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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 Mendeleev.[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 Mendeleev'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 promptlv 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[7], 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).[8] 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[9]; von Antropoff (1932-33) examined krypton/chlorine or bromine mixtures.[10] 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[4] in 1933, from considerations of ionic radii, that XeF_6, KrF_6 and perxenates should be preparable and at his suggestion an attempt[11] was made to synthesize a xenon fluoride. The attempt failed. Ironically a similar experiment,[12] 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[13] an oxyfluoride of platinum which proved to be the salt $O_2^+[PtF_6]^-$. This formulation implied that platinum hexafluoride was capable of oxidizing molecular oxygen, $O_{2(g)} + PtF_{6(g)} \longrightarrow O_2[PtF_6]^-_{(c)}$, 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 (e.g. XeO_4), +6(e.g. XeF_6) +4(e.g. XeF_4) and +2(e.g. XeF_2).[15,16]

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 (Rn, Xe or Kr) with electronegative ligands (e.g. F, O, OSO_2F, etc.). Here we see the drive of the electronegative ligand towards the light noble-gas configurations (particularly that of Ne). Clearly the drive of the fluorine atom to attain the 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

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

(a) V. M. McRae, R. D. Peacock, and D. R. Russell, Chem. Communs., (1969) 62.

(b) F. O. Sladky, P. A. Bulliner, and N. Bartlett, J. Chem. Soc., (1969) 2179.

(c) L. G. Cole, and G. W. Elverum, Jr., J. Chem. Phys., 20 (1952) 1543.

(d) R. A. Durie, Proc. Roy. Soc., A207 (1951) 388.

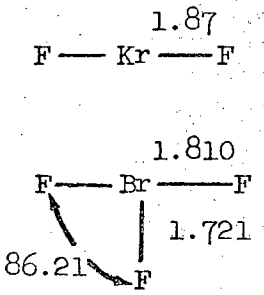
(e) G. R. Somayajula, J. Chem. Phys. 33 (1960) 1541.

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_2 or KrF_2, must be very like the bonding of two fluorine atoms to the halogen atom of halogen monofluoride: ($Cl(Br,I)F + 2F \rightarrow Cl(Br,I)F_3$). Certainly the approximately linear part of the T shaped BrF_3 molecule resembles the KrF_2 molecule as Table 1.2.2 shows.

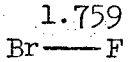
Table 1.2.2

Structural Comparison of KrF_2 with BrF and BrF_3
(distances in Å units)



C. Murchinson, S. Reichman, D. Anderson, J. Overend, and F. Schreiner, J. Amer. Chem. Soc., 90 (1968) 5690.

D. W. Magnuson, J. Chem. Phys. 27 (1957) 223.



D. F. Smith, M. Tidwell, and D. V. P. Williams, Phys. Rev. 77 (1950) 420.

The unique bond in BrF_3 is short, like the bond in the Br–F molecule. Undoubtedly, the KrF bond in KrF^+ like XeF^+ will be shorter than in KrF_2 and should resemble the Br–F molecule bond.

The XeF_4 molecule, which is square planar,[17] is similar to the approximately square IF_4 group in the IF_5 molecule[18].

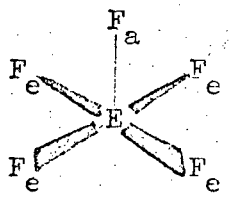
Presumably IF_4^-, like BrF_4^-, is also of D_{4h} geometry. The well characterized isoelectronic species XeF_5^+, IF_5 and TeF_5^- are very similar in shape, the bond lengths showing a decrease with increase in the atomic number (nuclear charge) of the central atom. The details are

Table 1.2.3

Comparison of Xenon Compounds with Related Molecules

(Internuclear Distances in Å Units)

EF_5 (C_{4v} symmetry)



	TeF_5^- (a)	IF_5 (c)	XeF_5^+ (b)
E - F_a	1.84	1.86	1.81
E - F_e	1.94	1.89	1.88
F_a - E - F_e(°)	79	~ 81	79

EO_4 (T_d symmetry)

	IO_4^- (d)	XeO_4 (e)
E-O	1.79	1.74

EO_3 (C_{3v} symmetry)

	IO_3^- (f)	XeO_3 (g)
E-O	1.82	1.76
O-E-O(°)	97	103

EO_6 (O_h symmetry)

	$[SbO_6]$ (h)	$[TeO_6]$ (i)	$[IO_6]$ (j)	$[XeO_6]$ (k)
E-O	1.97	1.83-1.95	1.93	1.86

References Table 1.2.3

(a) A. J. Edwards and M. A. Mouty, J. Chem. Soc., A (1969) 703.

(b) N. Bartlett, F. Einstein, D. F. Stewart, and J. Trotter, J. Chem. Soc., A (1967) 1190.

(c) G. R. Jones, R. D. Burbank, and N. Bartlett, Inorg. Chem., in press.

(d) R.W.G. Wyckoff, "Crystal Structures," Vol. 3, Interscience, New York, 1964.

(e) G. Gunderson, K. Hedberg, and J. L. Huston, Acta Cryst., A 25 S3 (1969) 124.

(f) B. S. Garrett, Report 1745,97. Oak Ridge National Lab., 1954; Structure Reports 18 (1954) 393.

(g) D. H. Templeton, A. Zalkin, J. D. Forrester, and S. M. Williamson in "Noble Gas Compounds," H. H. Hyman, Ed., The University of Chicago Press., Chicago and London, (1963) pp 229-237.

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

(i) S. Raman, Inorg. Chem., 3 (1964) 634.

(j) A. F. Wells, 'Structural Inorganic Chemistry' Third Edition, Oxford University Press, Oxford, 1962, p 335.

(k) J. Ibers, W. C. Hamilton, and D. R. MacKenzie, Inorg. Chem. 3 (1964)1412; A. Zalkin, J. D. Forrester, D. H. Templeton, S. M. Williamson, and C. W. Koch, J. Amer. Chem. Soc., 86 (1964) 3569; A. Zalkin, J. D. Forrester and D. H. Templeton, Inorg. Chem. 3 (1964) 1417.

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.

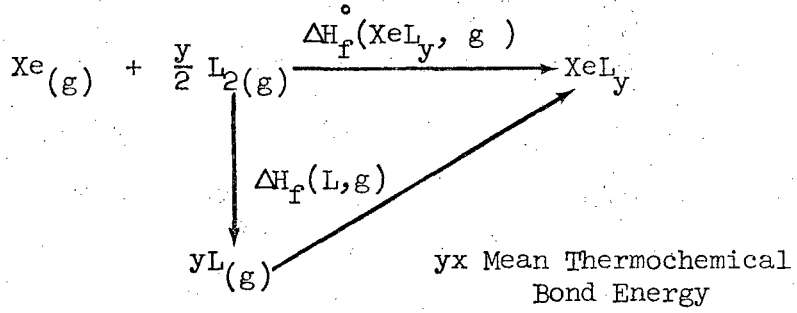
Table 1.2.3

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:



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.[20] 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})

Bond Energies

$SnCl_4$[a]	$SbCl_5$[a]			
75	61			
$SnCl_2$[b]	$SbCl_3$[a]	$TeCl_4$[a],[c],[d]		
90	75	56		
		$TeCl_2$	ICl_3[e]	
			<47	
			ICl[e]	$XeCl_2$
			58	<32 est.

Dissociation Energies[f]

GeO	AsO	SeO	BrO	KrO
158	115	101	56	<1
SnO	SbO	TeO	IO	XeO
127	89	81	47	9

*Lines connect molecules of related geometry.

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

(b) L. Brewer, G. R. Somoyajula, and E. Brackett, Chem. Revs., 63 (1963) p 111-121.

(c) K. J. Frederick, and J. H. Hildebrand, J. Amer. Chem. Soc., 60 (1938) 2522.

(d) J. H. Simons, J. Amer. Chem. Soc., 52 (1930) 3490.

(e) R. H. Lamoreaux, and W. F. Giauque, J. Phys. Chem., 73(1969) 755.

(f) L. Brewer, and G. M. Rosenblatt, Advances in High Temperature Chemistry, Vol. 2, Academic Press, Inc., New York, 1969, pp. 1-83.

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 (~ 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.

(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, 82; IF_5, 64; 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*

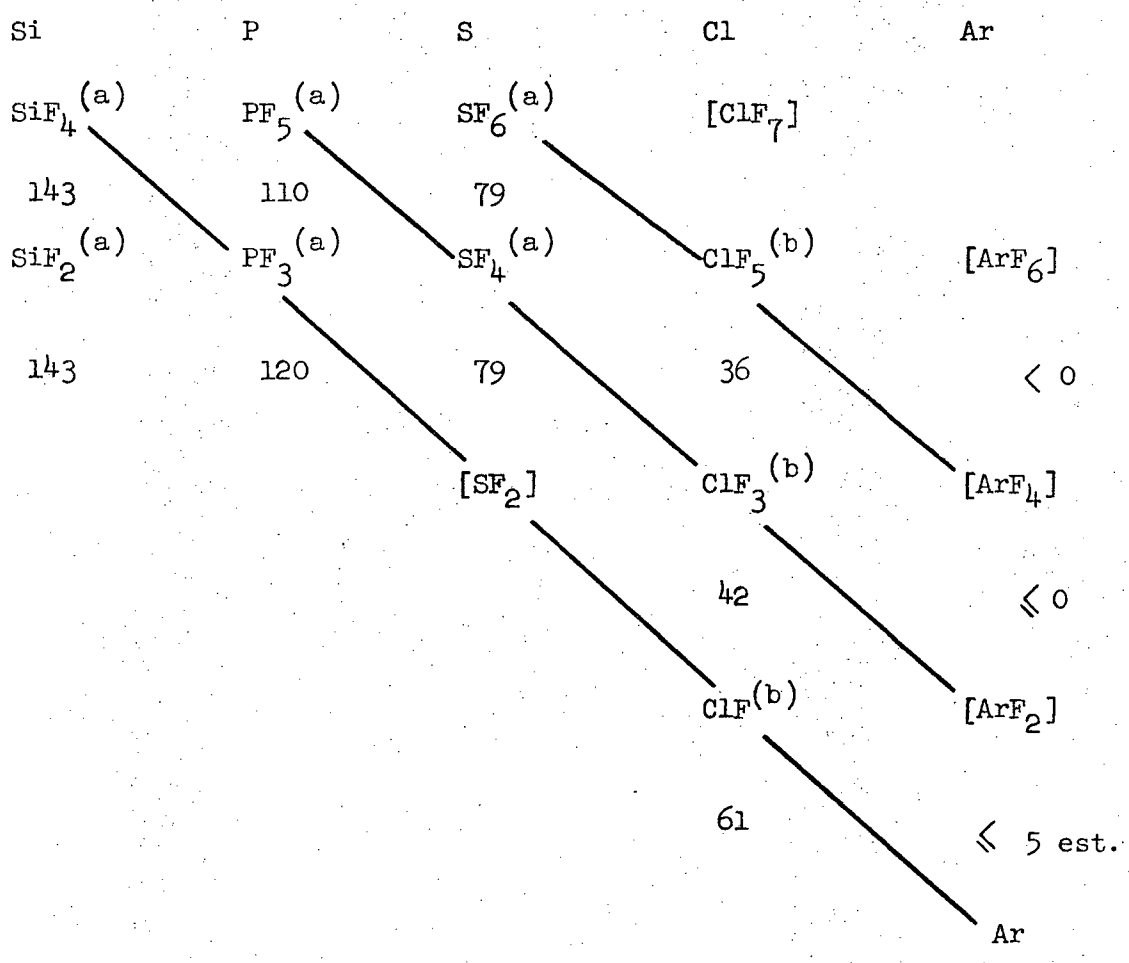


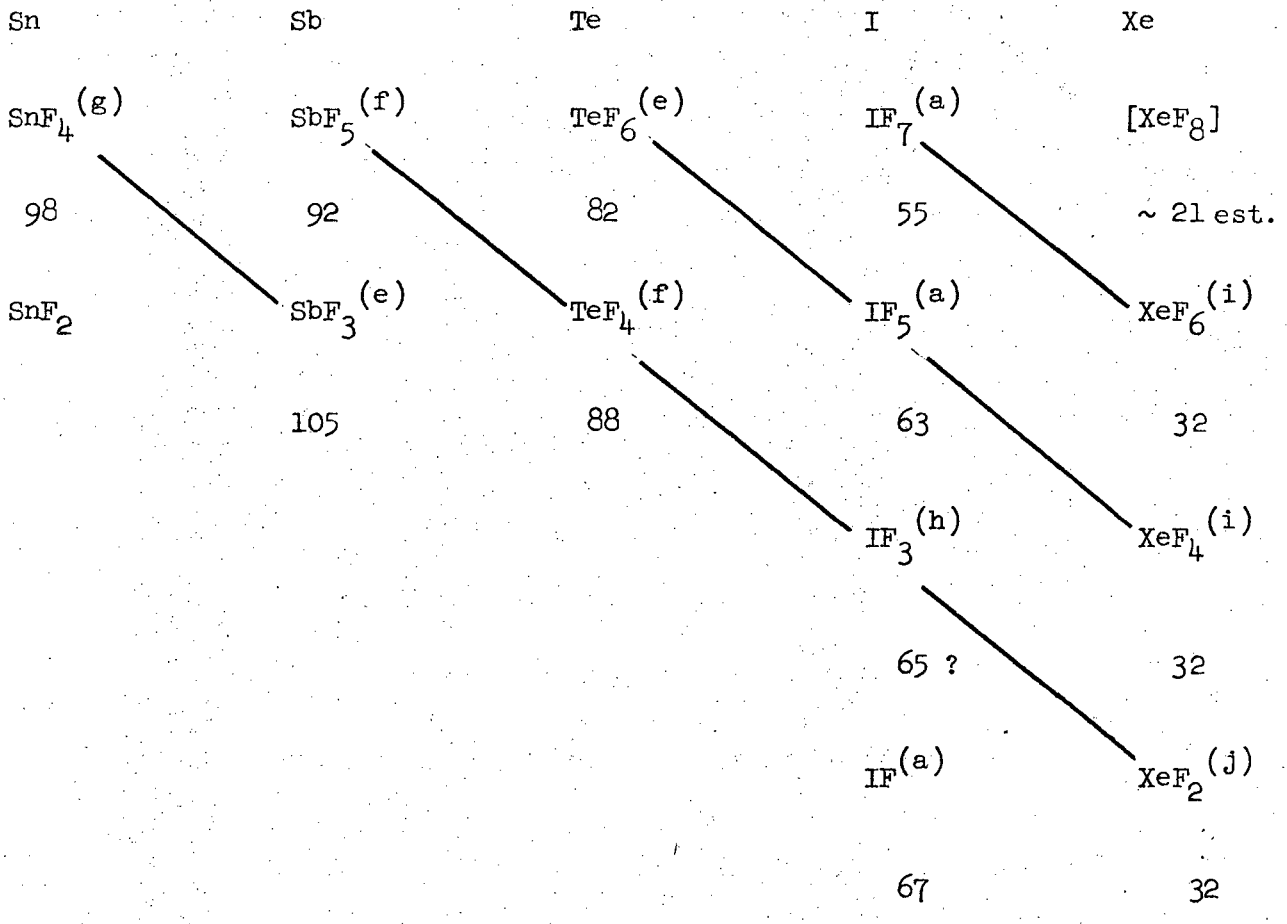
Table 1.2.5

(Mean Thermochemical Bond Energies (kcal $mole^{-1}$) for Noble-Gas Fluorides and Related Fluorides*)

Ge	As	Se	Br	Kr
GeF_4 (c)	AsF_5 (d)	SeF_6 (e)	$[BrF_7]$	
112	92	72		
GeF_2 (c)	AsF_3 (e)	SeF_4 (f)	BrF_5 (e)	$[KrF_6]$
113	116	76	45	$\leqslant$ 9 est.
		$[SeF_2]$	BrF_3 (e)	$[KrF_4]$
			48	$\leqslant$ 9 est.
			BrF (e)	KrF_2 (k)
			60	12

Table 1.2.5

(Mean Thermochemical Bond Energies (kcal mole^{-1}) for Noble-Gas Fluorides and Related Fluorides*)



*Geometrically related molecular species are cross-linked

Table 1.2. 5

References

(a) JANAF Thermochemical Data, The Dow Chemical Company, Midland, Michigan. U.S.A., (1969).

(b) National Bureau of Standards Report 10074 (July 1969).

(c) P. A. G. O'Hare, J. Johnson, B. Klamecki, M. Mulvihill and W. N. Hubbard, J. Chem. Thermodyn., 1 (1969) 177.

(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)

(f) M. Nichols, Ph.D. Thesis, University of Durham, 1958.

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

(h) L. Stein in Halogen Chemistry, V. Gutmann, ed., Academic Press, London and New York, (1967) Vol. 1, pp. 133-224.

(i) L. Stein and P. L. Plurien, in "Noble Gas Compounds," H. H. Hyman, Ed., The University of Chicago Press, Chicago and London (1963) p. 144.

(j) V. I. Pepekin, Yu. A. Lebedev, A. Apin, Zh. Fiz. Khim. 43 (1969) 1564.

(k) S. R. Gunn, J. Amer. Chem. Soc., 88 (1966) 5924; J. Phys. Chem., 71 (1967) 2934.

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[21] 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:

XeF_2	XeF_4	XeF_6
ΔS°_f - 26.5	-61	-96

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:

$$\Delta H_1 \left(Xe_{(g)} + 2F_{(g)} \longrightarrow XeF_{2(g)}\right) = -65 \text{ kcal mole}^{-1}$$

$$\Delta H_2 \left(XeF_{2(g)} + 2F_{(g)} \longrightarrow XeF_{4(g)}\right) = -61 \text{ kcal mole}^{-1}$$

$$\Delta H_3 \left(XeF_{4(g)} + 2F_{(g)} \longrightarrow XeF_{6(g)}\right) = -55 \text{ kcal mole}^{-1}$$

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 $ClF \rightarrow ClF_5$ involves approximately the same energy:

$$\Delta H_1 \left(ClF_{(g)} + 2F_{(g)} \longrightarrow ClF_{3(g)}\right) = -64 \text{ kcal mole}^{-1}$$

$$\Delta H_2 \left(ClF_{3(g)} + 2F_{(g)} \longrightarrow ClF_{5(g)}\right) = -56 \text{ kcal mole}^{-1}$$

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

$$\Delta H \left(Cl_{(g)} + F_{(g)} \longrightarrow ClF_{(g)}\right) = -61 \text{ kcal mole}^{-1}.$$

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 $BrF \longrightarrow BrF_5$.

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 XeF^+, KrF^+, ArF^+ etc., should also show stronger bonding than the neutral fluorides. This is so for XeF^+, where the bond energy is ca. 47 kcal $mole^{-1}$ (see 3.2.1.), in contrast to the mean bond energy in XeF_2 of 32 kcal $mole^{-1}$. The KrF^+ bond energy must certainly be greater than 12 kcal $mole^{-1}$ and it is argued that ArF^+ should also be a bound species.[22a] It should be appreciated, however, that the ArF^+ bond is unlikely to be as strong as the bond in its isoelectronic relative ClF. Unfortunately, the enormous electron affinity of the 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.: IF, 67; IF_3, 65(est.); IF_5, 63 kcal $mole^{-1}$) is much less dramatic than in the chlorine and bromine series, but there is a sharp decline with IF_7 (T.B.E. 55 kcal $mole^{-1}$). This represents an enthalpy change for the process:

$$IF_{5(g)} + {}^{2}F_{(g)} \longrightarrow IF_{7(g)} \quad = \quad -65 \text{ kcal mole}^{-1}$$

which contrasts with ΔH, for each previous fluorine ligand pair addition, of ca. 125 kcal $mole^{-1}$. It may be that this lower enthalpy derives in part from the ligand crowding in molecular IF_7. If so, we can be certain that the steric inhibition to 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 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[24] indicate the $5p \longrightarrow 5d$ 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 ~ 1100 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[28] ~ 160 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,[26] and recent work [25] suggests that outer orbitals may play a major role in the bonding, at least in the higher noble-gas oxidation states.[27]

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[29] 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^2sp^3 tungsten atom orbital hybridization (or its equivalent) is assumed for the σ bonds - π bonding involving the other d orbitals may also be admitted. Similarly, rhenium heptafluoride is assumed to involve d^3sp^3 rhenium σ orbital hybridization. Also, osmium tetroxide may be described in terms of four σ orbitals involving osmium sp^3 hybrids, plus π 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 [30] 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

Molecule	WF_6	TeF_6	ReF_7	IF_7	OsO_4	XeO_4
Symmetry	O_h [a]		D_{5h} + ? C_{2v}, C_s [b,c]		T_d [d]	
E-L (Å units)	1.833 [e]	1.83 [f]	---	1.825 [b]	1.74 [g]	1.74 [h]
f_r (mdyn/Å)	5.1 [i]	5.01 [j]	---	3-4 [k]	7.14 [d]	5.75 [d]
ν_1 (cm^{-1})	769 [a]	701 [a]	736 [e]	676 [e]	971	906 est
T.B.E. (kcal $mole^{-1}$)	121 [m]	82 [n]	100 est	55 [o]	127 [p]	21 [q]

UCRL-19658

(a) K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley, 1963.

