (Xe and H$_2$O) to be $-\alpha \frac{R_{\text{Xe}}R_{\text{H}_2\text{O}}}{r^6}$,
in which $R_{\text{Xe}}$ (=10.16 ml) and $R_{\text{H}_2\text{O}}$ (=3.75 ml) are the mole refractions
of Xe and H$_2$O, $\alpha$ = 51 kcal mole$^{-1}$, and $r$ is the average Xe-H$_2$O distance
in \AA units (the mole refraction is $4\pi N/3$ times the polarizability;
$N$ is Avogadro's number). With inclusion of terms for more distant
water molecules and other xenon atoms his value for the interaction
energy becomes -10.3 kcal mole$^{-1}$, which is in fair agreement with
the experimental value of -9.3 kcal mole$^{-1}$ given in Table 1.4.2. This
interaction energy is large compared to the 0.16 kcal mole$^{-1}$ lower
enthalpy of the clathrate 'ice' structure compared with ice I.

In the other common hydrate structure, which is the one usually
adopted by the "double hydrates," the cubic unit cell ($a = \sim 17\AA$)
contains 136 water molecules in a hydrogen bonded framework which
defines 16 small chambers, with the pentagonal dodecahedron as the
cage, and 8 large chambers, each formed by twenty-eight water molecules
at the corners of a hexakai-decahedron. The hexakai-decahedron has
4 hexagonal and 12 pentagonal faces. The large chambers accomodate
large molecules like chloroform and the smaller chambers, smaller
molecules like xenon and krypton. Thus chloroform and xenon yield
a hydrate of ideal composition CHCl$_3$ . 2Xe , 17 H$_2$O., i.e., 8CHCl$_3$:
16Xe. 136 H$_2$O.

Pauling$^{46}$ and Miller$^{57}$, independently, have proposed that clathrate
hydrate formation may be important in anesthesia. Certainly, xenon is
an effective anesthetic and that role must involve London dispersion interactions and not chemical bonding.

The recently reported\textsuperscript{58} binding of xenon to myoglobin is also, apparently, another example of enclathration. It may also be noted here that the large negative entropy of solution of argon in water\textsuperscript{59} may be due to the formation of an orientated water sheath about the dissolved atoms. Addition of small quantities of dioxane leads to a rapid increase in the entropy of solution, presumably because of the destruction of the argon water sheath.

\textbf{\(\beta\)-Hydroquinone and Phenol Clathrates.} Argon, krypton and xenon \(\beta\)-hydroquinone clathrates have been prepared and characterized by Powell.\textsuperscript{53} Clathrates involving other phenolic materials have also been described, principally those of phenol. It is of interest that Nikitin\textsuperscript{60} used the latter host-precursor in 1939, to attempt to prepare a phenol-radon clathrate. He was able to produce a mixed phenol clathrate of radon and hydrogen sulphide, but not a pure Rn clathrate. In 1940 he prepared a xenon-phenol clathrate and incidentally was the first to infer from this study that this and related compounds involved an inclusion type of association. Von Stackelberg and his associates\textsuperscript{61} have elucidated the structure of this and a number of other phenol clathrates, several of which were first prepared by them.

The ideal composition of the \(\beta\)-hydroquinone clathrates is \(G \cdot 3\mathcal{G} \cdot C_6H_4(OH)_2\). Typical compositions are represented in Table 1.4.3., where \(G\) is Ar, Kr and Xe. Structural analyses show that the noble-gas atoms are located in approximately spherical cages of hydrogen bonded hydroquinone molecules.\textsuperscript{51} The free diameter of the cage hole is \(\sim 4.2\AA\).
The β-hydroquinone structure is 82 cal mole\(^{-1}\) less favourable in free energy than the non-clathrate α form.\(^5\) Although the hydroquinone clathrates are usually derived from solutions this is not essential. The argon clathrate has been prepared by subjecting solid α-hydroquinone to argon pressures of 300 atm and above. Von Stackelberg\(^6\) has shown

Table 1.4.3.

**Table 1.4.3.**

<table>
<thead>
<tr>
<th>Noble-gas</th>
<th>β-Hydroquinone clathrates(^{(a)})</th>
<th>Phenol Clathrates(^{(b)})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G.3C(_6)H(_4)(OH)(_2)</td>
<td>mG.12C(_6)H(_5)OH</td>
</tr>
<tr>
<td>Noble-gas</td>
<td>C(_6)H(_4)(OH)(_2)</td>
<td>G</td>
</tr>
<tr>
<td></td>
<td>Ratio</td>
<td>kcal mole(^{-1})</td>
</tr>
<tr>
<td>Ar</td>
<td>3: 0.8</td>
<td>-6.0</td>
</tr>
<tr>
<td>Kr</td>
<td>3: 0.74</td>
<td>-6.3</td>
</tr>
<tr>
<td>Xe</td>
<td>3: 0.88</td>
<td>4.0</td>
</tr>
</tbody>
</table>

\(\Delta H^*\) represents the enthalpy change for the process: Host lattice (α form)\(^{(c)}\) + G(g) \(\rightarrow\) clathrate compound.

\(\Delta H^*\) represents the enthalpy change for the process: Host lattice (α form)\(^{(c)}\) + G(g) \(\rightarrow\) clathrate compound.


(b) P. H. Lahr, and H. L. Williams, J. Phys. Chem., 63 (1959) 1432.

that the phenol clathrates contain 12 phenol molecules per unit cell. The argon, krypton and xenon phenol clathrates have also been made directly from the gases and molten phenol at > 40°C.
Mössbauer Studies of Noble-Gas Clathrates. The value of Mössbauer studies in the further elucidation of the noble-gas clathrates has been briefly reviewed by Herber.\(^6^2\) Evidently the recoil-free fraction of the \(^{83}\)Kr-hydroquinone clathrate absorber is essentially constant between room temperature and \(\sim 150^\circ K\). The recoil free fraction increases very rapidly below this temperature. The results for \(T > 150^\circ K\) are what one would expect for a square well potential, but the low temperature results are open to several interpretations. The latter results are more typical of ordinary harmonic binding and suggest either the onset of phenomena normally associated with bulk materials (such as condensation and liquefaction), or "sticky" collisions with the cavity wall. The work on both xenon and krypton hydroquinone clathrates shows that the noble gas atoms are essentially in spherical sites -- single resonances only are observed.

The \(\gamma\)-ray transitions in the xenon halides have excess energy relative to atomic xenon in the \(\gamma\)-hydroquinone clathrate whereas the transitions in the tetroxide and perxenates have less energy. The isomer shifts are displayed as an energy level diagram in Figure 1.4.2. The excess energy of the \(\gamma\)-rays in the halides can be explained on the assumption that these compounds involve Xe \(p\) orbitals in bonding. These findings have been accounted for by Perlow and Perlow (see Fig. 1.4.2) as follows: The transfer of \(5p\) electrons from xenon increases the effective field acting on the Xe \(s\) electrons (5\(s\) and inner electrons) -- hence, \(\Delta s\) (the isomer shift) > 0. On the other hand, the oxygen containing compounds, having octahedral or tetrahedral symmetry, have appreciable 5\(s\)
Xenon isomer shifts *(a) 

\[ \begin{align*}
\text{XeF}_4 & : +0.40 \pm 0.04 \\
\{\text{XeCl}_4\} & : +0.25 \pm 0.08 \\
\{\text{XeCl}_2\} & : +0.17 \pm 0.08 \\
\text{XeF}_2 & : +0.10 \pm 0.12 \\
\text{CLATHRATE} & : 0 \\
\text{XeO}_4 & : -0.19 \pm 0.02 \\
\text{XeO}_6 & : -0.22 \pm 0.02 \\
\end{align*} \]

*The energies shown are to be added to the transition energy for the neutral atomic species.

admixture into their bonding orbitals and the direct effect of the transfer of $5s$ charge reduces the central charge density more than the shielding effect of $5p$ transfer increases it. Consequently, $\Delta s < 0$. Implicit in this explanation is the assumption that the enclathrated xenon is essentially an unperturbed xenon atom.

1.4.2. Noble-Gas Encapsulation in Zeolites

The encapsulation of noble-gases in zeolites is quite similar to the trapping of the gases in clathrates, but no simple stoichiometry appears to exist. Encapsulation does not appear to change the structure of the adsorbing zeolite. The process consists of forcing gas molecules into the pores of a suitable heat-stable material at elevated temperatures and pressures, and then trapping them by cooling the material in the presence of the gas, maintaining the high pressure until the cooling is complete. The most suitable host materials have so far proved to be the synthetic zeolites. These are dehydrated alumino-silicates, which are interlaced with regularly spaced channels which are of molecular dimensions. Pore and channel size in the synthetic zeolites can be controlled by varying the cation type of the zeolite. With this control, atoms or molecules above a given size can be excluded -- hence the term "molecular sieves." Presumably in the "encapsulation" process, the increased vibrational motion of the atoms in the zeolite lattice lowers the potential energy barrier and the increased kinetic energy of the gaseous atom aids in overcoming this barrier. In any event, the channels fill up with gas atoms. With suitable choice of zeolite, the weight of gas trapped per unit weight of zeolite is greater than for any known clathrate, e.g. up to 20 wt % argon has been encapsulated. Table 1.4.4 gives some representative findings. Encapsulation is not yet very effective for neon. The most effective zeolite pore diameter
(at room temperature) for argon and krypton atoms are about 3.82 and 4.0\textdegree, respectively. There are indications that the $^{85}$Kr encapsulates may be as stable as the clathrates (see 1.4.1).

### Table 1.4.4

Encapsulation of Argon and Krypton in Synthetic Zeolite Type A (a)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Cationic Composition of the zeolite</th>
<th>Initial Encapsulation pressure, atm</th>
<th>Quantity Encapsulated (g gas per 100 g zeolite)</th>
<th>At Start</th>
<th>After 30 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>20 / 80</td>
<td>2500</td>
<td>16.7</td>
<td>&lt;30% loss</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 / 60</td>
<td>2500</td>
<td>19.4</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60 / 40</td>
<td>2500</td>
<td>19.0</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>Kr</td>
<td>100% Na</td>
<td>4300</td>
<td>32.4</td>
<td>32.8*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60 / 40</td>
<td>4300</td>
<td>34.8</td>
<td>30.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82 / 8</td>
<td>4300</td>
<td>21.6</td>
<td>20.1</td>
<td></td>
</tr>
</tbody>
</table>

* The apparent increase most probably arises from analytical inaccuracy.


### 1.5 Gaseous Noble-Gas Cationic and Excited Atom Species

There are numerous reports of cationic species involving a noble-gas atom and some other atom or molecule. Two recent reviews have dealt with them. 63, 64
These transient species are usually produced by high energy radiation or bombardment with high energy particles (e.g. electrons) and have invariably been detected by mass spectroscopy. Since the noble-gas cations are isoelectronic with the neighbouring halogen atoms, they are anticipated to be more electronegative than them (because of their higher nuclear charge). It is to be expected, then, that the noble-gas cations should form bound species with other atoms and ligands. Now the electron affinity of these cationic species will, in many cases, approach the electron affinity of the noble-gas cation itself. This makes it unlikely that stable salts of cations containing helium and neon for use at ordinary temperatures and pressures will be isolated. There is more hope for Rn, Xe, Kr and Ar species. As mentioned earlier (see 1.2.3) certain argon cation species e.g. ArF+ may be isolateable as salts. However, KrF+ salts are more likely (see 2.2.1) and XeF+ salts are known (see 3.2.1.)

1.5.1 Hydride Cations

The simplest cation derivatives are the hydrides. They may be generated in ion-molecule reactions:

\[ G^+ + \text{H}_2 \rightarrow \text{GH}^+ + \text{H} \]

\[ G + \text{H}_2^+ \rightarrow \text{GH}^+ + \text{H} \]

The first reaction has been observed for Ar, Kr and Xe. The estimated proton affinities, i.e., \( \Delta H(G(g) + H^+(g) \rightarrow (GH)^+(g)) \) for the diatomic hydride cations are listed in Table 1.5.1. As may be seen from the thermochemical cycle in Figure 1.5.1., the electron affinity of \( \text{GH}^+(g) \)
Table 1.5.1
Proton affinities\(^{(a)}\) \(G_{p}\), and ionization potentials of the noble gases

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>(G_{p}) (eV)</td>
<td>1.8</td>
<td>2.2</td>
<td>3.0</td>
<td>&gt;4</td>
<td>&gt;6</td>
</tr>
<tr>
<td>I(0)(eV)</td>
<td>24.586</td>
<td>21.563</td>
<td>15.759</td>
<td>13.999</td>
<td>12.129</td>
</tr>
</tbody>
</table>


is equal to the electron affinity of the proton \((-13.6\text{ eV})\) minus the proton affinity of \(G\). This is so only if \(\Delta H(GH(g)\rightarrow G(g)+H(g))\) is zero. Thus the electron affinity of \(ArH^{+}\) should be \(\approx -10.6\text{ eV}\).

Figure 1.5.1
Relationship of ionization potential, proton affinity and hydride cation electron affinity

\[\begin{align*}
G(g) + H_{2}(g) & \rightarrow (GH)^{+} \\
& \downarrow 13.6\text{ eV} \quad E((GH)^{+}) \\
G(g) + H(g) & \rightarrow GH(g) \quad \Delta H\text{ diss} \approx 0(?)
\end{align*}\]

Note that \(E(XeH^{+}) \approx -7.6\text{ eV}\). This is encouraging. Xenonium salts may be preparable.

1.5.2 Excited Atom Reactions

Energy levels and radiative lifetimes of the noble gases are given in Table 1.5.2. The excitation energies of even the lowest excited
states of the noble-gases are greater than the ionization energies of many molecules. Accordingly, excited noble-gas atoms will often bring about associative ionization:

\[
G^* + X \rightarrow GX^+ + e
\]

The noble gases can therefore act as photosensitizers in much the same way as mercury. Thus, krypton sensitized dissociation of \(N_2\) has been established. Excited xenon atoms generate the short lived \(XeO\) molecule in the reaction:

\[
Xe^* + O_2 \rightarrow XeO^* + O
\]
2. Krypton Chemistry

So far, the chemistry of krypton has been limited to that of krypton difluoride and its derivatives. All efforts to confirm the synthesis of a tetrafluoride or higher fluoride of krypton have failed. These attempts have included the subjection of \( \text{KrF}_2/F_2 \) mixtures to high energy irradiation at low temperatures. Nor has any firm evidence appeared to support the existence of oxides, oxysalts or chlorides.

2.1. Krypton (I) Compounds

No \( \text{Kr}^+ \) salts have been claimed and the only established krypton(I) compound is the low temperature species, krypton-monofluoride radical.

2.1.1 The Krypton Monofluoride Radical

Although krypton monofluoride has only been generated in exceedingly small concentration, in krypton difluoride crystals subjected to \( \gamma \) radiation (1.3 MeV), it is, nevertheless, of interest because of the information the unpaired-electron probe yields on the nature of krypton-fluorine bonding. The radicals, which colour the host crystals violet, persist indefinitely at \(-196^\circ\) but disappear on warming to \(-153^\circ\). The \( \text{KrF} \) radical has one more electron than bromine monofluoride. Since this electron must be in an antibonding \( \sigma \) orbital, the \( \text{Kr}-\text{F} \) bond can amount only to a one electron bond. The bond strength may be comparable to the \( \text{KrF} \) bond in \( \text{KrF}_2 \) (mean thermochemical bond energy \( = 12 \) kcal mole\(^{-1}\)) but certainly weaker and presumably, at most, only half the strength of the bond in the \( \text{Kr-F}^+ \) ion (isoelectronic with \( \text{BrF} \), for which the thermochemical bond energy \( = 60 \) kcal mole\(^{-1}\)).
In an electron spin resonance study of the radical, hyperfine interaction of the electron spin with the $^{19}$F nucleus was observed, which was sufficient to show that the fluorine component of the anti-bonding orbital, containing the unpaired electron, is chiefly F2p$_{o}$, (2p$_{o}$ population, $c_{F}^{2}2p = 0.61$, whereas, $c_{F}^{2}2s = 0.04$). This is similar to the situation in XeF (see 3.1.1.). Furthermore, the findings indicated a lower fluorine character in the bonding orbitals of KrF, compared with XeF, which is in harmony with the greater electronegativity of krypton, than xenon.

2.2. Krypton (II) Compounds

2.2.1 Krypton Difluoride

Synthesis. Krypton difluoride was first characterized by Turner and Pimentel who prepared it by the u.v. photolysis of fluorine, suspended in a solid mixture of argon and krypton at 20 K. Although the first krypton compound to be prepared was described by its discoverers, Von Grosse and his coworkers, as the tetrafluoride, the properties ascribed to this material have been shown to be those of the difluoride.

Laboratory Preparation. Because the difluoride is thermodynamically unstable all successful syntheses have used krypton and fluorine mixtures held at low temperatures (usually -193°), and have involved either irradiation with γ rays, 1.5 Mev electrons, ultraviolet light, or 10 Mev protons, or electric discharge of the gaseous mixture. The last procedure is the simplest to reproduce and has been employed in several laboratories to make gram quantities of the fluoride. The essential apparatus is shown in Figure 2.2.1. The cleanest synthesis, which is also moderately efficient, involves the irradiation, at temperatures of less than -60, and approaching -196°, of the gaseous krypton and fluorine mixtures with 10 Mev protons.
Diagram of apparatus used for the preparation of krypton difluoride.

A: Polychlorotrifluoroethylene container for the collection and storage of the compound, attached to the glass apparatus by compression fittings. B and C: U-tubes of Pyrex glass with break-seals. D: Electrical discharge reaction vessel made of Pyrex glass (diameter, 60 mm.; height of wide portion, 200 mm.). Two copper disks of 20 mm. diameter and 5 mm. thickness, spaced 75 mm. apart, serve as electrodes. The leads to the electrodes are silver soldered into Kovar to glass seals.

E: Valve manifold to convert push-pull operation of magnetic piston pump into unidirectional gas circulation as indicated. Each individual valve consisted of a 10-mm. glass tube ground flat at the end, protruding into a wider tube and closed with a thin square piece of glass held in place by gravity. Application of a small pressure head from below (0.1 mm.) permits gas to flow upward. Downward flow is inhibited by the closure of the ground end of the glass tube by the square piece of glass. Arrangement of four valves in the way indicated in the figure permits use of the pumping action of each half stroke of the piston.

F: Magnetic piston pump after Brenschede. G: Piston of pump suspended from stainless steel spring. H: Solenoid. V1, V2, V3: Monel valves. With the reaction in progress valve 1 is kept closed while valves 2 and 3 are open. During the purification and sublimation of the product, first to tube C and then into tube B, valves 2 and 3 are closed to separate the pump from the rest of the system, and valve 1 is open to establish a connection to the vacuum line.

Since the proton beam passes effectively through a 0.03 cm thick aluminium window, the synthesis of this most oxidatively reactive of all fluorides can be carried out in an all aluminium vessel. (Aluminium is highly resistant to oxidative fluorination.) A 1-hr. irradiation at 54 mA yields ca. 1g of KrF₂. The G value for KrF₂ formation lies in the range 1 to 1.5 molecules/100 ev.⁶⁶

Krypton difluoride is most conveniently identified by its vibrational spectra and particularly by its Raman active \( \nu_{1} \) mode at 449 cm\(^{-1} \). The Raman spectrum is easiest to obtain since sapphire, which is chemically resistant to KrF₂, can be used as the container material. The very strong infrared band at 588 cm\(^{-1} \) also serves for ready identification -- silver chloride windows should be used. The instability of KrF₂ requires that the identification be carried out quickly and at the lowest possible temperature.

Thermodynamic Properties. Krypton difluoride is colourless both in the solid and vapour phases. It decomposes spontaneously at temperatures well below room temperature, the decomposition rate for the vapour at room temperature being \( \sim 10\% \) hr\(^{-1} \). The decomposition rate is substantially lower for the solid⁷⁴ and evidently negligible at Dry Ice temperature.⁷² The spontaneous dissociation has prevented the accurate determination of a number of the physical properties of KrF₂, but there is general agreement⁷²,⁷⁴ that its vapour pressure is ca. 30 mm Hg at 0°. The enthalpy of vapourization \( \Delta H_{sub} = 9.9 \text{ kcal mole}^{-1} \) has been derived from vapour pressure measurements over the limited temperature range \(-15.5 \) to \(15^\circ\).⁷⁴

Measurement of the heat of dissociation⁷⁹, at 93°, of a gaseous sample of the difluoride (which is rapidly decomposed at this temperature) has given a standard heat of formation \( \Delta H_f^{\circ} (\text{KrF}_2(g)) = 14.4 \pm 0.8 \text{ kcal mole}^{-1} \). The calorimetric measurements are supported by mass-spectrometric, appearance-
potential data. Although there is some ambiguity of interpretation, it is probable that the observed appearance potential $A(\text{Kr}^+, \text{KrF}_2) = 13.21 \pm 0.25$ ev, is appropriate for the process $\text{KrF}_2(g) + e \rightarrow \text{Kr}^+ + \text{F}_2(g) + 2e$.

If so, since $I(\text{Kr}) = 14.00$ ev, it follows that $\Delta H(\text{KrF}_2(g) \rightarrow \text{Kr}(g) + \text{F}_2(g)) = 0.79 \pm 0.25$ ev (i.e., $18 \pm 5$ kcal mole$^{-1}$).

The thermochemical average bond energy derived from the calorimetric data is 12 kcal mole$^{-1}$. This is the lowest average bond energy of any known fluoride. Indeed the atomization of $\text{KrF}_2$ involves a lower enthalpy than the atomization of molecular fluorine! Krypton difluoride should, of all oxidative fluorides, be closest in activity to atomic fluorine.

Although the $\text{KrF}^+$ ion is not established there is reason to believe that it occurs in the complex $\text{KrF}_2_2$, 2SbF$_5$ (see 2.2.2). As can be seen from Fig. 2.2.2, the electron affinity of $\text{KrF}^+$ equals the electron affinity of $\text{Kr}^+$ ($-I(\text{Kr}, g) = 14.0$ ev), less the difference in bond energy between $\text{KrF}^+$ and $\text{KrF}$. It is reasonable to suppose that the B.E. ($\text{KrF}^+$) is $\sim 2 \times$ B.E. ($\text{KrF}$).

A recent value for the appearance potential$^{76a}$ for $\text{KrF}^+$, $A(\text{KrF}^+, \text{KrF}_2) = 13.39$ ev. Since this corresponds to the process $\text{KrF}_2(g) \rightarrow \text{KrF}^+ + \text{F}_2(g) + e$, then from Fig. 2.2.2, $A(\text{KrF}^+, \text{KrF}_2) = \Delta H(\text{KrF}_2(g) \rightarrow \text{Kr}(g) + 2\text{F}(g)) + I(\text{Kr}) + \text{B.E.}(\text{KrF}^+)$. Therefore, the bond energy for the cation = $(13.39 - 14.00)$ ev $- \Delta H_{\text{at}}(\text{KrF}_2) \approx 37$ kcal mole$^{-1}$. This is approximately 3 times the mean thermochemical bond energy of $\text{KrF}_2$.

Figure 2.2.2

The Electron Affinity and Bond Energy of $\text{KrF}^+$
The Electron Affinity and Bond Energy of KrF$^+$

\[ \text{I}(\text{KrF}_2) = \text{I}(\text{Kr}) - \text{B.E.}(\text{KrF}^+) + \text{B.E.}(\text{KrF})(g) \]

\[ \text{B.E.}(\text{KrF}^+) = \text{I}(\text{Kr}) - \text{A}(\text{KrF}^+, \text{KrF}_2) + \Delta H_{at}(\text{KrF}_2) \]
Structural Features. Like its relative, xenon difluoride, KrF$_2$ is a symmetrical linear molecule (D$_{oo}$h). The Kr-F interatomic distance has been determined for the gaseous species by electron diffraction, (1.889 ± 0.010 Å) and rotational infrared spectroscopy (1.875 ± 0.002 Å). The infrared and Raman data are in agreement with the D$_{oo}$h molecular symmetry and the force constants $f_\alpha = 2.46$, $f_{rr} = -0.20$ and $f_\alpha = 0.21$ indynes$^{-1}$, obtained from the computed potential function $2V = f_\alpha (\Delta r_1^2 + \Delta r_2^2) + 2f_{rr} \Delta r_1 \Delta r_2 + r_0^2 f_\alpha \Delta \alpha^2$, where $\Delta r_1$ and $\Delta r_2$ are changes in the bond distances and $\Delta \alpha$ is the change in bond angle, have been interpreted (particularly the negative sign of $f_{rr}$, the bond-bond interaction constant) in terms of a considerable weight of a no-bond F Kr F structure in resonance admixture with (F-Kr)$^+$ F$^-$ (Kr-F)$^+$. The krypton difluoride molecule is related to the bromine trifluoride molecule. As may be seen from the molecular characteristics represented in Fig. 2.2.3, the Kr-F internuclear distance in KrF$_2$ is slightly greater than the Br-F distance in the approximately linear part of the BrF$_3$ molecule. The unique Br-F bond distance in BrF$_3$ is comparable to the internuclear separation in the bromine monofluoride molecule. The bonding associated with two longer bonds of BrF$_3$ is presumably similar to that involved in KrF$_2$. If four-electron, three-centre p$_o$ m.o. bonding is assumed, then each F ligand is, in effect, bonded to the central atom by one electron. The shorter, stronger bond in bromine monofluoride is consistent with electron-pair-bonding. Presumably, the bond length in KrF$^+$ will be similar to that in BrF and it may, like XeF$^+$ (see 3.2.6.), be slightly shorter than its halogen relative. Although crystalline krypton difluoride is not isostructural with xenon difluoride, it is, like the
Figure 2.2.3

Comparison of KrF₂ with BrF BrF₃ and XeF₂

\[
\begin{align*}
\text{F} & \text{Kr} \quad \text{F} \\
1.88 & \\
\text{F} & \text{Xe} \quad \text{F} \\
2.00 & \\
\end{align*}
\]

\[
\begin{align*}
\text{F} & \text{Br} \quad \text{F} \\
1.810 & \\
\text{Br} & \quad \text{F} \\
1.721 & \\
\end{align*}
\]

\[
\begin{align*}
\text{F} & \quad \text{Br} \\
1.759 & \\
\end{align*}
\]

Only the approximately linear BrF₂ part of the BrF₃ molecule is relevant for this comparison.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(v₁)</th>
<th>(v₂)</th>
<th>(v₃)</th>
<th>(f_r)</th>
<th>(f_{rr})</th>
<th>(f_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KrF₂</td>
<td>449</td>
<td>232.6</td>
<td>588</td>
<td>2.46</td>
<td>-0.20</td>
<td>0.21</td>
</tr>
<tr>
<td>(F)BrF₂*</td>
<td>531</td>
<td>613</td>
<td></td>
<td>3.00</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>XeF₂</td>
<td>515</td>
<td>213.2</td>
<td>558</td>
<td>2.84</td>
<td>0.13</td>
<td>0.20</td>
</tr>
</tbody>
</table>

*Only the approximately linear BrF₂ part of the BrF₃ molecule is relevant for this comparison.*
later, essentially a molecular assembly. The structure is not known with high precision, but is known that the molecules are oriented such that each fluorine ligand of one molecule is oriented towards a Kr atom of its nearest neighbour. The orientation and alignment of the molecules is consistent with an appreciable bond polarity. The effective volume of one molecule in crystalline KrF$_2$ which is $37.5 \, \text{Å}^3$, is similar to the XeF$_2$ value of $39.2 \, \text{Å}^3$.

Bond Polarity and Bond Type. Both $^{19}\text{F}$ n.m.r. studies of KrF$_2$ solutions in anhydrous hydrogen fluoride $\mathcal{F}$, and Mössbauer studies on the pure solid, have yielded data which have been interpreted in terms of the charge distribution in the linear molecule. In both studies close relationship of KrF$_2$ to the much more extensively studied XeF$_2$ molecule was assumed. The $^{19}\text{F}$ chemical shielding value, $\sigma_F$, relative to F$_2$, for KrF$_2$($\sigma_F \approx 370 \times 10^{-6}$) is much less than for XeF$_2$($\sigma_F = 629 \times 10^{-6}$).

The interpretation of these findings was based on the assumption that the bonding in KrF$_2$ as in XeF$_2$, is of the three-centre, four-electron, p$_g$ m.o. type and that the shielding arises from the paramagnetic term. On this basis, it has been argued that $q_F$ (KrF$_2$) = -0.45 e, whereas for XeF$_2$, $q_F = -0.73$ e. The lower polarity of the Kr-F bond, relative to the Xe-F bond, is readily rationalized in terms of the higher electronegativity of krypton than that of xenon (see 1.3.5). It is of interest that the $^{19}\text{F}$ n.m.r study of KrF$_2$ solutions in HF showed that there is no fluorine exchange with the solvent, even at 25°, in contrast with XeF$_2$ (see 3.2.1). It is to be expected that ionization to form KrF$^+$ is less favourable than for XeF$^+$ formation.

The KrF$_2$ charge distribution derived from the Mössbauer findings is similar to that from the n.m.r. data. Since the experimentally derived quadrupole interaction energy for KrF$_2$, $e^2qQ$ (where $e$ is the charge on the electron, $Q$ the quadrupole moment and $eq$ the field gradient) = $960 \pm 30$ m Hz,
is a consequence of an electric field gradient at the position of the krypton nucleus, there must be a non-spherical electron distribution about that nucleus. This is assumed to arise from the sharing of some krypton 4p electrons with the fluorine atoms. On the assumption of that only po orbitals are involved in the bonding, the interaction energy (for one electron transferred from krypton) \( e^2 Q (\text{KrF}_2) = + \frac{4}{5} e^2 Q \langle r^{-3} \rangle \), i.e., the field gradient due to one 4p electron is \( eq = + \frac{4}{5} e \langle r^{-3} \rangle \). However, atomic beam work had shown that for the \( 3p^2 \) state of Kr (i.e., for a \( 4p^55s \) configuration, where one electron has been removed from a p orbital) \( \frac{2}{5} e^2 Q \langle r^{-3} \rangle = 452.2 \text{ mH}_2 \). If \( \langle r^{-3} \rangle \) is approximately the same for \( \text{KrF}_2 \) and Kr, the interaction energy for the one p electron deficiency for the two cases, should be in the ratio 2:1; they are approximately so \( (960:452.2) \). This indicates, supposing the \( \langle r^{-3} \rangle \) assumption to be valid, that the electron transfer from the krypton atom to the fluorine ligands would be \( \sim 1 \) le. The authors of the Mössbauer study have pointed out that this finding can be simply rationalized (in valence bond terms) on the assumption that \( \text{KrF}_2 \) is a resonance hybrid of \( F^{\text{-}} \text{Kr}^{\text{+}} F^{-} \) and \( F \text{Kr}^{\text{+}} - F \). They point out that if the electronegativity of \( \text{Kr}^{\text{+}} \) and \( F \) are similar this would result in equal sharing of the bond electron pair in \( \text{KrF}^{\text{+}} \). Consequently, the krypton atom in \( \text{KrF}_2 \) would have a net deficiency of one 4p electron. An electron transfer of \( 1 \) le from the Kr atom to the ligands, however, seems rather high, particularly since a charge distribution of that size has been well substantiated for \( \text{XeF}_2 \) (see 3.2.1), and xenon is less electronegative than krypton. Furthermore Coulson's interpretation\(^{78}\) of the peculiar nature of the bond-bond interaction force constant requires considerable weight of the no-bond structure, \( F \text{Kr} F \), in the resonance admixture.
with $\text{F} (\text{Kr-F})^+$ and $(\text{F-Kr})^+ \text{F}^-$, which requirement of course reduces the Kr charge to less than +1. The form $\text{F}^– \text{Kr}^2+ \text{F}^-$ presumably does not make significant contributions to the bonding. It may be that inclusion of outer orbital character (e.g. 4d) of the krypton atom in the bonding model, used to interpret the Mössbauer findings, would have yielded a lower charge distribution. The physical properties of krypton difluoride are summarized in Table 2.2.1.

Table 2.2.1

Physical Properties of Krypton Difluoride

The Chemistry of Krypton Difluoride. As the thermodynamic instability of the compound towards dissociation suggests, it is a powerful oxidative fluorinator. In keeping with an anticipated fluorinating ability approaching that of atomic fluorine, it oxidizes chloride (of silver chloride infrared cell windows) to chlorine trifluoride and chlorine pentafluoride.\(^{73}\) Its interaction with water generates krypton and oxygen.\(^{72}\)

$$\text{KrF}_2 + \text{H}_2\text{O} \rightarrow \text{Kr} + 0.5\text{O}_2 + 2\text{HF}$$

Although clearly an unusual fluorinator, it has failed to oxidize xenon trioxide to the trioxide difluoride (see 3.5.2.) or indeed to any other xenon(VIII) oxyfluoride or fluoride. Furthermore, it has not proven possible to prepare $\text{XeF}_8$ (see 3.5.1.) by bringing $\text{XeF}_6$ into interaction with it.

There have been claims\(^{67}\) that the hydrolysis, by ice, of krypton difluoride (incorrectly identified\(^{72}\) as $\text{KrF}_4$) at -30 to -60° yields 2 to 3% of an acid and that hydrolysis by 0.35N barium hydroxide at 0 to 50° results in a yield of approximately 7% of the barium salt. These claims have not been substantiated.
The difficulty of preparing quantities of KrF$_2$ and problems of handling have resulted in meagre study. Undoubtedly, this scant attention will be remedied when the remarkable potential of the compound as an oxidative reagent is more generally appreciated. It is important to note the greater stability of the complex of KrF$_2$ with SbF$_5$ (see 2.2.2). Because of this, the complex may prove to be a more useful reagent than the parent fluoride.

### 2.2.2 Krypton Difluoride Complexes

The only established derivative of krypton difluoride is the briefly described complex with antimony pentafluoride, KrF$_2$, 2SbF$_5$. There are also indications that an arsenic pentafluoride complex forms at -78; but this compound dissociates readily at low temperatures. The antimony compound was formed by treating KrF$_2$ with SbF$_5$ in glass or KF containers. The components interact completely at -20°. The compound dissolves in excess antimony pentafluoride, which can be removed at 25°, to leave a colourless solid, KrF$_2$, 2SbF$_5$, m.p. ~ 50° (decomp. → KrF + F$_2$ + SbF$_5$). The solution in SbF$_5$ decomposes slowly at 25° although the decomposition of the solid at this temperature is very slow. Aqueous hydrolysis (either basic or slightly acid) liberates krypton, oxygen and fluorine monoxide.