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

(c) E. W. Kaiser, J. S. Muenter, W. Klemperer, W. E. Falconer, and W. A. Sunder, Bell Telephone Report, 1970.

(d) W. A. Yeranos, Bull. Soc. Chim. Belges, 74 (1965) 414.

(e) M. Kimura, V. Schomaker, D. W. Smith, and B. Weinstock, J. Chem. Phys., 48 (1968) 4001.

(f) Mean of 1.84 and 1.82Å quoted respectively by L. Pauling, and L. O. Brockway, Proc. Natl. Acad. Sci., 19 (1933) 68 and H. Braune, and S. Knoke, Z. Phys. Chem., (Leipzig) B21 (1933) 297.

(g) T. Ueki, A. Zalkin, and D. H. Templeton, Acta Cryst., 19 (1965) 157.

(h) C. Gunderson, K. Hedberg, and J. L. Huston, Acta Cryst., A 25 S3 (1969) 124.

(i) H. H. Claassen, J. Chem. Phys., 30 (1959) 968.

(j) K. O. Christy, and W. Sawodny, Inorg. Chem., 6 (1967) 1783.

(k) R. K. Khanna, J. Mol. Spectrosc., 8 (1962) 134.

(l) H. H. Claassen, E. L. Casner and H. Selig, J. Chem. Phys., 49 (1968) 1803.

(m) P. A. C. O'Hare, and W. N. Hubbard, J. Phys. Chem., 70 (1966) 3353.

(n) P. A. C. O'Hare, J. L. Settle, and W. N. Hubbard, Trans. Faraday Soc., 62 (1969) 558.

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

(p) Nat. Bur. Stand. Technical Note 270-4, U. S. Department of Commerce, Washington, D.C. (May 1969).

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

unstable species, whereas both OsO_3F_2 and XeO_3F_2 are known (the latter is kinetically stable to decompostion, 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.

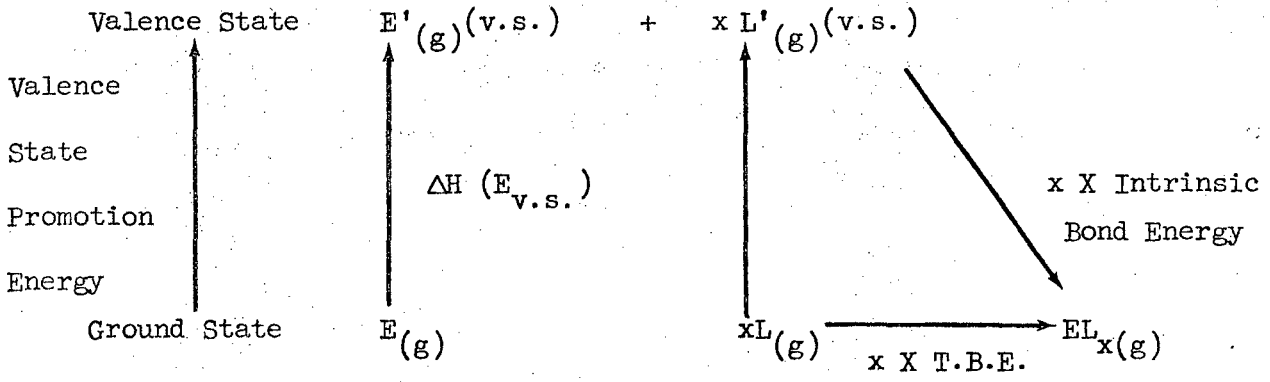
Table 1.3.1

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



the two cases. It is a reasonable assumption that a $^2\underline{P}$ 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_6 and TeF_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., $\Delta H(Te_{(g)}(\text{ground-state}) \longrightarrow Te_{(g)}(\text{valence-state}))$, exceeds the corresponding tungsten promotion by ~ 240 kcal g atom^{-1}. It is not inconceivable that this energy could represent the difference in the valence-state-promotion energies for $\underline{d}^2\underline{sp}^3$W and $\underline{sp}^3\underline{d}^2$ Te, each in an octahedral field of six fluorine ligands.

The oxides XeO_4 and OsO_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_4 formation exceeds that for OsO_4 formation by approximately 420 kcal mole^{-1}. It is possible that this derives from $\underline{d}$ (or $\underline{f}$) 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_2, 2.00Å, 2.8 mdyn/Å; XeF_4, 1.95Å, 3.02 mdyn/Å; XeF_6, 1.89Å, 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).

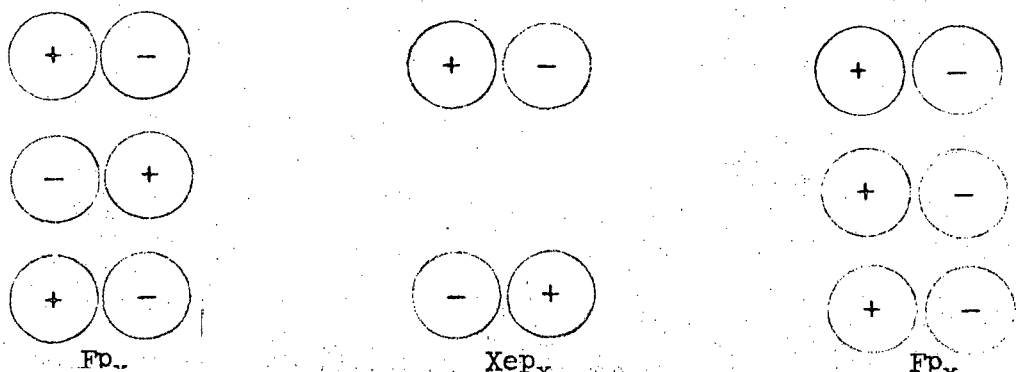
1.3.3. Bonding Without 'Outer' Noble-Gas Orbitals

There is a considerable weight of expert opinion[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.[23] In this model, XeF_2 is represented as primarily involving resonance between $F-Xe^+F^-$ and F^-Xe^+-F. This scheme preserves both classical concepts: the 'octet' and the 'electron-pair-bond.'

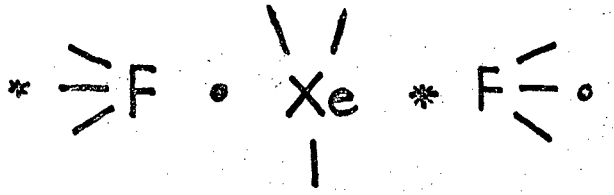
Halides. The widely accepted simple m.o. model, proposed independently by Pimentel[32] and Rundle[33], applies well to noble-gas-halides. It is of historical interest that in Pimentel's 1951 paper, which was devoted primarily to bonding in trihalide ions, he discussed the validity of his bonding scheme 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 pσ m.o.s. for XeF_2



from which they are derived. The best net bonding for the three atoms occurs when the arrangement is centro-symmetric. The observed $\underline{D_{\infty h}}$ 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 $\underline{p\sigma}$ m.o. system, the anti-bonding 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 binding has been termed 'semi-ionic'.[15] The best calculations place the net charge distribution to be close to the representation $F^{\frac{1}{2}-}Xe^{1+}F^{\frac{1}{2}-}$. 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.

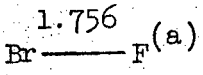
Bonding in the xenon tetrafluoride molecule may be dealt with similarly, by considering two three-centre orbitals at right angles.[33] The square planar geometry of the molecule is 'predicted' by this

Table 1.3.2.

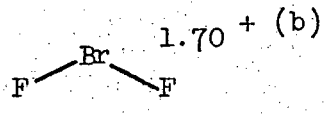
Comparison of Bond Lengths in XeF^+, XeF_2 and Bromine Fluorides

(internuclear distances in Å units)

'Electron-Pair-Bond' Species:

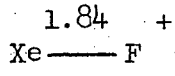


(a)



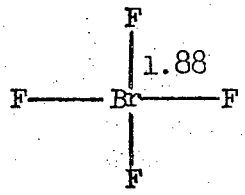
+ (b)

(C_{2v})

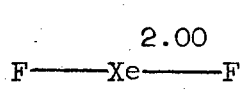


+ (c)

'Single-Electron-Bond' Species:



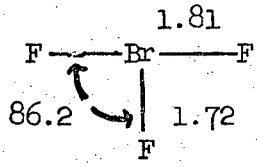
(D_{4h})



(e)

($D_{\infty h}$)

A Mixed Species:



(f)

(C_{2v})

(a) D. F. Smith, M. Tidwell, and D. V. P. Williams, Phys. Rev., 77 (1950) 420.

(b) A. J. Edwards and G. R. Jones, Chem. Commun., (1967) 1304.

(c) V. M. McRae, R. D. Peacock, and D. R. Russell, Chem. Communs., (1969) 26.

(d) W. G. Sly, and R. E. Marsh, Acta Cryst. 10 (1957) 378.

(e) S. Reichmann, and F. Schreiner, J. Chem. Phys., 51 (1969) 2355.

(f) D. W. Magnuson, J. Chem. Phys. 27 (1957) 223.

description as is the approximate charge distribution Xe^{+2} $(F^{-\frac{1}{2}})_4$. 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 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 Xe—F bond in XeF_2 to be weaker than in 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 XeF^+ to 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'

(Table 1.3.2.)

length would be represented as 1.68 - 1.76Å and the 'one-electron-bond' as 1.78 - 1.88Å. 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 XeF_2(2.00Å), XeF_4 (1.95Å), XeF_6, (1.89Å) (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.[35] There is also the possibility of greater 'outer' orbital participation of the central atom in bonding, the higher the oxidation state,[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 Xe–O bonds are shorter (XeO_3, 1.76; XeO_4, 1.74Å, see 3.4.4. and 3.5.4.) than Xe–F bonds and the Xe–O stretching force constants, e.g. $f_r(XeO_3)$ = 5.66 mdynes $Å^{-1}$ (3.4.4.), are greater than for Xe–F, e.g. $f_r(XeF_4)$ = 3.02 mdynes $Å^{-1}$ (3.3.1.), the mean thermochemical bond energy for XeO is $\leq$ 21 kcal $mole^{-1}$, which contrasts with the Xe–F value of 31 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. Xe 4f and 5d) play an insignificant role. Since the oxygen atom can receive two electrons, the simplest representation for the 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 Xe :⟶O. Of course, the appropriate valence-state of the oxygen atom for such a bond would be ^1D, which is 45.1 kcal $mole^{-1}$ above the ground ^3P state.[36] On this basis, then, the intrinsic Xe–O bond energy would be the mean thermochemical-bond-energy ($\leq$ 21 kcal $mole^{-1}$), plus the oxygen valence-state promotion energy ($\sim$ 45 kcal $mole^{-1}$), i.e., 65 kcal $mole^{-1}$, which is more in keeping with the vibrational spectroscopic data. Now the 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 $Xe^{1+} - O^{1-}$. Valence-state promotional enhancement of the bonding in the oxides may well account for the kinetic stability of XeO_3 and XeO_4.

1.3.4 Electron-Pair Repulsion Theory

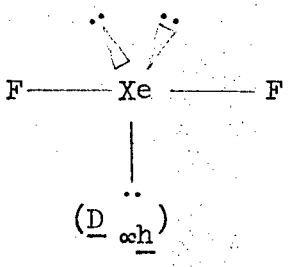
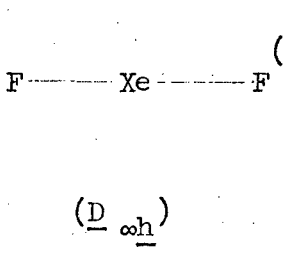
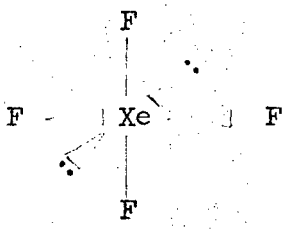
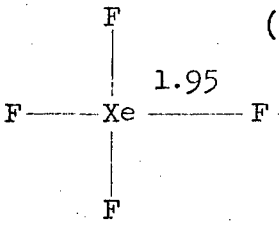
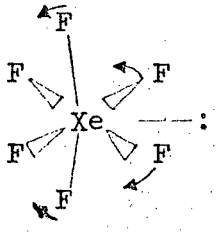
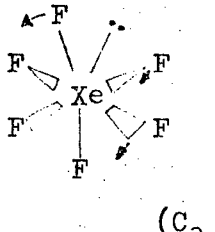
Although, as has been remarked, there has been considerable reluctance on the part of those providing bonding models for noble-gas compounds to admit the involvement of 'outer' noble-gas orbitals in bonding, it is striking that the theory which, almost without exception, has correctly predicted the geometrical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

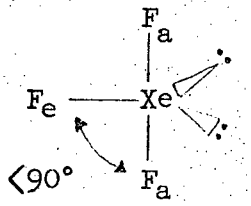
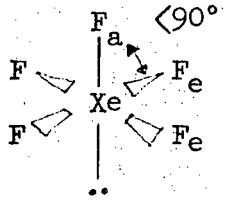
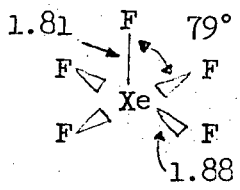
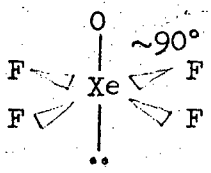
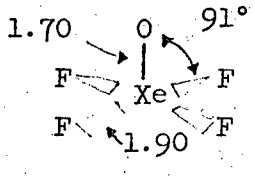
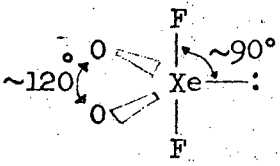
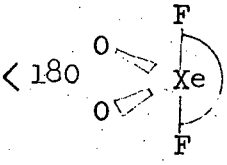
Electron Pair Repulsion Theory, which was first formulated independently by Tsuchida[37] and Powell and Sidwick[38], gained widespread appeal when it was rendered much more quantitative by Gillespie and Nyholm.[29] The theory assumes that each halogen-ligand bond to the central atom involves an electron-pair, 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').

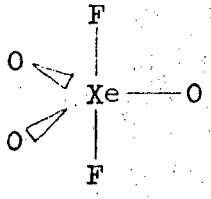
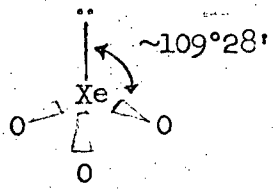
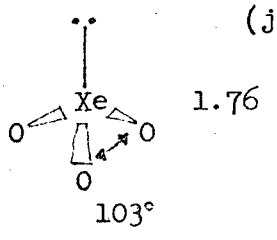
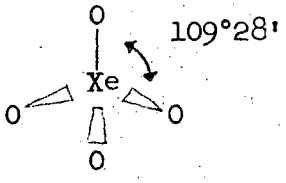
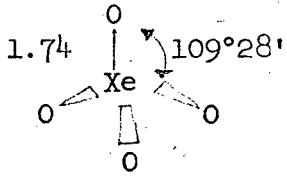
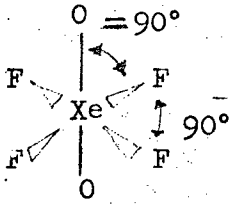
Shortly after the first reports of the noble-gas compounds, Gillespie[39] used the theory to predict the shape of a number of then unknown species.

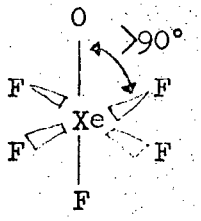
Table 1.3.3.

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

Species	Central Atom Coordination	Predicted Geometry	Observed Structure
XeF_2	5 - trigonal bipyramid (3 n-b e.p.; 2 b. e.p.)	 ($\underline{D}_{\infty h}$)	 ($\underline{D}_{\infty h}$) (a)
XeF_4	6 - pseudo octahedron (2 n- b. e.p.; 4b.e.p.)	 ($\underline{D}_{4h}$)	 ($\underline{D}_{4h}$) (b)
XeF_6	Either: 7 - pseudo pentagonal bipyramid (1 n-b. e.p; 6 b.e.p.)	 ($\underline{C}_{2v}$)	XeF_6 monomer is not octahedral. $XeF_{6(g)}$ undergoes rapid intramolecular rearrangement through $\underline{C}_{3v}$, $\underline{C}_{2v}$ and C_s symmetry species.(d) The cubic crystalline phase contains tetramers and hexamers which are essentially $XeF_5^+ F^-$ clusters.(e)
	or: 7 - face occupied octahedron (1 n-b. e. p.; 6 b. e. p.)	 ($\underline{C}_{3v}$)	

Species	Central Atom Coordination	Predicted Geometry	Observed Structure
XeF_3^+	5 - pseudo trigonal bi-pyramid (2 n-b.e.p.; 3 b. e.p.)	 ($Xe\text{-}F_a > XeF_e$)	unknown
XeF_5^+	6 - pseudo octahedron (1 n-b. e.p.; 5 b.e.p.)	 (C_{4v}) ($Xe - F_a < Xe - F_e$)	 (C_{4v}) (f)
$OXeF_4$	6 - pseudo octahedron (1,4 - e.b.; 1 n-b. e. p.; 4 b. e. p.)	 (C_{4v})	 (C_{4v}) (g)
O_2XeF_2	5 - pseudo trigonal bi-pyramid (2, 4 - e.b.; 1 n - b. e. p.)	 (C_{2v})	 (C_{2v}) (h)

Species	Central Atom Coordination	Predicted Geometry	Observed Structure
O_3XeF_2	5 - trigonal bipyramidal (3, 4 - e.b.; 2 b.e.p.)	 ($\underline{D}_{3h}$)	(i) Molecular Geometry Unknown
XeO_3	4 - pseudo tetrahedral (1 n-b.e.p.; 3, 4 - e.b.)	 ($\underline{C}_{3v}$)	(j)  ($\underline{C}_{3v}$)
XeO_4	4 - tetrahedral (4, 4 - e.b.)	 ($\underline{T}_d$)	(k)  ($\underline{T}_d$)
XeO_2F_4	6 - pseudo octahedral (2, 4 - e.b.; 4 e.p.b.)	 ($\underline{D}_{4h}$)	Compound Unknown

Species	Central Atom Coordination	Predicted Geometry	Observed Structure
$XeOF_5^+$	6 - pseudo octahedral (1, 4-e.b.; 5 b.e.p.)	 ($\underline{C}_{4v}$)	(ion unknown)

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[40] are as successful as the E.P.R. approach for less than six coordination. Thus, XeF_3^+ is predicted to be a T shaped species, the 'linear' F–Xe–F array being three-centre four-electron bonded (hence long, weaker, Xe–F bonds), the unique XeF bond being an electron pair bond (hence short). However, as we have seen, Rundle's approach fails for XeF_6 and IF_7.