Although the only structural information available on this compound is an infrared spectrum with strong bonds at 813 and 600-700 cm$^{-1}$, it is quite probable that the compound is the salt KrF$^+$_{[Sb$_{2}F_{11}]^{-}}$, analogous to XeF$^+$_{[Sb$_{2}F_{11}]^{-}}$ (see 3.2.6). Unfortunately, the stretching frequency anticipated for the cation (approximately that of the BrF molecule, 35 i.e., 672 cm$^{-1}$) lies in the region of Sb-F stretch. It will probably be necessary to solve the crystal structure to confirm the salt formulation. The salt
formulation accounts for the observation that the thermal stability of the complex is greater than that of isolated krypton difluoride. Note that the bond in the Kr-F⁺ ion (2.2.2) appears to be considerably stronger (T.B.E., ~ 30 kcal mole⁻¹, see above) than in the molecule (T.B.E., 12 kcal mole⁻¹).
Table 2.2.2

Physical Properties of Krypton Difluoride

Thermodynamic (a)

\[ \Delta H_{\text{sublimation}}, \text{kcal mole}^{-1} \sim 9.9 \]
\[ \text{Vap. Press, mm Hg, (T}^\circ\text{C)} 10 \pm 1 (-15.5)\); 29 \pm 2(0)3 \pm 3, (15.0^\circ) \]
\[ \Delta H^\circ_{f} \text{ 298.15}^\circ, \text{kcal mole}^{-1} \quad 14.4 \pm 0.8 \]
\[ \Delta H_{\text{at}} (\text{KrF}_2(g) \rightarrow \text{Kr}(g) + 2\text{F}(g)), \text{kcal mole}^{-1}, 23.4 \]
Mean Thermochemical Bond Energy, kcal mole^{-1}, 11.7

Solubility (b)

Anhydrous HF dissolves KrF_2 to \sim 16 \text{ moles / 1000 g HF at 20}^\circ.

\[ 19_F \text{ n.m.r. data}^{(b)} \]
(no F exchange for HF solutions). Chemical Shielding Values

\[ \sigma_F^{(2)}, \text{relative to F}_2\sigma_F^{(2)} = 0 : 374 \times 10^{-6} \text{ (4.6 moles / 1000 g HF)}, \]
\[ 362 \times 10^{-6} \text{ (16.4 moles / 1000 g HF) at 0}^\circ. \]

Infrared and Raman Data (c)

Infrared bands, cm\(^{-1}\)

|   | 232.65 | 580,596 vs | 1032 m |

Raman bands, cm\(^{-1}\)

|     | 449 (vapour) | 462.3 (solid) |

Assignments

fundamentals, cm\(^{-1}\)

|   | \(v_2\) | \(v_1\) | \(v_3\) | \(v_1 + v_3\) |

force constants (m dynes Å\(^{-1}\))

|     | \(f_r\), 2.46 | \(f_{rr}\), -0.20 | \(f_a\), 0.21 |

Molecular Structure (d)

\(D_{\infty h}\) symmetry, Kr-F internuclear distance, Å units 1.889 \pm 0.01
Crystallographic data (e)

Tetragonal unit cell, \( a = 6.533 \); \( c = 5.831 \text{Å} \); \( V = 248.91 \text{Å}^3 \); \( Z = 4 \);
\( D_{\text{calc}} = 3.24 \text{ g cm}^{-3} \)

Molecular Energetics (f)

Possible Process

\[ \text{Appearance Potentials, } A(Kr^+, KrF_2) = 13.21 \pm 0.25 \text{ ev} \ (KrF_2 + e \rightarrow Kr^+ + F_2 + 2e) \]
\[ A(KrF^+, KrF_2) = 13.71 \pm 0.20 \text{ ev} \ (KrF_2 + e \rightarrow KrF^+ + F + 2e) \]

(b) F. Schreiner, J. G. Malm, and J. C. Hindman, J. Amer. Chem. Soc. 87 (1965) 25.
(e) S. Siegel and E. Gebert, J. Amer. Chem. Soc. 86 (1964) 3896.
3. Xenon Chemistry

The chemical behaviour of xenon is appropriate for an element of Group VIII of the Periodic Table. The normal oxidation states are even numbered and range from +2 to +8. The +8 oxidation state is known only in the oxide, XeO4, the perxenates, XeO64-, and the trioxide difluoride, XeO3F2. The octafluoride is unknown. This pattern resembles that of osmium, where the octafluoride is unknown but the tetroxide, OsO4, and trioxide difluoride, OsO3F2, are well established compounds. Octafluorides would surely be ligand 'crowded' molecules and it may well be that the lack of success in attempts to make these compounds is associated with a large kinetic barrier (see 1.2.3 and 3.5.1.).

So far, the compounds of xenon all involve highly electronegative ligands (e.g., F, O, -OSO2F, -OTEF5). The fluorides are readily preparable from the elements and are thermodynamically stable and the other known compounds (e.g., oxides, oxyfluorides and oxysalts) have usually been derived from them. Xenon dichloride, which can be preserved only at low temperatures, has been made from the elements by trapping the products from a glow discharge at 20°K, but the only other established synthetic route to the xenon halides (see 3.2.2.) has involved the β decay of corresponding 129I anions (thus: 129IBr2 → 129XeBr2).

3.1 Xenon(I)

3.1.1 Xenon(I) Fluoride, The XeF Radical

The radical XeF' has been detected by Morton and Falconer in an electron spin resonance study of a single crystal of XeF4.
It is probable that the blue colour of the irradiated XeF$_4$ crystal was due to the XeF radical since the colour and the e.s.r. spectrum were observed to fade simultaneously and rapidly at 140$^\circ$K.

It has been inferred, from kinetic data, that the XeF radical is an intermediate in water oxidation and NO and NO$_2$ oxidation by XeF$_2$. It is also probable that the decomposition of FXeOSO$_2$F involves an XeF intermediate (FXeOSO$_2$F$\rightarrow$XeF$^+$ + SO$_3$F$^-$; 2XeF$^+$$\rightarrow$Xe + XeF$_2$; 2SO$_3$F$\rightarrow$S$_2$O$_6$F$_2$) since the overall chemical change is

$$2\text{FXeSO}_3\text{F} \rightarrow \text{Xe} + \text{XeF}_2 + \text{S}_2\text{O}_6\text{F}_2.$$  

Similarly, the decomposition of XeF$^+$OsF$_6^-$ is thought to involve charge transfer (XeF$^+$[OsF$_6$]$^-$$\rightarrow$XeF$^+$ + OsF$_6$) with subsequent XeF$^+$ disproportion. This accounts for the observed products: 3XeF$^+$[OsF$_6$]$^-$$\rightarrow$Xe$_2$F$_3$[OsF$_6$]$^-$ + Xe + 20sF$_6$.

Johnston and Woolfolk have shown that the first bond dissociation energy, $D_1 = \Delta H(\text{XeF}_2(g) \rightarrow \text{XeF}(g) + \text{F}(g))$, of XeF$_2$ is greater than the second. They suggest $D_1 = 54$ kcal mole$^{-1}$. Since the total bond energy of XeF$_2$ (see 3.2.1) is 64 kcal mole$^{-1}$, it follows that $D_2(\text{XeF}_2)$ i.e., B.E.(XeF$^+$) = would be 10 kcal mole$^{-1}$. However, should the bond energy in the XeF radical be less than $\Delta H(F) = 18.7$ kcal mole$^{-1}$, then dissociation $2\text{XeF} \rightarrow 2\text{Xe} + \text{F}_2$ would be favoured, but there is no evidence to indicate that this occurs. It is therefore more likely that the value for $D_1$ is closer to 44 kcal mole$^{-1}$, since then B.E(XeF) $\approx$ 20 kcal mole$^{-1}$. This value is still consistent with disproportion $2\text{XeF} \rightarrow \text{XeF}_2 + \text{Xe}$, for which, since $\Delta S \approx 0$, $\Delta G \approx -24$ kcal mole$^{-1}$.

It is obvious that the XeF radical should be a very effective F atom source.

The abundance of xenon isotopes, of differing nuclear spin, has provided for a much better definition of the XeF radical than was possible for KrF (see 2.1.1). The e.s.r. data given in Table 3.1.1,
Table 3.1.1

XeF Radical Data

Bond energy (kcal mole\(^{-1}\)): \(\sim 20\) 
\[\Delta H(2\text{XeF}(g) \rightarrow \text{XeF}_2(g) + \text{Xe}(g)) \text{ (kcal mole}\(^{-1}\)): \(\sim 24\) \] see text 

Source for e.s.r. characterization: \(\gamma\) - irradiation of XeF\(_4\) single crystal

(a) (b)

---

Principle values of the hyperfine interaction tensors\(^\ddagger\) and g tensors\(^*\): (b)

<table>
<thead>
<tr>
<th>Species</th>
<th>Xe(_|)</th>
<th>Xe(_\perp)</th>
<th>F(_|)</th>
<th>F(_\perp)</th>
<th>G(_|)</th>
<th>G(_\perp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{132}\text{XeF})</td>
<td>-</td>
<td>-</td>
<td>2649</td>
<td>540</td>
<td>1.9740</td>
<td>2.1251</td>
</tr>
<tr>
<td>(^{129}\text{XeF})</td>
<td>2368</td>
<td>1224</td>
<td>2637</td>
<td>526</td>
<td>1.9740</td>
<td>2.1251</td>
</tr>
<tr>
<td>(^{131}\text{XeF})</td>
<td>701</td>
<td>-</td>
<td>2653</td>
<td>-</td>
<td>1.9740</td>
<td>-</td>
</tr>
</tbody>
</table>

(\(^\ddagger\)Units are Mc, errors ± 10 mc. \(^*\)Errors ± 0.0008)

---

Comparison of Experimental Isotropic (A) and Anisotropic (B) Tensor Parameters with One Electron Parameters Theoretically Derived

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>A(_\text{obs}) [(8\pi \mu_B^2 \gamma / 3 \hbar]</th>
<th>%ns. spin (x \psi^2_{\text{ne}}(0)) popn.</th>
<th>B(_\text{obs}) [(2g\mu_B \gamma / 5\hbar]</th>
<th>%np spin (x &lt;r^{-3}&gt;_{\text{pn}}) popn.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{19}\text{F}(\underline{n} = 2))</td>
<td>1243</td>
<td>47,900 Mc</td>
<td>3</td>
<td>1243</td>
</tr>
<tr>
<td>(^{129}\text{Xe}(\underline{n} = 5))</td>
<td>1605</td>
<td>33,030 Mc</td>
<td>5</td>
<td>1605</td>
</tr>
</tbody>
</table>

indicate that the unpaired electron occupies an orbital possessing axial symmetry about the internuclear axis. Neglecting inner-shell polarization, the data indicate that this molecular orbital is largely derived from Xe 5p and F 2p, since the spin population corresponds to 4.9% Xe 5s, 36% Xe 5p, 2.6% F 2s and 47% F 2p. To a first approximation then XeF can be described in classical molecular orbital terms with the unpaired electron in the highest antibonding sigma orbital (\( \sigma^* \)).

Departure of the principal g-values of XeF from 2.0023 (free spin) must be associated with spin-orbit interaction of the ground \( \sum \) state with \( \Pi \) excited states of the molecule. The ground state configuration is written:

\[
\begin{align*}
&\left( \sigma 2p_F + \sigma 5p_{Xe}, \sigma_1 \right)^2; \left( \sigma 2p_F + \pi 5p_{Xe}, \pi 1_2 \right)^1; \\
&\left( \pi 2p_F - \pi 5p_{Xe}, \pi 3,4 \right)^1; \left( \sigma 2p_F - \sigma 5p_{Xe}, \sigma_2 \right)^1, \text{ or briefly} \\
&\begin{array}{c}
\sigma_1^2; \\
\pi 1,2; \\
\pi 3,4; \\
\sigma_2^1.
\end{array}
\end{align*}
\]

Of course \( \sigma_1 \) and \( \pi 1,2 \) are bonding orbitals and \( \pi 3,4 \) and \( \sigma_2 \) antibonding orbitals. The g shifts are attributed to the transitions:

\[
\begin{align*}
\sigma_1^2; \pi 1,2; \pi 3,4; \sigma_2^1 & \longrightarrow \sigma_1^2; \pi 1,2; \pi 3,4; \sigma_2^1 \\
\sigma_1^2; \pi 1,2; \pi 3,4; \sigma_2^1 & \longrightarrow \sigma_1^2; \pi 1,2; \pi 3,4; \sigma_2^1.
\end{align*}
\]

3.1.2 Xenon(I) Complexes

Several complex salts have been reported. The stoichiometry of these materials, e.g., XePtF\(_6\) and XeRhF\(_6\), implies either Xe(I) or Xe(II)\(_2\) species. The first compound is of particular interest since it was the first xenon compound to be reported in which the xenon valence electron configuration was unequivocally different from the supposed 'ideal' octet. This and the related XeRhF\(_6\) are formed spontaneously at ordinary temperatures by interaction of xenon gas with the hexafluoride
vapour: $\text{Xe}_2(g) + \text{MF}_6(g) \rightarrow \text{XeMF}_6(c)$. For the 1:1 stoichiometry it is essential to maintain a large excess of xenon over hexafluoride. The infrared data support the formulation of these materials as Pt(V) and Rh(V) compounds and their interaction with alkali fluoride in iodine pentafluoride (which is not an oxidizing solvent towards Pt(IV) or Rh(IV)) generates $A^+M^V_F_6$ salts. Of course, the $\text{Xe}^+$ species should be paramagnetic. So far there is no reliable magnetic or structural data to support the designation of the xenon in the solid materials as $\text{Xe}^+$ rather than $\text{Xe}_2^{2+}$ or $\text{Xe}_2^F^+$ (which would be appropriate for the formulation $\text{Xe}_2^F^+[\text{F}_5\text{Pt}^+-\text{PtF}_5^-]$). It is noteworthy that the material of composition $\text{XePtF}_6_2$ which is formed under conditions of twofold excess of $\text{PtF}_6$ over $\text{Xe}$, is an equimolar mixture of $\text{XeF}^+$ $[\text{PtF}_6^-]$ and $\text{PtF}_5$ (see 3.2.6.).

Considering, the established capability of $\text{PtF}_6$ to oxidize $\text{O}_2$ to $\text{O}_2^+$, the rapid formation of the $\text{XePtF}_6$ material from the gas phase, and the quinqueivalence of the platinum in the solid product, it is probable that this and $\text{XeRhF}_6$ represent true $\text{Xe}(I)$ compounds.
3.2 Xenon(II)

3.2.1 Xenon Difluoride

Xenon difluoride was first detected independently in two laboratories, and several effective syntheses were quickly reported. Laboratory Preparation. The static thermal method of preparation employing large excess of xenon over fluorine is the best way to make large quantities of the fluoride, indeed as Falconer and Sunder have shown, high yields of pure material can be obtained with Xe:F₂ molar ratios of ~2:1. The gaseous mixture is heated in a nickel or Monel vessel at 400°, quenched to room temperature and the difluoride isolated by vacuum sublimation.

A convenient preparation, which avoids the special metal equipment used in the last procedure, simply involves exposure to sunlight of Xe/F₂ mixtures (~1 at. total pressure) contained in dry Pyrex glass vessels, at room temperature. Other Syntheses. As might be expected, fluoride decomposition or excitation to provide atomic fluorine, when carried out in the presence of xenon, has been shown to yield xenon fluorides. When the technique allows for the separation of crystalline fluoride, either by continuous circulation of the energized gaseous mixture through cold traps (at 0° or below), or by providing energy to the fluoride-xenon system at room temperature or below, the xenon fluoride product has invariably proved to be XeF₂. Weeks, Chernick and Matheson were the first to exploit a cold trap in a circulating gas system to effect the preparation of high purity material. Others have exploited this feature in successful application to hot tube syntheses. The Weeks et al photosynthesis
employed irradiation of Xe/F$_2$ gaseous mixtures with light from a high pressure mercury arc (2500-3000A). Photosynthesis, with sunlight, involving Xe/OF$_2$ mixtures at $\sim$25° and Xe/O$_2$F$_2$ mixtures at 118° are also effective.

Gamma ray irradiation at $4 \times 10^6$ rads hr$^{-1}$ of 1:2 Xe/F$_2$ mixtures at 64° has been shown to yield 1:1 XeF$_2$/XeF$_4$ mixtures with a G-value (for Xe consumption) of 3.4 atoms per 100 ev absorbed in the gas mixture. The observations of Gard, Dudley and Cady that XeF$_2$ is formed in interaction of Xe with OF$_2$ (187°), OF$_3$OF (220-250°), and FSO$_3$F(170-180°), are consistent with syntheses involving, simply, interaction of Xe with F$_2$ derived from dissociation of the other reagent. The fluorination of xenon, at 200°, by iodine heptafluoride

$$Xe(g) + IF_7(g) \rightarrow XeF_2, IF_5(c)$$

is similarly dependent upon F$_2$, generated by pyrolysis $IF_7 \rightarrow IF_5 + F_2$. It is possible that xenon difluoride has also been observed as a product of the fission of a UO$_2$ - LiF mixture.

Of particular interest is the formation of XeF$_2$ as a product of the interaction of xenon with carbon tetrafluoride in a high voltage discharge and by the interaction of excited xenon ($^3$P$_1$) with perfluoro-cyclobutane:

$$Xe^+ + C_4F_8 \rightarrow XeF_2 + C_4F_6.$$ 

Thermodynamic Properties. Xenon difluoride is colourless as solid, liquid or gas. The vapour pressure of the solid at 25° is 4.55 mm; accordingly the solid develops large crystals easily at room temperatures. Although the melting point of supposedly pure XeF$_2$ has been variously given at 140, 130 ± 0.6, 134 ± 2 and 139.6 ± 0.2° (Ref. 84), the most reliable value is 129.03 ± 0.05°, as given by Schreiner et al.
Figure 3.2.1

Thermochemical Cycles for XeF₂ and Derived Species

From the thermochemical cycles:

\[ \text{B.E.}(\text{XeF}^+) = I(\text{Xe}) - A(\text{XeF}^+, \text{XeF}_2) + \text{Total B.E.}(\text{XeF}_2, g) \]

\[ I(\text{XeF}) = A(\text{XeF}^+, \text{XeF}_2) - D_1 (\text{XeF}_2, g) \]

\[ I(\text{XeF}) = I(\text{Xe}) + \text{B.E.}(\text{XeF}^+) - \text{B.E.}(\text{XeF}^+) \]
vapour pressure data given by the last workers, for the temperature range 0 - 115°, is also the most reliable, from which $\Delta H_{\text{sub}} = 13.2$ kcal mole$^{-1}$. The enthalpy of sublimation is in close agreement with the prior value of 13.3 kcal mole$^{-1}$, calculated by Jortner et al.,$^{103}$ assuming an electrostatic stabilization of the solid, involving a point charge of $-0.5\, e$ on each F ligand and $+1.\, e$ on the xenon atom.

Three values have been given for the enthalpy of formation of the difluoride: $\Delta H_f^o(\text{XeF}_2, g)$(kcal mole$^{-1}$), -25.9 from equilibrium constant data,$^{22}$ -28.2 ± 0.6 from a calorimetric study,$^{104}$ and -37 ± 10, from appearance potential studies.$^{105}$ The second value is preferred, from which the total thermochemical bond energy is 64 kcal mole$^{-1}$.

But Johnston and Woolfolk have evidence from kinetic studies,$^{85}$ involving XeF$_2$ and XeF$_4$ interactions with NO and NO$_2$, that the first bond dissociation energy for $\text{XeF}_2(g) \rightarrow \text{XeF}^+(g) + F(g)$ is much greater than the second. As has been discussed under the XeF$^+$ radical (3.1.1) reasonable values for the bond dissociations are $D_1$, 44 and $D_2$, 20 kcal mole$^{-1}$.

Figure 3.2.1

It will be appreciated from the thermochemical cycle given for XeF$_2$ in Figure 3.2.1, that the total bond energy of XeF$_2$ is related to the bond energy of XeF$^+$ by the equation

$$\text{T.B.E.}(\text{XeF}_2, g) = \text{B.E.}(\text{XeF}^+) + A(\text{XeF}^+, \text{XeF}_2) - I(\text{Xe}).$$

Since the last two experimentally observed quantities are 12.8 and 12.1 ev respectively, $\text{T.B.E.}(\text{XeF}_2, g) = 64 = \text{B.E.}(\text{XeF}^+) + 0.7$ ev (16 kcal mole$^{-1}$). Therefore the bond energy for XeF$^+$ is 48 kcal mole$^{-1}$, which is compatible with the greater strength and shortness of the Xe-F bond in the cation, compared with XeF$_2$ (see 3.2.6).
Table 3.2.1.

Physical Properties of Xenon Difluoride

Colourless crystals, liquid and vapour

(a) Triple point, 129.03°C

(a) $\Delta H_{\text{sublim.}}$, 13.2 ± 0.2 kcal mole$^{-1}$

(a) Vapour pressure(solid), $\log P_{\text{mm}}(T) = \frac{3057.67}{T} - 1.23521 \log T + 13.969736$


S°(solid): 57°C, 29.4 cal mole$^{-1}$ deg.$^{-1}$.

Thermodynamics of XeF$_2$ formation:

(b) $\Delta H_f^0$, g, 25°C, -25.903; 501°C, -25.491 kcal mole$^{-1}$

(b) $\Delta G_f^0$, g, 25°C, -17.858; 501°C, -5.222 kcal mole$^{-1}$

(c) $\Delta H_{\text{atomization}}$ (XeF$_2$ (g) $\rightarrow$ Xe(g) + 2F(g)), 64 kcal mole$^{-1}$

Mean Thermochemical bond energy, 32 kcal mole$^{-1}$.

1st bond dissociation energy, (d) ~54 kcal mole$^{-1}$ (but see text).

Solubility

Relative solubilities: BrF$_5$, very good; BrF$_3$, very good (but complex formation); IF$_5$, good (adduct formation); CH$_3$CN, good; HF, fair;

SO$_2$, fair; WF$_6$, poor; NH$_3$ very slight (e).

Solubility in H$_2$O (f):

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp(°C)</th>
<th>C(moles/1000g)</th>
<th>C(g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF (g)</td>
<td>-2.0</td>
<td>6.38</td>
<td>168</td>
</tr>
<tr>
<td>CH$_3$CN (h)</td>
<td>0</td>
<td>12.25</td>
<td>320</td>
</tr>
<tr>
<td>ONF, 3HF (i)</td>
<td>16.8</td>
<td>19.56</td>
<td>22.17</td>
</tr>
</tbody>
</table>

Electrical conductivity measurements support the essentially molecular nature of XeF$_2$ in all of the solutions, look under appropriate headings for IR, UV and n.m.r. spectra of these solutions.
Thermodynamics and kinetics of XeF₂ hydrolysis.

\[ \Delta G^\circ (\text{XeF}_2 \text{aq}) + \text{H}_2\text{O} \rightarrow \text{Xe}(g) + \frac{3}{2} \text{O}_2(g) + 2\text{HF(aq)} \] est. \( (j) \)

\[ \text{H}_2\text{O} \sim 53.4 \text{ kcal mole}^{-1}, \text{ hence } K_{eq} \sim 10^{4.0} \]

**Hydrolysis conditions**: 1st order rate constant \( \Delta E_{\text{activ.}} \) \( \Delta S_{\text{activ.}} \) Ref.

(0.01MHC104) \( 4.2 \times 10^{-4} \text{sec}^{-1}(25^\circ) \) 19.6 -8.1 \( (k) \)

Only XeF₂ \( \left\{ \begin{array}{l} 2.83 \pm 0.02 \times 10^{-5} \text{sec}^{-1}(0^\circ) \quad - \quad - \quad - \quad \} \end{array} \right\} \)

in \( \text{H}_2\text{O} \) \( \left\{ \begin{array}{l} 2.52 \pm 0.01 \times 10^{-4} \text{sec}^{-1}(25^\circ) \quad - \quad - \quad - \quad \end{array} \right\} \)

\( 1.2 \times 10^{12} \text{exp}(-18400/RT) \text{min}^{-1} \) 18.4±2.1 - - \( (j) \)

**Vibrational Spectra**:

**XeF₂ solid**:

<table>
<thead>
<tr>
<th>bands (cm(^{-1}))</th>
<th>IR (vs)</th>
<th>( \nu_3 )</th>
<th>( \nu_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>547</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>496</td>
<td>1.0</td>
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<td></td>
</tr>
<tr>
<td>108</td>
<td>0.33</td>
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<tr>
<td>assignment</td>
<td></td>
<td>lattice mode</td>
<td></td>
</tr>
</tbody>
</table>

**XeF₂, vapour**:

<table>
<thead>
<tr>
<th>bands (cm(^{-1}))</th>
<th>IR (w)</th>
<th>IR (vs)</th>
<th>IR (vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1070</td>
<td></td>
<td></td>
<td>213.2</td>
</tr>
<tr>
<td>560</td>
<td></td>
<td>560</td>
<td></td>
</tr>
<tr>
<td>assignment</td>
<td>( \nu_1 + \nu_3 )</td>
<td>( \nu_3 )</td>
<td>( \nu_2 )</td>
</tr>
</tbody>
</table>

**CH₃CN solution**:

<table>
<thead>
<tr>
<th>bands (cm(^{-1}))</th>
<th>IR (w)</th>
<th>IR (s)</th>
<th>IR (s)</th>
<th>IR (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1235</td>
<td></td>
<td>533</td>
<td></td>
<td>509</td>
</tr>
<tr>
<td>assignment</td>
<td>( \nu_3 )</td>
<td>( \nu_1 )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( \nu_3 \) (cm\(^{-1}\)) in other solvents:

- \( \text{CH}_3\text{NO}_2 \), 532; \( \text{dioxane} \) 530; \( \text{CCl}_4 \), 538
Ultraviolet Spectrum of XeF₂ Vapour (t)(u)(v)(w), (see also photoelectron spectra):

<table>
<thead>
<tr>
<th>Wavelength (Å)</th>
<th>Half width (cm⁻¹)</th>
<th>est. extinction coefficient e. mole⁻¹ cm⁻²</th>
<th>est. oscillator strength f</th>
</tr>
</thead>
<tbody>
<tr>
<td>2300</td>
<td>8249</td>
<td>0.86 x 10²</td>
<td>0.0033</td>
</tr>
<tr>
<td>1580</td>
<td>8060</td>
<td>1.12 x 10⁴</td>
<td>0.12</td>
</tr>
<tr>
<td>1425</td>
<td>(1000)</td>
<td>0.4 x 10⁴</td>
<td>0.02</td>
</tr>
<tr>
<td>1335</td>
<td>(1290)</td>
<td>0.4 x 10⁴</td>
<td>0.02</td>
</tr>
<tr>
<td>1215</td>
<td>(2070)</td>
<td>0.4 x 10⁴</td>
<td>0.03</td>
</tr>
<tr>
<td>1145</td>
<td>(2730)</td>
<td>0.6 x 10⁴</td>
<td>0.06</td>
</tr>
</tbody>
</table>

for assignments see references (t)(u)(x)(v)(y)

Rydberg Bands (v)(t)(u)(v):

Allowing for a systematic error of -18Å in the Rydberg data of references (t) and (v), this and the He I and II photoelectron data of reference (y) can be fitted by the two series:

\[ \nu_s = \{100, 160\} - \frac{109,737}{(n - 4.04)^2} \text{ cm}^{-1}; \ n = 6, 7. \]

and \[ \nu_d = \{100, 160\} - \frac{109,737}{(n - 2.42)^2} \text{ cm}^{-1}; \ n = 5, 6, \ldots \]

The \( \nu_s \) Rybergs are (v) the spin orbit split components of a \( 5\pi_u \rightarrow 6s \) transition.

The \( \nu_d \) Rybergs are probably the spin orbit components of a \( 5\pi_u \rightarrow 5d \) transition.
Photoelectron spectra (see also UV spectrum)\(\text{(y)\(z\)).\)

**Term Energies in Xe and XeF\(_2\)\(\text{(y)}\)**

<table>
<thead>
<tr>
<th>(\text{Xe},(\text{a}'))</th>
<th>(\text{Upper State})</th>
<th>(\text{Term, cm}^{-1})</th>
<th>(\text{XeF}_2)</th>
<th>(\text{Upper State})</th>
<th>(\text{Term, cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5p,(^2P_{3/2})6s)</td>
<td>30,400</td>
<td>(5,\Pi_u,(^2\Pi_{3/2})6s)</td>
<td>30,865</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5p,(^2P_{1/2})6s)</td>
<td>31,433</td>
<td>(5,\Pi_u,(^2\Pi_{1/2})6s)</td>
<td>30,080</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5p,(^2P_{3/2})6p)</td>
<td>19,322</td>
<td>(\text{---})</td>
<td>(\text{---})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5p,(^2P_{1/2})6p)</td>
<td>19,317</td>
<td>(\text{---})</td>
<td>(\text{---})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5p,(^2P_{3/2})5d)</td>
<td>16,668</td>
<td>(5,\Pi_u,(^2\Pi_{3/2})5d)</td>
<td>17,860</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5p,(^2P_{1/2})5d)</td>
<td>16,567</td>
<td>(5,\Pi_u,(^2\Pi_{1/2})5d)</td>
<td>16,600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5p,(^2P_{3/2})7s)</td>
<td>12,551</td>
<td>(\text{---})</td>
<td>(\text{---})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5p,(^2P_{1/2})7s)</td>
<td>12,590</td>
<td>(\text{---})</td>
<td>(\text{---})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Appearance potentials of ions \(\text{(z)}\(\text{(y)}\)**

<table>
<thead>
<tr>
<th>A.P. (ev)</th>
<th>(\text{XeF}_2^+)</th>
<th>12.28</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{XeF}_2^+)</td>
<td>12.78</td>
<td></td>
</tr>
</tbody>
</table>
### Observed and Calculated Ionization Potentials (eV) of XeF₂(y)

<table>
<thead>
<tr>
<th>Adiabatic Obs.</th>
<th>Vertical Obs.</th>
<th>0.92 K. T. Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.35 ± 0.01</td>
<td>12.42 ± 0.01</td>
<td>12.51 (5π₂u)</td>
</tr>
<tr>
<td>12.89 ± 0.01</td>
<td>12.89 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>ca 13.5</td>
<td>13.65 ± 0.05</td>
<td>11.79 (10g₂)</td>
</tr>
<tr>
<td>14.00 ± 0.05</td>
<td>14.35 ± 0.05</td>
<td>14.71 (3π₂g)</td>
</tr>
<tr>
<td>15.25 ± 0.05</td>
<td>15.60 ± 0.05</td>
<td>15.92 (4π₂u)</td>
</tr>
<tr>
<td></td>
<td>16.00 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>16.80 ± 0.05</td>
<td>17.35 ± 0.05</td>
<td>16.93 (6π₂u)</td>
</tr>
<tr>
<td>ca 22.5</td>
<td></td>
<td>25.24 (9g₂)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37.10 (5π₂u)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37.20 (8π₂g)</td>
</tr>
</tbody>
</table>

*There is an indication of a weak shoulder centered at 12.30 eV which may correspond to the true adiabatic IP for this band. However, it seems more likely that this lowest band is a hot one, arising from the appreciable excitation of the low frequency bending mode in the ground state of the neutral molecule.*
XeF$_2$ n.m.r. data

Microcrystalline solid, $25^\circ$; $^{19}$F$_{\text{p}}$, 612 p.p.m.; line width 6.0 G

HF solution (1 mole/1000g), $-19.5$: $^{19}$F$_{\text{p}}$ $^{129}$Xe$_{\text{p}}$ $^{129}$Xe

<table>
<thead>
<tr>
<th>Ref.</th>
<th>$^{19}$F$_{\text{p}}$ (p.p.m.)</th>
<th>$^{129}$Xe$_{\text{p}}$ (p.p.m.)</th>
<th>(c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a')</td>
<td>629</td>
<td>-</td>
<td>5,600</td>
</tr>
<tr>
<td>(c')</td>
<td>630.3</td>
<td>-3930</td>
<td>5,690</td>
</tr>
</tbody>
</table>

ONF, 3HF solutions (~ 1 mole/100g), 40°;

<table>
<thead>
<tr>
<th>Ref.</th>
<th>$^{19}$F$_{\text{p}}$ (p.p.m.)</th>
<th>(c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>631</td>
<td>5,640 ± 20</td>
</tr>
</tbody>
</table>

CH$_3$CN solution

<table>
<thead>
<tr>
<th>(h)</th>
<th>$^{19}$F$_{\text{p}}$ (p.p.m.)</th>
<th>(c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>610 ± 2</td>
<td>5,450 ± 20</td>
</tr>
</tbody>
</table>

n.m.r. single crystal data (d')

(rigid-lattice second moment $M_2'$ = $M_2$ + $4/45 \Delta \sigma^2 H_0^2$, )

$H_0$ = applied field strength $\Delta \sigma = \sigma_\perp - \sigma_\parallel$, where $\sigma_\perp$ and $\sigma_\parallel$ are the shielding $\perp$ and $\parallel$ to symmetry axis.)

$M_2$ Obs = 3.25 G$^2$, $M_2$ calc = 2.85 G$^2$ -- the difference probably represents thermal displacements (see crystal structure data)

$|\Delta \sigma| = (105 \pm 10) \times 10^6$

Mössbauer spectrum (e') (f') (see sections 1.4.1, 2.2.1, 3.2.2)

<table>
<thead>
<tr>
<th>splitting (mm/sec)</th>
<th>$e^2 Q Q$ (Mc/sec)</th>
<th>Isomer shift $U_{|}$ (mm/sec)</th>
<th>Electron transfer $h_{\perp}$ per bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4.2°K) 39.00 ± 0.10</td>
<td>2490</td>
<td>0.10 ± 0.12</td>
<td>1.43* 1.43*</td>
</tr>
</tbody>
</table>

$U_{\|}$ is the quadrupole coupling in units of the quadrupole coupling of a single $P_\perp$ hole.

* $h_{\perp}$ is the hole in the 5p shell, assuming that the bonding involves P$^+_g$ orbitals only.
Molecular structure

Vapour: $D_\infty h$ geometry established by IR and R data.(o)(u')

Rotational IR ($v_3$ band)(p) gives, $\alpha_3 = 3.31 \times 10^{-4}$ cm$^{-1}$,

$B_0 = 0.11350$ cm$^{-1}$, and $X_23 = -1.44$ cm$^{-1}$.

From $B_0$, the Xe-F bond length is $1.9773 \pm 0.0015$Å

Single crystal structure (see Figure 3.2.2)

Tetragonal unit cell(g'), $a = 4.315 \pm 0.003$; $c = 6.990 \pm 0.004$Å;

$V = 130.15$Å$^3$; $z = 2$.

$D_{\text{calc}} = 4.32$ g cm$^{-3}$. S. G. I4/mmm (D$^{17}_{4h}$)

Structural parameters(h'):

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th>(fermi units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe</td>
<td>(0.0)</td>
<td>0.0341 ± 0.0020</td>
<td>0.0083 ± 0.0006</td>
<td>(0.476)</td>
</tr>
<tr>
<td>F</td>
<td>0.2838 ± 0.0004</td>
<td>0.0635 ± 0.0022</td>
<td>0.0087 ± 0.0004</td>
<td>(0.550)</td>
</tr>
</tbody>
</table>

(values in parentheses were not varied; f are neutron scattering amplitudes)

Intramolecular distance Xe – F, 2.00 ± 0.01Å

Each Xe atom has 8 'non-bonded' F neighbours at 3.41Å

Each F atom has one F neighbour at 3.02Å (along c) and 4F at 3.09Å

Magnetic susceptibility (i')

$-x_M = 40-50 \times 10^{-6}$ e.m.u.

Bonding: Refs. (j')(k')(l')(m')(n')(o')(p')(q')(u')(g')(r')(s')(t')(u')(v')

Proposed energy levels: Refs. (w)(y)(u)(y)
References

Table 3.2.1.

(a) F. Schreiner, G. N. McDonald and C. L. Chernick, J. Phys. Chem. 72 (1968) 1162.
(h) H. Meinert and S. Rüdiger, Z. Chem. 7 (1967) 239.
(m) J. J. Turner and G. C. Pimentel, see reference (g) p. 101.
(n) D. F. Smith, see reference (g) p. 295.
(q) H. Meinert and G. Kauschka, Z. Chem. 2 (1969) 70.
(s) N. Bartlett and D. E. McKee, unpublished observation.
(v) J. J. Jortner, E. G. Wilson and S. A. Rice, see reference (g) p. 358.
(y) C. R. Brundle, M. B. Robin and G. R. Jones, in press.
(b') J. C. Hindman and A. Svirmickas, see reference (g) p. 251.
(c') T. H. Brown, E. B. Whipple and P. H. Verdier, see reference (g) p. 263.
(f') G. J. Perlow, C. E. Johnson and M. R. Perlow, see reference (g) p. 279.
(h') H. A. Levy and P. A. Agron, see reference (g) p. 221.
(o') L. C. Allen, see reference (g) p. 358.
(u') D. F. Smith, *J. Chem. Phys.* 38 (1963) 270; and see reference (g) p. 295.
The Kinetics of XeF₂ Formation. Rate studies of the interaction of xenon with fluorine have shown that the reaction is zero order in Xe.\textsuperscript{106, 107, 108} These same investigations indicate that the reaction is primarily heterogeneous. Weaver\textsuperscript{107} has noted a 1st order dependence of the reaction on F₂, which may be due to a slow step involving the dissociation of adsorbed fluorine molecules into adsorbed fluorine atoms. Evidently, the walls of nickel or Monel vessels have marked catalytic activity and CoF₃, NiF₂, and CaF₂ have been shown to be effective catalysts. However, metal fluorides cannot be catalytic agents in the photochemical synthesis, carried out in Pyrex vessels. Again, wall reactions may be involved, but there is no clear evidence for this at this time. Sinel'nikov et al.\textsuperscript{109} have shown that atomic fluorine (generated in a glow discharge) is capable of converting condensed xenon (at 77°K) to xenon difluoride (45% yield in 75 min.) From this, and the efficiency of the gas discharge synthesis, they have concluded that xenon activation is not necessary for xenon difluoride formation.

Structures Features. Infrared\textsuperscript{110, 111} and Raman\textsuperscript{112, 113, 114, 115, 110} spectroscopy have established the symmetrical linear (D₁h) geometry of the XeF₂ molecule. The vibrational spectroscopic data is given in Table 3.2.1. A high-resolution infrared study\textsuperscript{116} of the ν₂ stretching mode has provided a bond length of 1.9773 ± 0.0015Å for the vapour phase molecule. This bond length is similar to that in the molecule in the crystalline phase. The value given by Levy and Agron\textsuperscript{117, 118} from their single-crystal neutron diffraction study is 2.00± 0.01Å.

In crystalline XeF₂, the linear molecules are aligned parallel in a body-centered tetragonal array, the unit cell of which is shown in Figure 3.2.2. It is clear that there are strong interactions between molecules since each xenon atom has not only its 2 bound fluorine
Figure 3.2.2
The Unit Cell of Xenon Difluoride
atoms at 2.0 Å but also 8 fluorine atoms at 3.41 Å, the latter being fluorine ligands of the 8 nearest XeF$_2$ neighbours. This structural arrangement is compatible with the high enthalpy of sublimation of XeF$_2$ ($\Delta H_{\text{sub}} = 13.2$ kcal mole$^{-1}$) and Jortner et al have convincingly accounted for these features. They point to the considerable bond polarity in the XeF$_2$ molecule and account for $\Delta H_{\text{sub}}$ in terms of an electrostatic stabilization energy of 11.31 kcal mole$^{-1}$ (assuming the charge distribution in each molecule to be $-0.5\text{F}-\text{Xe}^{1+}-\text{F}^{0.5}$) and a dispersion energy of $\sim 2$ kcal mole$^{-1}$ — a total of $\sim 13.3$ kcal mole$^{-1}$.

It is evident from the packing arrangement that the region close to the equatorial plane of each XeF$_2$ molecule is avoided by neighbouring-molecule fluorine ligands. This may indicate that the 'non-bonding' valence electrons of the xenon atom provide very effective shielding of the xenon positive charge in this plane. It seems also that the effective volume of the xenon atom is considerable in crystalline XeF$_2$ (and even in its derivatives, see 3.2.6. and 3.2.7.). The molecular volume for XeF$_2$ is 65.1 Å$^3$. But in many fluorides (e.g., XeF$_6$, IF$_7$, IF$_6^+$AsF$_6^-$) the effective volume of each fluorine ligand is 17.8 Å$^3$. Therefore $\sim 29$ Å$^3$ of the effective molecular volume of XeF$_2$ can be attributed to an effective xenon(II) volume. This effective volume may largely derive from the shielding properties (or steric activity) of the 'non-bonding' xenon valence electrons.

Findings from nuclear magnetic resonance $^{119, 120, 121, 122}$ and Mössbauer studies $^{123, 124}$ (see 2.2.1. and 3.2.2.) have generally been interpreted in terms of considerable bond ionicity$^{125, 119, 123}$. Recent broad-line n.m.r. studies$^{120}$ show that the previous quantitative evaluations may be considerably in error, since much of the earlier n.m.r.
Experimental work was apparently carried out using rather impure XeF₂ samples. Nevertheless, bond polarity in XeF₂ must be high and is probably not very different from the value derived by Rice and his coworkers. 104

From the core-electron chemical-shift derived from X-ray electron spectroscopy (E.S.C.A.) of gaseous XeF₂, Karlsson et al. 126 have concluded that the positive charge on the xenon atom is ~+1 — a value in fair agreement with n.m.r. and Mossbauer findings. A high resolution HeI and HeII photoelectron spectroscopic study of the difluoride (involving valence electron promotion or ionization) has been reported by Robin and his coworkers. They have shown that the vertical ionization potentials of the first eight ionizations in the XeF₂ molecule compare well with the results of Gaussian Type Orbital calculations. The first two ionic states of XeF₂ are the \( \frac{2}{3} \) (12.42 ev) and \( \frac{1}{2} \) (12.89 ev) spin-orbit components formed by ionization from the highest filled \( \pi \) orbital (5\( \pi_u \)). They conclude that the XeF₂ molecule in these two states is essentially of the same size and shape as the ground state neutral species. This indicates that the 5\( \pi_u \) orbital is essentially non-bonding. The photoelectron spectrum of XeF₂ yields characteristic Rydberg energies which correlate with Rydberg excitation energies derived by Rice and his coworkers 128, 129, 130 from the XeF₂ ultraviolet spectral data. The interpretation given by the latter workers for the ultraviolet spectrum of XeF₂ is in terms of a semi-empirical LCAO molecular orbital description. The bonding models for XeF₂ have been presented earlier (see 1.3.3-4). Perhaps because of the wealth of data on the molecule and its simplicity, it has been the subject of many theoretical papers. The majority of these have depended upon molecular orbital
models which have excluded Xe outer orbitals (5d and 4f) from significant involvement. Coulson's review\(^\text{23}\) gives the essence of these models. On the other hand, more recently, Mitchell\(^\text{25}\) has concluded on the basis of model calculations, following the extended valence-bond method of Hurley, Lennard-Jones and Pople, that the XeF\(_2\) structure, with lowest energy is the localized electron pair structure F-Xe-F, which involves a contracted 5d\(_\text{Xe}\) orbital in the bonding. Mitchell, furthermore, argues that Coulson's favoured valence bond structure, F-Xe\(^+\)F\(^-\), is energetically unfavourable. However, the F-Xe\(^+\)F\(^-\) structure is claimed to be lower in energy than F-Xe\(^+\)F\(^-\) and hence to be more likely to contribute to the bonding description. Clearly, it will be some time before the question of outer Xe orbital participation in the bonding in the Xe compounds can be satisfactorily resolved.

**Non-aqueous XeF\(_2\) Chemistry.** Since XeF\(_2\) is easily made and is thermodynamically stable, at ordinary temperatures and pressures, it is a convenient source of other xenon(II) compounds. Furthermore, since the Xe-F mean thermochemical bond energy is one of the lower bond energies of known fluorides, being comparable to the mean bond energy of ClF\(_2\), XeF\(_2\) is, potentially, a strong oxidizer and fluorinator. Both of these aspects have been explored.

The fluorine ligands of the XeF\(_2\) may be substituted, by highly electronegative ligands, using the ligand protonic acids:

\[
\text{XeF}_2 + \text{HL} \rightarrow \text{FXeL} + \text{HF}
\]

\[
\text{FXeX} + \text{HL} \rightarrow \text{XeL}_2 + \text{HF}
\]

The high exothermicity of \(\Delta H_f\) (HF) is a major factor in bringing about the forward reaction. Solid products have been obtained for
$L = SO_3F \text{ and } ClO_4^{86}; OTeF_5^{131, 132}$ and possibly $O_2CCF_3^{133, 134}$. The perchlorates and trifluoroacetates are detonable. All of these compounds are described later (see 3.2.4. et. seq.). Efforts to generate $FXeCl$ or $XeCl_2$ by interaction of $XeF_2$ with HCl or $BCl_3$ have failed, xenon being eliminated quantitatively. 135

Although xenon difluoride is potentially a strong oxidizer it is frequently unreactive for kinetic reasons. Its stability in aqueous solution (see later) is typical of this kinetic inertness, although solutions in other solvents, e.g. CH$_3$CN 136, 137 and other organic solvents, 138 are also stable, if certain catalysts, particularly fluoro-acids, are absent. The difluoride is also soluble in the halogen fluorides, IF$_5$, BrF$_3$ and BrF$_5$ 139 and in anhydrous hydrogen fluoride. 140 Physical evidence, where available, has always shown the dissolved $XeF_2$ to be mono-molecular in solution 141, 142, 136, 138, 143 and to be geometrically similar to the gas phase species. Occasionally the solvents form complexes with the difluoride (e.g. IF$_5$ and BrF$_3$) and this limits their usefulness in preparations. Either BrF$_5$ 139 or acetonitrile 137, 142, 144, 136 (depending on the particular application) is a convenient solvent for $XeF_2$, but it is possible that ONF, 3HF (b.p. 94°) will also prove to be a very useful solvent for it. 143

The oxidizing capability of $XeF_2$ can be exploited by using a fluoride ion acceptor as catalyst. 139 Thus, a solution of iodine and $XeF_2$ in acetonitrile may be kept indefinitely (particularly if CsF is present, to absorb fluoroacids) but on introduction of HF or $BF_3$ the $XeF_2$ oxidizes the iodine to form iodine fluorides: $I_2 + XeF_2 \xrightarrow{F^- \text{ acceptor}} Xe + 2IF$; $IF + XeF_2 \xrightarrow{F^- \text{ acceptor}} Xe + IF_3$, etc. Oxidizable strong fluoride ion acceptors interact rapidly with the difluoride:
Solutions of xenon difluoride and benzene or other aromatics are stable until hydrogen fluoride is introduced, at which point the solutions become coloured, xenon evolves and HF and fluoroaromatics are formed. Thus, $4.1 \times 10^{-2} \text{ mole of benzene in interaction with } 1.26 \times 10^{-2} \text{ mole of XeF}_2 \text{ for } 2\frac{1}{2} \text{ hr. yields a distillate of composition; 88.72% benzene, 10.28% fluorobenzene, 0.7% } p\text{-difluorobenzene and 0.3% } o\text{-difluorobenzene. A tarry residue (0.640 g) contained monofluorobiphenyl, biphenyl, difluorobiphenyl and trifluorobiphenyl. Xenon difluoride fails to interact with perfluoro-olefins, even after several days, whereas it interacts with olefins to yield difluoro-olefins.}^{145} \text{ This may be due to the presence of some HF in the latter reaction. It is of interest that the } \text{vic } \text{difluorides formed in this reaction isomerize to the gem difluorides:}

\[ \text{XeF}_2 + \text{CH}_2 = \text{CH}_2 \rightarrow \text{CH}_2\text{FCH}_2\text{F} \rightarrow \text{CH}_3\text{CHF}_2 \]

\[ \text{CH}_3 - \text{CH} = \text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CHF}_2 \]

It seems likely that in all of these fluorination and oxidation reactions, the reaction takes place first by ionization of XeF$_2$ to XeF$^+$ (or related species) followed by electron transfer to give XeF$^+$ . As discussed above, the XeF species is very weakly bound and must be a very effective F atom source (see 3.1.1).

The Xe-F bond in XeF$^+$ (see above and 3.2.6.) is considerably stronger than in XeF$_2$, as is to be expected, since here we have essentially electron pair bonding involving Xe 5p (and possible 5d) orbitals in the bonding.
(See 1.3.1 - 4). This must contribute to the ready ionization of XeF₂.

A number of salts of the XeF⁺ ion have now been established and they are discussed in section 3.2.6. The ionization enthalpy ΔH°

\[(\text{XeF}_2(g) \rightarrow \text{XeF}^+(g) + \text{F}^-(g)) \approx +215 \text{ kcal mole}^{-1}\]

which compares with that for ONF, \(\Delta H°(\text{ONF}(g) \rightarrow \text{NO}^+(g) + \text{F}^-(g))\), of +208 kcal mole⁻¹.

There is no reason why a large number of XeL⁺ salts should not be derivable from the XeF⁺ salts or XeF₂ itself. It will probably be essential to use rather electronegative ligands L, and it will be necessary, for stable salts, that \(\sum (\text{lattice energy} - \text{ionization potential of the anion})\), should be more exothermic than the electron affinity of the cation.

The compounds which XeF₂ forms with XeF₄, IF₅, XeOF₄ and XeF₅⁺ (see 3.2.7.) preserve the essential form of XeF₂. The intermolecular bonding in these compounds is primarily coulombic and like that in solid XeF₂ itself. It is a consequence of the considerable bond polarity of XeF₂.

The aqueous solution chemistry of XeF₂. Xenon difluoride dissolves in water (\(\sim 250 \text{ g l}^{-1}\) at 0°C) with only very slight decomposition. The presence of molecular XeF₂ in the solution has been established by UV spectroscopy¹⁴¹ and electrical conductance.¹⁴⁶ The difluoride may be recovered by CCl₄ extraction or fractional distillation.¹⁴¹ Clearly, XeF₂ has remarkable kinetic stability, since \(\Delta G°(\text{XeF}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{Xe}(g) + \frac{1}{2}\text{O}_2(g) + 2\text{HF}(\text{aq})\) has been estimated to be \(-53.4 \text{ kcal mole}^{-1}\), from which \(K_{\text{eq}} = [\text{Xe}] [\text{O}_2]^{\frac{1}{2}} [\text{HF}]^2 / [\text{XeF}_2] [\text{H}_2\text{O}] \approx [\text{HF}]^2 / [\text{XeF}_2] \approx 10^{40}\). Neutral or acid solutions decompose rather slowly, the half-life being \(\sim 7 \text{ hr. at } 0°C\).¹⁴¹ So far, XeF₂ is the only established Xe(II) aqueous solution species. Decomposition in basic solution is very fast, the base catalytic effect being roughly in the order of base strength.
The hydrolysis products are xenon, oxygen, fluoride ions and hydrogen peroxide.

Evidently, in 0.01 M perchloric acid, XeF$_2$ oxidation of water proceeds with a first order rate constant of $4.2 \times 10^{-4}$ sec$^{-1}$ at 25°, with an activation energy of 19.6 kcal mole$^{-1}$ and $\Delta S$(activation) = -8.1 ev.

Two independent studies of the kinetics of XeF$_2$ hydrolysis, in water alone, have been reported. Fehér and Lörine studied the reaction at 0 and 25° and found the reaction to be first order, their rate constants being $2.83 \pm 0.02 \times 10^{-5}$ sec$^{-1}$ at 0° and $2.52 \pm 0.01 \times 10^{-4}$ at 25°. Legasov et al. similarly found first order kinetics with $k_1 = 1.2 \times 10^{12} \exp(-18400/RT)$ min$^{-1}$, for the temperature range 10-40°. From this study the activation energy is 18.4 ± 2.1 kcal mole$^{-1}$. Since the first bond dissociation of XeF$_2$ is known to exceed the second, the latter authors concluded that their observed activation energy was in keeping with XeF$^-$ radical formation in the first stage. Oxygen atom formation, in aqueous XeF$_2$ decomposition, is consistent with some of the oxidizing properties of aqueous XeF$_2$.

The specific conductance of $4 \times 10^{-4}$ ohm$^{-1}$ cm$^{-1}$, found for a saturated XeF$_2$ solution, at 0°, is probably that of hydrogen fluoride formed in the oxidation of water by the XeF$_2$. This finding in any case is consistent with the spectroscopic findings and suggests that at least 97% of the dissolved XeF$_2$ is initially present as molecular XeF$_2$. Furthermore, since $^{18}$F exchange between XeF$_2$ and aqueous HF proceeds only to the extent of ~ 0.8% after 2 hr. at 0° it is clear that reversible $F^-$ ion addition (e.g. XeF$_2$(aq) + F$^-$ (aq) $\rightarrow$ XeF$_3^-$ (aq)) or $F^-$ ion abstraction (e.g. XeF$_2$(aq) + HF$^-$ (aq) $\rightarrow$ XeF$^+$ (aq) + HF$_2^-$) are not significant processes in acid aqueous media.
The interaction of XeF$_2$ with water is not only catalyzed by base but also by species which have an affinity for fluoride ions. Of a variety of metal ions investigated, the order of the accelerating effect is the same as the order of the stability constants of their monofluoro complexes: Th$^{4+} >$ Al$^{3+} >$ Be$^{2+} >$ La$^{3+}$. These findings parallel the oxidizing behaviour of XeF$_2$ in non-aqueous solvents in which the stronger fluoride ion acceptors have greater effect in promoting oxidation by XeF$_2$. These findings suggest that the hydrolysis of XeF$_2$ may involve XeF$^{+}$ formation.

It is significant that, in spite of the considerable investigation of the chemistry of XeF$_2$, no evidence for a kinetically stable monoxide has appeared. It may be that the fleeting yellow colour reported by several investigators to accompany alkaline hydrolysis of XeF$_2$ is associated with the XeF radical, but it is more likely to be an unstable hydroxy species or oxide:

\[
H_2O + XeF_2 \rightarrow 2HF + Xe(OH)_2 \text{ or } XeO + H_2O
\]

It is possible that XeO, like its iodine analogue IF, could exist as an unstable polymer. Evidently, if XeO is formed as an intermediate in aqueous hydrolysis, its lifetime must be very short, since there is no evidence for higher oxide formation, such as might be anticipated from mutual oxidation-reduction reactions of the type: 2Xe0 $\rightarrow$ Xe + XeO$_2$. It is of interest that the disproportionation of hypoiodite, I$^- + IO_3^-$ $\rightarrow$ I$^- + IO_2^-$ is very slow compared with the iodide catalyzed reaction involving an activated complex \{I$^- + 2I$O_2^- + H^+$\}. The xenon counterpart of the latter would be unlikely to exist, since Xe(0) would not be retained. Evidently, XeO$_3$ introduced into an aqueous XeF$_2$ solution
is extensively consumed in the course of the interaction of XeF₂
with water, although an aqueous solution of XeO₃ itself can be kept
almost indefinitely.¹⁵¹ It has been presumed that the XeO₃ consumption
results from reduction by an XeO intermediate: \[
\text{XeO}_3(aq) + 2\text{XeO}_2 \rightarrow \text{Xe} + \text{O}_2
\]
but even an oxygen atom could serve as an
equally effective reducer [O] + \text{XeO}_3 \rightarrow \text{XeO}_2 + \text{O}_2. The interaction
of XeF₂ with water is in effect an oxygen atom source for bromate
oxidation to perbromate.¹⁵² This is perhaps the most dramatic example
of the oxidizing capability of XeF₂ since perbromates were previously
unknown and had been considered by some to be impossible to synthesize.

Aqueous XeF₂ solutions also oxidize \(^1⁴¹,¹⁵³\) chloride to chlorine, iodide and
iodate to periodate, Ce(III) to Ce(IV), Cr(III) to Cr(VI), Co(II) to Co(III)
and Ag(I) to Ag(II) and the fluoride has even been suggested as an
analytical reagent for I⁻ and Cr(III).¹⁵³ Alkaline solutions of Xe(VI)
are oxidized to Xe(VIII). The oxidation potentials have been estimated
for XeF₂ / Xe in acid solution to be 2.2 v and for XeO²⁻ / Xe in alkaline
solution to be 1.3 v. A polarographic study \(^1⁵⁴\) shows that acidified
XeF₂ solutions are reduced in a single step to xenon, at a potential
of \(\sim 0 v\) with respect to the \(\text{Hg}_2\text{SO}_4/\text{Hg}\) reference electrode.
Analysis and identification. The analysis of $\text{XeF}_2$ samples may be carried out conveniently by transferring known weights of the material to a small nickel weighing bottle (provided with a valve) containing an excess of degassed mercury. By keeping the bottle warm and the contents agitated, complete reduction of the difluoride occurs within a few hours:

$$\text{Hg} + \text{XeF}_2 \rightarrow \text{HgF}_2(\text{Hg}_2\text{F}_2) + \text{Xe}$$

Xenon production may be determined by gas measurement or by weight loss. The fluorine content is simply given by the increase in weight due to mercury fluoride formation. This method is easier than the earlier one which used hydrogen to reduce the difluoride: hydrolysis in base, with gas collection ($\text{Xe} + \frac{3}{2}\text{O}_2$) and mass spectrometric characterization, together with acidimetric analysis for the HF formed in the hydrolysis:

$$\text{H}_2\text{O} + \text{XeF}_2 \rightarrow 2\text{HF} + \text{Xe} + \frac{5}{2}\text{O}_2$$

or iodimetric titration, on the basis of the reaction:

$$\text{XeF}_2(\text{aq}) + 2\text{I}^- \rightarrow \text{Xe} + 2\text{F}^- + \text{I}_2$$

have also been used effectively.

Perhaps the most sensitive test for the presence of $\text{XeF}_4$ and $\text{XeF}_6$ in the difluoride sample is the melting point ($129.02^\circ$). The distinctive infrared absorptions of $\text{XeF}_2$ (555 cm$^{-1}$), $\text{XeF}_4$ (590 cm$^{-1}$) and $\text{XeF}_6$ (broad band, 530-610 cm$^{-1}$) serve to detect the presence of a few percent of each of the fluorides in a sample of any one — down to ~ 1% of $\text{XeF}_4$ in $\text{XeF}_2$ can be detected. The advent of laser Raman spectroscopy has now made identification or detection of very small quantities or concentrations of $\text{XeF}_2$ rather easy. A dry glass container is satisfactory.
for sample holding and the band due to symmetric XeF$_2$ stretch ($v_1$) at 497 cm$^{-1}$ is extremely strong and well removed from bands attributable to the other xenon compounds. An X-ray powder photograph will readily confirm whether the bulk of a solid sample is or is not XeF$_2$ -- a 10% abundance could well be missed however.

3.2.2 Xenon Dichloride and Dibromide

**Synthesis.** The synthesis of xenon dichloride was first claimed by Meinert$^{156}$ who subjected a 1:1:1 mixture of Xe, F$_2$ and SiCl$_4$ or CCl$_4$ to a high frequency discharge (25 MHz, 150-350 mA), at -80°. This yielded colourless crystals which decomposed at ~ +80°. Mass-spectroscopy of the reaction product gave a strong XeCl$^+$ spectrum. The compound was not characterized further. Presumably interaction of F$_2$ with the tetrachloride (of Si of C) generates Cl atoms, essential for XeCl$_2$ formation.

The compound has also been prepared, using the matrix isolation technique, by Nelson and Pimentel.$^{157}$ In this preparation, a Xe : Cl$_2$ mixture of 200-100 : 1 was passed through a microwave discharge (2450 Mc, RK 5609, Raytheon Corp.) and then condensed upon a cesium iodide optical window, maintained at or close to 20°K. Infrared spectra were recorded in the range 400-200 cm$^{-1}$. An absorption centered at 313 cm$^{-1}$ was shown to be due to XeCl$_2$.

Xenon dichloride (and a number of other xenon compounds) have been detected$^{158}$ by Mössbauer Spectroscopy, as products of the $\alpha$ decay of their $^{129}$I relatives:

$$^{129}\text{I}Cl_2 \xrightarrow{\alpha} ^{129}\text{XeCl}_2$$
Table 3.2.2
Comparison of XeCl₂ with other Xe Dihalides and KrF₂

<table>
<thead>
<tr>
<th></th>
<th>XeF₂</th>
<th>XeCl₂</th>
<th>XeBr₂</th>
<th>KrF₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infrared $v_3$ (cm⁻¹)</td>
<td>547(a)</td>
<td>313(b)</td>
<td>--</td>
<td>580(a)</td>
</tr>
<tr>
<td>force const. $k_{r-rr}$ (m. dynes/Å)</td>
<td>2.60(b)</td>
<td>1.317(b)</td>
<td>--</td>
<td>2.59(b)</td>
</tr>
<tr>
<td>Mössbauer Splitting (mm/sec)</td>
<td>39.0±0.1</td>
<td>28.2±0.1</td>
<td>22.2±0.4</td>
<td>--</td>
</tr>
<tr>
<td>Electron transfer per bond²</td>
<td>0.72</td>
<td>0.52</td>
<td>0.41</td>
<td>0.5(e)</td>
</tr>
</tbody>
</table>

*See also Figure 1.4.2

*The electron transfer per bond, from the noble-gas atom to each ligand, is derived on the supposition that outer orbitals of the noble-gas atom e.g. Xe 5d are not involved in the bonding, and that the bonding is primarily po.


Although of value in the study of structure and bonding the last technique does not, of course, lend itself to the preparation of macroscopic quantities of the xenon compounds.

**Thermodynamic features.** As discussed in Section 1.2.3., the greater bond energy of \( \text{Cl}_2 \) relative to \( \text{F}_2 \) and the lower thermochemical bond energy of chlorides relative to fluorides, together indicate that xenon chlorides should be thermodynamically unstable (see Figure 1.2.4). The failure to prepare the xenon chlorides from the fluorides in metathetical reactions e.g., \( \text{XeF}_2 + \text{HCl} \) (or \( \text{BCl}_3 \)) \[ \rightarrow \left. -70^\circ \right. \text{Xe} + \text{Cl}^+ + 2\text{HF} \) (or \( \text{BF}_n\text{Cl}_{3-n} \)) and the evident instability of the dichloride, show that this is so.

**Structure and bonding.** The infrared absorption at 313 cm\(^{-1}\), observed in the spectrum of the matrix isolated material at 20\(^\circ\)K, has been convincingly attributed to the \( \nu_3 \) (asymmetric \( \text{Xe} - \text{Cl} \) stretch) mode of \( \text{XeCl}_2 \). Since no other absorption (attributable to the symmetric stretch, \( \nu_1 \)) was observed, the molecular symmetry is evidently \( \text{D}_{\infty h} \) (the bending mode, \( \nu_2' \) is expected to be \(< 200 \text{ cm}^{-1} \), i.e. below the limit of detection in this study).

The asymmetric stretching force constant \( k_{\text{rr}} \) given in Table 3.2.3, shows that the \( \text{Xe} - \text{Cl} \) bond is weak compared with the difluoride \( \text{Xe} - \text{F} \) and \( \text{Kr} - \text{F} \) bonds.

**Table 3.2.2.**

The Mössbauer effect is uniquely suited to study the process of xenon compound formation by \( \beta \) decay of \(^{129}\text{I} \) compounds. The new molecules are formed one at a time in the decay and each molecule signals its formation, and the details of its structure, through its contribution to the hyperfine spectrum of the \( \gamma \)-radiation. This radiation is emitted from the \(^{129}\text{Xe} \) nucleus, the 39.6 keV first excited state of which is
populated in the $\gamma$ decay of $^{129}\text{I}$. This state decays with a mean life $\tau = 1.46 \pm 0.06 \times 10^{-9}$ sec, usually by internal conversion, but by $\gamma$ emission in 8% of the cases. The excited $^{129}\text{Xe}$ nuclear state (spin and parity $\frac{3}{2}^+$) has a quadrupole moment $\mathbf{e}Q$, which results in a doublet absorption spectrum if the electric field gradient $\mathbf{e}Q \left(= \frac{\partial^2 V}{\partial z^2}\right)$ does not vanish. Therefore less symmetrical ligand arrangements (i.e. non spherical, non $O_n$ or non $T_d$) give rise to a resonance splitting. The splitting is proportional to $\mathbf{e}Q$. On the basis of a calibration against spectroscopic and atomic-beam studies of the quadrupole coupling caused by a single hole in the 5p electron shell of $^{131}\text{Xe}$, and comparison of $^{129}\text{Xe}$ and $^{131}\text{Xe}$ Mössbauer splittings in $\text{XeF}_4^{158}$, a quadrupole splitting of 27.3 mm/sec, is assigned to the loss of one $\text{P}_z$ electron (symmetry axis $z$) or a pair of $\text{P}_x$ or $\text{P}_y$ electrons. This interpretation assumes that the only xenon orbitals involved in the bonding are the $5s$ and $5p$, the latter having prime importance in forming $\sigma$ molecular orbitals.

The observed data for $\text{XeCl}_2$ are given in Table 3.2.2. It is clear, from the comparison with the $\text{XeF}_2$ and $\text{XeBr}_2$ data, that the bond polarity decreases in the sequence $\text{XeF}_2 > \text{XeCl}_2 > \text{XeBr}_2$. This is in harmony with the decrease in electronegativity of the ligands $F \to Br$. It is doubtful, however, if any of the bonds are as polar as the figures given in Table 3.2.2. indicate (see section 2.2.1). The figures probably represent upper limits for bond polarity. If there is significant Xe 5d orbital participation in the bonding as Mitchell asserts, $^{25}\text{a}$ this must have appreciable influence on the electric field gradient, in which case the splitting calibration just referred to will not be valid.
Other properties. Nothing is known of the long term stability of the dichloride and heavier halides, nor the highest temperature at which they may be safely stored. Nor is anything known of the reaction chemistry of XeCl$_2$, although it is clear from thermodynamic considerations that it is potentially a powerful oxidizer and chlorinator. Attempts to make XeCl$^+$ salts have failed.$^{135}$

Xenon Dibromide. The dibromide of xenon has been detected by Mössbauer Spectroscopy as a product of the $\beta$ decay of its $^{129}$I relative:

$$\text{IBr}_2 \rightarrow \text{XeBr}_2$$

It is to be expected that XeBr$_2$ will be much less stable than the chloride. Nothing further is known about the compound.

3.2.3 Xenon(II) Oxide and Hydroxide

It is of interest that XeO$_2$(g) was detected spectroscopically$^{159}$ as a bound gas phase species prior to 1962. The bond energy for this species is given as 9 kcal mol$^{-1}$ (See Table 1.2.4. and section 1.2.3). Xenon(II) oxide has not been isolated in the condensed phase however—not even by matrix isolation techniques.

There are indications that the hydrolysis of XeF$_2$ gives rise to xenon(II) oxide or hydroxide, this being a plausible explanation for the fleeting yellow colour observed, occasionally, to accompany the XeF$_2$ decomposition (see section 3.2.1, aqueous XeF$_2$ chemistry). Since IO$^-$ is a kinetically rather stable species$^{150}$, similar stability would have been expected for XeO.
It is probable that monomeric XeO would be much less favourable energetically than the oxygen bridged polymer. (It is conceivable that the brown solid reported to be \((\text{IF})_n\) by Schmeisser and Scharf is a fluorine bridge polymer). Polymeric XeO would presumably be a helical polymer with linear or near linear \(-(O-\text{Xe-O})-\) groups and a non-linear \(\text{Xe-O-Xe}\) bond. The fleeting yellow product of \(\text{XeF}_2\) hydrolysis could be such a polymer. Of course, \((\text{XeO})_n\) is anticipated to be thermodynamically unstable.
3.2.4. Xenon(II) Fluoride Fluorosulphate and Related Compounds

Although, so far, it has not proved possible to derive xenon(II) oxide or xenon dichloride by metathesis from the difluoride, several ligands have been successfully substituted for fluoride. One or both of the fluorine ligands of XeF$_2$ may be substituted. Compounds of this type were first reported independently by Bartlett and Sladky$^{86}$ and by Musher.$^{133}$ In the monosubstitution derivatives, the known ligands are -OSO$_2$F, -OCIO$_3$, -OTeF$_5$, and -OC(O)CF$_3$. It is probable that other highly electronegative ligands, (e.g., -OCF$_3$; -OSF$_5$ and even -SF$_5$) will also prove to be effective.

General synthetic procedure. The preparation of the monosubstituted XeF$_2$ derivatives has generally involved interaction of the fluoride with the appropriate anhydrous acid:

$$\text{XeF}_2 + \text{HL} \rightarrow \text{FX-L} + \text{HF}$$

The considerable exothermicity of $\Delta H^\circ_{\text{r}}$(HF) = -64.92 kcal mole$^{-1}$ provides the main driving force for these reactions. In the cases of the fluorosulphate and perchlorate, the difluoride is treated with an equimolar amount of acid at temperatures of $-75^\circ$ or lower and the hydrogen fluoride generated is removed as thoroughly as possible at the lowest possible temperature. The perchlorate and trifluoroacetate are kinetically unstable and detonate easily. The pentafluoro tellurate is the most stable$^{131}$ of the established compounds.

General structural features. The available structural data show that the linear three-centre-atomic feature of XeF$_2$ is maintained when one of the fluorine ligands is substituted. So far, all effective ligands are highly electronegative -OR groups. The Xe-O bond is longer (and presumably weaker) than the Xe-F bond. These features are exemplified
Figure 3.2.3

The Molecular Structure of FXeO$_2$S$_2$F

Precision of bond lengths is ca. 0.01 Å (uncorrected for thermal motion). The angles F(1)-Xe-O(1) and Xe-O(1)-S are 177.5 ± 0.4° and 123.4 ± 0.6°.
by the structure of the fluorosulphate \(^86\) which is shown in Figure 3.2.3. Evidently, the Xe-F bond is shorter than in XeF\(_2\) itself and it

Figure 3.2.3.

The Molecular Structure of FXeOS\(_2\)F

is as though the bonding were tending to Xe\(^+\)SO\(_3\)F\(^-\) (see 3.2.6), i.e., the resonance form F-Xe\(^+\)SO\(_3\)F\(^-\) has greater weight than F Xe\(^+\)OSO\(_2\)F. The similarity of the Xe-F features of the vibrational spectra shown in Table 3.2.3 indicate that the Xe-F bond in all of the known FXeL compounds, is similar to that in FXeOS\(_2\)F.

Stability and reactions. The fluorosulphate and perchlorate are thermodynamically unstable and the latter is dangerously explosive. The fluorosulphate has been kept for many weeks at 0° but has a half life of only a few days at \(\sim 20°\) and decomposes smoothly when molten according to the equation \(^86\)

\[
2FXeSO_3F \rightarrow XeF_2 + Xe + S_2O_6F_2.
\]

Presumably, this involves radical formation: FXeSO\(_3\)F \(\rightarrow\) FXe + SO\(_3\)F, and the yellow green colour gives some support to this. The equilibrium \(^{161}\)

2SO\(_3\)F \(\rightarrow\) S\(_2\)O\(_6\)F\(_2\) is well known \(^{161}\) and as has been discussed under XeF\(^-\) (section 3.1.1), all evidence indicates that the radical disproportionates:

2XeF \(\rightarrow\) Xe + XeF\(_2\). So far it has not proved possible to obtain (ClO\(_4\))\(_2\) from the perchlorate, the decomposition usually being complex (yielding mainly ClO\(_3\), some Cl\(_2\)O\(_7\), O\(_2\), Xe and ClO\(_2\)) and occasionally proceeding with explosive violence. In contrast, the pentafluoroorthotellurate is thermally quite stable (to 120° in prefluorinated vessels) and can be\(^{131}\) distilled (liquid) unchanged at 53° (0.01 mm Hg).