Of course, it can be argued that the electron repulsion rules would be appropriate for bonds containing less than electron pairs. Thus, IF_7 could be represented as involving 7 single-electron bonds (see Linnett, loc. cit.) and XeF_6 as 6 single-electron bonds and a non-bonding electron pair. However, the similarity of the IF bonds in IF and 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,[41, 39, 42] their estimates usually being extrapolations from Pauling values[43] for the neighbouring elements or otherwise dependent on them. Sanderson[42] has taken a somewhat different approach, his values being based on his electronegativity equalization principle and related concepts[44] -- 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[41] has derived electronegativity

coefficients via a variant of the original Pauling method.[43] Other estimates given by Rundle[33] 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

He	Ne	Ar	Kr	Xe	Rn	Ref.
0.4-0.6	0.70	0.94	1.09	1.30	1.4-1.5	(a)
		0.95	1.11	1.30		(b)
				1.31	2.12	(c)

Electronegativity Coefficients of The Noble-Gases

He	Ne	Ar	Kr	Xe	Rn	Ref.
2.5-3.0	4.4	3.5	3.0	2.6	2.3-2.5	(a)
4.5	4.0	2.9	2.6	2.25	2.00	(d)

(a) Bing-Man Fung, J. Phys. Chem. 64, 596 (1965).

(b) R. J. Gillespie, "Noble-Gas Compounds," H. H. Hyman, Ed., The University of Chicago Press, Chicago and London, 1963, p. 333.

(c) R. T. Sanderson, Inorg. Chem. 2 (1963) 660; R. T. Sanderson, J. Inorg. Nucl. Chem. 7 (1958) 288.

(d) R. E. Rundle, J. Amer. Chem. Soc. 85 (1963) 112.

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, α, 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

Noble-Gas Atom diameters, ionization potentials, static polarizabilities and heat of adsorption on activated charcoal.

	He	Ne	Ar	Kr	Xe
Atomic Diameter[a] crystal lattice (Å)		3.2	3.84	3.96	4.36
Atomic Diameter[a] viscosity (Å)	2.7	2.8	3.42	3.6	4.05
1st ionization potential[b] (eV)	24.586	21.563	15.759	13.999	12.129
Static polarizability[c] α (Å^3)	0.204	0.392	1.63	2.465	4.01
Heat of adsorption on activated charcoal[d] (kcal/g-atom) at temp(°C) indicated in parentheses	0.54 (very low)	1.13(-182)	3.93(-105)	5.32(-50)	8.74(-25)

(a) G. A. Cook, Ed., "Argon, Helium and The Rare Gases," 2 Vols, Interscience Publishers, New York, London, 1961, Vol I, p. 13.

(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]

Noble-Gas	Decomp. Temp. (°C, 1 atm press)	H_2O Dissocn. Press. (amt, at 0°C)	ΔH_f° (kcal mole^{-1}) G. 5.75 H_2O	Cubic unit cell constant (Å)	$\Delta H(G_{(g)}$ + host lattice) kcal mole^{-1}	D_2O Decomp. Temp. (°C, 1 atm. press.)
Ar	-42.8	105	- - -	- - -		
Kr	-27.8	14.5	13.9	- - -	6.5	-25.1
Xe	-3.4	1.5	16.7	11.97	9.3	- 3.2
Rn		1	- - -			

[a] The values in this table, are taken from G. A. Cook, ref (a) Table 1.4.1, p 164, except for those under $\Delta H(G_{(g)}$ + 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[45] for the case of the noble-gas hydrates, the energy of the electronic dispersion interaction between two molecules A and B is

$$W = - \frac{3}{2} \frac{\alpha_A \alpha_B E_A E_B}{r^6 (E_A + E_B)} .$$

In this equation α_A and α_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 H_2O 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[46] a hydrate of the gas (1898). Hydrates of krypton, xenon and radon were prepared somewhat later.[47] All have the general ideal formula 8 G. 46 H_2O. The gas atoms are held in 'cages' in a pseudo-ice water lattice.

In 1949, Powell and Guter[48] 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[49] to be hydrogen bonded networks of the 'host' species(β-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.'[50] 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[51] 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 β-hydroquinone and gaseous argon), compared to a value of 5.4 kcal g-atom^{-1}, derived[51] 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.[50]

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: [52] argon amounts to ~ 8.8 wt % of the argon β-hydroquinone compound (which has an 'ideal' stoichiometry $[C_6H_4(OH)_2]_3Ar$). 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 β-hydroquinone clathrate has already proved useful[53] as a carrier for radioactive ^{85}Kr.

Noble-gas hydrates. The crystal structures of the simple-noble-gas hydrates were established[54] by Claussen in 1951. Structural features, of the clathrate hydrates generally, have been reviewed by Jeffrey and McMullen.[55] 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.[56]

All noble-gas hydrates contain a common structural feature.[55] This is a pentagonal dodecahedral arrangement of water molecules, shown in

Figure 1.4.1

The 12Å Hydrate-Clathrate Structure[a]

[a]After L. Pauling, Science 134 (1961) 15.

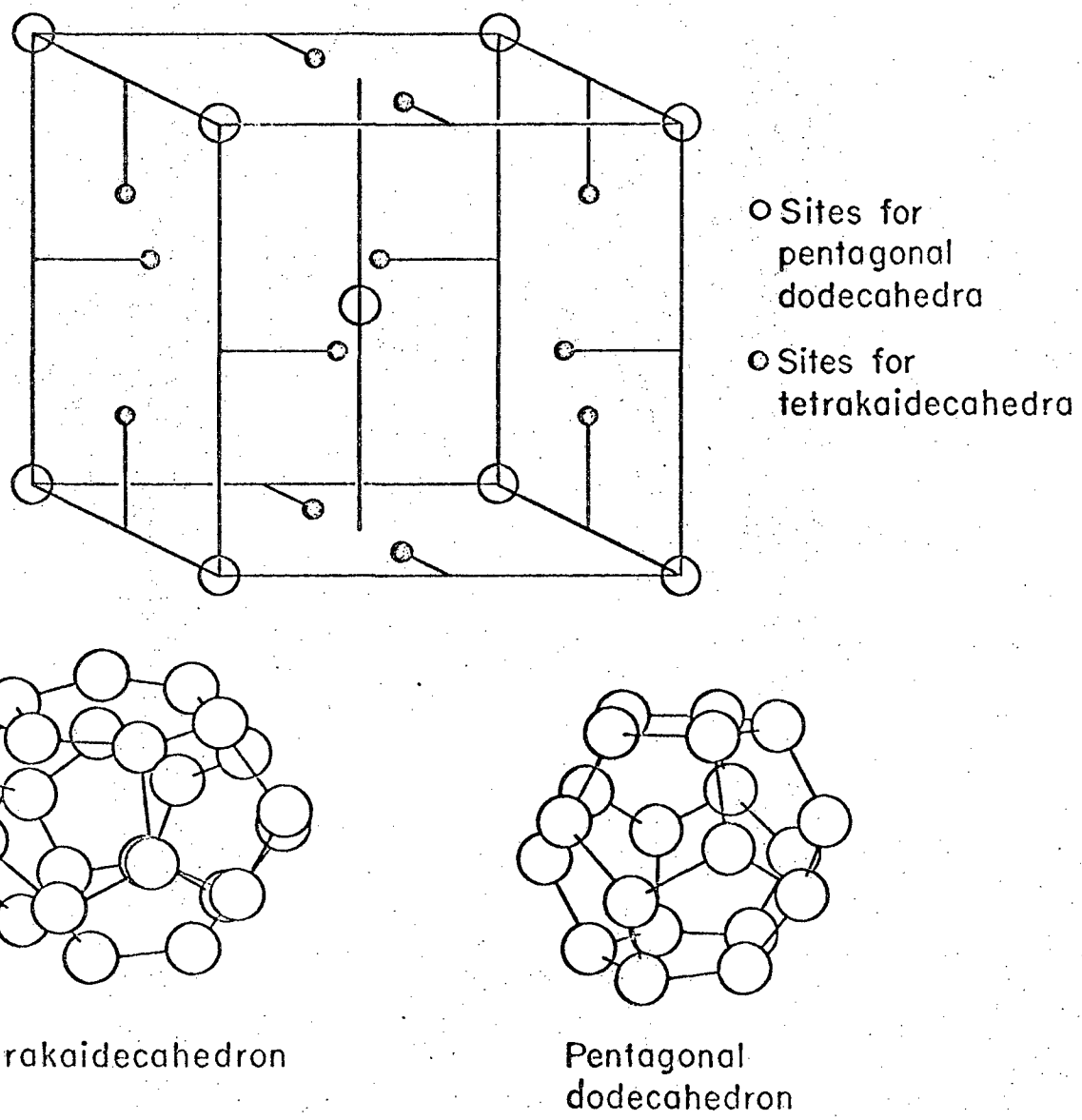


Figure 1.4.1

Figure 1.4.1. In these $H_{40}O_{20}$ 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, $a_o \approx 12\text{Å}$, the $H_{40}O_{20}$ units are linked by other water molecules to form a pseudo-body-centered array in which the two $H_{40}O_{20}$ 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_h^3 - Pm3n) 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° 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 2.75Å, which is essentially the same as the value for ordinary ice, which is 2.76Å. 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.[46] He points out that in the crystal $8Xe.46\ H_2O$, two xenon atoms are in pentagonal dodecahedra chambers, and the 20 water molecules are at a distance of 3.85Å from the xenon atom. For each of the six xenon atoms

in tetrakaidecahedral chambers, there are 12 water molecules at 4.03A and 12 at 4.46Å from the xenon atom. Using the dispersion energy equation given above, and assuming $E_{H_2O} \approx E_{Xe} \approx 1.57$ x the first ionization potential of xenon (280 kcal mole^{-1}), Pauling derives the interaction energy for two molecules (Xe and H_2O) to be = - a $R_{Xe}R_{H_2O}/r^6$, in which R_{Xe}(=10.16 ml) and R_{H_2O}(=3.75 ml) are the mole refractions of Xe and H_2O, a = 51 kcal mole^{-1}, and r is the average Xe—H_2O distance in Å units (the mole refraction is 4_π 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 = ~ 17Å) 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_2O., i.e., 8$CHCl_3$. 16Xe. 136 H_2O.

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[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[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.

β-Hydroquinone and Phenol Clathrates. Argon, krypton and xenon β-hydroquinone clathrates have been prepared and characterized by Powell.[53] Clathrates involving other phenolic materials have also been described, principally those of phenol. It is of interest that Nikitin[60] used the latter host-precurser 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[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 β-hydroquinone clathrates is G. 3β-$C_6H_4(OH)_2$. 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.[51] The free diameter of the cage hole is ~ 4.2Å.

The β-hydroquinone structure is 82 cal mole^{-1} less favourable in free energy than the non-clathrate α form.[52] 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[63] has shown

Table 1.4.3.

Noble-gas-β-hydroquinone and phenol clathrates

Noble-gas	β-Hydroquinone clathrates(a) ideal formula: $G.3C_6H_4(OH)_2$		Phenol Clathrates(b) formula: $mG.\ 12\ C_6H_5OH$	
	$C_6H_4(OH)_2$: G Ratio	ΔH_β^* kcal mole^{-1}	m	ΔH_β^* kcal mole^{-1}
Ar	3: 0.8	-6.0	2.92	-9.85
Kr	3: 0.74	-6.3	2.14	-8.97
Xe	3: 0.88		4.0	-8.8

ΔH_β^* represents the enthalpy change for the process: Host lattice $(\beta form)_{(c)} + G_{(g)} \longrightarrow$ clathrate compound.

(a) H. M. Powell, J. Chem. Soc., (1950) 298, 300 and 468. W. C. Child, Jr., Quart. Revs., (1964) 321.

(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.[62] Evidently the recoil-free fraction of the ^{83}Kr-hydroquinone clathrate absorber is essentially constant between room temperature and ~ 150°K. The recoil free fraction increases very rapidly below this temperature. The results for T > 150°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 liquifaction), 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.

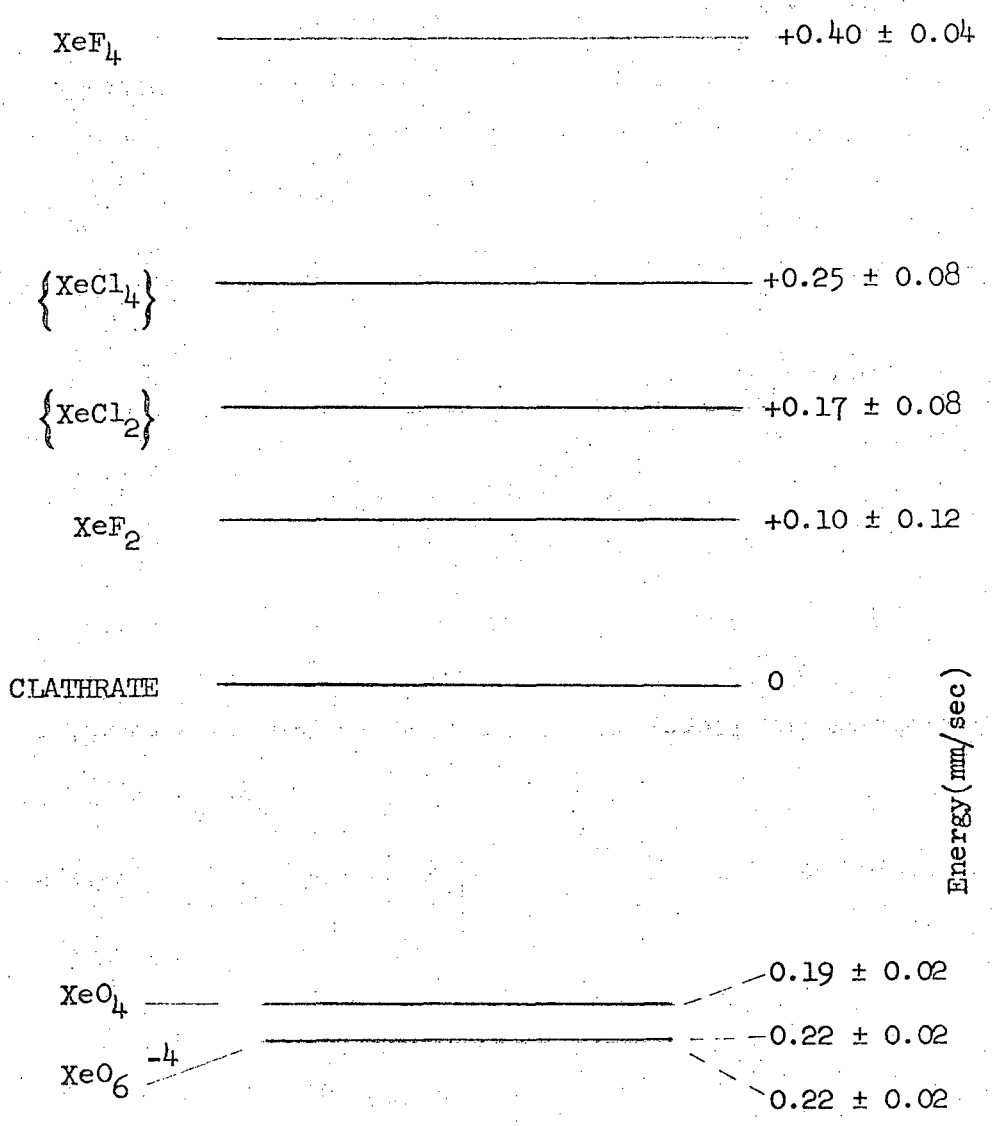
The γ-ray transitions in the xenon halides have excess energy relative to atomic xenon in the β-hydroquinone clathrate whereas the transitions in the tetroxide and perxenates have less energy. The isomer shifts are displayed as an energy level diagram in Figure 1.4.2. The excess energy of the γ-rays in the halides can be explained on

(Figure 1.4.2)

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 (5s and inner electrons) -- hence, Δs (the isomer shift) > 0. On the other hand, the oxygen containing compounds, having octahedral or tetrahedral symmetry, have appreciable 5s

Figure 1.4.2

Xenon isomer shifts*(a)



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

(a)As given by G. J. Perlow and M. R. Perlow, J. Chem. Phys., 48(1968) 958.

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[45] 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 4.0Å, 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]

Gas	Cationic Composition of the zeolite K/Na ratio	Initial Encapsulation pressure, atm	Quantity Encapsulated (g gas per 100 g zeolite) At Start	After 30 days
Ar	20 / 80	2500	16.7	<30% loss
	40 / 60	2500	19.4	"
	60 / 40	2500	19.0	"
Kr	100% Na	4300	32.4	32.8*
	60 / 40	4300	34.8	30.2
	92 / 8	4300	21.6	20.1

* The apparent increase most probably arises from analytical inaccuracy

(a) Work of L. H. Schaffer and W. J. Sesuy, quoted in "Argon, Helium and The Rare Gases," G. A. Cook, Ed., Interscience, Vol 1, New York 1961, p 230.

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:

$$G^+ + H_2 \longrightarrow GH^+ + H$$

$$G + H_2^+ \longrightarrow GH^+ + H$$

The first reaction has been observed for Ar, Kr and Xe. The estimated proton affinities, i.e., $\Delta H(G_{(g)} + H^+_{(g)} \longrightarrow (GH)^+_{(g)})$ 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 $GH^+_{(g)}$

Table 1.5.1

Proton affinities,[a] Gp, and ionization potentials of the noble gases

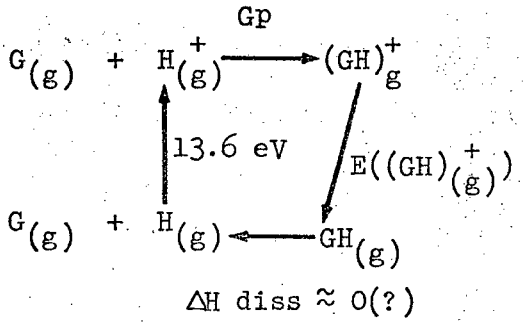
	He	Ne	Ar	Kr	Xe
Gp (eV)	1.8	2.2	3.0	⩾4	⩾6
I(G)(eV)	24.586	21.563	15.759	13.999	12.129

[a] G. Von Bunan, Fortschr. Chem. Forschung, 5(2) (1965) 374.

is equal to the electron affinity of the proton (-13.6 eV) minus the proton affinity of G. This is so only if $\Delta H(GH_{(g)} \longrightarrow G_{(g)} + H_{(g)}$ is zero. Thus the electron affinity of ArH^+ should be ≈ - 10.6 eV.

Figure 1.5.1

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



Note that $E(XeH^+)$ ≈ - 7.6 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

Table 1.5.2

Energy levels of the noble-gases and their radiative lifetimes[a]

	Metastables				Ions		
	$2\,^3S$	$2\,^1S$	$2\,^1P$		^2S		
He	19·81	20·61	21·21	—	24·58	—	ev
	—	—	0·56	—	—	—	nsec.
	$^3P_2$	$^3P_1$	$^3P_0$	$^1P_1$	$^2P_{3/2}$	$^2P_{1/2}$	
Ne	16·61	16·67	16·71	16·84	21·56	21·66	ev
	—	21	—	1·5	—	—	nsec.
Ar	11·55	11·62	11·72	11·82	15·75	15·93	ev
	—	8·1	—	1·8	—	—	nsec.
Kr	9·91	10·03	10·56	10·64	14·00	14·66	ev
	—	3·4	—	3·3	—	—	nsec.
Xe	8·31	8·43	9·44	9·57	12·13	13·43	ev
	—	3·8	—	3·2	—	—	nsec.

[a]From B. Brocklehurst, Quart. Revs., 22 (1968) 147.

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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:[63]

$$G^* + X \longrightarrow GX^+ + e$$

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:[63]

$$Xe^* + O_2 \longrightarrow XeO^* + O$$

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[65] or higher fluoride of krypton have failed. These attempts have included the subjection of KrF_2/F_2 mixtures to high energy irradiation at low temperatures.[66] Nor has any firm evidence appeared to support the existence of oxides, oxysalts[67] or chlorides.