These compounds have considerable potential as oxidizers, in reactions in which the substituted ligand is transferred to a more electropositive centre, but little has, so far, been reported on these aspects.
### Table 3.2.3.
Comparison of FXeO$_2$F, and Related Compounds

<table>
<thead>
<tr>
<th>Colour</th>
<th>FXeO$_2$F$^\text{(a)}$</th>
<th>FXeOCl$_3$$^\text{(a)}$</th>
<th>FXeOTeF$_5$$^\text{(b)}$</th>
<th>FXeOCOCF$_3$$^\text{(c)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colourless</td>
<td>Colourless</td>
<td>v. pale yellow</td>
<td>pale yellow?</td>
<td></td>
</tr>
<tr>
<td>m.p. ($^\circ$C)</td>
<td>36.6</td>
<td>16.5</td>
<td>-24</td>
<td>(detonates)</td>
</tr>
<tr>
<td>b.p. ($^\circ$C)</td>
<td>sublimable</td>
<td>(detonates)</td>
<td>53(0.01 torr)</td>
<td></td>
</tr>
<tr>
<td>Half-life at ~ 20°C</td>
<td>~ 1 week</td>
<td>rapid decomposition of melt.</td>
<td>$\infty$</td>
<td>~ 10 hrs.</td>
</tr>
<tr>
<td>Unit cell</td>
<td>$a=9.88$, $b=10.00$, $c=10.13\AA$ (all±0.01Å)</td>
<td>Powder patterns show that FXeOCl$_3$ is similar to FXeO$_2$F</td>
<td>but not isomorphous with it.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$z=8$, space group $D^\text{15}_h$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvents</td>
<td>CH$_3$CN</td>
<td>CH$_3$CN</td>
<td>CH$_3$CN, CCl$_4$</td>
<td></td>
</tr>
<tr>
<td>$^{19}\text{F n.m.r. data}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta_\text{p} (\text{p.p.m.})$</td>
<td>-</td>
<td>-</td>
<td>37(F(Te))</td>
<td></td>
</tr>
<tr>
<td>($^{19}\text{F, CF}_3\text{COOH} = 0$)</td>
<td>-</td>
<td>-</td>
<td>66.3(F(Xe))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td>(in CH$_3$CN soln.)</td>
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</table>
Infrared and Raman bands & assignments

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<tr>
<th>IR(a)(d)</th>
<th>R(a)(d)</th>
<th>IR(a)(d)</th>
<th>R(a)(d)</th>
<th>IR(e)</th>
<th>IR(in CH₃CN)(c)</th>
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<td>253s</td>
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</tr>
<tr>
<td>620 vs</td>
<td>614w</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>636m</td>
<td>638mw</td>
<td></td>
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</tr>
<tr>
<td>798s</td>
<td>800w</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>722vs</td>
<td>726w</td>
<td></td>
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<tr>
<td>758sh</td>
<td>754w</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>970-1220</td>
<td>970-1220</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1210vs</td>
<td>1197w</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1018vs</td>
<td>1014 mw</td>
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<td></td>
</tr>
<tr>
<td>1048sh</td>
<td>1032 vw</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1393s</td>
<td>1390w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1243 vw</td>
<td>1202 mw</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1730</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( \delta(Xe-O) \) \( \delta(Xe-O-C) \) \( \lambda(S-F) \)
Table 3.2.4

References


(e) F. O. Sladky, unpublished observation.
Interaction of the FXeOR compounds with one mole of the anhydrous acid HOR, generates the bis compound: 86, 132, 134 (see section 3.2.5)

\[
FXeOR + HOR \rightarrow Xe(OR)\_2
\]

Attempts to prepare mixed compounds (e.g. by interaction of HSO\(_3\)F with FXeOTeF\(_5\)) have so far failed: 162

\[
FXeOTeF\_5 + HSO\(_3\)F \rightarrow HF, S\(_2\)O\(_6\)F\(_2\), F\(_2\)TeOTeF\(_5\), Xe, O\(_2\)
\]

It is possible that the F-ligand in the FXe-OR compounds can be donated to strong fluoride ion acceptors (like AsF\(_5\) and SbF\(_5\)):

\[
FXe-OR + AsF\_5 \rightarrow [XeOR]^+ [AsF\_6]^- ?
\]

since FXeOTeF\(_5\) forms a 1:1 complex with AsF\(_5\): 131, of which preliminary studies indicate the salt formulation. 162 The interaction of FXeOTeF\(_5\) with CsF: 131

\[
FXeOTeF\_5 + CsF \rightarrow TeF\_6 + (FXeO^-Cs^+) \rightarrow CsF + Xe + \frac{1}{2}O\_2
\]

raises the possibility of isolating FXeO\(^-\) salts by careful control of reactions of this kind. Much can probably be achieved, in exploring the chemistry of these compounds, by exploiting the solvent properties of CH\(_3\)CN (which is oxidatively rather inert).

3.2.5 Xenon(II) bis Fluorosulphate and Related Compounds

Stability and Reactions. The disubstituted derivatives of XeF\(_2\) are less well characterized than their monosubstituted relatives. The compounds are obtained 86, 132, 134 by treating XeF\(_2\) with two moles of the anhydrous acid
or by allowing the FXeOR relative to interact with one mole of acid. As discussed in section 3.2.4, attempts to prepare unsymmetrical RO-Xe-OR compounds have failed. The bis fluorosulphate decomposes more readily than FXeOSO\(_2\)F:

\[
\text{spontaneous at } 20^\circ \\
\text{Xe(OSO}_2\text{F})_2 \rightarrow \text{Xe} + (\text{SO}_3\text{F})_2
\]

and the meagre available evidence indicates that this lower stability of the bis compounds will prove to be general. The decomposition of the fluorosulphate provides very pure (SO\(_3\)F\(_2\)) but, unfortunately, this mode of decomposition is not general and the perchlorate\(^86\), orthotellurate\(^132\) and trifluoroacetate\(^134\) decompose as indicated (the first and last being dangerously explosive materials):

\[
\begin{align*}
\text{Xe(CIO}_4)_2 & \rightarrow 20^\circ \rightarrow \text{Xe} + (\text{CIO}_3)_x + O_2 (+ \text{some Cl}_2O_7) \\
\text{Xe(OTeF}_5)_2 & \rightarrow 120^\circ \rightarrow \text{Xe} + F_5\text{Te-0-TeF}_5 + O_2 (+ \text{some TeF}_6) \\
\text{Xe(OOCOF}_3)_2 & \rightarrow 20^\circ \rightarrow \text{Xe} + C_2F_6 + 2CO_2 \\
& \text{t}_1:17\text{hr.}
\end{align*}
\]

Table 3.2.4

Physica data on the bis compounds is given in Table 3.2.4. Fluorosulphonic acid will displace the perfluororthotelluric acid\(^162\):

\[
\text{Xe(OTeF}_5)_2 + \text{HOSO}_2\text{F} \rightarrow \text{Xe(OSO}_2\text{F})_2 + 2\text{HOTeF}_5
\]

but attempts to displace the telluric acid with HOOCOF\(_3\)\(^162\) have led to
Table 3.2.4.
Physical Properties of Xe(OSO$_2$F)$_2$ and Related Compounds

<table>
<thead>
<tr>
<th></th>
<th>Xe(OSO$_2$F)$_2$ (a)</th>
<th>Xe(OClo$_3$)$_2$ (a)</th>
<th>Xe(OTeF$_5$)$_2$ (c)</th>
<th>Xe(OCOCF$_3$)$_2$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>pale yellow</td>
<td>pale yellow</td>
<td>colourless</td>
<td>pale yellow</td>
</tr>
<tr>
<td>m.p. ($^\circ$C)</td>
<td>43-45 (decomp.)</td>
<td>- -</td>
<td>35-37</td>
<td>- -</td>
</tr>
<tr>
<td>Solvents</td>
<td>CH$_3$CN</td>
<td>CH$_3$CN</td>
<td>CH$_3$CN,CCl$_4$</td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td></td>
<td>(explosive with</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_5$O$_2$, acetone, benzene)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unit Cell</td>
<td>a = 7.82Å (b)</td>
<td>- -</td>
<td>a = 15.6Å (d)</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td>b = 13.5</td>
<td></td>
<td>b = 8.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = 6.78</td>
<td></td>
<td>c = 12.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\beta$ = 96$^\circ$</td>
<td></td>
<td>z = 4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>z = 4</td>
<td></td>
<td>space group</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cmca</td>
<td></td>
</tr>
<tr>
<td>Vibrational Spectra(cm$^{-1}$)</td>
<td>See Table 3.2.5</td>
<td>IR</td>
<td>R</td>
<td>IR</td>
</tr>
<tr>
<td></td>
<td></td>
<td>780 w</td>
<td></td>
<td>701 w</td>
</tr>
<tr>
<td></td>
<td></td>
<td>705 vs</td>
<td></td>
<td>692 m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>628 vs</td>
<td></td>
<td>510</td>
</tr>
<tr>
<td></td>
<td></td>
<td>647m</td>
<td></td>
<td>$\nu$(Xe-0-)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\nu$(Te-F)$^+$</td>
<td></td>
<td>970-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\nu$(Te-O$^-$)</td>
<td></td>
<td>1240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>475m</td>
<td></td>
<td>1240</td>
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<td></td>
<td></td>
<td>434 m</td>
<td></td>
<td>$\nu$(C-F)</td>
</tr>
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<td></td>
<td></td>
<td>300 w</td>
<td></td>
<td>1730</td>
</tr>
<tr>
<td></td>
<td></td>
<td>320 w</td>
<td></td>
<td>$\nu$(C=0)</td>
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<tr>
<td></td>
<td></td>
<td>237 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>178 wv</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>131 vs</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8(0-Xe-0)?</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) M. Wechsberg and N. Bartlett, to be published.
(d) F. O. Sladky, unpublished information.
Table 3.2.5
Raman Frequencies and Assignments for \( \text{FXeOS}_2\text{F} \), \( \text{Xe(OS}_2\text{F})_2 \) and \( \text{S}_2\text{O}_6\text{F}_2 \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \nu(S-O) )</th>
<th>( \nu(S-O) )</th>
<th>( \nu(S-F) )</th>
<th>( \delta(0-S-0) )</th>
<th>( \rho_w(S-F) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{XeOS}_2\text{F} )</td>
<td>1390w</td>
<td>1197w</td>
<td>970w</td>
<td>800w</td>
<td></td>
</tr>
<tr>
<td>( \text{Xe(OS}_2\text{F})_2 )</td>
<td>1425w</td>
<td>1238mw</td>
<td>959mw</td>
<td>823w</td>
<td>601s</td>
</tr>
<tr>
<td>( \text{S}_2\text{O}_6\text{F}_2 )</td>
<td>1497mw</td>
<td>1251vs</td>
<td>880m</td>
<td>824s</td>
<td>798vs</td>
</tr>
</tbody>
</table>

\( \nu(s-o) \) terminal, \( \nu(s-o) \) bridge, \( \nu(s-f) \) terminal

\( \nu = \) stretching, \( \delta = \) deformation, \( \rho_w = \) wagging


decomposition:

\[ \text{Xe} \left( \text{OTeF}_5 \right)_2 + 2 \text{HOOCCF}_3 \rightarrow \text{Xe} + 2 \text{HOTeF}_5 + 2 \text{CO}_2 + \text{C}_2 \text{F}_6 \]

Structural features. The available structural evidence, which is primarily infrared and Raman data, suggest that the xenon atom is symmetrically placed between the two OR groups. The Raman data for Xe(OSO₂F)₂ and related SO₃F compounds given in Table 3.2.5 supports the R-O-Xe-O-R formulation but suggests that the molecule is not centrosymmetric.

3.2.6 XeF₂ as a Fluoride Ion Donor

Compounds of composition XeF₂²MF₅ (where M is a quinquevalent metal atom) have been known since 1963 but several years passed before they were shown to be salts containing the XeF⁺ ion. Indeed, strong fluoride ion acceptors, such as AsF₅ and the metal pentafluorides, readily withdraw a fluoride ion from XeF₂ and three classes of salt have been established: XeF⁺[MF₆]⁻, (XeF₂, MF₅); XeF⁺[M₂F₁₁]⁻, (XeF₂, 2MF₅) and \( \text{Xe}_2\text{F}_3[\text{MF}_6]^- \) (2XeF₂, MF₅). It is quite possible that the range of salts is more extensive than this since the phase study by Maslov et al. of the XeF₂-SbF₅ system established the compounds XeF₂, SbF₅; XeF₂, 1.5 SbF₅; XeF₂, 2SbF₅ (proved to be XeF⁺[SbF₆]⁻) and XeF₂, 6SbF₅.

Laboratory preparation. It is possible to prepare the XeF₂ salts by simply fusing XeF₂/MF₅ mixtures but the fluoroarsenates cannot be made in this way. It is better to prepare the compounds from a solvent and bromine pentafluoride (b.p. 41.3 °C) has proved to be excellent for this purpose. Typically, the difluoride and appropriate pentafluoride are weighed (by difference) in the desired molar ratio, into a Kel-F tube.
Figure 3.2.4.
The Molecular Structure of XeF²⁺[Sb₂F₁₁]⁻.
which is then attached to a vacuum line. Bromine pentafluoride is distilled on to the \( \text{XeF}_2 / \text{MF}_5 \) mixture, which is allowed to dissolve at room temperature. By removing the \( \text{BrF}_5 \) slowly, well-crystalline, homogeneous material may be obtained.

**Structural features.** The molecular structure \(^{165}\) of \( \text{XeF}^+[\text{Sb}_2\text{F}_{11}]^- \) is represented in Figure 3.2.4. The structure establishes the existence of a short-bonded \( \text{XeF} \) species, the properties of which, as may be seen from the comparison with IF molecule in Table 1.2.1, are consistent with its designation as \( \text{XeF}^+ \). It is clear from the Raman spectra \(^{87}\) of the compounds \( \text{XeF}_2, 2\text{MF}_5 \) that they are structurally similar to \( \text{XeF}^+ [\text{Sb}_2\text{F}_{11}]^- \). All are characterized by strong bands in the 600-621 cm\(^{-1}\) region assigned to the \( \text{XeF}^+ \) stretch. The rather short \( \text{Xe} \cdots \text{F} \) distance of 2.35Å between the cation and anion, in the antimony salt, indicates a small Van der Waals radius for the positively charged Xe atom.

The Raman data for the \( \text{XeF}_2, \text{MF}_5 \) compounds show the formulation \( \text{XeF}^+ [\text{MF}_6]^+ \) to be appropriate, the vibrational characteristic of the \( \text{XeF}^+ \) species being very like that of the \( \text{XeF}^+ [\text{XeF}_2]^- \). Not only is there evidence of a weak interaction of the \( \text{XeF}^+ \) ion with the \( \text{MF}_6^- \) but some interaction between the \( \text{XeF}^+ \) ions is also indicated. It should be noted that I-Cl forms a chain polymer and it may well be that the \( \text{XeF}^+ \) species tends to that behaviour.

The crystal structure of \( 2\text{XeF}_2 \text{AsF}_5 \) proves \(^{164}\) the formulation \( \text{Xe}_2\text{F}_3^+ [\text{AsF}_6]^- \) to be appropriate. The cation is planar and \( \tau^- \) shaped and is represented in Figure 3.2.5. The Raman spectra of this salt and the other \( 2\text{XeF}_2, \text{MF}_5 \) compounds establish that the latter also contain the \( \text{Xe}_2\text{F}_3^+ \) ion. \(^{87}\) This ion has a similar shape to that observed in the \( \text{H}_2\text{F}_3^- \) and \( \text{I}_5^- \) ions.
Figure 3.2.5
A Comparison of the \( \text{Xe}_2\text{F}_3^+ \), \( \text{H}_2\text{F}_3^- \) and \( \text{I}_5^- \) ions.

\[ \text{[Xe}_2\text{F}_3]^+ \]

\[ \begin{align*}
&\text{Xe} \quad \text{F} \\
&178(2)^\circ \\
&
\end{align*} \]

\[ \begin{align*}
&\text{Xe} \quad \text{F} \\
&151(2)^\circ \\
&2.14 \ (0.03) \ \text{Å} \\
&1.90 \ (0.03) \ \text{Å}
\end{align*} \]

\[ \text{[H}_2\text{F}_3]^- \]

\[ \begin{align*}
&\text{F} \quad \text{H} \\
&2.35 \ (0.02) \ \text{Å} \\
&130-139
\end{align*} \]

\[ \text{I}_5^- \]

\[ \begin{align*}
&\text{I} \\
&185(0.5)^\circ \\
&95 \ (0.5)^\circ \\
&3.17 \ (0.015) \ \text{Å} \\
&2.82 \ (0.015) \ \text{Å}
\end{align*} \]
The near linearity of the \( \text{FXe} \cdots \text{F} \) assemblies indicates that the cation resembles two \( \text{XeF}_2 \) molecules sharing a common F atom. The bond length disparity shows, however, that the five centre system is tending to \( \text{F-Xe}^+\text{F-} \cdot \cdot \cdot \text{F} \cdot \cdot \cdot \text{F-Xe}^+ \cdot \cdot \cdot \text{F} \). It is perhaps of significance that the \( \text{Xe}_2\text{F}_3^+ \) salts show little evidence of interaction of the cation with the anion -- highly polarizing \( \text{XeF}_2^+ \) ions are adequately "neutralized" by the bridging fluoride ligand.

Reactions. The fluoride ion donor ability of \( \text{XeF}_2 \) is comparable to that of nitrosyl fluoride and the available thermochemical data indicate that

\[
\Delta H^\circ(\text{XeF}_2(g) \rightarrow \text{XeF}^+(g) + \text{F}^-(g)) = +215 \text{ kcal mole}^{-1}
\]

(see section 3.2.2 and Figure 3.2.1). The increase in the \( \text{Xe-F} \) bond energy (48 kcal mole\(^{-1}\) in the cation, 32 in \( \text{XeF}_2 \)) in cation formation contributes to fluoride ion donor ability of the difluoride. It is a better \( \text{F}^- \) donor than \( \text{XeF}_4 \) but inferior to \( \text{XeF}_6 \).

An important aspect of the \( \text{XeF}^+ \) species is its high electron affinity. Since \( E(\text{XeF}^+) = B.E.(\text{XeF}^+) - B.E.(\text{Xe-F}) - I(\text{Xe}) \) (see Figure 3.2.1.), the electron affinity must be in the range 10 - 11 eV. This value is consistent with the decomposition of the salt \( \text{XeF}^+\text{[OSF}_6^- \) to \( \text{OSF}_6 \) and xenon:

\[
3\text{XeF}^+[\text{OSF}_6^-] \rightarrow [\text{Xe}_2\text{F}_3]^+[\text{OSF}_6^-] + 20\text{OSF}_6 + \text{Xe}
\]

In the \( [\text{Xe}_2\text{F}_3]^+ \) ion, each \( \text{XeF}^+ \) species receives electron density from the associated \( \text{F}^- \) ion (for which \( I(\text{F}^-) = 83 \text{ kcal mole}^{-1} \)). Thus the assembly becomes a multicentre bonded system, with a lower electron affinity than \( \text{XeF}^+ \).

So far, the salts have not been used as reagents but the acid catalysis of \( \text{XeF}_2 \) oxidation and fluorination reactions, referred to in section 3.2.2, implies that the \( \text{XeF}^+ \) or \( \text{Xe}_2\text{F}_3^+ \) ions are the effective oxidizers.

The known salts are briefly described in Table 3.2.6.
Table 3.2.6.

Some Physical Properties of XeF$^{+}$[MF$_6$]$^{-}$, XeF$^{+}$[M$_2$F$_{11}$]$^{-}$ and Xe$_2$F$_3$$^{+}$[MF$_6$]$^{-}$ Salts

<table>
<thead>
<tr>
<th>XeF$^{+}$[MF$_6$]$^{-}$ Salts</th>
<th>As$^a$</th>
<th>Ru$^a$</th>
<th>Os</th>
<th>Ir$^{a,b}$</th>
<th>Pt$^a$</th>
<th>Ta$^b$</th>
<th>Nb$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>pale yellow-green</td>
<td>pale yellow-green</td>
<td>brown* yellow-green</td>
<td>orange-red</td>
<td>pale yellow</td>
<td>pale yellow</td>
<td></td>
</tr>
<tr>
<td>m.p. ($^\circ$C)</td>
<td>-</td>
<td>110-1</td>
<td>-</td>
<td>152-3</td>
<td>82-3</td>
<td>52-3</td>
<td>30-5</td>
</tr>
<tr>
<td>Xe-F Stretch (Raman, cm$^{-1}$)$^{a}$</td>
<td>-</td>
<td>604,599</td>
<td>-</td>
<td>608,602</td>
<td>609,602</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Unit Cell</td>
<td>isomorphous</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
</tbody>
</table>

*a = 11.1, b = 7.96, c = 7.24Å, z = 4

Space group Pnma

*unstable
**XeF⁺[M$_2$F$_{11}$]$^-$ Salts**

<table>
<thead>
<tr>
<th>M</th>
<th>Sb</th>
<th>Ru</th>
<th>Ir</th>
<th>Pt</th>
<th>Ta</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>yellow$^c$</td>
<td>bright-green$^a$</td>
<td>orange-yellow$^a$</td>
<td>dark red$^a$</td>
<td>pale yellow$^b$</td>
<td>pale yellow$^b$</td>
</tr>
<tr>
<td>m.p. (°C)</td>
<td>63$^c$, $^a$</td>
<td>49-50$^a$</td>
<td>69-70$^a$</td>
<td>-</td>
<td>82-3$^b$</td>
<td>42-7$^b$</td>
</tr>
<tr>
<td>Xe-F Stretch$^a$ (Raman, cm$^{-1}$)</td>
<td>621</td>
<td>604,598</td>
<td>612,601</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Unit Cell**

<table>
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<th>Ru</th>
<th>Os</th>
<th>Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>pale yellow-green</td>
<td>yellow-green</td>
<td>yellow-brown</td>
<td>yellow-green</td>
</tr>
</tbody>
</table>

**Xe$_2$F$_3$⁺[MF$_6$]$^-$ Salts**

<table>
<thead>
<tr>
<th>M</th>
<th>As$^{e,a}$</th>
<th>Ru$^a$</th>
<th>Os$^a$</th>
<th>Ir$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>pale</td>
<td>pale</td>
<td>pale</td>
<td>pale</td>
</tr>
<tr>
<td>m.p. (°C)</td>
<td>99-100$^{e,a}$</td>
<td>98-99$^a$</td>
<td>-</td>
<td>92-93$^a$</td>
</tr>
<tr>
<td>XeF Stretch$^a$ (Raman, cm$^{-1}$)</td>
<td>600,588</td>
<td>593,579</td>
<td>593,582</td>
<td>592,578</td>
</tr>
</tbody>
</table>

**Unit Cell**

- a = 15.443
- b = 8.678
- c = 20.888
- β = 90.13
- z = 12
Table 3.2.6.
References


3.2.7 **Molecular Adducts of XeF₂**

Shortly after the preparation of the first xenon compounds a fluoride of xenon was isolated which was initially thought to be a second crystalline modification of XeF₄. A three-dimensional X-ray structural analysis quickly showed, however, that the compound was a 1:1 molecular adduct of XeF₂ and XeF₄. The molecular dimensions of the molecules are not significantly different from those of the pure components (see Table 3.3.4.). Several other adducts of XeF₂ have since been prepared in which the XeF₂ molecule is essentially indistinguishable from the molecule in crystalline XeF₂.

Established 1:1 compounds are XeF₂, XeF₄, XeF₂, IF₅, XeF₂, XeOF₄, and XeF₂[XeF₅⁺][AsF₆⁻] have been reported. Some physical properties of the compounds are given in Table 3.2.7.

**Table 3.2.7.**

| Some Physical Properties of XeF₂ Adducts |

Preparation. The adducts may be very conveniently prepared by mixing the components in the appropriate molar proportions. By fusing the mixture, or dissolving it in a suitable solvent (e.g. acetronitrile) a homogeneous sample is produced. The 1:1 XeF₂, IF₅ adduct may also be made by heating a xenon/IF₇ mixture to 200°:

\[
Xe + IF₇ \xrightarrow{200°} XeF₂, IF₅
\]

Structure and bonding. Attention has already been drawn to the semi-ionic nature of the bonding in XeF₂ (see sections 1.3.3. and 3.2.2.), and the excellent agreement with the experimental enthalpy of vaporization given by the lattice energy calculation for XeF₂(cryst) based on coulombic...
Table 3.2.7.

<table>
<thead>
<tr>
<th></th>
<th>XeF₂, XeF₄ (a)</th>
<th>XeF₂, IF₅ (b)</th>
<th>XeF₂, XeOF₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td></td>
<td>colourless solids</td>
<td></td>
</tr>
<tr>
<td>m.p. (°C)</td>
<td>98</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>ν₁ (XeF₂) cm⁻¹</td>
<td>- -</td>
<td>495</td>
<td>494</td>
</tr>
<tr>
<td>Xe- F bond length (Å)</td>
<td>2.010 (a = 0.006)</td>
<td>2.007 (a = 0.009)</td>
<td>- - -</td>
</tr>
<tr>
<td>Unit cell</td>
<td>a = 6.64</td>
<td>a = 7.65 ± 0.01 Å</td>
<td>a = 7.56 ± 0.01 Å</td>
</tr>
<tr>
<td></td>
<td>b = 7.33 ± 0.01 Å</td>
<td>c = 10.94 Å</td>
<td>c = 11.36</td>
</tr>
<tr>
<td></td>
<td>c = 6.40 ± 0.01 Å</td>
<td>z = 4</td>
<td>z = 4</td>
</tr>
<tr>
<td></td>
<td>θ = 92°40 ± 5'</td>
<td>space group P4/m</td>
<td>space group P4/m</td>
</tr>
<tr>
<td>z = 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>space group P2₁/c</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Bond length in XeF₂(c) = 2.00 ± 0.01 Å

(c) N. Bartlett and M. Wechsberg, to be published.
interactions between $-\frac{1}{2}F-Xe^{+}-F^{-\frac{1}{2}}$ molecules. The crystal structure of XeF$_2$, XeF$_4$ shows that similar coulombic interactions between the XeF$_2$ and XeF$_4$ molecules are responsible for the ordered close packed structure. Undoubtedly, all of the XeF$_2$ molecular complexes owe their existence to appreciable coulombic interactions between the interacting species.

The crystal structure of the 1:1 XeF$_2$, IF$_5$ compound, illustrated in Figure 3.2.6., nicely illustrates the nature of the intermolecular interactions. Each molecule is surrounded by an approximately cubic arrangement of molecules of the other kind. The detailed arrangement is consistent with close packing of the molecules and with electrostatic attraction of the negatively charged fluorine ligands of one molecular species for the positively charged central atom of the other. The attraction of the fluorine ligands of XeF$_2$ for the iodine atoms of the IF$_5$ molecules is particularly important. The disposition of the fluorine ligands in a layer of XeF$_2$ molecules is determined by the orientation of the nearest IF$_5$ molecules as illustrated. Where superimposed IF$_5$ molecules, in adjacent layers, are base to base, the sandwiched XeF$_2$ molecules orient to make short I-F contacts. On the other hand, the XeF$_2$ molecules are oriented away from the IF$_5$ molecules where they abut apex to apex.

This arrangement suggests that the iodine atom bears an appreciable positive charge which is effectively shielded by fluorine ligands but not by the non-bonding valence electron pair. Presumably, the non-bonding pair is concentrated significantly on the $c$ axis rendering the IF$_5$ molecule pseudo-octahedral. Consequently, the centres of the faces of the pseudo-octahedron on the 'pair' end of the molecule would
Figure 3.2.6.
The Crystal Structure of XeF$_2$, IF$_5$

A portion of the structure selected to indicate the basal to basal and apical to apical environment of IF$_5$ molecules. The "cells" which have been drawn through Xe atoms to assist in spacial perception should not be confused with the unit cell.
Figure 3.2.6.

The Crystal Structure of XeF$_2$, IF$_5$

INTERATOMIC DISTANCES (Å) AND ANGLES (°)
WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

a. In IF$_5$ molecule

- I-F(1) 1.817(10) 1.862(10)*
- I-F(2) 1.873(5) 1.892(5)*
- F(1)···F(2) 2.395(9) F(2)···F(2$^I$) 2.615(8)
- F(1)-I-F(2) 80.9(0.2)

b. In XeF$_2$ molecule

- Xe-F(3) 2.007(9) 2.018(9)*

b. Attractive interactions between XeF$_2$ and IF$_5$

- F(3)···I 3.142(7) F(2)···Xe 3.516(5)**
- F(2)···Xe$^II$ 3.361(6)**

c. Intermolecular F···F contacts

- F(1)···F(1) 2.621(19) F(2)-F(2$^{III}$) 2.929(12)
- F(2)···F(2$^{II}$) 2.953(8) F(2)-F(3) 3.418(8)
- F(2)···F(3$^{III}$) 3.214(8) F(2)-F(3$^{II}$) 2.901(7)
- F(3)···F(3$^{IV}$) 2.961(14)

* Corrected for thermal motion, assuming that F atom rides on heavy atom. All other distances were uncorrected.

** Roman numbers refer to atoms at symmetry equivalent positions, where I = (y,-x,z), II = (1/2-y, 1/2+x, 1/2+z), III = (1/2-x, 1/2-y,1/2-z) IV = (1-y,x,z).
effectively possess positive charge (the 'pair' screening being poor in this direction). The fluorine ligands of the XeF$_2$ molecules align approximately as this model dictates.

The Xe-F interatomic distance of 2.007 (± 0.009) Å in the XeF$_2$ molecules is not significantly different from that observed in crystalline XeF$_2$ (2.00 ± 0.01 Å).

Although IF$_5$ and BrF$_5$ are known to be geometrically similar$^{20}$, the latter does not form a stable adduct with XeF$_2$. Presumably, this is because the charge on the (more electronegative) Br atom is less than on the I atom and perhaps also because the central-atom charge screening by the F ligands in BrF$_5$ is more effective than in IF$_5$. It is of interest that the XeOF$_4$ adduct with XeF$_2$ is much less stable than is XeF$_2$, IF$_5$ negative. This is compatible with the greater screening of the positive charge on the Xe(VI) atom in XeOF$_4$ compared with the iodine charge screening in IF$_5$. In XeOF$_4$, the basal fluorine ligands are in the same plane as the xenon atom, i.e. $\angle F_a$-Xe-$F_b = 91^\circ$, whereas in IF$_5$, $\angle F_a$-I-$F_b = 80^\circ$.

The interaction of XeF$_2$ with the XeF$_5^+$ ion is not surprising in view of the close similarity of XeF$_5^+$ and IF$_5$ (see section 3.4.5).
3.3. Xenon (IV) Compounds

Xenon tetrafluoride is the only xenon(IV) compound available in macroscopic quantities, so far characterized unambiguously. The tetrachloride and tetrabromide have been detected by Mössbauer spectroscopy, as products of the \( \beta \) decay of \( ^{129}\text{Xe} \rightarrow ^{129}\text{Xe} \).

3.3.1 Xenon Tetrafluoride

**Historical and preparative.** Xenon tetrafluoride was first reported in 1962, by Claassen, Selig and Malm. They prepared it by heating mixtures of xenon and fluorine, at about 6 atm., in a 1:5 ratio at 400° in a sealed nickel can. These conditions are close to optimum for XeF\(_4\) preparation and the static synthesis remains the most convenient one for the preparation of gram lots. A hot-tube flow method is claimed to yield good quality tetrafluoride, if the F\(_2\)/Xe molar ratio is 4:1 and the residence time in the hot zone of a nickel tube, at 300°, is 1 min. 17\( ^b \) A flow system, designed for continuous production of the tetrafluoride, using a F\(_2\)/Xe molar ratio 3:1 and a furnace temperature of 560° has also been described. 173 There are indications, however, that considerable care must be exercised, if high purity XeF\(_4\) is to be obtained by the flow method.

Thus, the earlier erroneous report, that 'xenon tetrafluoride' (prepared by the hot-tube flow method) interacts with SbF\(_5\): 
\[
\text{XeF}_4 + 2\text{SbF}_5 \rightarrow \text{XeF}_2 + 2\text{SbF}_3
\]
was undoubtedly due to the sample of supposed tetrafluoride having been largely difluoride. However, even the static method is far from perfect. As Weinstock and his coworkers have demonstrated, it is not possible to prepare XeF\(_4\) pure (see Figure 3.3.1 and thermodynamic features) by the thermal method, therefore, if high purity material is desired, it is necessary either to resort to chemical purification.
or else submit the sample to tedious fractionation.102

An essentially quantitative yield of XeF₄ has been claimed for the electric discharge method.174 A F₂/Xe molar ratio of 2:1 (operating pressure 2 to 15 mm) in a reaction vessel at -78°C yielded XeF₄ quantitatively. Like the hot-tube flow method this lends itself to continuous operation.

The tetrafluoride also forms 175 when F₂/Xe mixtures (2.6 - 2.08:1) are irradiated with Co - γ rays or 1.5 MeV electrons, without cooling of the sample. When the reaction vessel is cooled well below 0°C, so as to freeze out any XeF₂ (the first reaction product), the yield of XeF₄ is very small. Utilization of absorbed energy must be efficient since initial G values, based on xenon consumption, are in the range 5 to 15 atoms per 100 eV absorbed. XeF₄ is relatively stable to γ-radiation with an initial G value of 0.6 to 1.8 at 45°C. An independent study176 involving 1.6 MeV electrons agrees with the above findings.

Laboratory preparation. Xenon tetrafluoride is difficult to separate from the difluoride by physical means (the two have similar vapour-pressure relationships and also form a 1:1 adduct - see section 3.2.7.) and to circumvent this, it has often been the practice to employ F₂/Xe ratios (2:1) and temperatures of ~450-500°C, which conditions generate minimal XeF₂ but XeF₆ as a major impurity. The XeF₆ (approximately 1/3 of the product) is removed by treating the mixture with sodium fluoride, which forms a complex with it at room temperature.81 A more general chemical purification169, which effectively eliminates XeF₂ and XeF₆ simultaneously, exploits the inferior fluoride ion donor ability of XeF₄ compared to XeF₂ or XeF₆. With this purification, conditions
which maximize the \( \text{XeF}_4 \) production, may be employed. Such a product, which will contain small but significant quantities of \( \text{XeF}_2 \) and \( \text{XeF}_6 \) (in approximately equimolar amounts), is dissolved in bromine pentafluoride and an excess of arsenic pentafluoride is condensed upon the mixture. Since \( \text{XeF}_2 \) and \( \text{XeF}_6 \) form involatile salts, and since the solvent and \( \text{AsF}_5 \) may be removed quantitatively at 0° or below (at which temperatures the \( \text{XeF}_4 \) has a very low vapour pressure), the \( \text{XeF}_4 \) can be isolated by subsequent vacuum sublimation, at 20°.

\[
\begin{align*}
\text{XeF}_2 & \quad \text{0° in static vacuum} \quad \text{XeF}_2^+ [\text{AsF}_6^-] \\
\text{XeF}_4 & \quad + \quad \text{AsF}_5 \ (\text{excess}) \quad \xrightarrow{\text{vacuum}} \quad \text{XeF}_4 + \text{AsF}_5^- \cdot \text{BrF}_5 \quad \xrightarrow{20°} \quad \text{XeF}_4 \uparrow \\
\text{XeF}_6 & \quad \text{in BrF}_5 \text{ soln.} \quad \quad \text{XeF}_5^+ [\text{AsF}_6^-] 
\end{align*}
\]

Samples purified in this way melt (117°) at the same temperature as those obtained by repeated fractional sublimation and give identical broad line \( ^{19}\text{F} \) n.m.r. spectra. It is best to make the crude \( \text{XeF}_4 \) in a nickel or Monel vessel after the method of Claassen et al., but the purification is best carried out in Kel-F vessels.