2.1. Krypton (I) Compounds

No 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[68], in krypton difluoride crystals subjected to γ 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° but disappear on warming to -153°. The KrF radical has one more electron than bromine monofluoride. Since this electron must be in an antibonding σ orbital, the Kr-F bond can amount only to a one electron bond. The bond strength may be comparable to the KrF bond in KrF_2 (mean thermochemical bond energy[69] = 12 kcal $mole^{-1}$) but certainly weaker and presumably, at most, only half the strength of the bond in the $Kr\text{-}F^+$ ion (isoelectronic with 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 σ orbital, containing the unpaired electron, is chiefly F 2pσ, (2pσ 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.

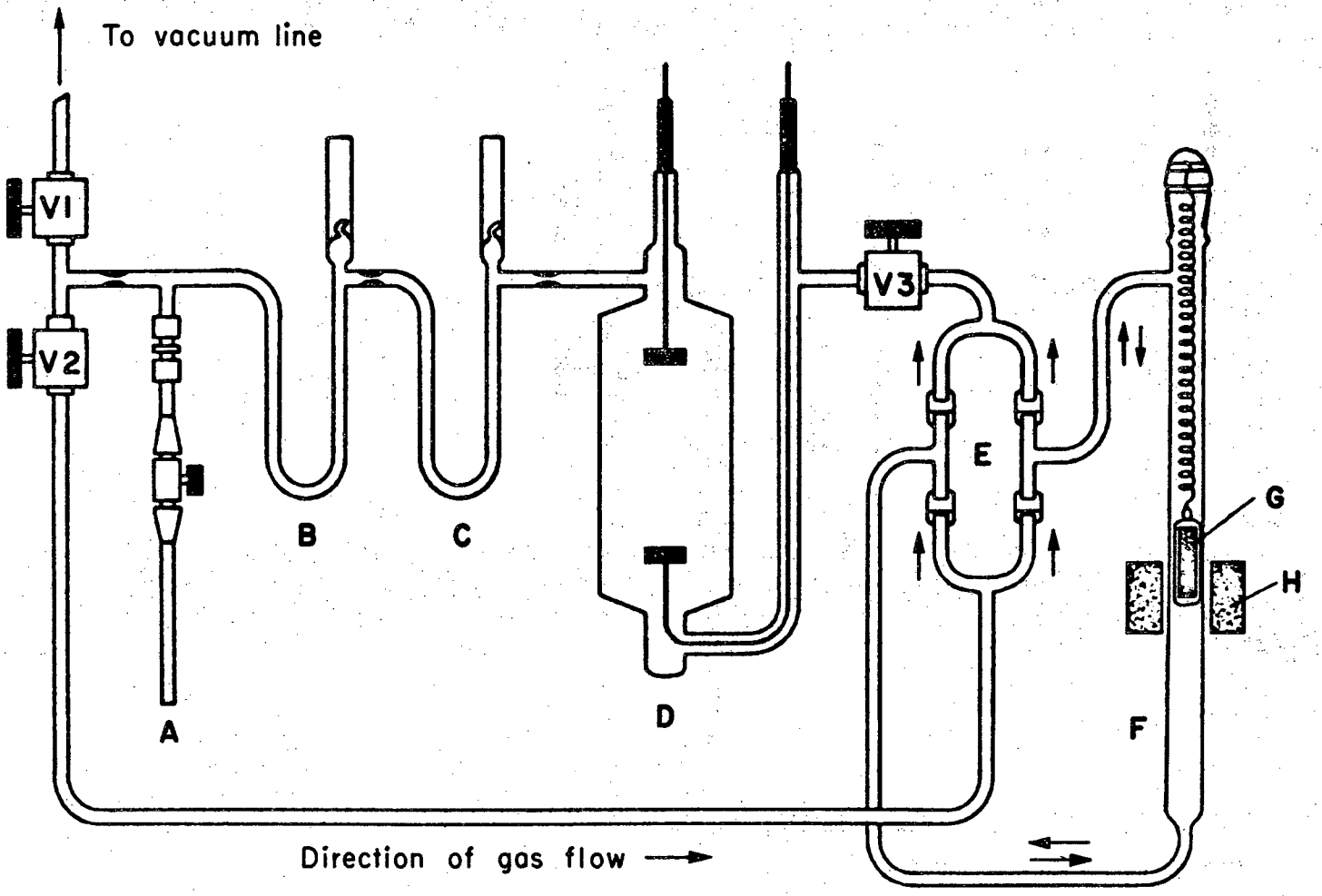
2.2. Krypton (II) Compounds

2.2.1 Krypton Difluoride

Synthesis. Krypton difluoride was first characterized by Turner and Pimentel[70] 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[65] 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[69] 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,[71] ultraviolet light,[70] or 10 Mev protons[66], or electric discharge of the gaseous mixture.[65, 72] 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.[66, 69]

Figure 2.2.1



XBL704-2667

Figure 2.2.1

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.[a] 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.

(a) W. Brenschede, Z. Physik. Chem. (Leipzig) A 178 (1936-1937) 74.

Figure 2.2.1

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 5μa yields ca. 1g of KrF_2. The G value for KrF_2 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 ν_1 mode at 449 cm^{-1}. The Raman spectrum is easiest to obtain since sapphire, which is chemically resistant to KrF_2 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 KrF_2 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 ~10% $hr.^{-1}$. The decomposition rate is substantially lower for the solid [74] and evidently negligible at Dry Ice temperature.[72] The spontaneous dissociation has prevented the accurate determination of a number of the physical properties of KrF_2, but there is general agreement[72,74] that its vapour pressure is ca. 30 mm Hg at 0°. The enthalpy of vapourization ΔH_{sub} = 9.9 kcal $mole^{-1}$ has been derived from vapour pressure measurements over the limited temperature range -15.5 to 15°.[74]

Measurement of the heat of dissociation[69], at 93°, of a gaseous sample of the difluoride (which is rapidly decomposed at this temperature) has given a standard heat of formation ΔH_f° $(KrF_{2(g)})$ = 14.4 ± 0.8 kcal $mole^{-1}$. The calorimetric measurements are supported by mass-spectrometric, appearance-

potential data.[75] Although there is some ambiguity of interpretation, it is probable that the observed appearance potential $A(Kr^+, KrF_2)$ = 13.21 ± 0.25 ev, is appropriate for the process $KrF_{2(g)} + e \rightarrow Kr^+ + F_{2(g)} + 2e$. If so, since I(Kr) = 14.00 ev, it follows that $\Delta H(KrF_{2(g)} \rightarrow Kr_{(g)} + F_{2(g)})$ = 0.79 ± 0.25 ev (i.e., 18 ± 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 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 KrF^+ ion is not established there is reason to believe that it occurs in the complex KrF_2, $2SbF_5$ (see 2.2.2). As can be seen from Fig. 2.2.2, the electron affinity of KrF^+ equals the electron affinity of Kr^+ ($-I(Kr,g)$ = 14.0 ev), less the difference in bond energy between KrF^+ and KrF. It is reasonable to suppose that the B.E. (KrF^+) is ~ 2 x B.E. (KrF).

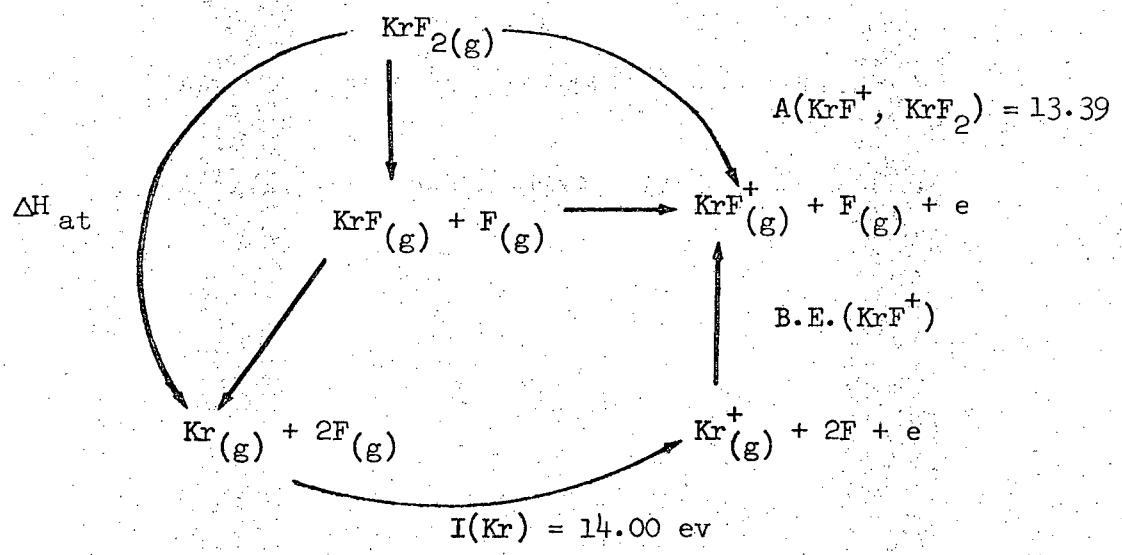
A recent value for the appearance potential[76a] for KrF^+, $A(KrF^+, KrF_2)$ = 13.39 eV. Since this corresponds to the process $KrF_{2(g)} \rightarrow KrF^+ + F_{(g)} + e$, then from Fig. 2.2.2, $A(KrF^+, KrF_2) = \Delta H\ (KrF_{2(g)} \rightarrow Kr_{(g)} + 2F_{(g)}) + I(Kr) + B.E.(KrF^+)$. Therefore, the bond energy for the cation = (13.39 - 14.00) eV - $\Delta H_{at}(KrF_2) \approx 37$ kcal $mole^{-1}$. This is approximately 3 times the mean thermochemical bond energy of KrF_2.

Figure 2.2.2

The Electron Affinity and Bond Energy of KrF^+

Figure 2.2.2

The Electron Affinity and Bond Energy of KrF^+



$$I(KrF_{(g)}) = I(Kr) - B.E.(KrF^+_{(g)}) + B.E.\ (KrF_{(g)})$$

$$B.E.(KrF^+_{(g)}) = I(Kr) - A(KrF^+,\ KrF_2) + \Delta H_{at}(KrF_2)$$

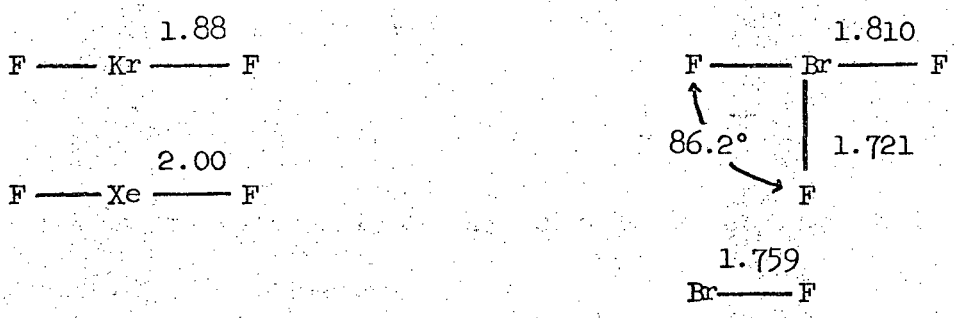
Structural Features. Like its relative, xenon difluoride, KrF_2 is a symmetrical linear molecule ($D_{\infty h}$).[70, 73] The Kr-F interatomic distance has been determined for the gaseous species by electron diffraction,[76] (1.889± 0.010Å) and rotational infrared spectroscopy[77] (1.875 ± 0.002Å). The infrared and Raman data are in agreement with the $D_{\infty h}$ molecular symmetry and the force constants $f_r = 2.46$, $f_{rr} = -0.20$ and f_α 0.21 indynes^{-1}, obtained[73] from the computed potential function $2V = f_r(\Delta r_1^2 + \Delta r_2^2) + 2f_{rr}\Delta r_1 \Delta r_2 + r_o^2 f_\alpha \Delta\alpha^2$, where Δr_1 and Δr_2 are changes in the bond distances and $\Delta\alpha$ is the change in bond angle, have been interpreted [78] (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 $(F\text{-}Kr)^+ F^-$, $F^-(Kr\text{-}F)^+$. 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 pσ 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 [79] it is, like the

Figure 2.2.3

Comparison of KrF_2 with BrF, BrF_3 and XeF_2

Figure 2.2.3

Comparison of KrF_2 with BrF BrF_3 and XeF_2



	Frequencies (cm^{-1})			Force Constants (md/Å)		
Molecule	ν_1	ν_2	ν_3	f_r	f_{rr}	f_α
KrF_2	449	232.6	588	2.46	-0.20	0.21
$(F)BrF_2$*	531		613	3.00	0.15	
XeF_2	515	213.2	558	2.84	0.13	0.20

*Only the approximately linear BrF_2 part of the BrF_3 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 $Å^3$, is similar to the XeF_2 value of 39.2 $Å^3$.

Bond Polarity and Bond Type. Both ^{19}F n.m.r. studies of KrF_2 solutions in anhydrous hydrogen fluoride[72], and Mössbauer studies[80] 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}F chemical shielding value, σ_F, relative to F_2, for KrF_2($\sigma_F \sim 370 \times 10^{-6}$) 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, pσ 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}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[80] 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 ±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 $4\underline{p}$ electrons with the fluorine atoms. On the assumption of that only $\underline{p\sigma}$ orbitals are involved in the bonding, the interaction energy (for one electron transferred from krypton) $e^2qQ(KrF_2) = +\frac{4}{5} e^2Q \langle r^{-3} \rangle$, i.e., the field gradient due to one $4\ \underline{p\sigma}$ 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 $4\underline{p}^5 5\underline{s}$ configuration, where one electron has been removed from a p orbital) $\frac{2}{5} e^2Q \langle r^{-3} \rangle = 452.2\ mH_2$. If $\langle r^{-3} \rangle$ is approximately the same for 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 $\sim$ 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 KrF_2 is a resonance hybrid of $F - Kr^+ F^-$ and $\overline{F}\ Kr^+ - F$. They point out that if the electronegativity of Kr^+ and F are similar this would result in equal sharing of the bond electron pair in KrF^+. Consequently, the krypton atom in KrF_2 would have a net deficiency of one $4\underline{p\sigma}$ electron. An electron transfer of 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 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 Kr F, in the resonance admixture

with $\overline{F}\ (Kr\text{-}F)^+$ and $(F\text{-}Kr)^+\ F^-$, which requirement of course reduces the Kr charge to less than +1. The form, $F\text{-}\ Kr^{2+}\ F^-$, 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]

$$KrF_2 + H_2O \longrightarrow Kr + 0.5O_2 + 2HF$$

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 XeF_8 (see 3.5.1.) by bringing XeF_6 into interaction with it.

There have been claims[67] that the hydrolysis, by ice, of krypton difluoride (incorrectly identified[72] as 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 [81] 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 KelF 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. $\longrightarrow Kr_2 + F_2 + SbF_5$). 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 $KrF^+[Sb_2F_{11}]^-$, analogous to $XeF^+[Sb_2F_{11}]^-$ (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 $Kr\text{-}F^{+}$ ion (2.2.2) appears to be considerably stronger (T.B.E., $\sim$ 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)

ΔH sublimation, kcal mole^{-1} ~ 9.9

Vap. Press, mm Hg, (T°C) 10 ± 1 (- 15.5°); 29 ± 2 (0°); 73 ± 3, (15.0°)

$\Delta H_f°$ 298.15°, kcal mole^{-1} 14.4 ± 0.8

ΔH_{at} ($KrF_{2(g)} \longrightarrow Kr_{(g)} + 2F_{(g)}$), kcal mole^{-1}, 23.4

Mean Thermochemical Bond Energy, kcal mole^{-1}, 11.7

Solubility (b)

Anhydrous HF dissolves KrF_2 to ~ 16 moles / 1000 g HF at 20°

^{19}F n.m.r. data (b)

(no F exchange for HF solutions). Chemical Shielding Values

$\sigma_F^{(2)}$, relative to F_2, $\sigma_{F_2}^{(2)}$ = 0 : 374 x 10^{-6} (4.6 moles / 1000 g HF), 362 x 10^{-6} (16.4 moles / 1000 g HF) at 0°.

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

	ν_2	ν_1	ν_3	$\nu_1 + \nu_3$
fundamentals, cm^{-1}	232.6	449	588	

force constants (m dynes A^{-1}) f_r, 2.46; f_{rr} -0.20 ; f_α, 0.21

Molecular Structure (d)

$D_{\infty h}$ symmetry, Kr-F internuclear distance, Å units 1.889 ± 0.01

Crystallographic data (e)

Tetragonal unit cell, a = 6.533; c = 5.831Å; V = 248.9Å^3; Z = 4;

D_{calc}, 3.24 g cm^{-3}

Molecular Energetics (f)

Appearance Potentials, $A(Kr^+, KrF_2)$ = 13.21 ± 0.25 ev ($KrF_2 + e \rightarrow Kr^+ + F_2 + 2e$) Possible Process

$A(KrF^+, KrF_2)$ = 13.71 ± 0.20 ev ($KrF_2 + e \rightarrow KrF^+ + F + 2e$)

(a) S. R. Gunn, J. Amer. Chem. Soc. 88 (1966) 5924; S. R. Gunn, J. Phys. Chem. 71 (1967) 2934.

(b) F. Schreiner, J. G. Malm, and J. C. Hindman, J. Amer. Chem. Soc. 87 (1965) 25.

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

(d) W. Harshbarger, R. K. Bohn, and S. H. Bauer, J. Amer. Chem. Soc. 89 (1967) 6466.

(e) S. Siegel and E. Gebert, J. Amer. Chem. Soc. 86 (1964) 3896.

(f) P. A. Sessa and H. A. McGee, J. Phys. Chem. 73 (1969) 2078.

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, XeO_4, the perxenates, XeO_6^{4-}, and the trioxide difluoride, XeO_3F_2. The octafluoride is unknown. This pattern resembles that of osmium, where the octafluoride is unknown but the tetroxide, OsO_4, and trioxide difluoride, OsO_3F_2, 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, $-OSO_2F$, $-OTeF_5$). 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 ^{129}I anions (thus: $^{129}IBr_2^- \xrightarrow{\beta} {}^{129}XeBr_2$).

3.1 Xenon(I)

3.1.1 Xenon(I) Fluoride, The XeF Radical

The radical $XeF^{\cdot}$ has been detected by Morton and Falconer[82, 83] in an electron spin resonance study of a single crystal of XeF_4

γ-irradiated at 77°K. 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[83] to fade simultaneously and rapidly at 140°K.

It has been inferred, from kinetic data, that the XeF radical is an intermediate in water oxidation[84] and NO and NO_2 oxidation[85] by XeF_2. It is also probable that the decomposition of $FXeOSO_2F$ involves an XeF intermediate ($FXeOSO_2F \longrightarrow XeF^{\cdot} + SO_3F^{\cdot}$; $2XeF^{\cdot} \longrightarrow Xe + XeF_2$; $2SO_3F \rightarrow S_2O_6F_2$) since the overall chemical change[86] is $2FXeSO_3F \longrightarrow Xe + XeF_2 + S_2O_6F_2$. Similarly, the decomposition of $XeF^+OsF_6^-$ is thought to involve charge transfer ($XeF^+[OsF_6]^- \rightarrow XeF^{\cdot} + OsF_6$) with subsequent $XeF^{\cdot}$ disproportion. This accounts for the observed[87] products: $3XeF^+[OsF_6]^- \longrightarrow Xe_2F_3^+[OsF_6]^- + Xe + 2OsF_6$.

Johnston and Woolfolk have shown[85] that the first bond dissociation energy, $D_1 = \Delta H(XeF_{2(g)} \longrightarrow XeF_{(g)} + F_{(g)})$, 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 $D_2(XeF_2)$ i.e., B.E.($XeF^{\cdot}$) = would be 10 kcal $mole^{-1}$. However, should the bond energy in the XeF radical be less than $\Delta H_f(F)$ = 18.7 kcal $mole^{-1}$, then dissociation $2XeF \rightarrow 2Xe + F_2$ 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) ≈ 20 kcal $mole^{-1}$. This value is still consistent with disproportion $2XeF \rightarrow XeF_2 + Xe$, 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}): ~ 20

$\Delta H(2XeF_{(g)} \longrightarrow XeF_{2(g)} + Xe_{(g)})$ (kcal mole^{-1}): ~ -24

} see text

Source for e.s.r. characterization: γ - irradiation of XeF_4 single crystal (a) (b)

Principle values of the hyperfine interaction tensors‡ and g tensors*: (b)

Species	$Xe_{\parallel}$	$Xe_{\perp}$	$F_{\parallel}$	$F_{\perp}$	$g_{\parallel}$	$g_{\perp}$
^{132}XeF	- -	- -	2649	540	1.9740	2.1251
^{129}XeF	2368	1224	2637	526	1.9740	2.1264
^{131}XeF	701	- -	2653	- -	1.9740	- -

(‡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 (b)

Nucleus	A_{obs}	$[8\pi g\beta\gamma/3h] \times \psi^2_{ns}(0)$	%ns. spin popn.	Nucleus	B_{obs}	$[2g\beta\gamma/5h] \times \langle r^{-3}\rangle_{np}$	% np spin popn.
$^{19}F(n=2)$	1243	47,900 Mc	3	$^{19}F(n=2)$	703	1,515 Mc	47
$^{129}Xe(n=5)$	1605	33,030 Mc	5	$^{129}F(n=5)$	382	1,052 Mc	36

(a) W. E. Falconer and J. R. Morton, Proc. Chem. Soc. (1963) 95.

(b) J. R. Morton and W. E. Falconer, J. Chem. Phys. 39 (1963) 427.

indicate that the unpaired electron occupies an orbital possessing axial symmetry about the internuclear axis. Neglecting inner-shell polarization, the data indicate that this σ 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$^{\cdot}$ can be described in classical molecular orbital terms with the unpaired electron in the highest antibonding sigma orbital (σ^*). Departure of the principal g-values of XeF from 2.0023 (free spin) must be associated with spin-orbit interaction of the ground Σ state with Π excited states of the molecule. The ground state configuration is written: $(\sigma\, 2p_F + \sigma\, 5p_{Xe}, \sigma_1)^2$; $(\pi\, 2p_F + \pi\, 5p_{Xe}, \pi_{1,2})^4$; $(\pi\, 2p_F - \pi\, 5p_{Xe}, \pi\, 3,4)^4$; $(\sigma\, 2p_F - \sigma\, 5p_{Xe}, \sigma_2)^1$, or briefly σ_1^2; $\pi_{1,2}^4$; $\pi_{3,4}^4$; σ_2^1. Of course σ_1 and $\pi_{1,2}$ are bonding orbitals and $\pi_{3,4}$ and σ_2 antibonding orbitals. The g shifts are attributed to the transitions:

$$\sigma_1^2\,;\ \pi_{1,2}^4\,;\ \pi_{3,4}^4\,;\ \sigma_2^1 \longrightarrow \sigma_1^2\,;\ \pi_{1,2}^4\,;\ \pi_{3,4}^3\,;\ \sigma_2^2$$

$$\sigma_1^2\,;\ \pi_{1,2}^4\,;\ \pi_{3,4}^4\,;\ \sigma_2^1 \longrightarrow \sigma_1^2\,;\ \pi_{1,2}^3\,;\ \pi_{3,4}^4\,;\ \sigma_2^2$$

3.1.2 Xenon(I) Complexes

Several complex salts have been reported.[1, 14] 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: $Xe_{(g)} + MF_{6(g)} \longrightarrow XeMF_{6(c)}$. 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 $A^{I}M^{V}F_6$ salts. Of course, the 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 Xe^+ rather than Xe_2^{2+} or Xe_2F^+ (which would be appropriate for the formulation Xe_2F^+ $[F_5Pt\text{–}F\text{–}PtF_5]^-$). It is noteworthy that the material of composition $Xe(PtF_6)_2$ which is formed under conditions of twofold excess of PtF_6 over Xe, is[87] an equimolar mixture of XeF^+ $[PtF_6]^-$ and PtF_5 (see 3.2.6.).

Considering, the established[13] capability of PtF_6 to oxidize O_2 to O_2^+, the rapid formation of the $XePtF_6$ material from the gas phase, and the quinquevalence of the platinum in the solid product, it is probable that this and $XeRhF_6$ represent true Xe(I) compounds.

3.2 Xenon(II)

3.2.1 Xenon Difluoride

Xenon difluoride was first detected independently in two laboratories,[88, 3] and several effective syntheses were quickly reported.[89, 90, 91]

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,[15] indeed as Falconer and Sunder have shown[92] high yields of pure material can be obtained with $Xe:F_2$ 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[12, 93], which avoids the special metal equipment used in the last procedure, simply involves exposure to sunlight of Xe/F_2 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 XeF_2. Weeks, Chernick and Matheson [89] 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 [91, 94]. The Weeks et al photosynthesis [89]

employed irradiation of Xe/F_2 gaseous mixtures with light from a high pressure mercury arc (2500-3000Å). Photosynthesis, with sunlight, involving Xe/OF_2 mixtures[12] at ~25° and Xe/O_2F_2 mixtures[95] at -118° are also effective.

Gamma ray irradiation at 4×10^6 rads hr^{-1} of ~1:2 Xe/F_2 mixtures at 64° has been shown[96] 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[97] that XeF_2 is formed in interaction of Xe with OF_2 (> 187°), CF_3OF (220-250°), and FSO_3F(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[98]

$$Xe_{(g)} + IF_{7(g)} \longrightarrow XeF_2, IF_{5(c)}$$

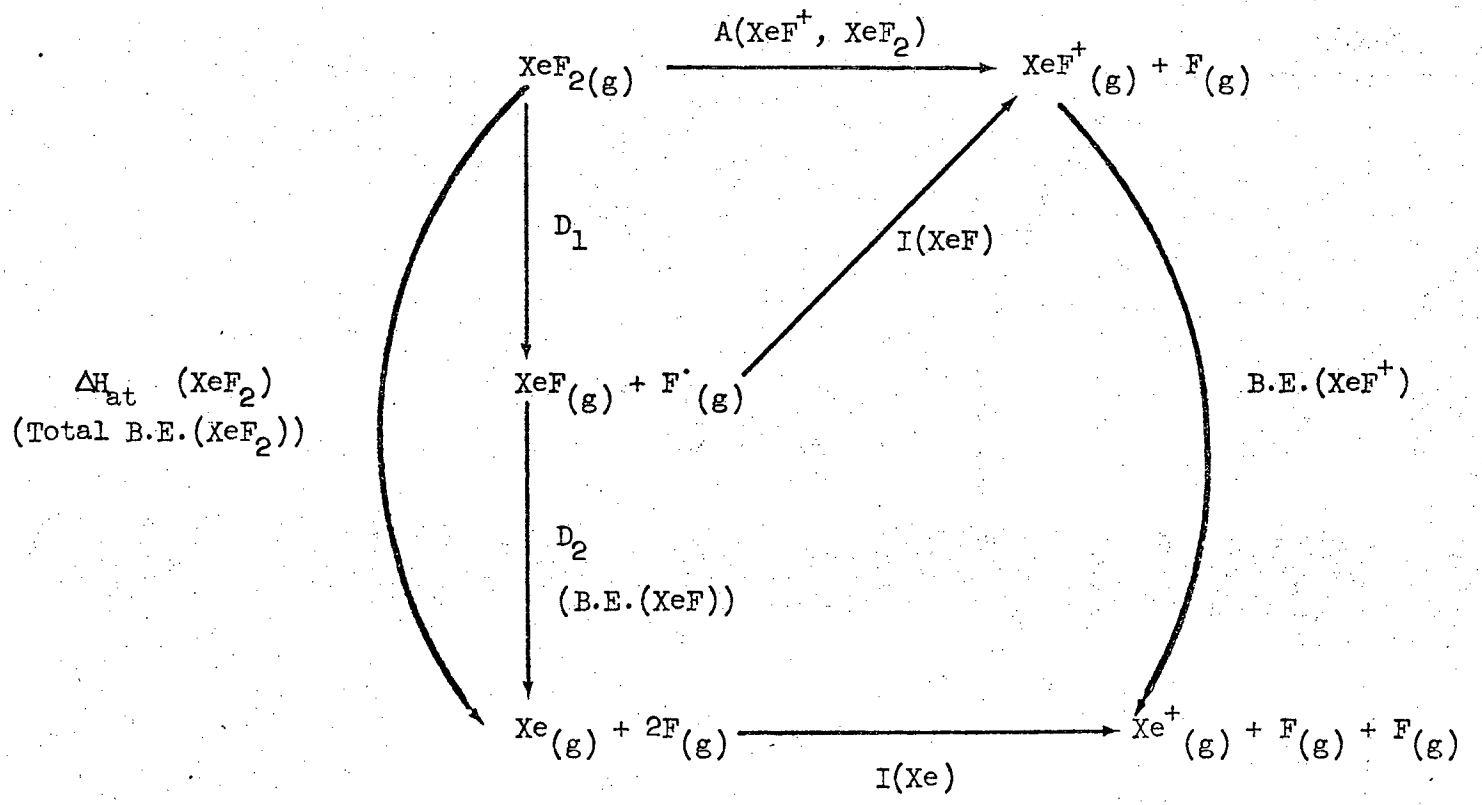
is similarly dependent upon F_2, generated by pyrolysis $IF_7 \longrightarrow IF_5 + F_2$. It is possible that xenon difluoride has also been observed[99] as a product of the fission of a UO_2 - LiF mixture.

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 [100] and by the interaction of excited xenon ($^3P_1$) with perfluoro-cyclobutane [101]: $Xe^+ + c\text{-}C_4F_8 \longrightarrow XeF_2 + c\text{-}C_4F_6$.

Thermodynamic Properties. Xenon difluoride is colourless as solid, liquid or gas. The vapour pressure of the solid[102] 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.[102] The

Figure 3.2.1

Thermochemical Cycles for XeF_2 and Derived Species



From the thermochemical cycles:

$$B.E.(XeF^+) = I(Xe) - A(XeF^+, XeF_2) + \text{Total } B.E.(XeF_2,g)$$

$$I(XeF) = A(XeF^+, XeF_2) - D_1\ (XeF_2,g)$$

$$I(XeF) = I(Xe) + B.E.(XeF^{\cdot}) - B.E.(XeF^+)$$

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vapour pressure data given by the last workers, for the temperature range 0 - 115°, is also the most reliable, from which ΔH 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: $\Delta H_f^\circ(XeF_2,g)$(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 $XeF_{2(g)} \rightarrow XeF^{\cdot}_{(g)} + F_{(g)}$ 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

$$T.B.E.(XeF_2,g) = B.E.(XeF^+) + A(XeF^+, XeF_2) - I(Xe).$$

Since the last two experimentally observed quantities are 12.8 and 12·1 ev respectively, $T.B.E.(XeF_2, g) = 64 = B.E.(XeF^+) + 0.7$ 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

Triple point,[a] 129.03°C

$\Delta H_{sublim.}$,[a] 13.2 ± 0.2 kcal mole^{-1}

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

S° (gas)[b]: 25°C, 62.057; 250°C, 69.715; 501°C, 75.345 cal mole^{-1} deg.$^{-1}$.

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

Thermodynamics of XeF_2 formation:

ΔH_f°, g,[b]: 25°C, -25.903; 501°C, -25.491 kcal mole^{-1}.

ΔG_f°, g,[b]: 25°C, -17.858; 501°C, -5.222 kcal mole^{-1}.

ΔH atomization ($XeF_{2\,(g)} \longrightarrow Xe_{(g)} + 2F_{(g)}$)[c], 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_3CN, good; HF, fair; SO_2, fair; WF_6, poor. NH_3 very slight[e].

Solubility in H_2O[f]: 25 g/l at 0°

HF[g]:	Temp(°C)	-2.0	12.25		29.95	
	C(moles/1000g)	6.38	7.82		9.88	
CH_3CN[h]:	Temp(°C)	0	21			
	C(g/l)	168	320			
ONF, 3HF[i]:	Temp(°C)	16.8	33.2	49.2	61.0	80.0
	C(moles/1000g)	16.3	19.56	22.17	25.38	30.55

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 XeF_2 hydrolysis.

$\Delta G°(XeF_{2(aq)} + H_2O \longrightarrow Xe_{(g)} + \frac{1}{2}O_{2(g)} + 2HF_{(aq)})$ est.[j]

≈ -53.4 kcal mole^{-1}, hence $K_{eq} \approx 10^{40}$

Hydrolysis conditions :	1st order rate constant	$\Delta E_{activ.}$	$\Delta S_{activ.}$	Ref.
(0.01MHClO$_4$)	4.2×10^{-4} sec^{-1}(25°)	19.6	-8.1	(k)
Only XeF_2 in H_2O	$2.83 \pm 0.02 \times 10^{-5}$ sec^{-1}(0°)	- -	- -	(l)
	$2.52 \pm 0.01 \times 10^{-4}$ sec^{-1}(25°)	- -	- -	(l)
	$1.2 \times 10^{12} \exp(-18400/RT)$ min^{-1}	18.4±2.1	- -	(j)

Vibrational Spectra:

XeF_2 solid:

bands (cm^{-1})	547 IR (vs)[m]	496 R (1.0)[n][o]	108 R (0.33)[n][o]
assignment	ν_3	ν_1	lattice mode

XeF_2, vapour:

bands (cm^{-1})	1070 IR (w)[n][o]	560 IR (vs)[o][n][p]	213.2 IR (vs)[o]
assignment	$\nu_1 + \nu_3$	ν_3	ν_2

CH_3CN solution:

bands (cm^{-1})	1235 IR (w)[h][q][r]	533 IR (s)[h][q][r][s]	509 R (s)[h]
assignment		ν_3	ν_1

ν_3 (cm^{-1}) in other solvents:

CH_3NO_2, 532; dioxane 530; CCl_4, 538

Ultraviolet Spectrum of XeF_2 Vapour[t][u][v][w], (see also photoelectron spectra):

Wavelength λ_{max}(Å)	Half width $\Delta\nu$(cm^{-1})	est. extinction coefficient e. $mole^{-1}$ cm^{-2} ϵ_{max}	est. oscillator strength f
2300	8249	0.86×10^2	0.0033
1580	8060	1.12×10^4	0.42
1425	(1000)	0.4×10^4	0.02
1335	(1290)	0.4×10^4	0.02
1215	(2070)	0.4×10^4	0.03
1145	(2730)	0.6×10^4	0.06

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

Rydberg Bands[y][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

$$\nu_s = \begin{Bmatrix}100,160\\103,950\end{Bmatrix} - \frac{109,737}{(n - 4.04)^2} \text{ cm}^{-1};\ n = 6, 7.$$

and $$\nu_d = \begin{Bmatrix}100,160\\103,950\end{Bmatrix} - \frac{109,737}{(n - 2.42)^2} \text{ cm}^{-1};\ n = 5, 6, \ldots$$

The ν_s Rydbergs are[y] the spin orbit split components of a $5\pi_u \longrightarrow 6s$ transition.

The ν_d Rydbergs are probably the spin orbit components of a $5\pi_u \longrightarrow 5d$ transition.

Photoelectron spectra (see also UV spectrum)[y][z]:

Term Energies in Xe and XeF_2[y]

Xe[a']		XeF_2	
Upper State	Term, cm^{-1}	Upper State	Term, cm^{-1}
$5p(^2P_{3/2})6s$	30,400	$5\pi_u(^2\Pi_{3/2})6s$	30,865
$5p(^2P_{1/2})6s$	31,433	$5\pi_u(^2\Pi_{1/2})6s$	30,080
$5p(^2P_{3/2})6p$	19,322		
$5p(^2P_{1/2})6p$	19,317		
$5p(^2P_{3/2})5d$	16,628	$5\pi_u(^2\Pi_{3/2})5d$	17,860
$5p(^2P_{1/2})5d$	16,567	$5\pi_u(^2\Pi_{1/2})5d$	16,600
$5p(^2P_{3/2})7s$	12,551		
$5p(^2P_{1/2})7s$	12,590		

Appearance potentials of ions [z][y]

	A.P.(ev)
XeF_2^+	12.28
XeF^+	12.78

Observed and Calculated Ionization Potentials (eV) of XeF_2 (y)

Adiabatic Obs.	Vertical Obs.	0.92 K. T. Calc.
12.35 ± 0.01 ‡	12.42 ± 0.01	12.51 ($5\pi_u$)
12.89 ± 0.01	12.89 ± 0.01	
ca 13.5	13.65 ± 0.05	11.79 ($10\sigma_g$)
14.00 ± 0.05	14.35 ± 0.05	14.71 ($3\pi_g$)
15.25 ± 0.05	15.60 ± 0.05	15.92 ($4\pi_u$)
	16.00 ± 0.05	
16.80 ± 0.05	17.35 ± 0.05	16.93 ($6\sigma_u$)
	ca 22.5	25.24 ($9\sigma_g$)
		37.10 ($5\sigma_u$)
		37.20 ($8\sigma_g$)

‡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° ; $^{19}F\sigma$, 612 p.p.m.; line width 6.0 G

HF solution (1 mole/1000g), - 19.5:

	Ref.	$^{19}F\sigma$ (p.p.m.)	$^{129}Xe\sigma$ (p.p.m.)	$J_{^{19}F - ^{129}Xe}$ (c/s)
	(b')	629	- -	5,600
	(c')	630.3	-3930	5,690

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

	Ref.			
	(i)	631	- -	5,640 ± 20
CH_3CN solution	(h)	610 ± 2	- -	5,450 ± 20

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

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

H_o = applied field strength $\Delta\sigma = \sigma_\perp - \sigma_{||}$, where $\sigma_\perp$ and $\sigma_{||}$ are the shielding $\perp$ and $||$ to symmetry axis.)

M_2 Obs = 3.25 G^2, M_2calc = 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)

	splitting (mm/sec)	e^2qQ (Mc/sec)	Isomer shift (mm/sec)	U_p ‡	h_p	Electron transfer per bond
(4.2°K)	39.00 ± 0.10	2490	0.10 ± 0.12	1.43*	1.43*	0.71*

‡ U_p is the quadrupole coupling in units of the quadrupole coupling of a single p_z hole.

* h_p is the hole in the 5p shell, assuming that the bonding involves P_σ orbitals only.

Molecular structure

Vapour: $\underline{D}_{\infty\,\underline{h}}$ geometry established by IR and R data[o] [u']

Rotational IR (ν_3 band)[p] gives, $\underline{\alpha}_3 = 3.31 \times 10^{-4}\,cm^{-1}$,

$\underline{B}_o = 0.11350\ cm^{-1}$, and $\underline{X}_{23} = -1.44\ cm^{-1}$.

From $\underline{B}_o$, the Xe-F bond length is $1.977_3 \pm 0.0015$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; $z = 2$.

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

Structural parameters[h']:

	$\underline{z}$	$\underline{\beta}$	$\underline{\beta}_{33}$	$\underline{f}$ (fermi units)
Xe	(0.0)	0.0341 ± 0.0020	0.0083 ± 0.0006	(0.476)
F	0.2838 ± 0.0004	0.0635 ± 0.0022	0.0087 ± 0.0004	(0.550)

(values in parentheses were not varied; $\underline{f}$ are neutron scattering amplitudes)

Intramolecular distance Xe — F, 2.00 ± 0.01Å

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

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

Magnetic susceptibility [i']

$-\chi_M = 40\text{-}50 \times 10^{-6}$ 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)(v)(u)(y)

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Table 3.2.1.

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The Kinetics of XeF_2 Formation. Rate studies of the interaction of xenon with fluorine have shown that the reaction is zero order in Xe.[106, 107, 108] These same investigations indicate that the reaction is primarily heterogeneous. Weaver[107] has noted a 1st order dependence of the reaction on F_2, 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 CoF_3, NiF_2 and CaF_2 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 [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.