\textbf{Thermodynamic Features.} A thorough study of equilibrium conditions in the \( \text{Xe}/\text{F}_2 \) system, as a function of temperature, has well defined conditions for maximizing the yield of each of the binary fluorides. The tetrafluoride is the most difficult to obtain in high purity, as perusal of the equilibrium constant data in Table 3.3.1 and Figure 3.3.1 reveal. It will be appreciated that low temperatures and high fluorine pressures will favour \( \text{XeF}_6 \) formation.
Table 3.3.1
Equilibrium Constants for the Xe/F_2 System

<table>
<thead>
<tr>
<th>Temp°K</th>
<th>298.15</th>
<th>523.15</th>
<th>573.15</th>
<th>623.15</th>
<th>673.15</th>
<th>723.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_1(XeF_2)</td>
<td>1.23 x 10^{13}</td>
<td>8.80 x 10^4</td>
<td>1.02 x 10^4</td>
<td>1670</td>
<td>360</td>
<td>29.8</td>
</tr>
<tr>
<td>K_2(XeF_4)</td>
<td>1.37 x 10^{11}</td>
<td>1.43 x 10^3</td>
<td>1.55 x 10^2</td>
<td>27.2</td>
<td>4.86</td>
<td>0.50</td>
</tr>
<tr>
<td>K_3(XeF_6)</td>
<td>8.2 x 10^5</td>
<td>0.944</td>
<td>0.211</td>
<td>0.0558</td>
<td>0.0182</td>
<td>0.0033</td>
</tr>
</tbody>
</table>

K_1 = (XeF_2)/(Xe)(F_2); K_2 = (XeF_4)/(XeF_2)(F_2); K_3 = (XeF_6)/(XeF_4)(F_2)

Underlined values are calculated.

Figure 3.3.1
Table 3.3.2

and low F_2 pressures and high temperatures favour XeF_2 formation. The tetrafluoride cannot of course be made pure by the thermal method (see under preparation). The ΔH_f° (XeF_4(g)) = -57.6 kcal mol^{-1} obtained from calorimetry agrees with that from photoionization studies (Table 3.3.2) and is therefore the most reliable value. Kinetic studies, involving interaction with NO or NO_2, have shown that the first bond dissociation energy of XeF_4 is considerably greater than the second. This is similar to the XeF_2 case.

Values for D_1 = 48 and D_2 = 15 kcal mol^{-1} have been indicated. 85

The tetrafluoride, unlike the Xe(IV) oxide and hydroxide systems, is stable with respect to disproportionation. This is consistent with the enthalpies and entropies of formation:

\[
\begin{align*}
\Delta H_f° \text{ (kcal mol}^{-1}) &\quad -28.2 &\quad -57.6 &\quad -82 \\
\Delta S_f \text{ (cal deg}^{-1} \text{ mole}^{-1}) &\quad -26.5 &\quad -61 &\quad -96
\end{align*}
\]
Figure 3.3.1. Pressure and Temperature Influence on XeF₂, XeF₄, and XeF₆ Formation

(a) Fig. 1. Equilibrium pressures of xenon fluorides as a function of temperature. Initial conditions: 125 mmol Xe, 275 mmol F₂ per 1000 ml.

(b) Fig. 2. Equilibrium pressures of xenon fluorides as a function of temperature. Initial conditions: 125 mmol Xe, 1255 mmol F₂ per 1000 ml.

(permission being requested from H. Selig and Academic Press)
Table 3.3.2

Some Physical Properties of XeF₄

Colourless crystals, liquid and vapour

Triple-point 390.25°K (117.10°C) (a)

Thermodynamic features:

Vapour pressure (solid), (275 to 390.25°K), \[ \log p_{\text{mm}} = -\frac{3226.21}{T} - 0.4343 \frac{1}{T} \log T + 12.301738 \] (a)

390.15°K : 817.97 mm. (only point for liquid XeF₄)

(XeF₂ is more volatile than XeF₄)

\[ \Delta H_{\text{sublim}} = 14.8 \pm 0.2 \text{ kcal mole}^{-1} \] (a)‡

15.3 ± 0.2 kcal mole⁻¹ (b)

Heat Capacity (cal deg⁻¹ mole⁻¹ (at 298.15°K))

<table>
<thead>
<tr>
<th>State</th>
<th>Calorimetric</th>
<th>Molecular Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>vapour</td>
<td>21.5</td>
<td>75.7 ± 0.4</td>
</tr>
<tr>
<td>solid</td>
<td>28.33</td>
<td>75.6 ± 0.4</td>
</tr>
</tbody>
</table>

Entropy

vapour: \( 73.0 \pm 2 \) (calc. from molecular data) \( 75.7 \pm 0.4 \) (a)

solid: \( 35.0 \)

Heat of Formation

\[ T^\circ \text{K} \quad \Delta H_f(g) \]

<table>
<thead>
<tr>
<th>T^\circ K</th>
<th>\Delta H_f(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>393</td>
<td>-57.6 kcal/mole (e)</td>
</tr>
<tr>
<td>298</td>
<td>-48 (f)</td>
</tr>
<tr>
<td>423</td>
<td>-53 ± 5 (g)</td>
</tr>
<tr>
<td>298.15</td>
<td>-51.5* (d)</td>
</tr>
</tbody>
</table>

‡ Preferred value

* XeF₄ sample may not have been pure
Mean Thermochemical Bond Energy ($E_{\text{Xe-F}}$)

31.7 kcal mole$^{-1}$ (based on $\Delta H_f^\circ = -51.5$, $\Delta H_f^\circ (F, g) = 18.8$ kcal mole$^{-1}$)

Density (X-ray) 4.10 (h); 4.04 (i) (j) g cm$^{-3}$

Solubility

<table>
<thead>
<tr>
<th>t°C</th>
<th>mole XeF$_4$</th>
<th>mole HF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000g HF</td>
<td>mole XeF$_4$</td>
</tr>
<tr>
<td>20</td>
<td>0.18</td>
<td>278</td>
</tr>
<tr>
<td>27</td>
<td>0.26</td>
<td>192</td>
</tr>
<tr>
<td>40</td>
<td>0.44</td>
<td>114</td>
</tr>
<tr>
<td>60</td>
<td>0.73</td>
<td>68</td>
</tr>
</tbody>
</table>

Diamagnetic Susceptibility

\[ x = -50.6 \times 10^{-6} \text{ (c.g.s. units)} \]

\[ -52 \pm 3 \times 10^{-6} \text{ (77 to 293°K)} \]

\[ -53 \times 10^{-6} \text{ (calculated)} \]

Ultraviolet Absorption Spectrum of XeF$_4$ (g)

<table>
<thead>
<tr>
<th>Wave Length (Å)</th>
<th>Half-Width, cm$^{-1}$</th>
<th>Estd. Extinction Coefficient (mole$^{-1}$ cm$^{-2}$)</th>
<th>Est. Oscillator Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>2280</td>
<td></td>
<td>398</td>
<td>0.009</td>
</tr>
<tr>
<td>2580</td>
<td>7000</td>
<td>160</td>
<td>0.003</td>
</tr>
<tr>
<td>1840</td>
<td>10000</td>
<td>4.75 x 10$^3$</td>
<td>0.22</td>
</tr>
<tr>
<td>1325</td>
<td>11200</td>
<td>1.5 x 10$^4$</td>
<td>0.80</td>
</tr>
</tbody>
</table>
### IR, Raman of XeF$_4$ (g)

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Fundamentals</th>
<th>wavenumbers $$(\text{cm}^{-1})$$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{1g}$</td>
<td>$\nu_1$ R</td>
<td>543 vs</td>
</tr>
<tr>
<td>$a_{2u}$</td>
<td>$\nu_2$ IR</td>
<td>291 s</td>
</tr>
<tr>
<td>$b_{1g}$</td>
<td>$\nu_3$ R</td>
<td>235 w</td>
</tr>
<tr>
<td>$b_{2g}$</td>
<td>$\nu_5$ R</td>
<td>502 vs</td>
</tr>
<tr>
<td>$b_{1u}$</td>
<td>$\nu_4$ inactive</td>
<td>221</td>
</tr>
<tr>
<td>$e_u$</td>
<td>$\nu_6$ IR</td>
<td>586 vs</td>
</tr>
<tr>
<td>$e_u$</td>
<td>$\nu_7$ IR</td>
<td>182 (calculated)</td>
</tr>
</tbody>
</table>

### Force Constants

<table>
<thead>
<tr>
<th>k</th>
<th>3.00 mdyn Å$^{-1}$ (q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{rr}$</td>
<td>0.12</td>
</tr>
<tr>
<td>$k_{rr}'$</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Crystal Structure

X-ray Diffraction (j)

monoclinic

P2_1/n

a = 5.050 ± 0.003 Å
b = 5.922 ± 0.003 Å
c = 5.771 ± 0.003 Å
β = 99.6 ± 0.1°

Z = 2

d = 4.04 g ml^-1

Xe-F = 1.93 Å

F-Xe-F 89.7° (σ = 0.9°)

Neutron-Diffraction (i)(a)(h)

Xe-F 1.953 ± 0.002 Å

F-Xe-F 90.0 ± 0.1°

See Figure 3.3.2

F N.M.R. Data (t)

Chemical Shift:

_{o_F} (p.p.m.; _o_{F_2} = 0)

Solid 482, 448

Liquid 445

HF Soln. 456, 452, 450

Coupling Constant:

J (Hz)

3836

3860, 3864, 3860
Broad Line N.M.R. Findings:

\[ \text{XeF}_4, \text{ microcrystalline solid} \]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{\text{ABS}} ) ** (p.p.m.)</td>
<td>218 ± 5</td>
</tr>
<tr>
<td>( \sigma_x )</td>
<td>0 ± 8</td>
</tr>
<tr>
<td>( \sigma_y )</td>
<td>261 ± 25 or 394 ± 25 ( \hat{z} )</td>
</tr>
<tr>
<td>( \sigma_z )</td>
<td>394 ± 25 or 261 ± 25</td>
</tr>
</tbody>
</table>

** The absolute scale values for chemical shifts are referred to the bare \( ^{19}\text{F} \) nucleus (\( v \)).

\( \hat{z} \) \( \sigma_x \) is the out of plane shielding (\( \text{D}_{4h} \text{XeF}_4 \)), \( \sigma_z \) is the shielding \( \parallel \) Xe-F bond, and \( \sigma_y \) is the in plane shielding perpendicular to the Xe-F bond.

\( \hat{z} \) If \( \sigma_z = 394 \) p.p.m. then \( \sigma_y = 261 \) p.p.m. or vice versa.

Mass Spectra (g)

<table>
<thead>
<tr>
<th>Ion</th>
<th>\text{XeF}_4^+</th>
<th>\text{XeF}_3^+</th>
<th>\text{XeF}_2^+</th>
<th>\text{XeF}^+</th>
<th>\text{Xe}^+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abundance</td>
<td>7</td>
<td>100</td>
<td>60</td>
<td>67</td>
<td>~800</td>
</tr>
</tbody>
</table>

Appearance Pot. (eV) 12.9(0.1) 12.1(0.1) 14.9(0.1) 13.3(0.1) 12.4(0.1)

Photoionization (x) spectra give \( \Delta H^o (\text{XeF}_4(g) \rightarrow \text{XeF}_3^+ (g) + F^- (g)) = 9.66 \text{ eV} \)

Electron Diffraction (y)

Radial distribution maxima: 1.94, 2.77 and 3.88 Å. Xe-F (\( \text{D}_{4h} \)) = 1.94 ± 0.01 Å.

Mossbauer Spectrum: See Table 3.4.1.
Table 3.3.2
References

(a) F. Schreiner, G. N. McDonald and C. L. Chernick, J. Phys. Chem. 72 (1968) 1162.
(e) See reference (c) p. 144; also supported by work of J. Berkowitz, ref. (x).
(f) S. R. Gunn and S. M. Williamson, Science 140 (1963) 177; see reference (c) p. 133.
(g) H. J. Svec and G. D. Flesch, Science 142 (1963) 954.
(i) S. Siegel and E. Gebert, J. Amer. Chem. Soc. 85 (1963) 240.
(k) See reference (c) p. 275.
(r) See reference (c) p. 287.
(t) R. Hoppe, Fortschr. Chem. Forsch. 2 (1965) 335.

(x) J. Berkowitz, Argonne National Laboratory, personal communication to N. Bartlett

(y) See reference (c) p. 238.
Figure 3.3.2 (i)

(i) The view of the XeF₄ crystal structure (a) along the b axis. The numbers give the elevation of the atoms in units of \( \frac{b}{100} \) above the plane of projection.

(a) See reference 17 b.
The Molecular Structure of XeF$_4$ as determined by X-ray diffraction$^\text{(a)}$. 

(a) See reference 17 b.
Thus, for the disproportionation: $2\text{XeF}_4(\text{g}) \rightarrow \text{XeF}_2(\text{g}) + \text{XeF}_6(\text{g})'$

$\Delta H^\circ = +5 \text{ kcal mole}^{-1}$ and $\Delta S \approx 0 \text{ cal deg}^{-1} \text{ mole}^{-1}$ and for $3\text{XeF}_4(\text{g}) \rightarrow \text{Xe}(\text{g}) + 2\text{XeF}_6$, $\Delta H^\circ = +9 \text{ kcal mole}^{-1}$ and $\Delta S \approx -9 \text{ cal deg}^{-1} \text{ mole}^{-1}$.

The enthalpy of vaporization of $\text{XeF}_4$, as in the case of $\text{XeF}_2$, is indicative of strong electrostatic interactions between $\text{XeF}_4$ molecules.

**Kinetic features.** Since $\text{XeF}_2$ is an intermediate in the formation of $\text{XeF}_4$, the kinetics of formation of the former (see section 3.2.1) are relevant to the latter. From a study\textsuperscript{178} of the thermally excited $\text{F}_2 + \text{Xe}$ reactions, with $\text{F}_2:\text{Xe}$ ratios of 16 or more and total pressures of 10 to 20 mm Hg, in the temperature range 190-250°, the $\text{XeF}_2$ formation was found to be zero order in $\text{F}_2$ and first order in $\text{Xe}$ (the reverse of the findings for the conditions which favour exclusive $\text{XeF}_2$ formation—see 3.2.1) and the $\text{XeF}_4$ formation, zero order in $\text{F}_2$ and first order in $\text{XeF}_2$. The thermal reactions were shown to be heterogeneous and a mechanism involving absorption and dissociation of $\text{F}_2$ on the nickel fluoride surface of the container has been proposed. The activation energy for $\text{F}_2 + \text{XeF}_2 \rightarrow \text{XeF}_4$ was deduced to be $\sim 13 \text{ kcal mole}^{-1}$.

**Structural features.** Vibrational spectroscopic\textsuperscript{179, 180, 181} and electron diffraction data\textsuperscript{182} have established the $\text{XeF}_4(\text{g})$ molecule to be square planar ($D_{4h}$), the latter study giving $\text{Xe}-\text{F}$ to be $1.94 \pm 0.01\text{Å}$. The crystallographic findings\textsuperscript{17} show that the size and shape of the isolated molecule is not significantly different in the crystal (see Figure 3.3.2). A neutron diffraction study\textsuperscript{17a} has shown the $\text{Xe}-\text{F}$ bond length in the solid to be $1.953 (0.004)\text{Å}$, the $\angle \text{FXeF} = 90.0 (0.02)^\circ$, and the amplitudes of vibration normal to the bond directions to be greater than in the bond direction. Thermal motion has also been indicated by the broad-line $^{19}\text{F}$ n.m.r. studies.\textsuperscript{177}
Bond Polarity and Bond Type. Nuclear magnetic resonance, Mössbauer and electron spectroscopy all indicate considerable charge migration Xe→F in the Xe-F bond.

The $^{19}$F chemical shift and $^{129}$Xe-$^{19}$F coupling constant (see Table 3.3.2) do not differ substantially from those obtained for the F-X bonds in the other xenon fluorides and the related fluorides BrF$_3$, IF$_5$ and TeF$_6$. The chemical shifts have been interpreted by Karplus and his coworkers in terms of a F ligand charge of -0.50. This evaluation assumed the bonding to involve primarily the F$_2$R and Xe$_5$R orbitals. On the other hand, Gutowsky and his coworkers on the basis of a localized bond description, using spd hybrid xenon orbitals, have concluded that the F-ligand charge is 0.49. A broad-line $^{19}$F n.m.r. study has shown that prior, similar, studies are erroneous, probably as a consequence of XeF$_2$ contamination. Experimental shielding values (see Table 3.3.2) are in quantitative and even, in some cases, qualitative disagreement with theoretical values obtained using a semi-empirical localized-orbital bonding scheme. It seems that more complete theoretical treatments, including delocalized orbitals, will be necessary to account for the observations.

The Mössbauer spectrum of XeF$_4$, which is discussed further in section 3.3.2, has been interpreted on the assumption of bonding involving Xe 5p orbitals. A F-ligand charge of -0.75 is assigned. This seems rather large and it may well be that the fault derives from the over-simplified bonding model. The chemical shift observed in the X-ray photoionization spectrum has been accounted for on the basis of a coulombic model, which assumes the central atom and ligands to be charged spheres. A F-ligand charge in the range -0.3 to -0.5 is compatible with the findings. (See section 3.4.2 and Table 3.4.4).
The most popular bonding descriptions have followed the lead of Pimentel and Rundle and generally emphasize the importance of the Xe 5p and F2p orbitals. Allen, Coulson and Jortner and Rice have reviewed the bonding models. Several authors have given energy level diagrams to account for the observed spectroscopic features. There are persistent claims also for the involvement of outer orbitals, particularly Xe 5d, in the bonding (See sections 1.3.1-4 and 3.2.2).

Chemical Properties. A number of the earlier studies involving XeF₄ are suspect because of the likelihood that the samples were contaminated with XeF₂ or XeF₆ or both (see under 'preparation' and 'thermodynamic features'). The tetrafluoride can be kept in thoroughly dried glass or quartz and can be stored indefinitely in Kel-F nickel or Monel containers.

The tetrafluoride undergoes instantaneous hydrolysis, with the formation of a transitory yellow species. The latter has been trapped at -80°C and, on the basis of infrared and e.s.r. examination, formulated as XeOF₂ (see section 3.3.3). The ultimate products of hydrolysis are Xe, O₂, HF and XeO₃ (see section 3.4.4). If the hydrolysis is carried out in strong base, perxenates are formed (see section 3.5.5); and if the hydrolysis occurs in aqueous KI, very little free O₂ is liberated, XeF₄ + 4I⁻ → Xe + 4F⁺ + 2I₂.

As with XeF₂, the low bond energy of XeF₄ causes it to be a strong oxidative fluorinator and it should compare with BrF₃ in oxidative capability. It seems, however, like XeF₂, to be kinetically rather inert. Solutions of XeF₄ in anhydrous HF (with which the fluoride does not undergo F-ligand exchange) are strongly oxidizing and fluorinate Pt metal to PtF₄. The neat compound oxidizes SF₄ to SF₆, oxidizes NO to ONF, but does not interact, at a measurable rate, with NO₂. The interaction of XeF₄ with H₂ does not
proceed at room temperature in the absence of a catalyst, but a slow
reaction occurs at 70° and this proceeds rapidly at 130°. The
tetrafluoride, in contrast with XeF₂, fluorinates perfluoropropane at
room temperature but gives similar products to XeF₂ in interaction
with the hydro-olefins (see section 3.2.2).

Attempts to prepare other Xe(IV) compounds by metathetical reactions
have met with little success. The interaction of XeF₄ with BCl₃ at -78° yields xenon and chlorine quantitatively:

\[ 3\text{XeF}_4 + 4\text{BCl}_3 \rightarrow \text{4BF}_4 + 3\text{Xe} + 6\text{Cl}_2 \]

There are indications, however, that (as in the XeF₂ case), the F-ligands
may be substituted by other highly electronegative ligands, since XeF₄
dissolved in trifluoroacetic anhydride is reported to yield a crystalline
compound considered to be Xe(OCOCF₃)₄. Clearly, ligands such as -O-C₁₀₃,
OS₂F and OTeF₅ are possible but there is no certainty that the compounds
will be stable to disproportionation or spontaneous reduction.

The fluoride ion donor ability of XeF₄ has been shown to be less
than that of XeF₂ or XeF₆ and this forms the basis of a chemical purification
for XeF₄. These findings are in harmony with the enthalpies of ionization
derived from photoionization studies by Berkowitz:

\[
\begin{align*}
\text{XeF}_2(\text{g}) & \rightarrow \text{XeF}^+ \text{(g)} + \text{F}^- \quad \Delta H^o(\text{eV}) = 9.45 \\
\text{XeF}_4(\text{g}) & \rightarrow \text{XeF}_3^+(\text{g}) + \text{F}^- \quad \Delta H^o(\text{eV}) = 9.66 \\
\text{XeF}_6(\text{g}) & \rightarrow \text{XeF}_5^+(\text{g}) + \text{F}^- \quad \Delta H^o(\text{eV}) = 9.24
\end{align*}
\]

The best fluoride ion acceptor (SbF₅) forms a crystalline solid (or solids) with XeF₄, probably containing XeF₃⁺ and there is also evidence for weaker fluoride ion acceptors (PF₅, AsF₅) forming compounds in BrF₃ solution. Reports that XeF₄ interacts with SbF₅ or TaF₅ to form XeF₂.
derivatives, \( \text{XeF}_2 \cdot \text{IF}_5 \) on dissolution in IF\(_5\), are certainly erroneous. It is probable that the XeF\(_4\) used in those studies was grossly contaminated with XeF\(_2\).

**Analysis of XeF\(_4\).** The solid is most conveniently tested for purity by a melting point determination (117.1\(^\circ\)) but its Raman spectrum is also highly characteristic and readily reveals the presence of XeF\(_2\) or XeF\(_6\) (see Table 3.3.2). The infrared spectrum readily characterizes the vapour.

Samples of XeF\(_4\) have been analyzed by reduction with hydrogen at 130\(^\circ\): \(^{192}\)

\[
\text{XeF}_4 + 2\text{H}_2 \rightarrow \text{Xe} + 4\text{HF}
\]

A more convenient analytical technique involves reduction with mercury:

\[
\text{XeF}_4 + 4\text{Hg} \rightarrow \text{Xe} + 2\text{Hg}_2\text{F}_2 \quad (\text{or} \quad 2\text{HgF}_2)
\]

The xenon may be measured tensimetrically or gravimetrically and the fluorine content is obtained from the weight of mercury fluoride formed. As has been remarked above, it has also been claimed that XeF\(_4\) may be analyzed iodimetrically, by dissolution in aqueous KI.

### 3.3.2 Xenon Tetrachloride

Efforts to prepare macroscopic quantities of XeCl\(_4\) and XeBr\(_4\) from XeF\(_4\) by metathetical reactions have failed, but the former has been detected \(^{158},^{199}\) by Mössbauer Spectroscopy as a product of the \( \beta \) decay of its \( \text{I}^{129} \) analogues: \( \text{I}^{129} \text{Cl}_4 \rightarrow \beta \rightarrow \text{XeCl} \). There is no evidence for the existence of XeCl\(_4\). The conditions for the observation of this species are essentially the same as for the dihalides described in section 3.2.3.
The chemical shift observed for XeCl₄ is shown in Figure 1.4.2 relative to shifts for the other xenon compounds. The Mössbauer data for the xenon halides are compared in Table 3.3.3. The quantities in Table 3.3.3

Mössbauer Data for the Xenon Halides

<table>
<thead>
<tr>
<th>Halide</th>
<th>Splitting (mm/sec.)</th>
<th>$e^2_q Q_{exc}$ (MHz)</th>
<th>5p Electron transfer</th>
<th>Electron transfer per bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>XeF₄</td>
<td>41.04 ± 0.07</td>
<td>2620</td>
<td>3.00</td>
<td>0.75</td>
</tr>
<tr>
<td>XeF₂</td>
<td>39.0 ± 0.1</td>
<td>2490</td>
<td>1.43</td>
<td>0.72</td>
</tr>
<tr>
<td>XeCl₄</td>
<td>25.6 ± 0.1</td>
<td>1640</td>
<td>1.88</td>
<td>0.47</td>
</tr>
<tr>
<td>XeCl₂</td>
<td>28.2 ± 0.1</td>
<td>1800</td>
<td>1.03</td>
<td>0.52</td>
</tr>
<tr>
<td>XeBr₂</td>
<td>22.2 ± 0.4</td>
<td>1415</td>
<td>0.81</td>
<td>0.41</td>
</tr>
</tbody>
</table>

the table have the same meaning and were derived in the same way as those discussed in section 3.2.3. Again, the bonding model assumes that the only Xenon orbitals participating in the bonding are the Xe 5p orbitals, hence the indicated bond polarities are probably not quantitatively reliable; the trends are probably correct.

3.3.3 Xenon Oxide Difluoride

Of the several claims for XeOF₂ in the literature, only one is supported with experimental evidence. The compound identified as XeOF₂ is the bright yellow solid formed by hydrolizing XeF₄ at -80°. This product gives neither an e.s.r. spectrum, nor an infrared D shift ($D_2O$ in place of $H_2O$), and contains only one atom of O. The observed infrared absorption bands have been assigned on the basis of $C_{2v}$ symmetry: 747 ($\nu_1$, $A_1$, Xe-O str.), 520 ($\nu_2$, $A_1$, Xe-F sym. str.) and 490 cm⁻¹.
(ν₄, B₂, Xe-F asym. str.). It is argued that these data are compatible with a structure

\[ \begin{array}{c}
\text{F} \quad \text{Xe} \quad \text{F} \\
\end{array} \]

with \( \angle \text{F-Xe-F} \) of about 90°, thus resembling ClF₃ and BrF₃ (see section 1.4.4). The Xe-O stretching force constant is 4.7 mdyne/Å on the basis of this model and assignments. This appears a little low, even allowing for a lower value with the lower oxidation state, since the force constant for XeO in XeOF₄ is 7.08 mdyne/Å (see section 3.4.2).

### 3.3.4 Xenon(IV) Oxide

Although XeO₂ has been postulated as an intermediate in the hydrolysis of XeF₄ (see section 3.4.4) there is no firm evidence for its existence.

### 3.3.5 F₄₋ₓ Xe(OR)ₓ Compounds

Apart from the report of the synthesis of Xe(OOCCF₃)₄ (see section 3.3.1), no other compounds in this class have yet been reported.

### 3.3.6 XeF₄ as a Fluoride Ion Donor and Acceptor

There is no evidence that XeF₄ can accept fluoride ion (or any other ion) and this provides for the ready removal of XeF₆ contaminant by absorption of the latter with alkali fluoride.

Although XeF₄ is a poorer F⁻ donor than either XeF₂ or XeF₆ (see section 3.3.1) it does form compounds with the best F⁻ acceptor, SbF₅. These may contain the XeF₃⁺ ion, but there is presently no evidence to support this. (See also sections 3.4.1 and 3.4.5)
3.3.7 Molecular Adducts of XeF₄

Only one molecular adduct of XeF₄ has been established, XeF₂, XeF₄. The crystal structure of this adduct shows it to be an ordered arrangement, in which, as may be seen from Table 3.3.4, each molecule possesses essentially the same size and shape as in the component solids. The bonding is presumably a consequence of the coulombic interactions.

Table 3.3.4

Intramolecular Distances in XeF₂, XeF₄ and their Components

<table>
<thead>
<tr>
<th></th>
<th>XeF₂</th>
<th>XeF₄(a)</th>
<th>XeF₄(b)</th>
<th>XeF₄(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe-F (Å) in XeF₂</td>
<td>(2) 2.010 (0.012)</td>
<td>(2) 2.00 (0.02)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe-F (Å) in XeF₄</td>
<td>(2) 1.972 (0.014)</td>
<td>(2) 1.945 (0.014)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-Xe-F in XeF₄</td>
<td>(2) 89.1° (0.8)</td>
<td>90.0 (0.02)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


XeF₂, XeF₄ Intermolecular Contacts

Xe(II) -- -- F-Xe(IV) distances (2) 3.28, (2) 3.42, (8) in range 3.61-3.69Å
Xe(IV) -- -- F-Xe(II) (6) in range 3.35-3.37Å

Compare with data in Figures 3.2.2 and Figures 3.3.1.

between positive charges on the Xe atoms and negative charges on the fluoride ligands of the surrounding molecules. The compound resembles other XeF₂ adducts (see section 3.2.8).
3.4 Xenon(VI) Compounds

The chemistry of Xe(VI) is limited to the fluoride XeF₆, the oxyfluorides XeOF₄ and XeO₂F₂, the oxide XeO₃, and complexes of these compounds. The trioxide is thermodynamically unstable with respect to the elements in their standard states and there are indications that this is also so for XeO₂F₂. The oxide is a powerful explosive. The oxyfluoride XeOF₄ and the fluoride are thermodynamically stable at ambient temperatures. All of the compounds, at least potentially, are strong oxidizers.

3.4.1. Xenon Hexafluoride

Preparation. The preparation of XeF₆ was first described in four independent and almost simultaneous reports. All preparations are carried out in nickel or Monel vessels and, in general, high F₂ pressures and lower temperatures favour XeF₆ formation. A 95% conversion to XeF₆ is obtained with F₂/Xe ratios of 20:1 at 50 atm. pressure (see section 3.3.1 and Table 3.3.1). The hexafluoride has also been reported as a product of the electric discharge of a 3:1 F₂:Xe mixture, the product being trapped at -78°. Furthermore, O₂F₂ is reported to oxidize XeF₄ to XeF₆ between -133 and -78°.

Laboratory Preparation. In order to obtain pure XeF₆ it is best to form the NaF·XeF₆ adduct, by mixing with NaF, the other xenon fluorides (XeF₂, XeF₄ and XeOF₄) likely to be present, being unable to form stable complexes with the NaF.

The apparatus and experimental procedures for XeF₆ synthesis are essentially as given under XeF₂ and XeF₄ but since higher fluorine pressures are desirable, the nickel or Monel vessels used to contain the hot mixtures should be strong enough to safely withstand 400 atmospheres
pressure of $F_2$. A $Xe/F_2$ ratio of 1:20 is satisfactory. The mixture is heated to $300^\circ$ for 16 hours. Excess fluorine is removed under vacuum at $-192^\circ$ and the crude $XeF_6$ condensed onto NaF (previously fluorinated and in appreciable excess). This mixture is warmed to $50^\circ$ for 2 hours then left at room temperature overnight. This serves to complex all of the $XeF_6$ as a NaF.$XeF_6$ adduct. Uncombined impurities ($XeOF_4$, $XeF_2$, $XeF_4$) are removed by pumping on the NaF mixture at temperatures up to $50^\circ$, to constant weight (an hour or so should suffice). The $XeF_6$ is then retrieved by heating to $125^\circ$ under vacuum, when the gas is rapidly evolved and may be collected in cold traps (nickel, Monel or Kel-F at $-196^\circ$).

The usual care should be taken to guard against $XeO_3$ formation (EXPLOSIVE) and it should always be assumed that the oxide may have formed in apparatus used for $XeF_6$ synthesis and handling.

Table 3.4.1

| Thermodynamic features. | Equilibrium studies$^{22}$ of the $Xe/F_2$ system have defined the optimum conditions for $XeF_6$ formation. The equilibrium constant data from these studies are given in Table 3.3.1 and the thermodynamic data and other physical data for $XeF_6$ are given in Table 3.4.1. It is of interest that the experimental equilibrium constant data suggest an entropy, $S^\circ$, for $XeF_6(g)$ which requires a molecular symmetry lower than $O_h$ (see below). Heat capacity and vapour pressure measurements$^{206}$ have provided accurate physical constants and also indicated structural changes in solid $XeF_6$ at 253.8 and 291.8$^\circ$K. The interpretation of these regions of anomalous heat capacity, in terms of changes between previously identified$^{207}$ crystalline modifications of $XeF_6$, has been questioned.$^{208}$ The high entropy of vapourization of the liquid$^{206}$ (32.74 e.v.) is |
Table 3.4.1

Some Physical Properties of XeF₆

The solid is colourless below m.p., the liquid and vapour are yellow-green. (a)(b)
m.p. (°C)(c): 49.48; phase changes (°C): 18.65, -19.35
b.p. (°C)(c): 75.57

Thermodynamic Features

Vapour density (b): "Molecular weight" (25.6°), 249.6; (24.8°), 245.5, 248 (t)
  Theor. XeF₆, 245.3.
Vapour pressure (mm)(b): 2.7 (0.04°); 23.43 (22.67°)
Vapour pressure equations: \( \log P_{\text{mm}} = -X / T + Y \)

Solid: Temp. Range (°K)  X  Y
  273.19 → 295.82(b)  3400.12  12.86125
  254  → 291.8 (c)  3313.5  12.5923
  291.8 → 322.38(c)  3093  11.8397

Liquid: (322.38 → 350°)(c)  \( \log P_{\text{mm}} = -6170.88 \cdot T - 23.67815 \log T + 80.77778 \)

Second virial coefficient, \( B \), \( (PV = RT + EP) \)(c) = -955 cm³ mole⁻¹

\( \Delta H \) sublim (kcal mole⁻¹): 15.6 (b); 13.2 (d)  \( \Delta H \) fus (kcal mole⁻¹): 1.37 (c)

\( \Delta S \) vap (cal deg⁻¹ mole⁻¹): 32.74

\( C_p \), solid (at 298.15 °K), (cal deg⁻¹ mole⁻¹)(c): 41.03

\( \Delta H_p \) (g) (kcal mole⁻¹)(298.15°K): 70.4(b); 82.9(e); 81(f)

\( \Delta S_p \) (g) (cal deg⁻¹ mole⁻¹): -97(b)

\( S^\circ \) (cal deg⁻¹ mole⁻¹)(c): Solid(298.15°K), 50.33; liquid (335°K), 61.10;
  Gas (335°K), 96.27; also (b) from Xe/F₂ equilibria, gas
  (298.15°K), 88.84 or 91.87

\( \Delta H^\circ \) (XeF₆(g) → XeF₅(g) + F⁻(g))(f): 9.24 ev (213 kcal mole⁻¹)
Solubility

<table>
<thead>
<tr>
<th>Anhydrous HF: (g)</th>
<th>Moles XeF₆ / Mole XeF₆</th>
<th>Moles HF / 1000 g HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>t(°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.8</td>
<td>3.16</td>
<td>15.8</td>
</tr>
<tr>
<td>21.7</td>
<td>6.06</td>
<td>8.25</td>
</tr>
<tr>
<td>28.5</td>
<td>11.2</td>
<td>4.46</td>
</tr>
<tr>
<td>30.25</td>
<td>19.45</td>
<td>2.57</td>
</tr>
</tbody>
</table>

Molar conductivity (g) of HF solutions (ohm⁻¹ cm²) in range 60-147 ohm⁻¹ cm² (0.75 - 0.02 mole l⁻¹)

XeF₆ gives yellow-green solutions in WF₆, IF₅ and BrF₅.