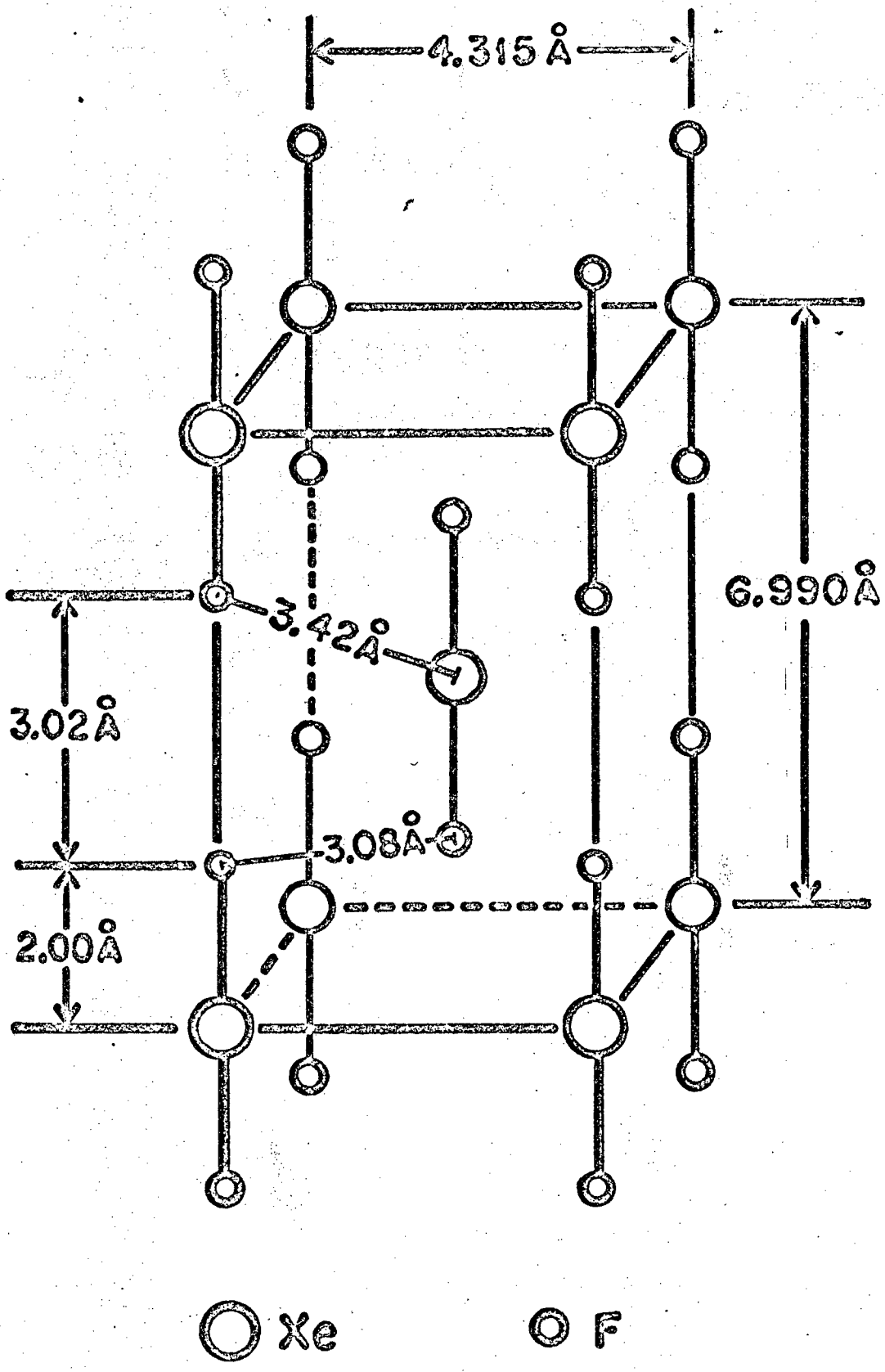
Structures Features. Infrared [110, 111] and Raman[112, 113, 114, 115, 110] spectroscopy have established the symmetrical linear ($D_{\infty h}$) geometry of the XeF_2 molecule. The vibrational spectroscopic data is given in Table 3.2.1. A high-resolution infrared study[116] of the ν_2 stretching mode 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[117, 118] from their single-crystal neutron diffraction study is 2.00± 0.01Å.

In crystalline XeF_2, 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 stong interactions between molecules since each xenon atom has not only its 2 bound fluorine

Figure 3.2.2

Figure 3.2.2

The Unit Cell of Xenon Difluoride



atoms at 2.0Å but also 8 fluorine atoms at 3.41Å, 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 (ΔH_{sub} = 13.2 kcal mole^{-1}) and Jortner *et al*[104] have convincingly accounted for these features. They point to the considerable bond polarity in the XeF_2 molecule and account for ΔH_{sub} in terms of an electrostatic stabilization energy of 11.31 kcal mole^{-1} (assuming the charge distribution in each molecule to be $^{-0.5}F\text{-}Xe^{+1}\text{-}F^{-0.5}$) and a dispersion energy of ~2 kcal mole^{-1} — a total of ~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 65.1Å^3. But in many fluorides (e.g., XeF_6, IF_7, $IF_6^+AsF_6^-$) the effective volume of each fluorine ligand is 17.8Å^3. Therefore ~ 29Å^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 XeF_2 samples. Nevertheless, bond polarity in XeF_2 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 XeF_2, 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.[127] They have shown that the vertical ionization potentials of the first eight ionizations in the XeF_2 molecule compare well with the results of Gaussian Type Orbital calculations. The first two ionic states of XeF_2 are the $^2\pi_{3/2}$ (12.42 ev) and $^2\pi_{1/2}$ (12.89 ev) spin-orbit components, formed by ionization from the highest filled π orbital ($5\pi_u$). They conclude that the XeF_2 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 XeF_2 yields characteristic Rydberg energies which correlate with Rydberg excitation energies derived by Rice and his coworkers[128, 129, 130] from the XeF_2 ultraviolet spectral data. The interpretation given by the latter workers for the ultraviolet spectrum of XeF_2 is in terms of a semi-empirical LCAO molecular orbital description.

The Bonding in XeF_2. The bonding models for XeF_2 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 [23] gives the essence of these models. On the other hand, more recently, Mitchell[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 5dσ Xe orbital in the bonding. Mitchell, furthermore, argues that Coulson's favoured valence bond structure, $F\text{-}Xe^{+}F^{-}$, is energetically unfavourable. However, the $F^{-}Xe^{2+}F^{-}$ structure is claimed to be lower in energy than $F\text{-}Xe^{+}F^{-}$ 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_5, 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:

$$XeF_2 + HL \longrightarrow FXeL + HF$$

$$FXeX + HL \longrightarrow XeL_2 + HF$$

The high exothermicity of ΔH_f (HF) is a major factor in bringing about the forward reaction. Solid products have been obtained for

L = SO_3F and ClO_4 [86] ; $OTeF_5$ [131, 132] and possibly O_2CCF_3 [133,134]. The perchlorates and trifluoroacetates are detonatable. 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_3CN [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: $I_2 + XeF_2 \xrightarrow{F^- \text{ acceptor}} Xe\uparrow + 2IF$; $IF + XeF_2 \xrightarrow{F^- \text{ acceptor}} Xe\uparrow + IF_3$, etc. Oxidizable strong fluoride ion acceptors interact rapidly with the difluoride:

$$XeF_2 + 2SO_3 \longrightarrow Xe\uparrow + S_2O_6F_2$$

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, 4.1×10^{-2} mole of benzene in interaction with 1.26×10^{-2} mole of XeF_2 for $2\frac{1}{2}$ hr. yields a distillate of composition; 88.72% benzene, 10.28% fluorobenzene, 0.7% p-difluorobenzene and 0.3% o-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] This may be due to the presence of some HF in the latter reaction. It is of interest that the vic difluorides formed in this reaction isomerize to the gem difluorides:

$$XeF_2 + \begin{cases} CH_2 = CH_2 \longrightarrow CH_2FCH_2F \longrightarrow CH_3CHF_2 \\ CH_3 - CH = CH_2 \longrightarrow CH_3CH_2\text{-}CHF_2 \end{cases}$$

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 $XeF^{\cdot}$. 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 5s) orbitals in the bonding

(See 1.3.1 - 4). This must contribute to the ready ionization of XeF_2. A number of salts of the XeF^+ ion have now been established and they are discussed in section 3.2.6. The ionization enthalpy $\Delta H°$ ($XeF_{2(g)} \longrightarrow XeF^+_{(g)} + F^-_{(g)}$) is $\approx$ + 215 kcal mole^{-1}, which compares with that for ONF, $\Delta H°(ONF_{(g)} \longrightarrow NO^+_{(g)} + F^-_{(g)})$, 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 XeF_2 itself. It will probably be essential to use rather electronegative ligands L, and it will be necessary, for stable salts, that $\sum$ (lattice energy — ionization potential of the anion), should be more exothermic than the electron affinity of the cation.

The compounds which XeF_2 forms with XeF_4, IF_5, $XeOF_4$ and XeF_5^+ (see 3.2.7.) preserve the essential form of XeF_2 . The intermolecular bonding in these compounds is primarily coulombic and like that in solid XeF_2 itself. It is a consequence of the considerable bond polarity of XeF_2 .

The aqueous solution chemistry of XeF_2. Xenon difluoride dissolves in water (~25g ℓ^{-1} at 0°) with only very slight decomposition. The presence of molecular XeF_2 in the solution has been established by UV spectroscopy[141] and electrical conductance.[146] The difluoride may be recovered by CCl_4 extraction or fractional distillation.[141] Clearly, XeF_2 has remarkable kinetic stability, since $\Delta G°(XeF_{2\,(aq)} + H_2O \longrightarrow Xe_{(g)} + \frac{1}{2}O_{2(g)} + 2HF_{(aq)})$ has been estimated[84] to be - 53.4 kcal mole^{-1}, from which $K_{eq} = [Xe][O_2]^{\frac{1}{2}}[HF]^2 / [XeF_2][H_2O] \approx [HF]^2 / [XeF_2] \approx 10^{40}$. Neutral or acid solutions decompose rather slowly, the half-life being ~ 7 hr. at 0°.[141] So far, XeF_2 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,[147] in 0.01 M perchloric acid, XeF_2 oxidation of water proceeds with a first order rate constant of 4.2×10^{-4} sec^{-1} at 25°, with an activation energy of 19.6 kcal $mole^{-1}$ and ΔS(activation) = -8.1 ev. Two independent studies of the kinetics of XeF_2 hydrolysis, in water alone, have been reported. Fehér and Lörine studied[148] 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*[84] 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 $XeF^{\cdot}$ 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 4×10^{-4} ohm^{-1} cm^{-1}, found[146] 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[146] 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. $XeF_{2(aq)} + F^-_{(aq)} \rightleftharpoons XeF^-_{3(aq)}$) or F^- ion abstraction (e.g. $XeF_{2(aq)} + HF_{(aq)} \rightleftharpoons XeF^+_{(aq)} + HF_2^-$) are not significant processes in acid aqueous media.

The interaction of XeF_2 with water is not only catalized by base but also by species which have an affinity for fluoride ions.[149] 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.[94, 141] 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:

$$H_2O + XeF_2 \xrightarrow{OH^-} 2HF + Xe(OH)_2 \text{ or } XeO.\ y\ H_2O$$

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: $2XeO \rightarrow Xe + XeO_2$. It is of interest that the disproportionation of hypoiodite, $IO^- + IO^- \rightarrow I^- + IO_2^-$ is very slow compared with the iodide catalyzed reaction[150] involving an activated complex $\left\{ I^- + 2IO^- + H^+ \right\}$. The xenon counterpart of the latter would be unlikely to exist, since Xe (0) would not be retained. Evidently, XeO_3 introduced[147] into an aqueous XeF_2 solution

is extensively consumed in the course of the interaction of XeF_2 with water, although an aqueous solution of XeO_3 itself can be kept almost indefinitely.[151] It has been presumed that the XeO_3 consumption results from reduction by an XeO intermediate: $XeO_{(aq)} + XeO_{3(aq)} \longrightarrow 2XeO_2$; $XeO_2 \longrightarrow Xe + O_2$, but even an oxygen atom could serve as an equally effective reducer $[O] + XeO_3 \longrightarrow XeO_2 + O_2$. The interaction of XeF_2 with water is <u>in effect</u> an oxygen atom source for bromate oxidation to perbromate.[152] This is perhaps the most dramatic example of the oxidizing capability of XeF_2 since perbromates were previously unknown and had been considered by some to be impossible to synthesize.

Aqueous XeF_2 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 XeF_2 / Xe in acid solution to be 2.2 v and for XeO?/Xe in alkaline solution to be 1.3 v. A polarographic study[154] shows that acidified XeF_2 solutions are reduced in a single step to xenon, at a potential of ~ 0 v. with respect to the Hg_2SO_4/Hg reference electrode.

Analysis and identification. The analysis of XeF_2 samples may be carried out conveniently[92] 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:

$$Hg + XeF_2 \longrightarrow HgF_2(Hg_2F_2) + Xe$$

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[89] which used hydrogen to reduce the difluoride. Hydrolysis in base[155], with gas collection ($Xe + \frac{1}{2}O_2$) and mass spectrometric characterization, together with acidimetric analysis for the HF formed in the hydrolysis:

$$H_2O + XeF_2 \longrightarrow 2HF + Xe + \tfrac{1}{2}O_2$$

or iodimetric titration, on the basis of the reaction:

$$XeF_{2(aq)} + 2I^- \longrightarrow Xe + 2F^- + I_2$$

have also been used effectively.[94]

Perhaps the most sensitive test for the presence of XeF_4 and XeF_6 in the difluoride sample is the melting point (129.02°)[102]. The distinctive infrared absorptions of XeF_2 (555 cm^{-1}), XeF_4 (590 cm^{-1}) and 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 XeF_4 in XeF_2 can be detected. The advent of laser Raman spectroscopy has now made identification or detection of very small quantities or concentrations of XeF_2 rather easy. A dry glass container is satisfactory

for sample holding and the band due to symmetric XeF_2 stretch (ν_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 Corpn.) 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 β decay of their ^{129}I relatives:

$$^{129}ICl_2^- \xrightarrow{-\beta} {}^{129}XeCl_2$$

Table 3.2.2

Comparison of $XeCl_2$ with other Xe Dihalides and KrF_2

		XeF_2	$XeCl_2$	$XeBr_2$	KrF_2
Infrared data	ν_3 (cm^{-1})	547[a]	313[b]	--	580[a]
	force const. k_r-k_{rr} ($m.$ dynes/Å)	2.60[b]	1.317[b]	--	2.59[b]
*Mössbauer data[c][d] (^{129}Xe)	Splitting (mm/sec)	39.0 ± 0.1	28.2 ± 0.1	22.2 ± 0.4	- - -
	e^2qQ (MH_2)	2490	1800	1415	960 ± 30[e]
	Electron transfer per bond‡	0.72	0.52	0.41	0.5[e]

*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 pσ.

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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 Cl_2 relative to 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., $XeF_2 + HCl \text{ (or } BCl_3) \xrightarrow{-70^\circ} Xe + Cl_2 + 2HF \text{ (or } BF_nCl_{3-n})$ [135]

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°K, has been convincingly attributed to the ν_3 (asymmetric Xe - Cl stretch) mode of $XeCl_2$. Since no other absorption (attributable to the symmetric stretch, ν_1) was observed, the molecular symmetry is evidently $\underline{D}_{\infty h}$ (the bending mode, ν_2, is expected to be < 200 cm^{-1}, i.e. below the limit of detection in this study).

The asymmetric stretching force constant $\underline{k}_r - \underline{k}_{rr}$, given in Table 3.2.3, shows that the Xe - Cl bond is weak compared with the difluoride Xe - F and Kr - F bonds.

Table 3.2.2.

The Mössbauer effect is uniquely suited to study the process of xenon compound formation by β decay of ^{129}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 γ-radiation. This radiation is emitted from the ^{129}Xe nucleus, the 39.6 keV first excited state of which is

populated in the $\underline{\beta}$ decay of ^{129}I. This state decays with a mean life $\tau = 1.46 \pm 0.06 \times 10^{-9}$ sec, usually by internal conversion, but by $\underline{\gamma}$ emission in 8% of the cases. The excited ^{129}Xe nuclear state (spin and parity $\frac{3}{2}+$) has a quadrupole moment eQ, which results in a doublet absorption spectrum if the electric field gradient eq ($= \partial^2 V/\partial z^2$) 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 qQ. On the basis of a calibration against spectroscopic and atomic-beam studies of the quadrupole coupling caused by a single hole in the $5\underline{p}$ electron shell of ^{131}Xe, and comparison of ^{129}Xe and ^{131}Xe Mössbauer splittings in XeF_4[158], a quadrupole splitting of 27.3 mm/sec, is assigned to the loss of one $5_{\underline{p_z}}$ electron (symmetry axis $\underline{z}$) or a pair of $5_{\underline{p_x}}$ or $5_{\underline{p_y}}$ electrons. This interpretation assumes that the only xenon orbitals involved in the bonding are the $5\underline{s}$ and $5\underline{p}$, the latter having prime importance in forming $\underline{\sigma}$ molecular orbitals.

The observed data for $XeCl_2$ are given in Table 3.2.2. It is clear, from the comparison with the XeF_2 and $XeBr_2$ data, that the bond polarity decreases in the sequence $XeF_2 > XeCl_2 > XeBr_2$. This is in harmony with the decrease in electronegativity of the ligands F→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 $5_{\underline{d}}$ orbital participation in the bonding as Mitchell asserts,[25a] 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 β decay of its ^{129}I relative:

$$IBr_2^- \xrightarrow{-\beta} XeBr_2$$

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 $XeO_{(g)}$ was detected spectroscopically[159] as a bound gas phase species prior to 1962. The bond energy for this species is given as 9 kcal $mole^{-1}$ (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 $(IF)_n$ by Schmeisser and Scharf [160] is a fluorine bridge polymer). Polymeric XeO would presumably be a helical polymer with linear or near linear -(O-Xe-O)- groups and a non-linear Xe-O-Xe bond. The fleeting yellow product of XeF_2 hydrolysis could be such a polymer. Of course, $(XeO)_n$ 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,[86, 131, 133] the known ligands are $-OSO_2F$, $-OClO_3$ $-OTeF_5$ and $-OC(O)CF_3$.[134] 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:

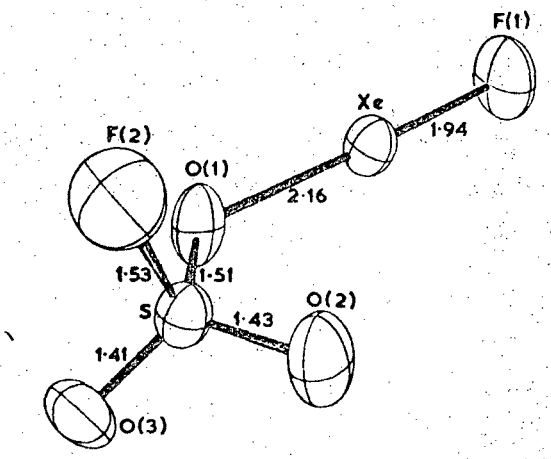
$$XeF_2 + HL \longrightarrow FX\text{-}L + HF$$

The considerable exothermicity of $\Delta H_f^\circ(HF)(= -64.92$ kcal mole$^{-1})$[19] provides the main driving force for these reactions. In the cases of the fluorosulphate and perchlorate[86, 135], the difluoride is treated with an equimolar amount of acid at temperatures of -75° 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 $FXeOSO_2F$



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 ± 06°.

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 $FXeOSO_2F$

is as though the bonding were tending to $XeF^+ SO_3F^-$ (see 3.2.6), i.e., the resonance form $F\text{-}Xe^+SO_3F^-$ has greater weight than $^-F\ Xe^+\text{-}OSO_2F$. 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 $FXeOSO_2F$.

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 ~ 20° and decomposes smoothly when molten according to the equation[86]

$$2FXeSO_3F \longrightarrow XeF_2 + Xe + S_2O_6F_2 .$$

Presumably, this involves radical formation: $FXeSO_3F \longrightarrow FXe + SO_3F$, and the yellow green colour gives some support to this. The equilibrium $2SO_3F \rightleftharpoons S_2O_6F_2$ is well known[161] and, as has been discussed under $XeF^{\cdot}$ (section 3.1.1), all evidence indicates that the radical disproportionates: $2XeF \longrightarrow Xe + XeF_2$. 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_2O_7, O_2, Xe and ClO_2) and occasionally proceeding with explosive violence.[135] In contrast, the pentafluoroorthotellurate is thermally quite stable (to 120° in prefluorinated vessels) and can be distilled[131] (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 $FXeOSO_2F$, and Related Compounds

	$FXeOSO_2F$[a]	$FXeOClO_3$[a]	$FXeOTeF_5$[b]	$FXeOCOCF_3$[c]
Colour	Colourless	Colourless	v. pale yellow	pale yellow?
m.p. (°C)	36.6	16.5	-24	(detonates)
b.p. (°C)	sublimable	(detonates)	53(0.01 torr)	"
Half-life at ~ 20°C	~ 1 week	rapid decomposition of melt.	∞	~ 10 hrs.
Unit cell	a=9.88, b=10.00, c=10.13Å(all±0.01Å) z=8, space group D_{2h}^{15} = Pbca[a]	Powder patterns show that $FXeOClO_3$ is similar to $FXeOSO_2F$ but not isomorphous with it.[a]	- - - -	- - - -
Solvents	CH_3CN	CH_3CN		CH_3CN, CCl_4
^{19}F n.m.r. data				
$\underline{o}_F$(p.p.m.)	- - -	- - -	37(F(Te))	- - - -
($\underline{o}_{CF_3COOH}$ = 0)	- - -	- - -	66.3(F(Xe)) (in CH_3CN soln.)	

	IR(a)(d)	R(a)(d)	IR(a)(d)	R(a)(d)	IR(e)	IR(in CH_3CN)(c)
Infrared and		253s		202m		
			$\underline{\delta}$(F-Xe-O)			
		243m		258s		
Raman bands	$\underline{\delta}$(Xe-OS)		$\underline{\delta}$(Xe-O-Cl)			
(cm^{-1})		395mw				
	$\underline{\rho}$(S-F)					
& assignments						
		433s				
	(?)					
			505vs	507vs	470m	
		540s	520sh 530sh	525ms	520m	510
	518vs	521vs				
	$\underline{\nu}$(Xe-F) + $\underline{\nu}$(Xe-O)		$\underline{\nu}$(Xe-F) + $\underline{\nu}$(Xe-O)		$\underline{\nu}$(Xe-F)+ $\underline{\nu}$(Xe-O-)	$\underline{\nu}$(Xe-F) + $\underline{\nu}$(Xe-O-)
		531m				
					623 s	
		536m	586s		704 vs	
	597w	584mw		593w		
					768 s	
	614m	616mw	620 628 } vs	614w 638mw		
	$\underline{\delta}$(O-S-O)				$\underline{\nu}$(Te-F)+ ν(Te-O-)	
	798s	800w	722vs 758sh	726w		
	$\underline{\nu}$(S-F)			754 770 } w		970-1220
	970vs	970w	$\underline{\delta}(ClO_3) + \underline{\rho}_r(ClO_3)$			$\underline{\nu}$(C-F)
	$\underline{\nu}$(S-O-)		+$\underline{\nu}$(Cl-O-)			
	1210vs	1197w	1018vs	1014 mw		
			1048sh	1032 vw		
	$\underline{\nu}$(S=O)		$\underline{\nu}$(Cl=O)			
	1393s	1390w		1243 vw		1730
			1215vs 1295w	1202 mw		
	$\underline{\nu}$(S=O)		$\underline{\nu}$(Cl=O)			$\underline{\nu}$(C=O)

Table 3.2.4
References

(a) N. Bartlett, M. Wechsberg, F. O. Sladky, P. A. Bulliner, G. R. Jones and R. D. Burbank, Chem. Commun. (1969) 703; N. Bartlett and F. O. Sladky, The Second European Fluorine Chemistry Symposium, Göttigen, August 28-31, 1968.

(b) F. O. Sladky, Angew Chem. Int. Ed. 8 (1969) 373.

(c) M. Eisenberg and D. D. DesMarteau, J. Inorg. Nucl. Chem. Letters 6 (1970) 29.

(d) P. A. Bulliner, Ph. D. Thesis, Princeton University, 1970.

(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)

$$FXeOR + HOR \longrightarrow Xe(OR)_2$$

Attempts to prepare mixed compounds (e.g. by interaction of HSO_3F with $FXeOTeF_5$) have so far failed:[162]

$$FXeOTeF_5 + HOSO_2F \longrightarrow HF,\ S_2O_6F_2,\ F_5TeOTeF_5,\ Xe,\ O_2$$

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):

$$FXe\text{-}OR + AsF_5 \longrightarrow \left[XeOR\right]^+\left[AsF_6\right]^- ?$$

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]

$$FXeOTeF_5 + CsF \begin{cases} \longrightarrow TeF_6 + (FXeO^-Cs^+) \longrightarrow CsF + Xe + \tfrac{1}{2}O_2 \\ \longrightarrow XeF_2 + CsOTeF_5 \end{cases}$$

raises the possibility of isolating $FXeO^-$ salts by careful control of reactions of thes kind. Much can probably be achieved, in exploring the chemistry of these compounds, by exploiting the solvent properties of CH_3CN (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 $FXeOSO_2F$:

$$Xe(OSO_2F)_2 \xrightarrow[\text{at } 20°]{\text{spontaneous}} Xe + (SO_3F)_2$$

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 $(SO_3F)_2$ 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):

$$Xe(ClO_4)_2 \xrightarrow{\sim 20°} Xe + (ClO_3)_x + O_2 \ (+ \text{ some } Cl_2O_7)$$

$$Xe(OTeF_5)_2 \xrightarrow{120°} Xe + F_5Te\text{-}O\text{-}TeF_5 + O_2 \ (+ \text{ some } TeF_6)$$

$$Xe(OCOCF_3)_2 \xrightarrow[t_{\frac{1}{2}}:17\text{hr.}]{\sim 20°} Xe + C_2F_6 + 2CO_2$$

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]:

$$Xe(OTeF_5)_2 + HOSO_2F \longrightarrow Xe(OSO_2F)_2 + 2HOTeF_5$$

but attempts to displace the telluric acid with $HOOCCF_3$[162] have led to

Table 3.2.4.

Physical Properties of $Xe(OSO_2F)_2$ and Related Compounds

	$Xe(OSO_2F)_2$ [a]	$Xe(OClO_3)_2$ [a]	$Xe(OTeF_5)_2$ [c]	$Xe(OCOCF_3)_2$ [e]
Colour	pale yellow	pale yellow	colourless	pale yellow
m.p. (°C)	43-45 (decomp.)	- - -	35-37	- - -
Solvents	CH_3CN	CH_3CN	CH_3CN, CCl_4 (explosive with C_2H_5OH, acetone, benzene)	CH_3CN
Unit Cell	a = 7.82Å [b] b = 13.5 c = 6.78 β = 96° z = 4	- - -	a = 15.6Å [d] b = 8.7 c = 12.9 z = 4 space group Cmca	- - -
Vibrational Spectra(cm^{-1})	See Table 3.2.5		IR: 780 w; 705 vs; 628 vs; 475m R: 701 w; 692 m; 647m; 434 m; 300 w; 320 w; 237 m; 178 vw; 131 vs ν(Te-F)+ ν(Te-O-); ν(Xe-O-); δ(O-Xe-O)?	IR: 510 ν(Xe-O-); 970-1240 ν(C-F); 1730 ν(C=O)

(a) N. Bartlett, M. Wechsberg, F. O. Sladky, P. A. Bulliner, G. R. Jones and R. D. Burbank, Chem. Commun. (1969) 703.

(b) M. Wechsberg and N. Bartlett, to be published.

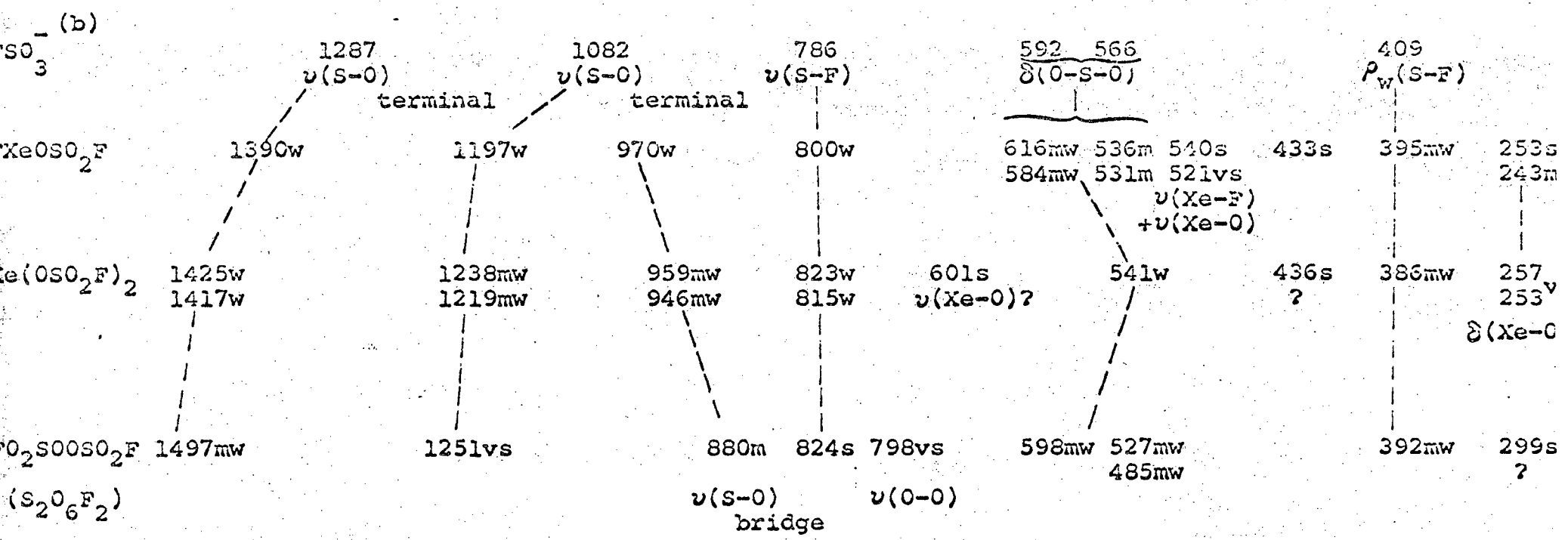
(c) F. O. Sladky, Angew Chem. Int. Ed. 8 (1969) 523.

(d) F. O. Sladky, unpublished information.

(e) M. Eisenberg and D. D. DesMarteau, Inorg. Nucl. Chem. Letters, 6 (1970) 29.

Table 3.2.5

Raman Frequencies and Assignments for $FXeOSO_2F$, $Xe(OSO_2F)_2$ and $S_2O_6F_2$.[a]



w = weak, m = medium, s = strong, v = very

υ = stretching, δ = deformation, ρ_w = wagging

(a) P.A. Bulliner, Ph.D. Thesis, Princeton University, 1970.

(b) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, 1963.

decomposition:

$$Xe(OTeF_5)_2 + 2HOOCCF_3 \xrightarrow{\sim 20^\circ} Xe + 2HOTeF_5 + 2CO_2 + C_2F_6$$

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 $Xe(OSO_2F)_2$ and related SO_3F compounds given in Table 3.2.5 supports the R-O-Xe-O-R formulation but suggests that the molecule is not centrosymmetric.

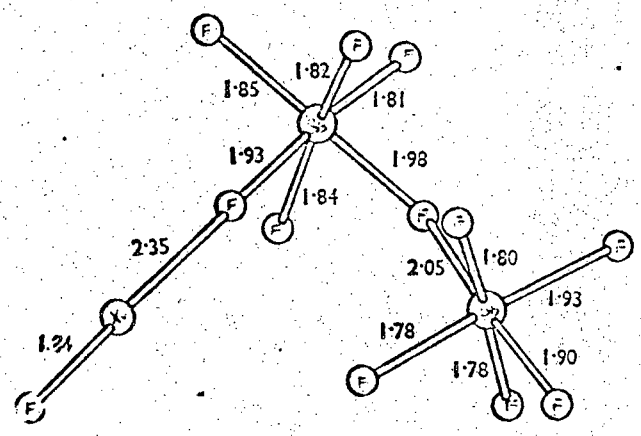
3.2.6 XeF_2 as a Fluoride Ion Donor

Compounds of composition XeF_2 $2MF_5$ (where M is a quinquevalent metal atom) have been known since 1963 [14, 163], but several years passed before they were shown to be salts containing the XeF^+ [164, 165, 87] ion. Indeed, strong fluoride ion acceptors, such as AsF_5 and the metal pentafluorides, readily withdraw a fluoride ion from XeF_2 and three classes of salt have been established[87] : $XeF^+[MF_6]^-$, (XeF_2,MF_5); $XeF^+[M_2F_{11}]^-$, $(XeF_2, 2MF_5)$ and $Xe_2F_3^+[MF_6]^-(2XeF_2,MF_5)$. It is quite possible that the range of salts is more extensive than this since the phase study by Maslov et al [166] of the XeF_2–SbF_5 system established the compounds XeF_2, SbF_5; XeF_2, 1.5 SbF_5; XeF_2, $2SbF_5$(proved[165] to be $XeF^+[SbF_6]^-$) and XeF_2, $6SbF_5$.

Laboratory preparation. It is possible to prepare the XeF_2 salts by simply fusing XeF_2 /MF_5 mixtures [165, 166, 167] 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°) has proved to be excellent for this purpose.[87] 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 $XeF^{+}[Sb_2F_{11}]^{-}$.



which is then attached to a vacuum line. Bromine pentafluoride is distilled on to the XeF_2/MF_5 mixture, which is allowed to dissolve at room temperature. By removing the BrF_5 slowly, well-crystalline, homogeneous material may be obtained.

Structural features. The molecular structure [165] of $XeF^+[Sb_2F_{11}]^-$ is represented in Figure 3.2.4. The structure establishes the existence of a short-bonded 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 XeF^+. It is clear from the Raman spectra[87] of the compounds XeF_2, $2MF_5$ that they are structurally similar to $XeF^+[Sb_2F_{11}]^-$. All are characterized by strong bands in the 600-621 cm^{-1} region assigned to the XeF^+ stretch. The rather short Xe ··· F distance

Figure 3.2.4.

The Molecular Structure of $XeF^+[Sb_2F_{11}]^-$.

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.

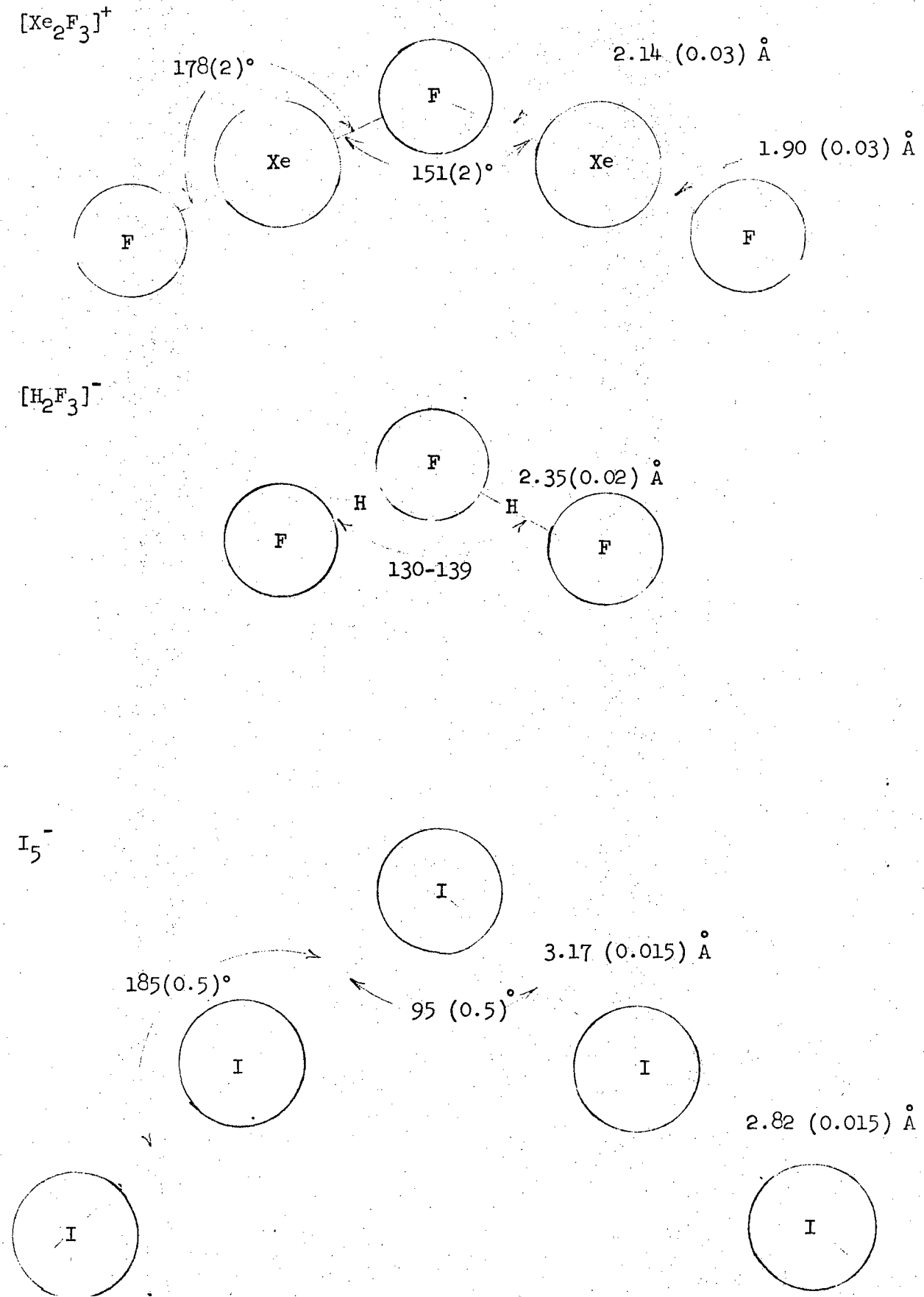
The Raman data for the XeF_2, MF_5 compounds show the formulation $XeF^+[MF_6]^-$ to be appropriate, the vibrational characteristic of the XeF^+ species being very like that of the $XeF^+[M_2F_{11}]^-$. Not only is there evidence of a weak interaction of the XeF^+ ion with the MF_6^- but some interaction between the XeF^+ ions is also indicated. It should be noted that I-Cl forms a chain polymer [168] and it may well be that the XeF^+ species tends to that behaviour.

The crystal structure of $2XeF_2, AsF_5$ proves [164] the formulation $Xe_2F_3^+[AsF_6]^-$ to be appropriate. The cation is planar and $\underset{\sim}{v}$ shaped and is represented in Figure 3.2.5. The Raman spectra of this salt and the other $2XeF_2$, MF_5 compounds establish that the latter also contain the $Xe_2F_3^+$ ion.[87] This ion has a similar shape to that observed in the $H_2F_3^-$ and I_5^- ions.

Figure 3.2.5

Figure 3.2.5

A Comparison of the $Xe_2F_3^+$, $H_2F_3^-$ and I_5^- ions.



The near linearity of the FXe··· F assemblies indicates that the cation resembles two XeF_2 molecules sharing a common F atom. The bond length disparity shows, however, that the five centre system is tending to $F\text{-}Xe^+F^-Xe^+\text{-}F$. It is perhaps of significance that the $Xe_2F_3^+$ salts show little evidence of interaction of the cation with the anion -- highly polarizing XeF^+ ions are adequately "neutralized" by the bridging fluoride ligand.