Dielectric Constant (i): (55°C), 4.10 ± 0.05

Dipole Moment (j): <0.03D

Magnetic Susceptibility: (k) χ_M = -(44.5 ± 0.5) x 10⁻⁶ cm³ mole⁻¹

Specific Conductance (i): (50°C): 1.45 ± 0.05 x 10⁻¹⁶ ohm⁻¹ cm⁻²

UV and Visible Absorption Spectrum (l): 3300 Å, strong, half-width 580 Å

First Ionization Potential: I(XeF₆(g))(f) (1016 Å) = 281.5 kcal mole⁻¹

Infrared and Raman Spectrum: non-octahedral (m)(n) monomer.

Solid (unknown crystalline form): (m):

R(cm⁻¹): 204?, 300 w, 404 vw, 583 s, 636 sh, 656 vs

Liquid: (m):

R(cm⁻¹) (54°C): 205?, 295 w, 370 vw, 403 vw, 506 vw, 574 sh, 585s (P), 637 sh, 654 vs (P)

(92°C): 205?, 295 w, 370 vw, 403 vw, 506 ms, 577 s, 616 sh, 650 vs.

Vapour:

IR (cm⁻¹)(n): 400 ms, 520 m, 563 mw, 616 s, 1036 vv, 1075w, 1118 vv, 1238 w

R (cm⁻¹) (94°C)(n): 520 s, 609 ms (P), also 206?
Electron Diffraction: Non octahedral molecular symmetry \((o)(p)(q)\)
Xe-F bond length: \(1.890\AA\)\(^{(o)}\)

Crystallographic Data:

Unit Cells: Cubic \((r)\) (stable between 103 and 301°K)\(^{(s)}\)

- \(a\_o (-80°C) = 25.06 (0.05) \AA\)
- Space group \(Fm\bar{3}c; z = \frac{14}{4} \) \(\text{XeF}_6\)
- \(d\text{ X-ray (g cm}^{-3}\) (-80°C) = 3.73 (0.02)

(See Figure 3.4.1)

Density \((c)\)

<table>
<thead>
<tr>
<th>(T^\circ K)</th>
<th>77.22</th>
<th>194.42</th>
<th>242.97</th>
<th>293.11</th>
<th>297.55</th>
<th>328.34</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d (g \text{ cm}^{-3}))</td>
<td>3.848(0.006)</td>
<td>3.751(0.007)</td>
<td>3.668(0.014)</td>
<td>3.465(0.013)</td>
<td>3.411(0.015)</td>
<td>3.173(0.03)</td>
</tr>
</tbody>
</table>
Table 3.4.1
References


(d) See reference (a) p. 39.

(e) See reference (a) p. 144.

(f) J. Berkowitz, Argonne National Laboratory, personal communication.

(g) See reference (a) p. 275.


(k) B. Volavsek, Mh. f Chemie 21 (1966) 1531.


indicative of polymerization in the liquid state. Two independent
vapour density measurements\textsuperscript{22, 209} show the hexafluoride to be
predominantly monomeric in the gas phase. The hexafluoride is much
more volatile than either XeF\textsubscript{2} or XeF\textsubscript{4}, although much less volatile
than other hexafluorides.

There is considerable disparity between the enthalpy of formation
from the equilibrium studies (-70.4 kcal mole\textsuperscript{-1}) and the value (-82.9
cal kcal mole\textsuperscript{-1}) from the heat of combustion of XeF\textsubscript{6} (XeF\textsubscript{6} + 3H\textsubscript{2} → Xe + 6HF).
Since the latter value is also in agreement with the value from photo-
ionization studies\textsuperscript{195}, it is preferred. This infers a mean thermochemical
bond energy for XeF\textsubscript{6} of 32 - 33 kcal mole\textsuperscript{-1}, which is, within the
experimental uncertainty, the same as the values derived for XeF\textsubscript{2} and
XeF\textsubscript{4}.

Although equilibrium studies\textsuperscript{22} showed no evidence of XeF\textsubscript{8} formation
it is of interest that the rate of exchange of \textsuperscript{18}F\textsubscript{2} with XeF\textsubscript{6} at 150°
was found to be a linear function of \textsuperscript{18}F\textsubscript{2} concentration, indicating
an associative mechanism.\textsuperscript{210}

Crystal and Molecular Structure. Although both a cubic and monoclinic
form of crystalline XeF\textsubscript{6} have been identified\textsuperscript{207} only the cubic structure
has been described in detail.\textsuperscript{211} (See Figure 3.4.1.) This structure
indicates that XeF\textsubscript{6} is effectively XeF\textsubscript{5}F\textsuperscript{+}, in the cubic phase. The

existence of both tetramers and hexamers in
the same unit cell indicates that the way in which the XeF\textsubscript{5} ion is
'bridged' by the F\textsuperscript{-} ions is not of prime importance. It should be noted,
however, that the 'bridging' F\textsuperscript{-} ions are not close to the four-fold axis
of the XeF\textsubscript{5} groups. This is consistent with the location of the non-
Figure 3.4.1

The Structural Units of XeF$_6$(cubic)\(^{(a)}\)

The cubic unit cell (space group Fm3c), \(a_0(-80^\circ C) = 25.06 \pm 0.05\AA\) contains 144 'XeF$_6$ units.' Ions of XeF$_5^+$ and F$^-$ are associated in tetrameric and hexameric units ((a) and (b) in the figure). There are 24 tetrarmers and 8 hexamers in the unit cell. Both right and left handed conformations of both tetraramers and hexamers occur.

The XeF$_5^+$ ions have similar size and shape in the tetraramers and hexamers. The F$^-$ ions 'bridge' the XeF$_5^+$ ions in each cluster type. The F$_5$Xe$^+---F^----XeF$_5^+$ bridges are unsymmetrical in the tetraramer but symmetrical in the hexamer, the chemically important bond lengths and angles are:

<table>
<thead>
<tr>
<th>Bond Distance (Å)</th>
<th>Hexamer</th>
<th>Tetramer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe-F$_{ap}$ (7.1)</td>
<td>1.76(3)</td>
<td>1.84(4)</td>
</tr>
<tr>
<td>Xe-F$_{bas}$ (8.3)</td>
<td>1.92(2)</td>
<td>1.86(3)</td>
</tr>
<tr>
<td>F$<em>{ap}$-F$</em>{bas}$</td>
<td>2.33(3)</td>
<td>2.29(6)</td>
</tr>
<tr>
<td>F$<em>{bas}$-F$</em>{bas}$</td>
<td>2.63(3)</td>
<td>2.54(13)</td>
</tr>
<tr>
<td>(\angle F_{ap}$-Xe-F$_{bas}$</td>
<td>80.0(0.6)$^\circ$</td>
<td>77.2(1.8)$^\circ$av.</td>
</tr>
<tr>
<td>(\angle F_{bas}$-Xe-F$_{bas}$</td>
<td>88.3(0.2)$^\circ$</td>
<td>87.2(4.5)$^\circ$av.</td>
</tr>
</tbody>
</table>

F$_5$Xe$^+---F^- 'bridge' distance (Å) | 2.56(2) | \{2.23(3) \ 2.60(3)\}

F$_5$Xe$^+---F^----XeF$_5^+$ 'bridge angle 118.8(0.3)$^\circ$ | 120.7(1.2)$^\circ$

The F$^-$ bridges 2XeF$_5^+$ groups in the tetraramer and 3 in the hexamer.

bonding (Xe(VI) valence electron pair on the four fold axis, trans to the unique Xe-F bond of the XeF$_5^+$ ion. Thus, the XeF$_5^+$ would appear to be pseudo octahedral. Note the similarity of the structure of (XeF$_6$)$_4^-$ to the structure of [XeF$_5^+$][AsF$_6$]$^{-}$ shown in Figure 3.4.5 (discussed in section 3.4.6). The XeF$_5^+$ unit in (XeF$_6$)$_x^-$ is almost indistinguishable from that observed in the XeF$_5^+$ salts.

From the limited structural information available on the monoclinic phase$^{207}$ it is probable that tetrameric units rather like those occurring in the cubic phase form the structural unit.

The entropy of vapourization indicates that the liquid is polymeric but the colour is similar to that of the vapour. It is possible that an appreciable proportion of the liquid is monomeric. The polymeric nature of the liquid is again attributable to F$^-$ bridging between XeF$_5^+$ units. The solutions of XeF$_6$ in HF$^{212}$ and WF$_6$$^{213}$ show a dependence of $^{19}$F n.m.r. chemical shift upon the temperature. These observations are simply explained by polymerization-depolymerization equilibria. The high conductivity of solutions in HF$^{214}$ suggests the ionization:

$$\text{XeF}_6(\text{soln.}) + \text{HF} \rightarrow \text{XeF}_5^+(\text{soln.}) + \text{HF}_2^- (\text{soln.})$$

Molecular XeF$_6$. The molecular structure of xenon hexafluoride in the gas phase has been the subject of much work and many papers. We still do not have a clear view of the structural features of isolated XeF$_6$ molecules. It is certain that the vapour at room temperature is not a collection of octahedral molecules. It is also evident that a large proportion of the molecules must be of non-octahedral symmetry. Electron diffraction data$^{215}$ have established that XeF$_6(g)$ has a very different
symmetry from that of TeF₆ and the data²¹⁶, ²¹⁷ have been interpreted²¹⁸, ²¹⁹ on the basis of non-centric molecular symmetry. Bartell et al ²¹⁷, ²¹⁸ concluded that the instantaneous molecular configurations encountered by incident electrons are predominantly in the broad vicinity of C₃ᵥ structures conveniently described as distorted octahedra, in which the Xe(VI) non bonding valence electron pair avoids the bonding pairs. Burbank et al ²¹⁹ found that a mixture of geometries of C₂ᵥ, C₃ᵥ and C₃ᵥ symmetry, each different symmetry having equal weight in the mixture, accounted for the observed electron diffraction data, within the limits of the experimental error. Bartell derives²¹⁷ Xe-F to be 1.890 ± 0.005 Å. Facile molecule inversion or intramolecular rearrangement is certainly compatible with the findings. Evidently, the major gas species are (or is) appreciably distorted, but Goodman ²²⁰ has persistently maintained, from theoretical considerations, that an O₅h ground state for XeF₆ would be separated by only very small energy from a triplet state of D₃d symmetry. Goodman predicts this triplet because his O₅h structure has 2 electrons populating an antibonding a₁g orbital (see Figure 3.4.2). The excitation of one of these electrons to generate a triplet requires little energy, but the state would be Jahn-Teller deformed to remove the orbital degeneracy. Goodman considers that a centro-symmetric distortion is required and since a D₄h distortion is not compatible with the observed electron diffraction data, concludes that D₃d symmetry is appropriate. Bartell allows that a D₃d species could be consistent with the electron diffraction findings. Unfortunately, a magnetic deflection molecular-beam experiment²²¹ has provided no evidence for a paramagnetic XeF₆ species, although this
does not necessarily deny the existence of a triplet species (if the spin-orbit coupling is sufficiently strong). It should also be noted however, that an electrostatic deflection molecular-beam experiment has provided no evidence for a dipolar $\text{XeF}_6$ species. Indeed $\mu(\text{XeF}_6)$ must be $< 0.03$ D and this is difficult to reconcile with non-centric structures. Claassen and his coworkers, from millimeter waveband studies, were unable to obtain evidence to support Bartell's inverting or pseudo rotator model. Raman and infrared data indicate that either the ground-state vapour molecules possess a symmetry lower than $\text{O}_h$ or they have some very unusual electronic properties that markedly influence the region of the spectrum usually considered the vibrational-rotational region. Clearly more work must be done to settle this important structural problem.

Bonding and Bond Polarity. Alone, of the first theoretical papers on the bonding in noble-gas compounds, the valence-shell-electron-pair-repulsion model predicted that the $\text{XeF}_6$ molecule would be non-octahedral (see section 1.3.4). The 3-centre-4-electron 'molecular orbital' model predicted an octahedral molecule (see section 1.3.3). It now appears however, that the 'non-bonding-valence electron-pair' in $\text{XeF}_6(g)$ does not have the 'bulk'(or steric activity) usually associated with such a 'pair'.

Evidently, even a Hückel molecular orbital model containing only $\text{Xe} 5\sigma, 5\pi$ atomic orbitals and a $p\sigma$ orbital in each F ligand, generates essentially the same structural predictions as the electron-pair-repulsion theory, and like it, predicts a larger distortion from $\text{O}_h$ symmetry than that observed.
The non-octahedral geometry and exceptional flexibility of the XeF$_6$ molecule, implied by the electron diffraction findings, have been interpreted in terms of a pseudo-Jahn-Teller effect. This explanation is probably best understood with the aid of Figure 3.4.2. This model supposes that the Xe 5d orbitals partake in the

Figure 3.4.2
Schematic Correlation Diagram Illustrating MO Energy Levels for an O$_{12}$ Molecule
bonding, the d orbital degeneracy having been removed by the ligand field. This model places a pair of electrons of the \( \begin{array}{c} \text{H} \\ \text{XeF}_6 \end{array} \) symmetry \( \text{XeF}_6 \) molecule in the antibonding orbital \( a_{1g}^* \). This orbital is supposedly very close in energy to the triply degenerate \( t_{1u}^* \) set of orbitals and indeed so close that certain deformations of the molecule can bring about considerable mixing of the ground and excited states. The \( t_{1u} \) deformation mode ought to have maximum effect in this regard and therefore be particularly favoured energetically. This is described as a pseudo-Jahn Teller effect. The amplitudes of vibration of the \( t_{1u} \) deformations indeed do appear to be large. A \( t_{1u} \) deformation is equivalent, geometrically, to a "lone-pair" pushing aside the ligands and protruding into the coordination sphere.

The same correlation diagram (Figure 3.4.2) is appropriate for Goodman's description. Goodman considers the represented \( \text{XeF}_6(\text{O}_h) \) species to be the ground state species but allows that the \( a_{1g}^* - t_{1u}^* \) energy gap is so small that there is an extensive population of the triplet state (suitably distorted to lift the orbital degeneracy of the \( t_{1u}^* \) set — a first order Jahn-Teller effect). Thus, according to this view, the \( \text{XeF}_6 \) population should contain octahedral and \( \text{D}_{3d} \) symmetry species, the concentration of the latter increasing with increasing temperature.

As in the case of the other fluorides, the \( ^{19} \text{F} \) n.m.r. data has been interpreted on the basis of bond polarities approximating to \( \text{Xe}^3+ - (\text{F}^0.5^-)_6 \). Both extreme theoretical approaches (one involving \( \text{Xe}5d \) orbitals, the other not) yielded this high bond polarity. Soft X-ray photoionization studies (involving the ejection of core electrons from the \( \text{Xe} \) atom) have shown that the charge withdrawn
from the xenon atom in XeF\textsubscript{6} is a little less than 3 times the charge withdrawn in XeF\textsubscript{2}. A charge somewhat less than 3+ on the Xe-atom is consistent with the findings (see Table 3.4.4 and section 3.4.2).

The ready ionization\textsuperscript{195}

\[
\text{XeF}_6(g) \rightarrow \text{XeF}_5^+(g) + F^-(g) \quad \Delta H = 9.24 \text{ eV}
\]

compared with XeF\textsubscript{4} and XeF\textsubscript{2}, the corresponding enthalpies of which are 9.66 and 9.45 eV respectively, is of considerable chemical importance and surely of significance to bonding theory. The enthalpy of ionization is approximately 0.6 eV less than anticipated on the basis of the XeF\textsubscript{2} and XeF\textsubscript{4} data. This is compatible with the greater stability of XeF\textsubscript{5}\textsuperscript{+} salts compared with XeF\textsubscript{3}\textsuperscript{+} and even XeF\textsuperscript{+} salts (see section 3.4.6). Evidently, the pseudo-octahedral geometry of the XeF\textsubscript{5}\textsuperscript{+} ion must be especially favourable. The IF\textsubscript{6}\textsuperscript{+} ion is also a very favourable species (thus IF\textsubscript{6}\textsuperscript{+} salts have greater stability than IF\textsubscript{4}\textsuperscript{+} salts\textsuperscript{227}, and IOF\textsubscript{5}\textsuperscript{+}, which is nearly octahedral, is not known to form IOF\textsubscript{4}\textsuperscript{+} salts).\textsuperscript{169}

As we have seen, the preference for the 'octahedral' geometry also shows up in the crystal structure of XeF\textsubscript{6}(cubic). It is possible that even in the molecular state, XeF\textsubscript{6} and IF\textsubscript{7} are close to XeF\textsubscript{5}\textsuperscript{+}F\textsuperscript{-} and IF\textsubscript{6}\textsuperscript{+}F\textsuperscript{-} ion pairs.

**Chemical Properties.** As befits its higher oxidation state, XeF\textsubscript{6} is a much more powerful oxidizer and fluorinator than XeF\textsubscript{2} or XeF\textsubscript{4}. It seems that XeF\textsubscript{6} has little of the kinetic stability noted in XeF\textsubscript{2} and XeF\textsubscript{4} chemical behaviour. Thus, unlike XeF\textsubscript{2} and XeF\textsubscript{4} it is not possible to store XeF\textsubscript{6} in glass or quartz. There is presumably a stepwise
interaction but these reactions are only effective for the formation of $\text{XeOF}_4$ and $\text{XeO}_3$: 

\[
2\text{XeF}_6 + \text{SiO}_2 \rightarrow 2\text{XeOF}_4 + \text{SiF}_4
\]

\[
2\text{XeOF}_4 + \text{SiO}_2 \rightarrow 2\text{XeO}_2\text{F}_4 + \text{SiF}_4
\]

\[
2\text{XeO}_2\text{F}_4 + \text{SiO}_2 \rightarrow 2\text{XeO}_3 + \text{SiF}_4
\]

The interaction with water similarly yields $\text{XeOF}_4$ and $\text{XeO}_3$ and the latter creates a hazard in $\text{XeF}_6$ handling. A large excess of water yields $\text{XeO}_3(\text{aq})$ as described in sections 3.4.4. and 3.4.5. Hydrolysis in strong base leads to the formation of perxenates, the 'ideal' disproportionation being

\[
2\text{XeF}_6 + 16\text{NaOH} \rightarrow \text{Na}_4\text{XeO}_6 + \text{Xe} + 12\text{NaF} + 8\text{H}_2\text{O}
\]

The 'disproportionation' can be much more complex than this (see section 3.4.5.). Hydrolysis in the presence of ozone generates perxenate much more efficiently. The hexafluoride interacts violently with $\text{H}_2$ to yield $\text{Xe}$ and $\text{HF}^{202}$ and with mercury to give $\text{Xe}$ and mercury fluorides.

The greater reactivity of $\text{XeF}_6$ is illustrated by its interaction with perfluoropropane which cleaves the molecule:

\[
2\text{XeF}_6 + 3\text{CF}_3\cdot\text{CF} = \text{CF}_2 \rightarrow 3\text{C}_2\text{F}_6 + 3\text{CF}_4 + 2\text{Xe}
\]

The tetrafluoride yields perfluoropropane and $\text{XeF}_2$ does not interact with the olefin. Cleavage of the carbon skeleton is not characteristic
of XeF$_6$ however, since it interacts with perfluorocyclopentane to generate the cyclopentane and lower xenon fluorides.$^{234}$

Efforts to prepare derivatives of XeF$_6$ other than oxyfluorides and oxides have so far failed. Thus, HCl and NH$_3$ interact with XeF$_6$ according to the following equations:$^{234}$

\[
\text{XeF}_6 + 6\text{HCl} \rightarrow \text{Xe} + 3\text{Cl}_2 + 6\text{HF}
\]

\[
\text{XeF}_6 + 8\text{NH}_3 \rightarrow \text{Xe} + 6\text{NH}_4\text{F} + \text{N}_2
\]

It is reasonable to suppose that substitution by highly electronegative groups, as in the case of XeF$_2$ (see section 3.2.4) can occur.

It is not surprising, in the light of the physical evidence on the considerable fluoride ion donor ability of XeF$_6$, that the fluoride should form XeF$_5^+$ salts with fluoride ion acceptors. The salts are described in section 3.4.6. The greater fluoride ion donor ability of XeF$_6$ and XeF$_2$ relative to XeF$_4$, provides for a chemical purification of the XeF$_4$ (see section 3.3.1).

Although there is no firm physical evidence to support complex anions XeF$_7^-$ and XeF$_8^{2-}$, the formation of salts with the alkali fluorides, of form AXeF$_7$ and A$_2$XeF$_8$, indicate that these anions may well exist. These 'salts' are described in section 3.4.7. The sodium salt, 2NaF.XeF$_6$, forms readily when the components are mixed at 50°, but decomposes under vacuum at 125°. This provides for the purification of XeF$_6$ (see laboratory preparation).

Analysis and Characterization. The hexafluoride is best characterized by its vapour infrared spectrum. It is necessary to use AgCl windows to withstand the chemical attack. Care should be taken to scan the 928 cm$^{-1}$ region for signs of XeOF$_4$ (the most common impurity). Analysis
can be carried out in much the same way as for XeF₄, by using H₂ or Hg as the reducing agent. The latter is preferred.

3.4.2 Xenon Oxide Tetrafluoride

Preparation. The oxyfluoride, XeOF₄, was first detected by mass-spectroscopy among the xenon fluorides. prepared by thermal excitation, and was soon isolated in macroscopic quantities by the partial hydrolysis of XeF₆.

\[ \text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF} \]

Unreacted XeF₆ and HF are removed by treatment with NaF (which forms compounds with both). The best reported procedure is that of Smith, who used a circulating-loop incorporating an infrared cell for monitoring the interaction. In this arrangement, air saturated with water vapour is bled into the circulating-loop, filled with XeF₆ near its saturation vapour pressure, and the XeF₆ consumption is monitored by following the intensity of the XeF₆ band at 520 cm⁻¹. Yields of 80%, based on XeF₆ consumption, have been obtained.

The static methods, involving interaction of XeF₆ with H₂O or SiO₂, are hazardous if not carried out with great care and it is probably better, if efficient and large scale synthesis are not important factors, to prepare the compound by heating Xe/F₂/O₂ mixtures to 235 °C, the Xe:F₂ ratio being ~ 1:4 and the oxygen in considerable excess (5 times the F₂ content). The last procedure yields XeF₄ as a major impurity, but the much greater volatility of
the XeOF$_4$ permits ready separation by vacuum distillation at \( \sim 0^\circ \). This method is no more hazardous than XeF$_6$ synthesis.

Whenever XeF$_6$ is handled in an apparatus, which has not been previously fluorinated or 'pickled' with XeF$_6$, the oxyfluoride XeOF$_4$ is produced. This occurs so readily that it was a source of some confusion in the early studies involving XeF$_6$.\(^{236}\)

**Some Physical Properties.** The hazards associated with the preparation of XeOF$_4$ have restricted its study. The limited physical data are summarized in Table 3.4.2.

### Table 3.4.2

The compound is colourless in all phases, is low melting (\(-46.2^\circ\)) and easily volatile.\(^{237}\) It is anticipated to be thermodynamically stable\(^{238}\) and all observations indicate that it is so.

The n.m.r. data (\(^{19}\)F, \(^{17}\)O, \(^{129}\)Xe, see Table 3.4.2) are consistent with the liquid being non-associated (unlike XeF$_6$) and the low electrical conductivity of the pure liquid shows that autoionization is very limited. Nevertheless, the liquid has a moderately high dielectric constant (24.6 at \(24^\circ\)) and dissolves the alkali fluorides, with considerable enhancement of the electrical conductivity.\(^{237}\) Thus, a 0.29 M CsF solution possesses a specific conductivity of \(8.5 \times 10^{-3}\) ohm$^{-1}$ cm$^{-2}$ at \(24^\circ\).\(^{237}\) Although XeOF$_4$ dissolves XeF$_6$ and is miscible with HF, the electrical conductance is not markedly effected by their addition.

**Structural Features.** Like the 'isoelectronic' halogen pentafluorides\(^{239}\) and XeF$_5^+$ (see sections 3.4.1 and particularly 3.4.6 for a structural comparison), XeOF$_4$ is known from n.m.r., \(^{121}\) vibrational\(^{180},\,114\) and microwave spectroscopy to be square-based pyramidal in shape, with the O- ligand apical (C$_{4v}$). The microwave data indicate that the Xe and
Table 3.4.2

Some Physical Properties of XeOF<sub>4</sub>

Colourless solid, liquid and vapour\(^{(a)}\).

m.p. \(^{(\circ\mathrm{C})}\):  
-28\(^{(a)}\)  
-41\(^{(b)}\)  
-40\(^{(c)}\)  
-46.2\(^{(d)}\)

<table>
<thead>
<tr>
<th>Vapour pressure(^{(b)})</th>
<th>T(\circ\mathrm{C})</th>
<th>(P_{mm})</th>
<th>Density ((g, \text{cm}^{-3})): (d = 3.168 - 0.0032T(^{(e)})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>29</td>
<td></td>
</tr>
</tbody>
</table>

Optical properties

Refractive index: \(^{(e)}\) (Cauchy relation) \(n = 1.40753 + \frac{4.870 \times 10^5}{\lambda^2} \pm 0.0003\)

(Measurements at 4358 and 4471\(\AA\)) Temp. Coeff. of \(n\): -0.00049

Molar refraction: \(^{(e)}\) \(R_D(25\circ\mathrm{C}) = 18.24 \text{ cc mole}^{-1}\)

Dipole Moment\(^{(f)}\) 0.65 \pm 0.09 D; Dielectric Constant \((24\circ\mathrm{C})\): 24.6 \(^{(d)}\)

Volume Susceptibility\(^{(c)}\) \(-x_v = 0.82\)

Infrared and Raman Spectra \(^{(g)}\)(\(^{(h)}\))

- Symmetry

\(|\begin{array}{c|c|c}
\text{C} & \nu\text{v} & \text{IR} \\
\hline
\text{IR} & & \\
\hline
\text{R} & & \\
\hline
\text{a}_1 & \nu_1 & 926 \text{ s} \\
\hline
\text{a}_1 & \nu_2 & 576 \text{ m} \\
\hline
\text{a}_1 & \nu_3 & 294 \text{ s} \\
\hline
\text{b}_1 & \nu_4 & 527 (4) \\
\hline
\text{b}_1 & \nu_5 & 230 \text{ (calc.)}
\end{array}|\)
Molecular dimensions

Microwave spectroscopy

\[ \text{Xe-O: } 1.703 \pm 0.015 \text{ Å} \]
\[ \text{Xe-F: } 1.900 \pm 0.005 \]
\[ \text{Xe-O-Xe-F: } 91.8 \pm 0.5^\circ(1) \]

\section*{N.M.R. Spectra}

\[ ^{17}O \text{ Shift: } \sigma_o = -313 \pm 2 \text{ ppm (} \sigma, H_2^{17}O = 0), J(^{129}\text{Xe-}^{17}O \text{ coupling}) = \]
\[ + 692 \pm 10 \text{ cps (j)} \]

\[ ^{19}F \text{ Shift: } \sigma_F = -100.27 \text{ ppm (} \sigma_F, \text{CCl}_3F = 0)^{(c)}; = 330 \text{ ppm (} \sigma_F, F_2(g) = 0)^{(k)(1)(m)} \]
\[ J(^{129}\text{Xe-}^{19}F \text{ coupling}) = 1127^{(1)}, 1124^{(c)} \]

\[ ^{129}\text{Xe Shift: } \sigma_{^{129}\text{Xe}} = -5511 \text{ ppm (} \sigma_{^{129}\text{Xe}}, \text{Xe}(g) = 0)^{(m)} \]

\section*{Photoelectron Spectroscopy}

\[ \Delta E(\text{XeOF}_4(g)) = 7.02 \pm 0.13 \text{ eV (relative to Xe}(g)) \]

\section*{Electrical Conductivity}

Specific conductivity (at 24°C): \(1.03 \times 10^{-5} \ \text{ohm}^{-1} \ \text{cm}^{-2}\), increases markedly with CsF or

RbF added: specific conductance (0.29M CsF soln. in XeOF_4): \(8.5 \times 10^{-3} \ \text{ohm}^{-1} \ \text{cm}^{-2}\)
Positive ions: all uni-positive ions observed but $\text{XeOF}_3^+ / \text{XeOF}_4^+$ ratio $\approx 100:1$

Negative ions: $\text{XeF}^-, \text{XeF}_2^-, \text{XeF}_3^-, \text{XeF}_4^-, \text{XeOF}_3^-$
Table 3.4.2

References


(b) D.F. Smith, Science 140 (1963) 899.


(f) J. F. Martins and E. B. Wilson, Jr., J. Mol Spectrosc. 26 (1968) 410.


(h) See reference (a) p. 287.


(k) See reference (a) p. 251.

(l) A. C. Rutenberg, Science 140 (1963) 993.

(m) See reference (a) p. 263.


(o) See reference (a) p. 47.
4 F-ligands, are very nearly coplanar (4.0-Xe-F = 91.8 ± 0.5°). The Xe-F bond length (1.900 ± 0.005 Å)\textsuperscript{239} is very similar to that found for XeF\textsubscript{6} (1.890 Å)\textsuperscript{217} and significantly shorter than for XeF\textsubscript{4} (1.95 Å)\textsuperscript{17a}. The Xe-0 bond length (1.703 ± 0.015 Å) is shorter than observed in either XeO\textsubscript{3} (1.76 Å)\textsuperscript{240} or XeO\textsubscript{4} (1.74 Å)\textsuperscript{241}. The force constants given in Table 3.4.3, derived from the vibration data, are consistent with these observations, the Xe-0 bond evidently being stronger than

<table>
<thead>
<tr>
<th>Table 3.4.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparison of Bond Stretching Force Constants (mdyne A\textsuperscript{-1}) of XeOF\textsubscript{4} with those of Related Molecules</td>
</tr>
<tr>
<td>k\textsubscript{r}(Xe-F)</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>XeOF\textsubscript{4}</td>
</tr>
<tr>
<td>3.21(a)</td>
</tr>
<tr>
<td>7.11(a)</td>
</tr>
</tbody>
</table>

(a) D. F. Smith, \textit{Science} 140 (1963) 899.
(e) W. A. Yeranos, \textit{Bull. Soc. Chim. Belges} 74 (1965) 414. This value was derived using a Urey-Bradley force field and an assumed value for \nu\textsubscript{1}.\textsuperscript{*} Converting this to a valence-force-field value yields a k\textsubscript{r}(Xe-0) of 6.7 mdynes A\textsuperscript{-1}.

in XeO\textsubscript{3} or XeO\textsubscript{4}.

Bonding and Bond Polarity. The observed geometry is as predicted by valence-electron-repulsion theory,\textsuperscript{39} and by the three-centre-four-electron bond description\textsuperscript{32,33} (see section 1.3). In the former
representation the molecule is pseudo-octahedral (the non-bonding valence electron pair being on the 4-fold molecular axis trans to the oxygen atom.†

The X-ray photo electron spectrum \(^{126}\) of XeOF\(_4\) yields a Xe core-electron chemical shift intermediate between XeF\(_4\) and XeF\(_6\) as shown in Table 3.4.4. These data show that the ligands remove electron density from the xenon atom (the expelled core electrons being more bound than in atomic xenon). The XeOF\(_4\) shift is seen to be closer to that of XeF\(_6\) than that of XeF\(_4\). The shifts have been interpreted quantitatively in terms of a simple coulombic model.\(^{126}\)

This assumes a spherical, positively charged, xenon atom of charge +\(q\) and radius \(r_V\) and spherical, negatively charged ligands at a distance \(R_L\).

† The steric activity of an oxygen ligand appears to be comparable to that of a non-bonding-valence-electron-pair, thus XeO\(_3\) (see section 3.4.4) is pseudo-tetrahedral with \(\angle O-Xe-O = 130^\circ\).
from the Xe atom. Thus, for $\text{XeOF}_4$

$$\Delta E_{\text{XeOF}_4} = -(q - q_0) \left( \frac{1}{r_v} - \frac{1}{r_F} \right) - q_0 \left( \frac{1}{r_v} - \frac{1}{r_F} \right)$$

and by equating the first term with $\Delta E_{\text{XeF}_4}$ or $\frac{2}{3} \Delta E_{\text{XeF}_6}$

$$\Delta E_{\text{XeOF}_4} = \Delta E_{\text{XeF}_4} \left( \text{or } \frac{2}{3} \Delta E_{\text{XeF}_6} \right) - q_0 \left( \frac{1}{r_v} - \frac{1}{r_F} \right).$$

Thus, the dependence of $q_0$ upon $r_v$ has been evaluated and compared with a similar interdependence for the xenon fluorides. The findings are as follows:

<table>
<thead>
<tr>
<th>Xe valence shell radius (Å)</th>
<th>1.5</th>
<th>1.4</th>
<th>1.3</th>
<th>1.2</th>
<th>1.1</th>
<th>1.0</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-ligand charge $q_0$</td>
<td>1.5</td>
<td>0.91</td>
<td>0.64</td>
<td>0.47</td>
<td>0.36</td>
<td>0.28</td>
<td>0.22</td>
</tr>
<tr>
<td>F-ligand charge $q_F^*$</td>
<td>0.63</td>
<td>0.48</td>
<td>0.37</td>
<td>0.30</td>
<td>0.20</td>
<td>0.16</td>
<td>0.13</td>
</tr>
</tbody>
</table>

(*essentially constant for all xenon fluorides)

They show, no matter what the choice of the Xe valence-shell radius, that the oxygen ligand withdraws more electron density than a fluorine ligand. This is compatible with the valence-electron-pair theory, if multiple bonding is allowed for the Xe-O bond, but is also in harmony with the three-centre orbital model, which, in its simplest representation, yields a charge distribution $\text{Xe}^+ \left( \text{F}^{-2} \right)_4 \text{O}^{-1}$ for the oxyfluoride. In the latter view the Xe-O bond is a semi-ionic bond, $\text{Xe}^+:\text{O}^-$. The considerable polarity of the Xe-O bond predicts a large dipole moment for $\text{XeOF}_4$ ($> 4 \text{D}$), if the non-bonding valence electron pair is sterically inactive.
(i.e., in the Xe 5s orbital). Since the observed dipole moment\textsuperscript{239}
is only 0.65 ± 0.09D, at least considerable Xe valence-shell polarization
occurs, or else the non-bonding 'pair' resides in a sterically active
orbital (e.g., an sp hybrid).

The $^{170}$ n.m.r. spectrum of $^{170}$XeF$_4$ shows a resonance ($\sigma$, -313 ppm
relative to H$_2$\textsuperscript{170}) down field from aqueous XeO$_3$\textsuperscript{242, 243} which has been
interpreted\textsuperscript{230} in terms of greater double bond character for Xe-O in XeOF$_4$
than in XeO$_3$(aq). The resonance is, however, to higher field than many
'double-bond' oxygen compounds, ($\sigma$, -500 to -600 ppm relative to H$_2$\textsuperscript{170}).

A localized orbital model (employing Xe 5d crystals) has been given,\textsuperscript{119}
to account for the observed n.m.r. chemical shifts and coupling constants.

Ligand Exchange in the System XeO$_2$F$_2$/XeOF$_4$. A $^{19}$F n.m.r. study and $^{18}$F
radiotracer investigation in the system XeO$_2$F$_2$/XeOF$_4$ has shown the half
life for F-ligand exchange to be < 7 min. at 0° and > 4 sec. at 70°,
but a detailed kinetic study was not carried out.

Chemical Properties of XeOF$_4$. The oxyfluoride hydrolyses further, evidently
in stepwise fashion\textsuperscript{235}:

\[
\text{XeOF}_4 + \text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 2\text{HF}
\]

\[
\text{XeO}_2\text{F}_2 + \text{H}_2\text{O} \rightarrow \text{XeO}_3 + 2\text{HF}
\]

but it has not proved possible to control the hydrolysis to generate
macroscopic yields of XeO$_2$F$_2$. The usual product is XeO$_3$\textsuperscript{229} The
oxyfluoride interacts similarly with SiO$_2$, especially at elevated
temperatures. The ready formation of XeO$_3$ renders investigations
of XeOF$_4$ (also XeF$_4$ and XeF$_6$) hazardous, particularly if carried
out in oxide containing apparatus.
Adducts of XeOF$_4$ with alkali fluorides (CsF, RbF, KF but not NaF) may contain the XeOF$_5$" ion, or polymers of it (see Section 3.4.9). The adducts formed with strong fluoride ion acceptors (see section 3.4.8) probably contain the XeOF$_3^+$ ion. The 1:1 molecular adduct formed between XeF$_2$ and XeOF$_4$ has been discussed in section 3.2.7. The formation and structure of this adduct are consistent with the high bond polarities discussed above.

**Analysis and Characterization.** The compound is most readily characterized and detected by infrared or Raman spectroscopy (the Xe-O stretch at 926(IR), 920(R), is very characteristic, particularly in conjunction with the Xe-F stretch at 608 vs (IR), 567 vs(R)). Analysis has been accomplished by interaction of XeOF$_4$ with H$_2$ in a nickel can at 300°:

\[ \text{XeOF}_4 + 3\text{H}_2 \rightarrow \text{Xe} + \text{H}_2\text{O} + 4\text{HF} \]

but it is probable that similar reduction with mercury would prove to be more convenient.

### 3.4.3. Xenon Dioxide Difluoride

**Preparation.** Mass spectroscopy gave the first indications of the existence of XeO$_2$F$_2$. It was subsequently prepared by Huston by mixing XeO$_3$ with XeOF$_4$. The latter is distilled onto the former which is cooled to dry-ice temperature. (Dry ice is used to minimize detonating the XeO$_3$ by thermal shock.) The XeO$_3$ is allowed to dissolve in the XeOF$_4$ (overnight). The resulting mixture of XeO$_2$F$_2$, XeOF$_4$ and XeF$_2$ is fractionally distilled in a Kel-F apparatus. The XeOF$_4$ being more volatile is readily removed. The difluoride is slightly more volatile than XeO$_2$F$_2$. It is possible that chemical purification could be
Table 3.4.5

Some Physical Properties of $\text{XeF}_2$  

Colourless solid, liquid and vapour\(^{(a)}\)

m.p. \(30.8^\circ\text{C}\)\(^{(a)}\)

\(\Delta H_f^\circ (\text{XeF}_2\text{(g)})\) estimated\(^{(b)}\): \(+56\text{ kcal mole}^{-1}\)

Volume Susceptibility \(\chi_V = -0.86\)\(^{(c)}\)

Infrared and Raman (liquid and solid)\(^{(d)}\)

<table>
<thead>
<tr>
<th>Raman</th>
<th>Infrared (Ar matrix)</th>
<th>Assignment</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td>Liquid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>205 ms</td>
<td>198 w</td>
<td>(v_4(a_1))</td>
<td></td>
</tr>
<tr>
<td>224 w</td>
<td>223 vw</td>
<td>(v_5(a_2))</td>
<td></td>
</tr>
<tr>
<td>315 vs</td>
<td>313 ms</td>
<td>(v_9(b_2))</td>
<td></td>
</tr>
<tr>
<td>350 ms</td>
<td>333 ms</td>
<td>(v_3(a_1))</td>
<td></td>
</tr>
<tr>
<td>537 vs</td>
<td>490 s</td>
<td>(v_2(a_1))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(v_5 + v_9)</td>
<td>541(B1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(v_5 + v_7)</td>
<td>547(B2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>?</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(v_8(b_2))</td>
<td></td>
</tr>
<tr>
<td>769 w</td>
<td>788 vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>814 w</td>
<td></td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>850 vs</td>
<td>845 vs</td>
<td>(v_1(a_1))</td>
<td></td>
</tr>
<tr>
<td>882 s</td>
<td>905 w</td>
<td>(v_6(b_1))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>?</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(v_1 + v_8)</td>
<td>1433(B2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>
Mass spectra

(a) Positive ions: \( \text{XeO}_2\text{F}_2^+ (0.89) \), \( \text{XeO}_2\text{F}^+ (0.66) \), \( \text{XeOF}_2^+ (4.8) \), \( \text{XeO}_2^+ (1.6) \), \( \text{XeF}_2^+ (3.3) \), \( \text{XeOF}^+ (2.3) \), \( \text{XeO}^+ (2.3) \), \( \text{XeO}^+ (1.0) \), \( \text{XeF}^+ (4.1) \).

Negative ions: \( \text{XeF}^- \), \( \text{XeF}_2^- \), \( \text{XeOF}^- \) - no evidence for heavier ions.

(b) S. R. Gunn, J. Amer. Chem. Soc. 87 (1965) 2290.
achieved by complexing the XeF₂ with AsF₅ (see section 3.4.1) but this supposes that XeO₂F₂ does not form a salt or adduct with AsF₅.

Physical Properties. The solid, liquid and vapour are colourless and the solid low melting (29.5 - 30.5°). Although thermodynamically unstable, with respect to XeF₂ and O₂, it can be kept at room temperature for several days in preconditioned Kel-F containers.

Table 3.4.5

The vibrational spectra, represented in Table 3.4.5, indicate that the molecule is of Cᵥ⁻² symmetry. Such an assignment is compatible with the observation that the isoelectronic species IO₂F₂⁻ is of Cᵥ⁻² symmetry, being pseudo trigonal bipyramidal (A) 0-I-0 = 180°; 4 F-I-F = 110°).

Chemical Properties. The compound interacts with XeF₆, with liquifaction, to yield XeOF₄:

\[
\text{XeF}_6 + \text{XeO}_2\text{F}_2 \rightarrow 2\text{XeOF}_4
\]

It rapidly hydrolyses in moist air to yield XeO₃ but a faint ozone like odour, reminiscent of XeO₄, can be discerned.

Analysis. The compound has been analyzed by decomposing it in a quartz container at 300°. The mixtures of Xe, O₂ and SiF₄ were

\[
\text{XeO}_2\text{F}_2 + \text{SiO}_2 \rightarrow 1.0 \text{Xe} + 1.5 \text{O}_2 + 0.45 \text{SiF}_4 \quad \text{Found}
\]

\[
1.0 \text{Xe} + 1.5 \text{O}_2 + 0.5 \text{SiF}_4 \quad \text{Calculated}
\]

analyzed mass spectrographically, with relative sensitivities to the 3 gases calibrated by means of a known mixture.
3.4.4 Xenon Trioxide

**Historical Note and Preparation.** In their first report on the synthesis of XeF₄, Claassen, Selig and Malm noted that the hydrolysis of the solid yielded initially a yellow solid (now considered to be XeOF₂, see section 3.3.3) which dissolved to yield a clear, pale yellow solution. Cady and his coworkers, in their first report of XeF₆, noted that the hydrolysis of the fluoride yielded a solution containing an oxidizing xenon species which they assumed to be xenic acid Xe(OH)₆. Simultaneously with the latter investigation, Smith observed that XeF₆ exposed to moist air yielded a solid product, which proved to be xenon trioxide. Independently, Williamson and Koch discovered that the solid recovered by evaporation of a hydrolysed XeF₄ solution was also XeO₃.

Since XeO₃ is a powerful explosive, great care must be exercised in its preparation (and indeed in the handling of XeF₄ and XeF₆ since the oxide is formed when these interact with moisture). The oxide is most efficiently prepared from XeF₆ and two detailed procedures have been given. The method given by Huston and his coworkers is probably the safer. Figure 3.4.3 illustrates the experimental arrangement for the controlled hydrolysis. The XeF₆, contained in a U-shaped Monel vessel, has a vapour pressure of ~30 mm at room temperature, and this vapour is swept in a stream of dry nitrogen into water contained in a Teflon bottle:

\[
\text{XeF}_6(g) + 3\text{H}_2\text{O}(l) \rightarrow 6\text{HF(aq)} + \text{XeO}_3(\text{aq})
\]

The hydrolysis of gram amounts takes several hours. It is essential that a stream of dry nitrogen be maintained at all times, since water.
Figure 3.4.3

Apparatus for Hydrolysis of Xenon Hexafluoride
should not gain entrance to the XeF₆ container.

If it is necessary to remove the HF from the aqueous solution, this can be achieved by treating the solution with magnesium oxide (MgO + 2HF → MgF₂ + H₂O) to make a slightly alkaline slurry. Following filtration through a sintered glass filter of medium porosity, the magnesium in solution is removed by passage through a column of hydrous zirconium oxide, converted to the nitrate form by exhaustive washing with 0.1 M HNO₃.

The aqueous XeO₃ solutions may be kept indefinitely if oxidizable impurities are excluded. It is important to exercise the greatest care if the solution is evaporated to dryness since the solid oxide may detonate.

Table 3.4.6.

Physical Properties. The oxide is colourless. The solid deliquesces at humidities greater than ~25%. The enthalpy of sublimation has been estimated from mass spectrometric observations²³⁸ to be 30 ± 10 kcal mole⁻¹. Calorimetry has given²⁴⁸ ΔH° = + 96 kcal mole⁻¹ from which an Xe-O bond energy of ~17.5 kcal mole⁻¹ has been derived.

The XeO₃ molecule is pyramidal and almost identical in shape and size to the IO₃⁻ ion.²⁴⁹,²⁴⁰ The bond angles O-Xe-O are closer to T₂₁ angles than right angles. The structure is shown in Figure 3.4.4.

Bonding and Bond Polarity. The pseudo-tetrahedral geometry of the XeO₃ molecule conforms to the representation of the bonding as Xe electron-pair donation, Xe⁺: → O⁻, the Xe orbitals being sp³ hybrids. This model also implies that the oxygen ligand valence state might be a singlet (see section 1.3). The shortness of the Xe-O bonds relative to Xe-F bonds and the higher force constants of the former...
Table 3.4.6

Some Physical Properties of XeO₃

Colourless, hygroscopic, detonatable solid with low vapour pressure at 20°.

Thermodynamic Features

\[ \Delta H \text{ sublimation (est): } 30 \pm 10 \text{ kcal mole}^{-1}(a) \]

\[ \Delta H_f^0 (298.15^\circ K)(s): + 96 \pm 2 \text{ kcal mole}^{-1} (b) \]

Mean thermochemical bond energy:

\[ \frac{27.5 - \Delta H \text{ sublim}}{3} : 17.5 \pm 4 \text{ kcal}(a) \]

\[ S^0, \text{XeO}_3(g) = 68.69 \text{ cal deg}^{-1} \text{ mole}^{-1} (c) \]

Index of refraction: \( n = 1.79(d) \)

Vibrational Spectra(e)

Infrared Spectrum(f)

(solid)

\[ \nu_1(A) \quad 770 \text{ cm}^{-1} \]

\[ \nu_2(A) \quad 311 \]

\[ \nu_3(E) \quad 820 \]

\[ \nu_4(E) \quad 298 \]

Xe-O stretch force constant \( k_r^* \): 5.66 mdyn/Å

Raman Spectrum (of 2.0 M aqu. soln.)

\[ \nu_1 \quad C^3Y \quad 780 \text{ cm}^{-1} \quad (p) \]

\[ \nu_2 \quad 344 \]

\[ \nu_3 \quad 833 \]

\[ \nu_4 \quad 317 \]
**Crystal Structure (X-ray)**

Orthorhombic

\[a = 6.163 \pm 0.008 \, \text{Å}\]

\[b = 8.115 \pm 0.010\]

\[c = 5.234 \pm 0.008\]

\[d_{\text{x-ray}}: 4.55 \, \text{g cm}^{-3}\]

\[z = 4\]

\[V = 262 \, \text{Å}^3\]

\[V_{\text{mole}} = 39.4 \, \text{cm}^3\]

Space group: \(P2_12_12_1\)

**Xe-O**

\[1.74 \pm 0.03 \, \text{Å}\]

\[1.76\]

\[1.77\] \quad av. \, 1.76 \, \text{Å}

\[\text{Xe-O} \quad 108 \pm 2^\circ\]

\[100.\]

\[101.\] \quad av. \, 103^\circ

See Figure 3.4.4

---

(a) S. R. Gunn, J. Amer. Chem. Soc. 87 (1965) 2290.


(f) See reference (b) p. 295.

Figure 3.4.4

The Molecular Shape and Packing In XeO₃ (cryst)

(See Table 3.4.5. for unit cell data)
Figure 3.4.4

(see Table 3.4.3) indicate that the intrinsic Xe-O bond energies are greater than the intrinsic Xe-F bond energies. As has already been remarked (see section 1.3.2) there are indications that the intrinsic energies of Xe-O bonds are not significantly different from transition metal oxygen-ligand bonds, usually considered multiple, e.g. Os-O in OsO$_4$. The greater strength of the Xe-O bonds, relative to Xe-F, may therefore be a consequence of the greater electron affinity of singlet oxygen (1D) or alternatively, a result of multiple bonding of the oxygen to xenon. The latter explanation implies the involvement of 'outer' Xe orbitals (e.g. Xe 5d).

The considerable kinetic stability of the xenon oxides must be of significance to bonding theory but this point has not been given serious theoretical consideration. This kinetic stability contrasts with the evident kinetic instability of the chlorides and 'heavier' halides. Presumably the difference lies in a readier formation, on the part of the halogen ligands, of an energetically favourable ligand diatomic, by electron transfer back to the Xe atom:

\[ \text{L} \text{Xe} \leftrightarrow \text{Xe} \text{L} \]

\[ \text{Xe} \text{L} \leftrightarrow \text{L} \text{Xe} \]

There must be considerable polarity in the Xe-O bond and the 3 near-neighbour Xe---O distances of 2.8, 2.89 and 2.90 Å must represent coulombic interactions -Xe$^+$ Xe ---O$^-$. The low volatility of the compound is compatible with such interactions.
Chemical Properties. The thermodynamic instability of the solid oxide and its high solubility and kinetic stability in aqueous solution has resulted in most work on the oxide being involved with aqueous solutions. The chemistry of the aqueous solutions is discussed in the following section.

The oxide also forms salts with the alkali hydroxides (see section 3.4.11) and with alkali fluorides and chlorides (see section 3.4.12). Cationic derivatives are not known. There is also some evidence for ester like alcohol intermediates, in the oxidation of alcohols. A solution of XeO₃ in t-butyl alcohol has been titrated with potassium or rubidium t-butoxide, using a pH meter with glass-calomel electrodes. The titration curves are similar to those given by glacial acetic acid in the same solvent and have end points at 1:1 molar ratio. Unstable precipitates formed during the titration, analysis of which, indicated empirical formulas t-BuO-XeO₂-M.t-BuOH or MHXeO₄.2t-BuOH (M = K or Rb). Attempts to isolate a XeO₃-t butyl alcohol ester failed and XeO₃ was lost on concentration beyond 0.4 M — vapour phase decomposition of ester-like species is possible.

Analysis. The trioxide is most conveniently analyzed by iodometric titration. Excess sodium iodide is added to an aqueous acid:

\[
\text{XeO}_3 + 6\text{I}^- + 6\text{H}^+ \rightarrow \text{Xe} + 3\text{H}_2\text{O} + 3\text{I}_2 \text{ solution.}
\]

The liberated \( \text{I}_2 \) is titrated with standard thiosulphate to an amylose end point. It is of interest that if acid is added before the \( \text{I}^- \) any perxenate decomposes to Xe(VI) and oxygen, whereas if \( \text{I}^- \) is added first, all of the oxidizing power is captured as triiodide.
3.4.5. Aqueous Xenon Trioxide ('Xenic Acid')

Preparation. Aqueous $\text{XeO}_3$ solutions are prepared as described under $\text{XeO}_3$. Solutions more concentrated than 2M in $\text{XeO}_3$ may be obtained. Solution calorimetric measurements have yielded $\Delta H_f(\text{XeO}_3 \rightarrow \text{H}_2\text{O})$.

Physical Properties. The physical properties of aqueous $\text{XeO}_3$ are given in Table 3.4.7, at 298.15°C to be $+99.94 \pm 0.24$ kcal mole$^{-1}$. This implies $\Delta H_{\text{soln.}} = 3.9 \pm 2$ kcal mole$^{-1}$. The $\text{Xe}/\text{Xe}(\text{VI})$ redox potentials, derived from the aqueous solution calorimetric data, show $\text{XeO}_3$ to be one of the strongest oxidants in aqueous media:

$$\text{Acid}, \quad \text{Xe}_2(g) + 3\text{H}_2\text{O}(l) \rightarrow \text{XeO}_3(aq) + 6\text{H}^+(aq) + 6\text{e}^-, \quad E_\text{A}^\circ = 2.10 \pm 0.01 \text{V}$$

$$\text{Base}, \quad \text{Xe}_2(g) + 70\text{H}^-(aq) \rightarrow 70\text{HXeO}_4^-(aq) + 3\text{H}_2\text{O} + 6\text{e}^-, \quad E_\text{B}^\circ = 1.24 \pm 0.01 \text{V}$$

Table 3.4.7

These potentials may be compared with those of the well known oxidizers $\text{Ce(IV)}$ ($E^\circ = -1.61 \text{V}$) and $\text{O}_3$ ($E^\circ = -2.07 \text{V}$). Xenic acid is reduced at the dropping mercury electrode in a single step to xenon.

The Raman spectrum of 2M soln. of $\text{XeO}_3$ establishes that the primary solution species is molecular $\text{XeO}_3$. This is further supported by the low electrical conductivity of the solution. A $^{17}$O n.m.r. study shows that the oxygen ligands undergo fast exchange with the solvent, equilibrium being established within 3 min at $23 \pm 10^\circ$. The $^{17}$O chemical shift ($-278 \pm 2$ p.p.m. with respect to water) is in the same range as those of perchloric acid ($-288$) and $\text{BrO}_3^-$, $\text{ClO}_3^-$ and $\text{ClO}_4^-$ ($-297, -287, -288$). This study also confirmed that $\text{XeO}_3$
Table 3.4.7

Some Physical Properties of Aqueous XeO₃

Solubility of XeO₃ in water: \( \geq 2 \, \text{M} \)\(^{(a)}\)

Thermodynamic Features \( \Delta H \) soln.\(^{(b)}\):

\[
\Delta H_f^\circ (\text{XeO}_3 \rightarrow \text{H}_2\text{O}, 298.15^\circ\text{K}): \quad 3.9 \pm 2.0 \text{ kcal mole}^{-1} \nonumber
\]

\[
\Delta S_f^\circ = -70 \pm 4 \text{ cal deg}^{-1} \text{ mole}^{-1} \nonumber
\]

\[
\Delta G_f^\circ (\text{XeO}_3 \rightarrow \text{H}_2\text{O}, 298.15^\circ\text{K}): \quad 120.8 \pm 1.2 \text{ kcal mole}^{-1} \nonumber
\]

Electrode potentials of the Xe/XeO₃ couple:

Acid:

\[
E^\circ_{\text{A}} (\text{Xe}(\text{g}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{XeO}_3(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^-) = 2.10 \pm 0.01 \text{ V} \nonumber
\]

Base:

\[
E^\circ_{\text{B}} (\text{Xe}(\text{g}) + 7\text{OH}^-(\text{aq}) \rightarrow \text{HXeO}_4(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) + 6\text{e}^-) = 1.24 \pm 0.01 \text{ V} \nonumber
\]

Equilibrium constant\(^{(a)}\)

\[
K_e = (6.7 \pm 0.5) \times 10^{-4} \nonumber
\]

Raman Spectrum. See Table 3.4.5

Electrical Conductivity\(^{(a)}\)

Molar conductance (0.02 M Xe(VI) soln.): \(< 0.04 \) at 25°

Molal Freezing Point Depression\(^{(a)}\):

\[
1.95 \pm 0.15^\circ \nonumber
\]


may be extracted from aqueous solution with CHCl₃. An equilibrium constant, $6.7 \pm 0.5 \times 10^{-4}$, has been reported for the process:

$$\text{HXeO}_4^- (aq) \rightarrow \text{XeO}_3(aq) + \text{OH}^- (aq)$$

This accounts for the variation in the UV spectrum as a function of pH. Shoulders at 210 and 250 m\(\mu\) which are evident in acid media are presumably associated with XeO₃ and a shoulder which appears at 265 m\(\mu\) in strong base may be associated with HXeO₄⁻. The isolation of salts e.g., CSHXeO₄, (see section 3.4.11) support this rational.

**Disproportionation.** In strong base XeO₃ (HXeO₄⁻?) disproportionates. The yield of perxenate at ~25° is ~33% for NaOH solutions of 0.25 → 4.2M and KOH solutions of 2 → 3.6M. Higher OH⁻ concentration and higher temperatures increase the yield. With LiOH the yield of perxenates is claimed to be 50% or higher. The disproportionation is complex and there are probably several routes to perxenate. In at least one experiment, however, the reaction appeared to be: $4\text{HXeO}_4^- + 50\text{OH}^- \rightarrow 3\text{HXeO}_6^{2-} + \text{Xe} + 3\text{H}_2\text{O}$. Complexes of Xe(VI) and Xe(VIII) do play a role in KOH (where a yellow solid appears) and NaOH (yellow solution), but must have small influence in LiOH solution where no appreciable amount of Xe(VI).Xe(VIII) complex appears to be formed. A complex of composition K₄XeO₆.2XeO₃ has been isolated from the KOH/XeO₃(aq) system but other complexes probably occur. Evidence has been presented to show that these Xe(VI).Xe(VIII) complexes decompose predominantly according to the equation:

$$[\text{Xe}_1 + y \text{O}_4 + 3 \text{Xe}] \rightarrow [\text{XeO}_4] + y\text{Xe} + 1.5y\text{O}_2$$
It appears that the higher the perxenate concentration the less likely is the XeO$_3$ to disproportionate as follows:

$$2\text{XeO}_3 \rightarrow [\text{XeO}_2] + [\text{XeO}_4];\ [\text{XeO}_2] \rightarrow \text{Xe} + \text{O}_2$$

The better than 50% yield of perxenate obtained in certain NaOH solutions and the LiOH system indicate that XeO$_3$ (HXeO$_4^{-}$) also interacts with a lower oxidation state than Xe(VI). The sequence XeO$_3$ + [XeO$_2$] $\rightarrow$ [XeO$_4$] + [XeO]; [XeO] $\rightarrow$ Xe + $\frac{1}{2}$O$_2$, appears more likely than XeO$_3$ + [XeO] $\rightarrow$ [XeO$_4$] + Xe, since XeF$_2$(aq) is known to reduce XeO$_3$(aq).

**Oxidation of Inorganic Ions.** The oxidizing capability of XeO$_3$(aq) is in accord with the oxidation potentials cited above. Iodide is oxidized$^{253, 151}$ rapidly in acid solution (but this is slow above pH 7), and calorimetry gives$^{251}$: $\Delta H(\text{XeO}_3(\text{aq}) + 9\text{I}^{-}(\text{aq}) + 6\text{H}^{+}(\text{aq}) \rightarrow \text{Xe}(\text{g}) + 3\text{I}_3^{-}(\text{aq}) + 3\text{H}_2\text{O}(1)) = -219.63 \pm 0.06 \text{kcal mole}^{-1}$. Bromide and chloride are also oxidized to the free halogen.$^{151}$

Acidic Mn(II) solutions are oxidized to MnO$_2$ over several hours and after a day or two MnO$_4^{-}$ is detectable. In 2M HClO$_4$, I$_2$ is oxidized to iodate and the rate is greater in 6M acid. Under the latter conditions, Br$_2$ is oxidized to BrO$_3^{-}$. The kinetics of the interaction of XeO$_3$(aq) with Pu(III) solutions have been explored.$^{255}$ The reaction is:

$$6\text{Pu}^{3+} + \text{XeO}_3 + 6\text{H}^{+} \rightarrow 6\text{Pu}^{4+} + \text{Xe} + 3\text{H}_2\text{O} \ (\text{in HClO}_4 \ \text{acid})$$

and the rate law is $-d[\text{Pu}^{3+}]dt = k[\text{Pu}^{3+}][\text{XeO}_3]$. The activation enthalpy, free energy and entropy are $\Delta H^{\ddagger} = 15.3 \pm 2.1$; $\Delta G^{\ddagger} = 20.2 \pm 0.1$ kcal mole$^{-1}$ and $\Delta S^{\ddagger} = 16 \pm 6.9$ cal deg$^{-1}$ mole$^{-1}$. Although the studies
did not provide for a decisive mechanism for the reaction, a two
electron change producing Pu(V), which then reacts with Pu(III)
to form Pu(IV), appears most plausible. A photochemically induced
oxidation of Neptunium(V) by XeO_3(aq) has been reported:

\[ 6\text{NP(V)} + \text{Xe(VI)} \rightarrow 6\text{NP(VI)} + \text{Xe} \]

The reaction is first order in XeO_3, the rate expression being
\[ -d[\text{NP(V)}]/dt = k_1[\text{XeO}_3] \]
for which \( k_1 \times 10^6 \, (\text{sec}^{-1}) = 6.28 \pm 0.58. \)
The formation of excited XeO_3: XeO_3 + hv \rightarrow XeO_3^* , appears to
be the rate-controlling step. It is noteworthy that the thermal
reaction is very slow. Since we may expect XeO_3 to be a 'two
electron oxidizer,' two NP(V) ions would need to be oxidized simultaneously
(NP(VII) is not a realistic species). (The effective oxidizer here may
not contain Xe but be a derivative of a XeO_3 + H_2O \xrightarrow{hv} \text{reaction}.)

**Oxidation of Organic Compounds.** Since periodate is highly specific
for the oxidation of vic-diols, their oxidation by XeO_3(aq) has also
been investigated. The XeO_3 solution interacts readily with vic-
diols and primary alcohols in neutral or basic solution but there is
no interaction in acid. The vic-diols yield carboxylic acids or CO_2
from the terminal -OH group. This contrasts with IO_4^- oxidations,
which yield aldehydes (IO_3^- being the reduction product). It may
be that this difference in behaviour has to do with the absence of
stable aqueous oxidation states of the xenon below Xe(VI).

Xenon trioxide has been recommended as an analytical reagent
for the determination of primary and secondary alcohols in aqueous
solution, the products being CO_2 and H_2O. The oxidation of tertiary
alcohols is slow. Similarly, carboxylic acids may also be quantitatively oxidized to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \).

3.4.6. Complexes of \( \text{XeF}_6 \) with \( \text{F}^- \) Acceptors

A number of adducts involving \( \text{XeF}_6 \) in combination with recognized \( \text{F}^- \) acceptors have been reported. They include the following 1:1 adducts (m.p. (°C) given in parentheses): \( \text{XeF}_6 \cdot \text{AsF}_5 \) (130.5°) 259, 260, 261; \( \text{XeF}_6 \cdot \text{BF}_3 \) (90°) 259; \( \text{XeF}_6 \cdot \text{SbF}_5 \) 234; \( \text{XeF}_6 \cdot \text{GeF}_4 \) (sub.) 262; \( \text{XeF}_6 \cdot \text{PtF}_5 \) (~100°) 263, 264; \( \text{XeF}_6 \cdot \text{IrF}_5 \) (116°) 169; \( \text{XeF}_6 \cdot \text{RuF}_5 \) (118°) 227. The X-ray structures of the 1:1 adducts with \( \text{PtF}_5 \) and \( \text{AsF}_5 \) have shown them to be \( \text{XeF}_5^+ \) salts 264, 265 (see Figure 3.4.5). The \( \text{Ir} \) and \( \text{Ru} \) compounds are isostructural with the \( \text{Pt} \) compound. 227 In view of the observation that the cubic form of \( \text{XeF}_6 \) is essentially \( \text{XeF}_5^+ \text{F}^- \) (see Figure 3.4.1) it seems probable that all of the 1:1 adducts are \( \text{XeF}_5^+ \text{ salts} \). However, the following \( \text{XeF}_6 \) adducts (with \( \text{F}^- \) acceptors) may also contain \( \text{XeF}_5^+ \) ions, in clusters with bridging with \( \text{F}^- \) ions: \( 2\text{XeF}_6 \cdot \text{AsF}_5 \) (110°) 261; \( 2\text{XeF}_6 \cdot \text{PF}_5 \) 261; \( 2\text{XeF}_6 \cdot \text{SbF}_5 \) 234; \( 2\text{XeF}_6 \cdot \text{PtF}_5 \) 263; \( 2\text{XeF}_6 \cdot \text{IrF}_5 \) (135°) 169; \( \text{XeF}_6 \cdot 2\text{SbF}_5 \) (103°) 234; \( 4\text{XeF}_6 \cdot \text{GeF}_4 \); \( 2\text{XeF}_6 \cdot \text{GeF}_4 \) 262; \( 4\text{XeF}_6 \cdot \text{SnF}_4 \) and \( 2\text{XeF}_6 \cdot \text{SnF}_4 \) 266.

**Preparation.** The complexes may be prepared simply by fusing the neat components or by dissolving them in non-reductive solvents (e.g. \( \text{BrF}_5 \) or \( \text{HF} \)). Alternatively, \( \text{XeF}_6 \) may be formed in situ, thus, \( \text{XeF}_5^+ \text{[PtF}_6^- \) and \( 2\text{XeF}_6 \cdot \text{PtF}_5 \) have been isolated 263 from \( \text{Xe}_2\text{F}_2/\text{PtF}_5 \) mixtures where the fluorine pressures and the reaction temperature favoured \( \text{XeF}_6 \) formation. The same mixtures yielded \( \text{XeF}_5^+ \) and \( \text{Xe}_2\text{F}_3^+ \text{[PtF}_6^- \) salts (see section 3.2.6) at low fluorine concentrations.
Figure 3.4.5
The Molecular Structure of $\text{XeF}_5^+[\text{AsF}_6^-]^+$.†

Some Physical and Chemical Properties. The compounds are colourless if the acceptor fluoride is a non-transition element fluoride and appropriately coloured if it is a transition metal derivative. All of the compounds are rather low melting and evidently dissociate readily. 266, 262

Although the crystal structures of $\text{XeF}_5^+[\text{PtF}_6]$ and $\text{XeF}_5^+[\text{AsF}_6]$ clearly indicate the ionic formulation they show the cation to possess considerable polarizing capability. The $\text{XeF}_5^+[\text{AsF}_6]$ structure, represented in Figure 3.4.5, shows the $\text{AsF}_6^-$ ion appreciably distorted as a consequence of those F-ligands of $\text{AsF}_6^-$ near the xenon atoms being attracted to the xenon. This is consistent with the charge of $\sim +3$ which the xenon(VI) atom is considered to bear.

Hydrolysis of these $\text{XeF}_6$ compounds occurs very readily. An almost quantitative yield of $\text{Xe(VI)}$ in solution has been reported. 266 The salts have considerable potential as oxidizers and fluorinators, but there are no reports on these aspects of the compounds.

3.4.7 $\text{XeF}_6$ Adducts with $\text{F}^-$ Donors

A number of compounds have been reported involving $\text{XeF}_6$ in combination with recognized fluoride ion donors. The following alkali fluoride compounds have been reported: 267, 268

$\text{CsF}.\text{XeF}_6$ (yellow, $\rho 4.72$ g cm$^{-3}$) $\xrightarrow{50^\circ}$ $2\text{CsF}.\text{XeF}_6$ (cream coloured) $\xrightarrow{400^\circ}$ CsF

$\text{RbF}.\text{XeF}_6$ (colourless) $\xrightarrow{0^\circ}$ $2\text{RbF}.\text{XeF}_6$ (colourless) $\xrightarrow{400^\circ}$ RbF

$2\text{KF}.\text{XeF}_6$ (colourless) $\xrightarrow{250^\circ}$ KF

$2\text{NaF}.\text{XeF}_6$ (colourless) $\xrightarrow{250^\circ}$ NaF
Lithium compounds do not form. Other reports\textsuperscript{204, 232} mention NaF.XeF\textsubscript{6} and give a decomposition temperature (under vacuum) of 125°. This decomposition temperature presumably applies to the 2NaF.XeF\textsubscript{6} compound, since there is no evidence for a 1:1 compound.\textsuperscript{268} As mentioned in section 3.4.1, the reversible compound formation of XeF\textsubscript{6} with NaF provides a convenient method for the purification of XeF\textsubscript{6}, since XeF\textsubscript{2}, XeF\textsubscript{4}, and XeOF\textsubscript{4} (the common impurities in an XeF\textsubscript{6} preparation) do not complex with NaF.

The enthalpies of dissociation of the 1:1 adducts:

\[ 2\text{Cs(Rb)F.XeF}_6 \rightarrow \text{Cs}_2(\text{Rb}_2)F_2 \cdot \text{XeF}_6 + \text{XeF}_6 \]

have been derived from vapour pressure-temperature measurements to be 14.0 and 8.7 kcal mole\textsuperscript{-1} respectively.

A compound with nitrosyl fluoride \textsuperscript{269} 2NOF.XeF\textsubscript{6}, is presumably closely related to the alkali fluoride compounds. The occurrence of infrared and Raman bands at 2310 and 2305 cm\textsuperscript{-1} indicate the presence of NO\textsuperscript{+} cations. The band at 540 cm\textsuperscript{-1} is presumably associated with Xe-F stretch. This is the only structural information available for the F\textsuperscript{-} donor compounds. It does support the expectation that they are salts of general formulae A\textsuperscript{+}[XeF\textsubscript{7}]\textsuperscript{-} and (A\textsuperscript{+})\textsubscript{2}[XeF\textsubscript{8}]\textsuperscript{2-}. Presumably, these anions, like XeF\textsubscript{6} itself, will exhibit steric activity of the non-bonding-valence-electron-pair.

The adducts are extremely reactive chemically and react violently with water. The hydrolysis presumably gives a quantitative yield of Xe(VI) in solution, since Xe is not evolved. Hydrolysis of CsXeF\textsubscript{7} in moist air yields CsXeO\textsubscript{3}F (see section 3.4.11). Dissolution of the latter yields CsHXeO\textsubscript{4}.\textsuperscript{268}
3.4.8 XeOF₄ Complexes with Fluoride Ion Acceptors

As in the case of XeF₆, antimony pentafluoride forms a complex with XeOF₄ which is stable at room temperature. Excess SbF₅ yields a material of composition XeOF₄·2SbF₅ (m.p. ~ 70°). A complex, 2XeOF₄·VF₅ is also reported. Arsenic pentafluoride forms an adduct with XeOF₄ at -78° but this does not exist at room temperature, even under pressures of one or two atmospheres of AsF₅. This contrasts with the XeF₆ behavior and it is clear that complex formation using AsF₅ may be used as a convenient chemical method for separating XeOF₄ and XeF₆. There is no firm structural information on the XeOF₄ complexes with the fluoride acceptors, but it is probable that they are salts of the XeOF₃⁺ ion, which is presumably pseudo-trigonal bipyramidal (the oxygen ligand being in an equatorial position).

3.4.9 XeOF₄ Complexes with Fluoride Ion Donors

The oxide tetrafluoride complexes readily with CsF, RbF, KF and NOF. The trend in thermal stabilities of the alkali fluoride complexes is similar to that observed in the XeF₆ complexes, namely Cs > Rb > K. The NOF complex, ONF.XeOF₄, dissociated readily (m.p. 40°, v.p. 30 mm Hg at 23°) thermogravimetric analysis indicates the following stoichiometries:

\[
\begin{align*}
\text{CsF}.\text{XeOF}_4 \xrightarrow{125°} 3\text{CsF}.\text{XeOF}_4 \xrightarrow{275°} 3\text{CsF}.\text{XeOF}_4 \xrightarrow{400°} \text{CsF} \\
3\text{RbF}.\text{XeOF}_4 \xrightarrow{50°} 3\text{RbF}.\text{XeOF}_4 (?) \xrightarrow{400°} \text{RbF} \\
3\text{KF}.\text{XeOF}_4 \xrightarrow{90°} 6\text{KF}.\text{XeOF}_4 \xrightarrow{250°} \text{KF}
\end{align*}
\]

The MF₂XeOF₄ adducts are chemically reactive and bulk samples dissolve exothermically in water but xenon is not evolved. When allowed to stand in moist air, HF is evolved and MXeO₃F salts (see section 3.4.12) are formed.
The $\text{XeOF}_5^-$ ion may occur in these $\text{XeOF}_4$ complexes but it is more probable that polymeric species involving $\text{XeOF}_4$ molecules 'bridged' by $\text{F}^-$ ions, like the $\text{XeF}_6$ tetramers and hexamers (see Figure 3.4.1) will be found.

3.4.10 $\text{XeOF}_2\text{F}_2$ Adducts

Adducts of $\text{XeOF}_2\text{F}_2$ have not been reported but it is possible that both $\text{XeOF}^+$ and $\text{XeOF}_3^-$ salts will be preparable. The cation should be structurally akin to $\text{XeO}_3^-$ and the anion pseudo-octahedral.

3.4.11 Xenates(VI)

**Preparation.** Mono alkali xenates of empirical formula $\text{M}\text{XeO}_4\cdot 1.5\text{H}_2\text{O}$ ($\text{M} = \text{Na, K, Rb, Cs}$) have been prepared$^{271}$ by lyophilization of $\text{0.1 M XeO}_3$ and alkali hydroxide in 1:1 ratio. The cesium salt has also been prepared by interaction of $\text{XeO}_3(\text{aq})$ in the presence of $\text{F}^-$. $^{247}$ A barium salt has also been claimed$^{141}$ and questioned.$^{151}$

**Physical Properties.** The infrared spectra of the salts are represented in Table 3.4.8. The salts are colourless and are considerably more stable (kinetically) than $\text{XeO}_3^-$, particularly when anhydrous. They are susceptible to detonation, particularly if they contain excess $\text{XeO}_3^-$. The salts are insoluble in methyl, ethyl and t-butyl alcohols, $\text{CHCl}_3$ and $\text{CCl}_4$.

The infrared spectra show that the salts do not contain perxenate.$^{271}$ Evidently the sodium salt is structurally different from the heavier alkali salts. Infrared absorptions at 3500 and 1600 cm$^{-1}$ indicate that the former contains hydroxyl groups. All are characterized by a strong band or bands in the region 770-810 cm$^{-1}$ -- presumably associated with $\text{Xe-O}$ stretch.

Table 3.4.8
### Table 3.4.3.

Infrared Spectra (cm\(^{-1}\)) of Monoalkali Xenates(VI)

<table>
<thead>
<tr>
<th>Empirical Formula</th>
<th>3120vw 1430vw 783s 741s 721s 699s 386s 341s,316s</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHXeO(_4) (a)</td>
<td>3500w 1600w 1360m 770-800s 730sh 625s 469s 340-370m</td>
</tr>
<tr>
<td>K(Rb)HXeO(_4) (a)</td>
<td>3500w 1600w 1360m 770-800s 730sh ~480s 340-370m</td>
</tr>
<tr>
<td>Cs(_2)HXeO(_4) (b)</td>
<td>3120vw 1430vw 783s 741s 721s 699s 386s 341s,316s</td>
</tr>
</tbody>
</table>


**Chemical Properties.** The xenates disproportionate on dissolution in water to Xe(0) and Xe(VIII). Like the oxide itself the xenates(VI) oxidize I\(^{-}\) to I\(_2\) and this has served as the basis for their analysis.

### 3.4.12 Complexes of XeO\(_3\) with F\(^{-}\) and Cl\(^{-}\) and Br\(^{-}\) Donors

Alkali fluoro-xenates (VI) MXeO\(_3\)F\(^272\), and chloro-xenates(VI)\(^273\) have been prepared. Brief mention has also been made of CsXeO\(_3\)Br\(^272\).

**Preparation.** The MXeO\(_3\)F salts (M: K, Rb, Cs) are prepared from aqueous solution. The Cs\(^+\) and Rb\(^+\) salts have been made by neutralizing the XeF\(_6\) hydrolysis product (0.5M) with 2M alkali hydroxide, to pH 4. Evaporation of the solution yields crystals. These are washed with ice cold water and are best stored in a desiccator. All of the salts may also be prepared by evaporating a solution prepared by mixing equal volumes of 0.5M XeO\(_3\)(aq) and 1M KF(aq) and containing a few drops of HF.

The chloro-xenate CsXeO\(_3\)Cl is prepared similarly although acetonitrile may be used as the solvent. A white crystalline precipitate is obtained after 3 hours following mixing of an ice-cold solution of ~2.0 ml of 1.5 M CsCl with 0.4 ml of 1.5M XeO\(_3\)(aq).
Physical Properties. The fluoro-xenates(VI) are claimed to be the most thermally stable of the solid oxygenated Xe(VI) compounds. Even the chloro-xenate is considerably more stable than XeO₃.

The infrared spectra of the MXeO₃F salts are characterized by bands at 812(s), 761(m), 380(w) and 333(w) cm⁻¹ but no bands were observed in the usual Xe-F stretching region (500-600 cm⁻¹). This finding is compatible with the crystal structure of the potassium salt. This structure shows XeO₃ units linked in infinite chains by bridging F atoms. The geometry of the XeO₃ moiety is very similar to that of XeO₃ itself, as may be seen from the representation of the xenon coordination group in Figure 3.4.6.

Figure 3.4.6.
The Xenon Coordination Geometry in KXeO₃F

Angles

₀Xe-O₂ 101.1(8)°
₀Xe-O₂ 97.8(7)°
₀Xe-O₃ 100.5(1.2)°
₀Xe-F₂ 85.3(5)°
₀₂Xe-F₁ 77.2(6)°
F₂-Xe-F₁ 98.7(2)°
₀₁Xe-F₁ 87.6(1.1)°
₀₁Xe-F₂ 85.8(1)°
The xenon first coordination sphere is a grossly distorted square based pyramid with one of the O-ligands apical. To a first approximation the F-ligands are $F^-$ species -- the Xe-F bonds are certainly much longer and (from the infrared evidence) weaker than in the fluorides. Presumably the non-bonding-valence-electron-pair occupies the sixth apical position of the pseudo-octahedral complex. The $F^-$ ligands presumably lower the positive Xe charge and lower its polarizing power - so enhancing the stability of the XeO$_3$ group.

Since the infrared spectrum of the chloro-xenate shows some similarities to those of the fluoro-xenates (818(s), 793(s), 766(m), 749(m), 663(w) and 400(m) cm$^{-1}$) the structure may be similar to that of KXeO$_3$F.

Chemical Properties. The fluoro xenates do not decompose thermally below 200° but lose substantial quantities of Xe and O$_2$ above 260°. Some samples exploded above 300°. The cesium chloro-xenate is stable to ~ 150°, and explodes at 205° in vacuo leaving CsCl. Addition of concentrated H$_2$SO$_4$ to CsXeO$_3$Cl yields Cl$_2$, chlorine oxides, O$_2$ and Xe.
3.5 Xenon (VIII) Compounds

The octafluoride of xenon is unknown and available evidence indicates that should it be preparable it will not be thermodynamically stable under ordinary conditions of temperature and pressure (see section 1.2). The trioxide difluoride and XeO₄ are the only known molecular compounds of Xe(VIII). The perxenates are the best characterized Xe(VIII) compounds and the alkali metal salts have considerable thermal stability (presumably kinetic). The pattern of known compounds of Os(VIII) with F and O- ligands is similar, OsO₄ and OsO₃F₂ being known and OsF₆, OsOF₆ and OsO₂F₄ unknown.

3.5.1 Xenon Octafluoride

Although, in an early report, a claim was made for the preparation of XeF₆, this has not been substantiated and much further work has failed to support the existence of this compound. In a thorough study of equilibria in the Xe/F₂ system Weinstock et al. found no evidence for XeF₆, even at high F₂/Xe ratios and moderate temperatures (see section 1.2).

3.5.2 Xenon Trioxide Difluoride

Xenon trioxide difluoride has been prepared by interaction of XeF₆ with solid sodium perxenate contained in a Kel-F tube. This interaction produces a larger quantity of other xenon compounds, principally XeO₄⁻. The compound was detected mass spectrometrically, XeO₃F₂⁺ being observed. Xenon tetroxide is formed in small quantities along with XeO₃F₂. These two compounds have comparable volatilities, both being sufficiently volatile at -78°C to yield characteristic
mass spectra. Since $\text{XeO}_2\text{F}_2$ is more volatile than $\text{XeO}_2\text{F}_2$ (see section 3.4.3) the former is probably symmetrical and non-polar. This indicates that the $D_{3h}$ geometry shown is probable. This would be consistent with all theoretical predictions (see section 1.3).

### 3.5.3 Other Xenon(VIII) Oxyfluorides

Although, in view of the six energetically favourable Xe-F bonds, $\text{XeOF}_6$, at first sight, appears to be a thermodynamically favourable formulation, the low enthalpy of formation of IF$_7$ from IF$_5$ for the process: $\text{IF}_5(g) + \text{F}_2(g) \rightarrow \text{IF}_7(g)$ (see section 1.2), suggests that the compound may be thermodynamically unstable and hence demanding of a special synthetic approach. No such objections apply to the $\text{OXeF}_5^+$ ion and it may be that the parent oxyfluoride can be prepared from salts of this ion.

The oxyfluoride $\text{XeOF}_4$ may well be preparable. The $\Delta H^\circ$ may be no more unfavourable than +10 to 20 kcal mole$^{-1}$.

### 3.5.4 Xenon Tetroxide

Preparation. Xenon tetroxide was first prepared by the interaction of concentrated sulphuric acid with xenates(VIII) at room temperature. Sodium or barium perxenate($\text{Na}_4\text{XeO}_6$; $\text{Ba}_2\text{XeO}_6$), dried in a vacuum desiccator, is contained in the side-arm of an all Pyrex apparatus. It is tapped
slowly into cold (-5°) reagent grade sulphuric acid, contained in a bulb below the side-arm. With care an approximately 34 percent yield of the tetroxide is obtained. The barium salt is more satisfactory than the sodium. The gaseous tetroxide is condensed in liquid nitrogen cooled traps as a yellow solid. If the mixing of the reactants is too fast or massive, the tetroxide decomposes with 'flashes of fire' and negligible XeO₄ yields are obtained. The tetroxide is readily purified by vacuum sublimation into a trap at -78°.

Table 3.5.1.

Physical Properties. The limited data available on XeO₄ are given in Table 3.5.1. The vapour pressure of XeO₄ is ~25mm at 0° and the volatility at -78° is sufficient to provide for mass spectrometric detection. Usually, decomposition to Xe and O₂ occurs before the sample reaches 0° and the decomposition can be violent - samples have exploded at -40°. This instability is in accord with the heat of formation, obtained by detonating several gaseous samples at ~25°: \( \Delta H^\circ (\text{XeO}_4(g) \rightarrow \text{Xe}(g) + 2\text{O}_2(g)) = -153.5 \text{ kcal mole}^{-1} \). This enthalpy indicates a mean thermochemical bond energy of 21.1 kcal, which is a little greater than the value for XeO₃.

The infrared spectrum of gaseous samples were obtained using nickel cells having either silver chloride or polyethylene windows. The findings and their interpretation are given in Table 3.5.1. The vibrational data indicate the molecule to be tetrahedral and this is borne out by the electron diffraction findings. The Xe-O stretching force constant is lower than in the case of XeOF₄, which suggests that the Xe-O bond in XeO₄ is weaker. This is supported by the bond
Table 3.5.1  

Some Physical Properties of XeO₄

The solid is yellow.

Thermochemical Features

\[ \Delta H_f^o (g) (298.15 \text{°K}): +153.5 \text{kcal(a)}; \text{mean thermochemical bond energy: 21.1 kcal(a)} \]

Vapour pressure, mm (°C) (b): 3(-35°), 10(-16°), 25(0°)

Vibrational spectra

<table>
<thead>
<tr>
<th>Infrared:</th>
<th>Obs.(b)</th>
<th>Calc.(c)</th>
</tr>
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<tbody>
<tr>
<td>( \nu_1 )</td>
<td></td>
<td>906</td>
</tr>
<tr>
<td>Supports T₄</td>
<td>( \nu_2 )</td>
<td>301</td>
</tr>
<tr>
<td>symmetry(b)(c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>877 (PQR)</td>
<td>876</td>
</tr>
<tr>
<td></td>
<td>870</td>
<td>885</td>
</tr>
<tr>
<td>( \nu_4 )</td>
<td>306 (PQR)</td>
<td>305</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>314</td>
</tr>
</tbody>
</table>

Urey-Bradley Force Constants(c) (mdynes Å⁻¹): K, 5.75; H, 0.10; F, 0.5; k, 0.05

Molecular Geometry

Xe-O Bond Length: P-R separation(b) yields Xe-O = 1.6Å ± 0.2

Electron diffraction(d) confirms T₄ symmetry and gives Xe-O = 1.736 ± 0.002 Å

(a) S. R. Gunn, J. Amer. Chem. Soc. 87 (1965) 2290.
length of 1.736 Å obtained from electron diffraction data, this being ~0.04 Å longer than the Xe-O bond in XeOF₄.²³⁹

Since the Xe-O bond strength in XeOF₄ appears to be greater than in XeO₄, it may be that the charge removal from the Xe atom by the 4 O- ligands in XeO₄ is less than the charge removal by the 4 F-ligands and 1 O-ligand in the oxide tetrafluoride. If each Xe-O bond involves a net charge distribution Xe⁺-O⁻ (as in Xe: → 0⁻), this would yield a central-atom charge of +4 for XeO₄ and only +3 for XeOF₄ (assuming 3 centre-4-electron bonds ½F·Xe⁺1·F⁻½). However, the ligand repulsions for the oxide would be greater than for the oxyfluoride. The chemical shift derived from the Mössbauer spectrum of XeO₄ has been interpreted¹⁵⁸ as indicative of a charge of +1.7 on the xenon atom, whereas the same authors argue that the Xe-atom positive charge in XeF₄ is +3. These values seem too disparate and the bonding assumptions upon which these numbers are based are probably at fault. (the only Xe orbitals assumed to be involved are the 5s and 5p).

Chemical Properties. Although potentially an oxidizing agent of great power, nothing has been reported on the chemical properties of the tetroxide.

Analysis and Identification. The tetroxide is probably most readily identified by its strong infrared bands at 877 and 305.7 cm⁻¹. Mass spectra²⁷⁸ show the typical isotope pattern of xenon repeated every 16 mass units up to XeO₄. Conventional analysis has been achieved²³⁸ by decomposing a sample with a spark (thermal decomposition would suffice) followed by cooling of the sample to -196° (to retain Xe), the oxygen then being measured with a Toepler pump. Subsequently, the xenon was measured in a like manner.
3.5.5 The Xenates(VIII) - 'Perxenates'

So far, attempts to prepare perxenates and other oxysalts of xenon by oxidizing Xe with powerful oxidizers in aqueous media have failed. All of the oxysalts are derived from the fluorides.

Preparation. Perxenates were first described by Malm, Holt and Bane.\(^{155}\) They found that the hydrolysis of XeF\(_6\) in strong sodium hydroxide generated Xenon gas and a precipitate of hydrated sodium perxenate. The reaction has been studied in detail\(^{151}\) and it is known that Xe(VI) is the immediate product of the hydrolysis, the formation of perxenate proceeding slowly at room temperature with initial half-times ranging from 2 to 20 hours. The reaction is catalyzed by impurities of unknown composition. The production of perxenate in these hydrolysis experiments obeys the stoichiometry represented in the equation.

\[
2\text{XeF}_6 + 4\text{Na}^+ + 16\text{OH}^- \rightarrow \text{Na}_4\text{XeO}_6 + \text{Xe} + O_2 + 12\text{F}^- + 8\text{H}_2\text{O}
\]

Evidently, the disproportionation of pure XeO\(_3\) solution in base is much slower\(^{151}\) and it is claimed\(^{170}\) that only \(\sim 33\%\) yields of perxenate are obtained over a NaOH range of 0.25 to 4.2 M and a KOH range of 2 to 3.6 M. It seems that high perxenate concentrations suppress the disproportionation\(^{235}\) but high [OH\(^-\)] concentrations lead to yields of Xe(VIII) in excess of 50%. This implies that a xenon species of oxidation state lower than Xe(VI) is contributing to the oxidation of XeO\(_3\) to perxenate (see section 3.4.5 for a fuller discussion of XeO\(_3\) disproportionation).
The most efficient synthesis of perxenate is provided by ozonizing a pure XeO$_3$ solution in 1 M NaOH. Since the solubility of sodium perxenate in water is only \~0.025M the salt precipitates out nearly quantitatively. Washing with a little cold water readily removes excess base. The salt is a white crystalline powder which may contain from 0.6 to 9 molecules H$_2$O per xenon atom depending on the drying procedure. The preparation of the potassium salt, K$_4$XeO$_6$. H$_2$O, requires greater care, since a mixed valence product K$_4$XeO$_6$.2XeO$_3$ readily precipitates.

Physical Properties. The perxenates are colourless, thermally stable solids. The hydrated sodium salt becomes anhydrous at 100° and decomposes abruptly at 360° and the barium salt decomposes at \~300°. The latter is almost insoluble in water a saturated solution at \~25° being only 2.3 x 10$^{-5}$ M. The solubility of the perxenates decreases in the sequence Na$^+$ > Li(1.0 x 10$^{-3}$M) > Am$^3+(6.1 x 10^{-5}$M) > Ba$^{2+}$(2.3 x 10$^{-5}$). Solutions of the alkali salts are strongly basic, the pH corresponding approximately to the liberation of 1 mole of OH$^-$ per mole of the compound dissolved:

$$\text{Na}_4\text{XeO}_{6} + \text{H}_2\text{O} \rightarrow \text{HXeO}_6^{3-} + \text{OH}^- + 4\text{Na}^+$$

The ultraviolet spectra of the perxenate solutions are pH dependent. Isobestic points at 220 and 270 m$\mu$ indicate that two principle species contribute to the spectra. Potentiometric titrations suggest the following equilibria:

$$\text{HXeO}_6^{3-} + \text{H}^+ \leftrightarrow \text{H}_2\text{XeO}_6^{2-} \quad (pK_A \sim 10.5)$$

$$\text{H}_2\text{XeO}_6^{2-} + \text{H}^+ \leftrightarrow \text{H}_3\text{XeO}_6^- \quad (pK_A \sim 6)$$
### Table 3.5.2

Some Physical Properties of Perxenates

<table>
<thead>
<tr>
<th>Crystallographic Data</th>
<th>( \text{Na}_4\text{XeO}_6 \cdot 6\text{H}_2\text{O} ) (a)</th>
<th>( \text{Na}_4\text{XeO}_6 \cdot 8\text{H}_2\text{O} ) (b) (c)</th>
<th>( \text{K}_4\text{XeO}_6 \cdot 9\text{H}_2\text{O} ) (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Space group</strong></td>
<td>Pbca</td>
<td>Pbcn</td>
<td>Pbc21</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>18.44 ± 1</td>
<td>11.864 ± 5</td>
<td>9.049 ± 4</td>
</tr>
<tr>
<td><strong>b</strong></td>
<td>10.103 ± 7</td>
<td>10.426 ± 5</td>
<td>10.924 ± 4</td>
</tr>
<tr>
<td><strong>c</strong></td>
<td>5.873 ± 5</td>
<td>10.358 ± 5</td>
<td>15.606 ± 6</td>
</tr>
<tr>
<td><strong>( d_{\text{X-ray}} ) (g cm(^{-3}))</strong></td>
<td>2.59</td>
<td>2.33 ± 5</td>
<td>2.35</td>
</tr>
<tr>
<td><strong>( d_{\text{measured}} )</strong></td>
<td>&gt; 2.17</td>
<td>2.38</td>
<td>---</td>
</tr>
<tr>
<td><strong>z</strong></td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>Xe-O (Å)</strong></td>
<td>(2) 1.86 (2)</td>
<td>(2) 1.88 (1)</td>
<td>1.86 (1)</td>
</tr>
<tr>
<td><strong>av. 1.840 (s)</strong></td>
<td>(2) 1.87 (2)</td>
<td>(2) 1.85 (1)</td>
<td></td>
</tr>
<tr>
<td><strong>Xe-O-Xe-O</strong></td>
<td>89 (1)°</td>
<td>89.3 (8)°</td>
<td>88.8 to 91.2 (7)°</td>
</tr>
<tr>
<td></td>
<td>87 (1)</td>
<td>89.0 (8)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>88 (1)</td>
<td>87.4 (8)</td>
<td></td>
</tr>
</tbody>
</table>

(See Figure 3.5.1)

<table>
<thead>
<tr>
<th>Vibrational Data(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8 M cesium perxenate solution:</td>
</tr>
<tr>
<td>Raman bands (cm(^{-1}))</td>
</tr>
<tr>
<td>Infrared bands (cm(^{-1}))</td>
</tr>
<tr>
<td>( \text{Na}_4\text{XeO}_6 \cdot 0.4\text{H}_2\text{O} ) (solid):</td>
</tr>
<tr>
<td>Raman bands (cm(^{-1}))</td>
</tr>
</tbody>
</table>

Oxidation Potentials(f)

Xe(VIII) - Xe(VI), Acid: 3.0 V; Base: 0.9 V.
Table 3.5.2

References

(a) A. Zalkin, J. D. Forrester and D. H. Templeton, Inorg. Chem. 3 (1964) 1417.
Figure 3.5.1

The Crystal Structure of Na₄XeO₆·6H₂O †

†Reproduced with permission from A. Zalkin, J. D. Forrester and D. H. Templeton, Inorg. Chem. 3 (1964) 1417.
$\text{Na}_2(\text{H}_2\text{O})_6^{++}$ Layer in $\text{Na}_4\text{XeO}_6 \cdot 6\text{H}_2\text{O}$
$\text{Na}_2\text{XeO}_6$ Layer
In $\text{Na}_4\text{XeO}_6 \cdot 6\text{H}_2\text{O}$
The interpretation of the solution properties is also complicated by the reduction of Xe(VIII) to Xe(VI):

\[ \text{H}_3\text{XeO}_6^- \rightarrow \text{HXeO}_4^- + 0.5\text{O}_2 + \text{H}_2\text{O} \]

This decomposition is more rapid the lower the pH.

Table 3.5.2
Figure 3.5.1
The crystal structures of several perxenates, including a hexahydrate, octahydrate and a nonahydrate have been determined and the findings are summarized in Table 3.5.2.

The structure of Na₄XeO₆·6H₂O is shown in Figure 3.5.1. The perxenate ion is seen to be octahedral. Much of the water in the hydrates is coordinated to the cations but the perxenate oxygen ligands are also hydrogen bonded to water molecules.

The Xe-O bond length, 1.84-1.88Å is slightly shorter than the Xe-F bond in XeF₆ (1.89Å) and much longer than in XeO₄ (1.74Å) and XeO₃ (1.76Å). As may be seen in Table 1.2.3, the size and shape of the perxenate ion is what one would have anticipated on the basis of the data for antimonates(V), tellurates(VI) and periodates.

The vibrational spectra of aqueous solutions of the perxenates suggest that a high concentration of symmetrical XeO₆⁴⁻ ions occurs in the concentrated (1.8 M cesium perxenate) solutions, but certain details imply the presence of other ionic forms. The vibrational spectra are included in Table 5.3.2. The intense highly polarized Raman band at 685 cm⁻¹ in the solution spectrum is very close to the 683 cm⁻¹ band in the solid Na₄XeO₆·0.4H₂O. It is very probably the totally symmetrical octahedral \( \nu_1 \) band. This stretching frequency
is compatible with the Xe-O bond length and is suggestive of a slightly stronger (intrinsic) bond than the Xe-F bond in XeF$_6$.

**Bonding and Bond Polarity.** The Mössbauer spectra of the perxenates imply chemical shifts which are very close to that of XeO$_4^{2-}$ and the derived Xe positive charge is indistinguishable from that obtained for the Xe-atom in XeO$_4$.

The bonding in XeO$_6^{4-}$ can be dealt with in terms of the Rundle-Pimentel theory, which in its simplest form represents the ion in terms of three 3-centre-4-electron bonds involving (formally) Xe$^{2+}$ (configuration 5s$^0$ 5p$^6$) and 6 0$^-$ components, each 3-centre-4-electron bond arising from a linear array (see Figure 1.3.2):

\[ \text{0} \quad \text{Xe}^{2+} \quad \text{0}^- \]

The high bond polarity of this model accounts for the greater intrinsic bond strength of Xe-O in [XeO$_6$]$^{4-}$ relative to XeF in Xe-F$_6$.

Alternatively, if d orbitals are involved in the bonding, the ion can be represented as an sp$^3$d$_2$ hybrid system, each Xe-O bond involving one bonding electron pair. In molecular orbital terms, this implies the involvement of two Xe 5d orbitals in generating 2 e$_g$ orbitals, by the agency of a ligand field effect. The simplest m.o. scheme would be as shown in Figure 3.5.2. There is, of course, no proof that Xe 5d orbitals are involved in the bonding.

Figure 3.5.2.
Figure 3.5.2.

A Simple Molecular Orbital Scheme for XeO$_6^{4-}$ involving Xe 5d orbitals
Chemical Properties. Perxenate solutions are powerful and rapid oxidizing agents, the Xe(VIII) being reduced to Xe(VI). Iodide is oxidized to I₂, even in 1M base. Similarly Br⁻ is oxidized to Br₂ at pH 9 or less and Cl⁻ to Cl₂ in dilute acid. Also in dilute acid perxenate immediately converts Mn²⁺ to MnO₄⁻. Iodate is oxidized to IO₄⁻ and Co(II) to Co(III) in base as well as acid. It should be noted that the oxidations in acid, to be effective, must be fast enough to compete with the rapid evolution of oxygen.

Americium perxenate, Am₄⁺(XeO₆)₃·4O H₂O, prepared from basic solutions of Am(III) is of low solubility in water (4.6 x 10⁻⁵ M) but it dissolves in acid to form Am(VI) and Am(V) solutions. Up to 80% Am(VI) has been obtained by this technique. The formal oxidation potentials for Am(III) - Am(VI) and Am(V) are, respectively, 1.75 and 1.83 V.

Analysis. It is evidently characteristic of perxenate that rapid decomposition to Xe(VI) occurs in acid media. Thus, if a solution of perxenate is first acidified, then iodide is added, only six equivalents of oxidizing power per mole of xenon are measured as iodine liberated. If iodide is added before the acid all eight oxidizing equivalents are measured. This can be useful in assessing the Xe(VI) impurity in a sample of perxenate. The iodine liberated is determined using thiosulphate according to standard procedures.
4. Radon Chemistry

4.1 Introduction

Prior to 1962, when Fields, Stein and Zirin reported a fluoride\textsuperscript{285}, there was no evidence for a true compound of radon, although the low first ionization potential (10.75 eV), hinted at chemical activity. In their pioneering work on radon, Ramsay and Soddy demonstrated\textsuperscript{286} that it did not react with metals and a large number of other substances. Nikitin was able\textsuperscript{287} to prepare clathrates of radon, including hydrogen chloride, hydrogen bromide and hydrogen sulphide clathrates and he was thus able to separate radon from helium and neon.

Unfortunately, there are no stable isotopes of radon and the longest lived 'natural' isotope, $^{222}\text{Rn}$, has a half-life of only 3.83 days. This isotope is derived from the decay of $^{226}\text{Ra}$ (usually in chloride solutions). Experimental difficulties arise not only from the radiation hazard, but also from radiation decomposition of the reagents employed in the studies. The latter factor rules out the utility of large-scale experimentation (even allowing that large quantities of $^{222}\text{Rn}$ could be collected).

4.2. Compounds of Radon

Since the Xe-F bond energy (32 kcal in all 3 fluorides) is much greater than that of Kr-F in KrF$_2$ (~12 kcal) and this follows the trend observed in the fluorides of the other groups (see section 1.2.3), we anticipate the Rn-F bond to be at least as energetic as that of Xe-F. It also appears likely that chlorides and oxides (RnCl$_2$, RnO$_2$, RnO$_3$, RnO$_4$ etc.) would be thermodynamically more stable than in the case of their xenon counterparts. Evidently\textsuperscript{288} however, radon, like astatine, is markedly more metallic than the element above it in its group.
So far, there is evidence only for a fluoride and attempts to prepare chlorides and oxides, directly and from the fluoride, have failed. A claim for the oxidation of Rn by strong aqueous oxidizers has been refuted and efforts to oxidize Rn with ozone and with sodium perxenate in aqueous media have failed to 'fix' the gas.

4.2.1. Radon Fluorides - RnF₂ (?)

In their initial reports, Stein and his coworkers established that Rn combines with fluorine at 400° to give a compound of low volatility which is reduced by hydrogen only at temperatures above 200°. More recent work has shown that Rn interacts spontaneously with fluorine and all of the stable interhalogen fluorides (e.g. 2BrF₃ + 3Rn → Br₂ + 3RnF₂(?)) except IF₅ and is even oxidized by the [NiF₆]²⁻ ion. In these experiments, gaseous Rn from a 5-curie radium chloride solution, dried by passing through a column of calcium sulphate and purified by distillation at -78° (to remove radiolytic hydrogen and oxygen), was condensed onto the various reagents held in Kel-F tubes. The mixtures were agitated at room temperature, for an hour or so, after which the Rn was found to be in the liquid phase. Removal of the excess reagent (BrF₅ or BrF₃ or ClF₃) in a vacuum at room temperature yielded, in all cases, a white solid containing all of the activity. All of the solids appear to be the same material, and to be identical to the fluoride prepared earlier.

Since the fluoride interacts with water without generating radon oxides and leaves little Rn activity in the aqueous phase it is probable that the compound is RnF₂: RnF₂ + H₂O → Rn + ½O₂ + 2HF. From the observation that AsF₅ will not oxidize Rn, whereas BrF₃ will, the standard free energy of formation of RnF₂ has been set between the limits of -29 and -51 kcal mole⁻¹.
Stein and his coworkers have shown that the fluoride decomposes above 250° in a vacuum. Evidently, the radon fluoride does not vapourise as a molecular species. Electromigration studies of the radon fluoride dissolved in bromine trifluoride or anhydrous hydrogen fluoride have established that the radon is present as a cation. The species RnF⁺ and Rn₂F₃⁺ would seem more reasonable than Rn²⁺. Presumably, the fluoride is ionic - both Rn²⁺(F⁻)₂ and RnF⁺(F⁻) are consistent with the known properties.

Although complex salts containing RnF⁺, Rn₂F₃⁺ or even Rn²⁺ appear feasible there is no evidence for such compounds at this stage. So far, no effort has been made to oxidize Rn with the more powerfully oxidizing hexafluorides. Since I(Rn) = 10.75, whereas I(Xe) = 12.1 eV, it is obvious that PtF₆ should oxidize Rn (See section 3.1.2) and it seems likely that IrF₆ and possibly OsF₆ could also oxidize the gas spontaneously at ordinary temperatures.

Some Practical Applications. The formation of radon compounds provides for the metering and location of the gamma radiation source, radon, at a specific site by bringing it into chemical interaction with fluorine, a halogen fluoride, or platinum hexafluoride. Thus, the Rn activity can be readily transferred to some ideal location, then 'fixed'. Removal of the 'fixed' Rn from the chosen site may be achieved by reduction (or hydrolysis). Encapsulated, involatile Rn compounds may replace the radon "seeds" or needles presently in medical use.

Radon occasionally produces hazardous radiation levels in uranium mines. It is feasible that this problem can be overcome by circulating the air through bubblers or packed towers containing oxidizing agents.
The Chemistry of Krypton, Xenon and Radon

Text References


35. See reference 20 pages 133-224.


62. R. H. Herber as in ref 55, pp. 1-42.
76a. See reference 195.
79. S. Siegel and E. Gebert, J. Amer. Chem. Soc. 86 (1964) 3896.
84. V. A. Iogasov, V. M. Prusakov, B. B. Chaiyevov, Russ. J. of
Phys. Ch., 42 (1968) 610.
86. N. Bartlett, M. Wechsberg, F. O. Sladky, P. A. Bulliner, G. R. Jones and
(A) (1960) 2179.
89. J. L. Weck, C. L. Chernick and M. S. Matheson, J. Amer. Chem.
Soc. 84 (1962) 4612.
324 (1963) 214.
28 (1966) 909.
98. N. Bartlett and D. F. McKee, unpublished observation.
102. F. Schreiner, C. N. McDonald and C. L. Chernick, J. Phys. Chem. 62
(1965) 1434.
112. See reference 14 page 39.
113. See reference 14 page 101.
114. See reference 14 page 295.
115. See reference 14 page 304.
118. See reference 14 page 211.
121. See reference 14 page 251.
122. See reference 14 page 263.
124. See reference 14 page 279.


128. See reference 14 page 358.


137. H. Meinert and S. Rüdiger, Z. Chem. 7 (1967) 239.


140. See reference 14, page 275.


154. B. Jaselskis, Science 146 (1964) 263.
156. H. Meinert, Z. Chem. 6 (1966) 71.
175. See reference 14, page 81.
180. See reference 14, page 287.
182. See reference 14, page 238.
189. See reference 14, p. 158.
191. See reference 14, p. 73.
192. See reference 14, p. 144.
193. N. Bartlett, Endeavour XXII (1964) 3.
194. A. Iskraut, R. Taubenest and E. Schumacher, Chimia 18 (1964) 188.
195. J. Berkowitz, Argonne National Laboratory, personal communication.
196. N. Bartlett and N. K. Jha, unpublished observation.
201. See reference 14, p. 64.
210. See reference 14, p. 68.
235. See reference 14, p. 106.
236. See reference 14, p. 50.
245. See reference 168, Volume III.
248. See reference 14, p. 149.
249. See reference 14, p. 229.


291. See reference 14 p. 113.

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