Reactions. The fluoride ion donor ability of XeF_2 is comparable to that of nitrosyl fluoride and the available thermochemical data indicate that $\Delta H^\circ(XeF_{2(g)} \longrightarrow XeF_{(g)}^+ + F_{(g)}^-) = +215$ kcal mole^{-1} (see section 3.2.2 and Figure 3.2.1). The increase in the Xe-F bond energy (48 kcal mole^{-1} in the cation, 32 in XeF_2) in cation formation contributes to fluoride ion donor ability of the difluoride. It is a better F^- donor than XeF_4 but inferior to XeF_6.[169]

An important aspect of the XeF^+ species is its high electron affinity. Since $E(XeF^+)$ = B.E.(XeF^+) - B.E.(Xe-F)-I(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 $XeF^+[OsF_6]^-$ to OsF_6 and xenon:

$$3XeF^+[OsF_6]^- \longrightarrow [Xe_2F_3]^+[OsF_6]^- + 2OsF_6 + Xe$$

In the $[Xe_2F_3]^+$ ion, each XeF^+ species receives electron density from the associated F^- ion (for which $I(F^-) = 83$ kcal mole^{-1}). Thus the assembly becomes a multicentre bonded system, with a lower electron affinity than XeF^+.

So far, the salts have not been used as reagents but the acid catalysis of XeF_2 oxidation and fluorination reactions, referred to in section 3.2.2, implies that the XeF^+ or $Xe_2F_3^+$ ions are the effective oxidizers.

The known salts are briefly described in Table 3.2.6.

Table 3.2.6.

Some Physical Properties of $XeF^+[MF_6]^-$, $XeF^+[M_2F_{11}]^-$ and $Xe_2F_3^+[MF_6]^-$ Salts

$XeF^+[MF_6]^-$ Salts

M =	As[a]	Ru[a]	Os	Ir[a]	Pt[a]	Ta[b]	Nb[b]
Colour	pale yellow-green	pale yellow-green	brown*	yellow-green	orange-red	pale yellow	pale yellow
m.p. (°C)	- -	110-1	- -	152-3	82-3	52-3	30-5
Xe-F Stretch (Raman, cm^{-1})[a]	- -	604,599	- -	608,602	609,602	- -	- -
Unit Cell[a]	← isomorphous →					- -	- -

a = 11.1, b = 7.96, c = 7.24Å, z = 4

Space group Pnma

*unstable

$XeF^+[M_2F_{11}]^-$ Salts

M =	Sb	Ru	Ir	Pt	Ta	Nb
Colour	yellow[c]	bright-green[a]	orange-yellow[a]	dark red[a]	pale yellow[b]	pale yellow[b]
m.p. (°C)	63[c,d]	49-50[a]	69-70[a]	- -	82-3[b]	42-7[b]
Xe-F Stretch (Raman, cm^{-1})[a]	621	604,598	612,601	- -	- -	- -
Unit Cell		← isomorphous →			← isomorphous →	

$Xe_2F_3^+[MF_6]^-$ Salts

M =	As[e,a]	Ru[a]	Os[a]	Ir[a]
Colour	pale yellow-green	pale yellow-green	pale yellow-brown	pale yellow-green
m.p. (°C)	99-100[e,a]	98-99[a]	- -	92-93[a]
XeF Stretch (Raman, cm^{-1})[a]	600,588	593,579	593,582	592,578
Unit Cell		← isomorphous →		

a = 15.443
b = 8.678
c = 20.888
β = 90.13
z = 12

Table 3.2.6.

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3.2.7 Molecular Adducts of XeF_2

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 XeF_4. A three-dimensional X-ray structural analysis[170] quickly showed, however, that the compound was a 1:1 molecular adduct of XeF_2 and XeF_4. 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 XeF_2 have since been prepared in which the XeF_2 molecule is essentially indistinguishable from the molecule in crystalline XeF_2. Established 1:1 compounds are XeF_2, XeF_4[170]; XeF_2, IF_5[18], XeF_2, $XeOF_4$[135] and $XeF_2[XeF_5]^+[AsF_6]^-$ [135] and the 1:2 compounds XeF_2, $2IF_5$[142] and XeF_2, $2([XeF_5]^+[AsF_6]^-)$[135] have been reported. Some physical properties of the compounds are given in Table 3.2.7.

Table 3.2.7.

Some Physical Properties of XeF_2 Adducts

Preparation. The adducts may be very conveniently prepared by mixing the components[135, 98, 171] in the appropriate molar proportions. By fusing the mixture, or dissolving it in a suitable solvent (e.g. acetronitrile)[142] a homogeneous sample is produced. The 1:1 XeF_2, IF_5 adduct may also be made[98] by heating a xenon/IF_7 mixture to 200°:

$$Xe + IF_7 \xrightarrow{200°} XeF_2,\ IF_5$$

Structure and bonding. Attention has already been drawn to the semi-ionic nature of the bonding in XeF_2 (see sections 1.3.3. and 3.2.2.), and the excellent agreement, with the experimental enthalpy of vapourization, given by the lattice energy calculation for $XeF_{2(cryst)}$, based on coulombic

Table 3.2.7.

Some Physical Properties of XeF_2 Adducts

	XeF_2, XeF_4 [a]	XeF_2, IF_5 [b]	XeF_2, $XeOF_4$
Colour	← colourless solids →		
m.p. (°C)		98	29
$\underline{\nu}_1(XeF_2)$ cm^{-1}	- - -	495	494
Xe^{II}-F bond length* (Å)	2.010 ($\underline{\sigma}$ = 0.006)	2.007 ($\underline{\sigma}$ = 0.009)	- - -
Unit cell	a = 6.64 b = 7.33 } ±0.01Å c = 6.40 $\underline{\beta}$ = 92°40 ± 5' z = 2 space group $P2_1/c$	a = 7.65 } ± 0.01Å c = 10.94 z = 4 space group I4/m	a = 7.56 ± 0.01Å c = 11.36 z = 4 space group I4/m

*Bond length in $XeF_{2(c)}$ = 2.00 ± 0.01Å

(a) J. H. Burns, R. D. Ellison and H. A. Levy, Acta. Cryst. 18 (1965) 11.

(b) G. R. Jones, R. D. Burbank and N. Bartlett, Inorg. Chem. 9 (1970) in press.

(c) N. Bartlett and M. Wechsberg, to be published.

interactions between $^{-\frac{1}{2}}F\text{-}Xe^{+1}\text{-}F^{-\frac{1}{2}}$ molecules. The crystal structure[170] 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[18], illustrated in Figure 3.2.6., nicely illustrates the nature of the intermolecular interactions. Each molecule is surrounded by an approximately cubic

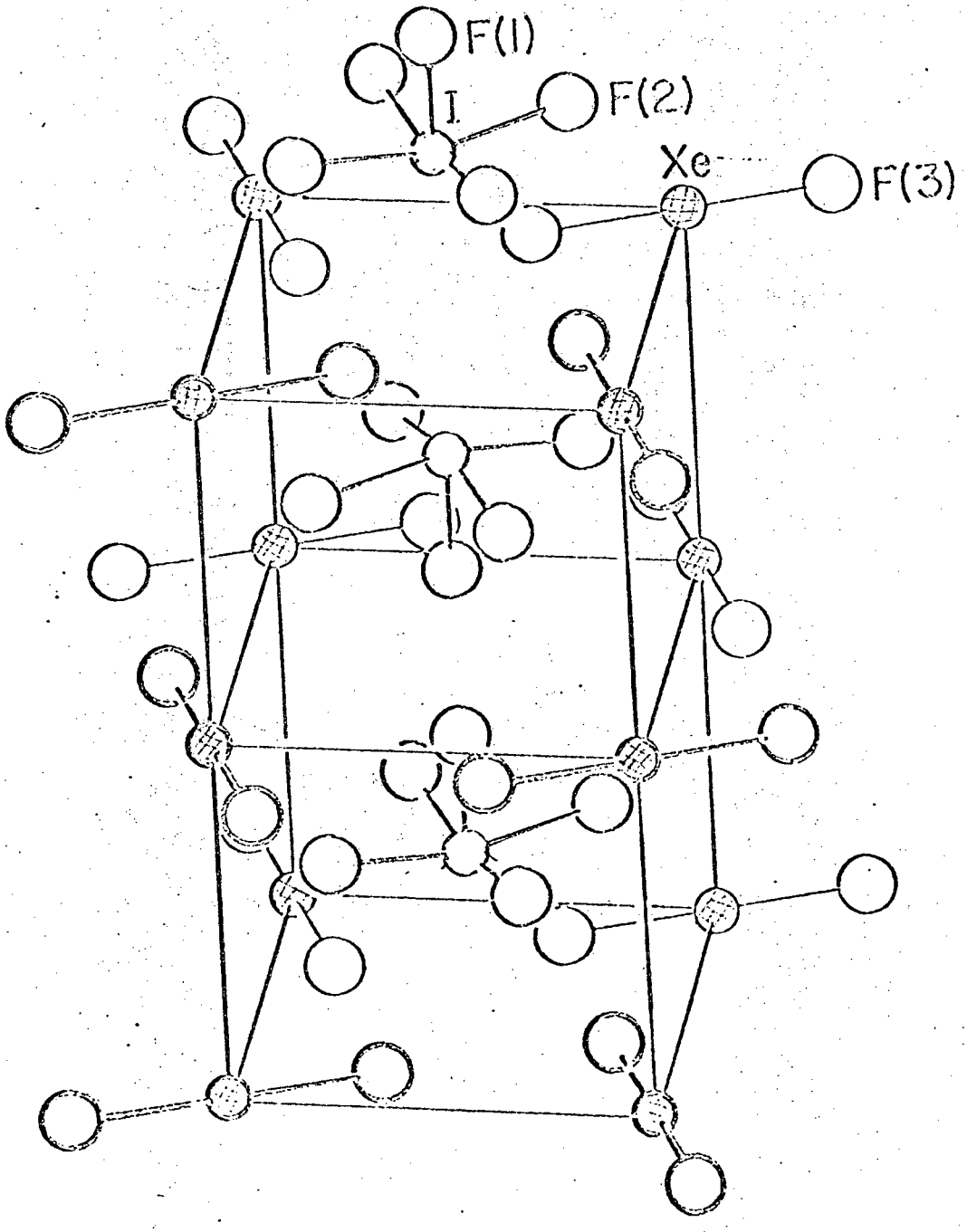
Figure 3.2.6.

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)*	

c. 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)**		

d. 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 (σ 0.009) Å in the XeF_2 molecules is not significantly different from that observed in crystalline XeF_2 (2.00 ± 0.01A).

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. $\angle F_a\text{-}Xe\text{-}F_b = 91^\circ$, whereas in IF_5, $\angle F_a\text{-}I\text{-}F_b = 80^\circ$.

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 β decay of $^{129}IX_4 \longrightarrow {}^{129}XeX_4$.

3.3.1 Xenon Tetrafluoride

Historical and preparative. Xenon tetrafluoride was first reported[2], 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[172] 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.[17b] 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: $XeF_4 + 2SbF_5 \longrightarrow XeF_2, 2SbF_5$! , 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[22] 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,[169]

or else submit the sample to tedious fractionation.[102]

An essentially quantitative yield of XeF_4 has been claimed for the electric discharge method.[174] A F_2/Xe molar ratio of 2:1 (operating pressure 2 to 15 mm) in a reaction vessel at -78°, yielded XeF_4 quantitatively. Like the hot-tube flow method this lends itself to continuous operation.

The tetrafluoride also forms [175] when F_2/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°, so as to freeze out any XeF_2 (the first reaction product), the yield of XeF_4 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. XeF_4 is relatively stable to γ-radiation with an initial G value of 0.6 to 1.8 at 45°. An independent study[176] 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 F_2/Xe ratios (2:1) and temperatures of ~ 450-500°, which conditions generate minimal XeF_2 but XeF_6 as a major impurity. The XeF_6 (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 purification[169], which effectively eliminates XeF_2 and XeF_6 simultaneously, exploits the inferior fluoride ion donor ability of XeF_4 compared to XeF_2 or XeF_6. With this purification, conditions

which maximize the XeF_4 production, may be employed. Such a product, which will contain small but significant quantities of XeF_2 and XeF_6 (in approximately equimolar amounts), is dissolved in bromine pentafluoride and an excess of arsenic pentafluoride is condensed upon the mixture. Since XeF_2 and XeF_6 form involatile salts, and since the solvent and AsF_5 may be removed quantitatively at 0° or below (at which temperatures the XeF_4 has a very low vapour pressure), the XeF_4 can be isolated by subsequent vacuum sublimation, at 20°.

$$\left.\begin{matrix} XeF_2 \\ XeF_4 \\ XeF_6 \end{matrix}\right\} + AsF_5(\text{excess}) \xrightarrow[-AsF_5,-BrF_5]{0^\circ \text{ in static vacuum}} \begin{matrix} Xe_2F_3^+[AsF_6]^- \\ XeF_4 \\ XeF_5^+[AsF_6]^- \end{matrix} \xrightarrow[20^\circ]{\text{vacuum}} XeF_4 \uparrow$$

in BrF_5 soln.

Samples purified in this way melt (117°) at the same temperature as those obtained by repeated fractional sublimation and give identical broad line ^{19}F n.m.r. spectra[177].

It is best to make the crude XeF_4 in a nickel or Monel vessel after the method of Claassen et al[2], but the purification is best carried out in Kel-F vessels.

Thermodynamic Features. A thorough study of equilibrium conditions in the Xe/F_2 system, as a function of temperature,[22] 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 XeF_6 formation

Table 3.3.1

Equilibrium Constants for the Xe/F_2 System[22]

Temp°K	298.15	523.15	573.15	623.15	673.15	773.15
$K_1(XeF_2)$	$\underline{1.23 \times 10^{13}}$	$\underline{8.80 \times 10^{4}}$	$\underline{1.02 \times 10^{4}}$	$\underline{1670}$	$\underline{360}$	29.8
$K_2(XeF_4)$	$\underline{1.37 \times 10^{11}}$	1.43×10^{3}	1.55×10^{2}	27.2	4.86	0.50
$K_3(XeF_6)$	$\underline{8.2 \times 10^{5}}$	0.944	0.211	0.0558	0.0182	0.0033

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

Underlined values are calculated

Figure 3.3.1

Table 3.3.2

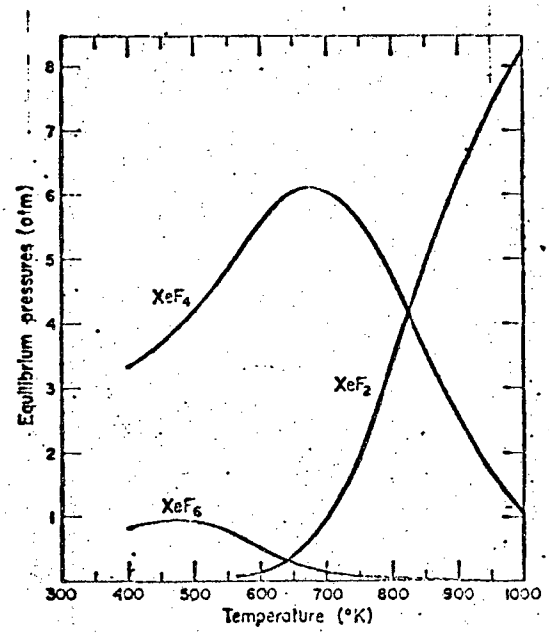
and low F_2 pressures and high temperatures favour XeF_2 formation. The tetrafluoride cannot of course be made pure by the thermal method (see under preparation). The $\Delta H_f^\circ\ (XeF_{4(g)})$=-57.6 kcal $mole^{-1}$ obtained from calorimetry agrees with that from photoionization studies (Table 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 $mole^{-1}$ 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:

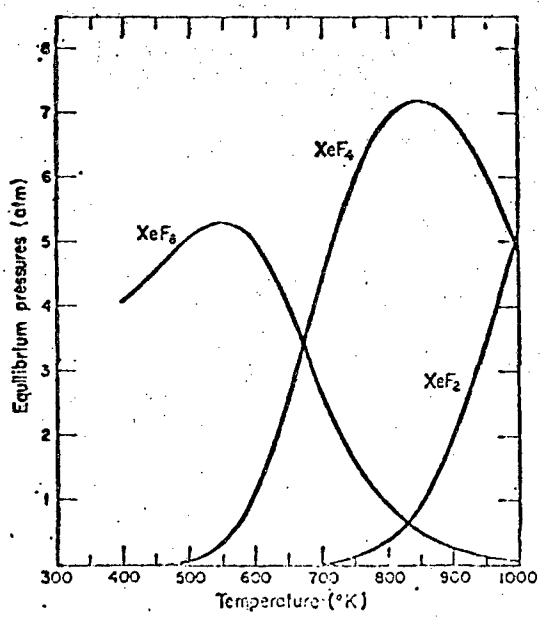
	$XeF_{2(g)}$	$XeF_{4(g)}$	$XeF_{6(g)}$
ΔH_f° (kcal $mole^{-1}$)	-28.2	-57.6	-82
ΔS_f (cal deg^{-1} $mole^{-1}$)	-26.5	-61	-96

Figure 3.3.1.

Pressure and Temperature Influence on XeF_2, XeF_4 and XeF_6 Formation



a. Fig. 1. Equilibrium pressures of xenon fluorides as a function of temperature. Initial conditions: 125 mmoles Xe, 275 mmoles F_2 per 1000 ml.



b. Fig. 2. Equilibrium pressures of xenon fluorides as a function of temperature. Initial conditions: 125 mmoles Xe, 1225 mmoles F_2 per 1000 ml.

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

Table 3.3.2

Some Physical Properties of XeF_4

Colourless crystals, liquid and vapour

Triple-point 390.25°K (117.10°C) (a)

Thermodynamic features:

Vapour pressure (solid), (275 to 390.25°K), $\log p_{mm} = -\frac{3226.21}{T} - 0.43434 \log T + 12.301738$ (a)

390.15°K : 817.97 mm. (only point for liquid XeF_4)

(XeF_2 is more volatile than XeF_4)

ΔH_{sublim} = 14.8 ± 0.2 kcal $mole^{-1}$ (a)‡

15.3 ± 0.2 kcal $mole^{-1}$ (b)

Heat Capacity (cal deg^{-1} $mole^{-1}$ (at 298.15°K))

vapour: (a) 21.5

solid: (c) 28.334

Entropy vapour: (a) 73.0 ± 2

(calc. from molecular data) 75.7 ± 0.4 (a); 75.6 ± 0.4 (d)

solid: *(c) 35.0

Heat of Formation

T°K	$\Delta H_{f(g)}$	
393	-57.6 kcal/mole (e)	- 58 (x)
298	-48 (f)	
423	-53 ± 5 (g)	
298.15	-51.5‡ (d)	

‡ Preferred value

*XeF_4 sample may not have been pure

Mean Thermochemical Bond Energy (E_{Xe-F})

31.7 kcal $mole^{-1}$ (based on ΔH_f° = - 51.5, ΔH_f° (F,g) = 18.8 kcal $mole^{-1}$)

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

Solubility In Anhydrous HF(k)

t°C	mole XeF_4 / 1000g HF	mole HF / mole XeF_4
20	0.18	278
27	0.26	192
40	0.44	114
60	0.73	68

Diamagnetic Susceptibility χ mole (c.g.s. units)

- -50.6×10^{-6} (~20°) (l)
- $-52 \pm 3 \times 10^{-6}$ (77 to 293°K) (m)
- -53×10^{-6} (calculated) (n)

Ultraviolet Absorption Spectrum of XeF_4 (g) (o)

Wave Length(Å)	Half-Width, cm^{-1}	Estd. Extinction Coefficient $mole^{-1}$ cm^{-2}	Est. Oscillator Strength
2280		398	0.009
2580	7000	160	0.003
1840	10000	4.75×10^3	0.22
1325	11200	1.5×10^4	0.80

IR, Raman of XeF_4 (g) (p)(q) (r)

Symmetry	Fundamentals	(cm^{-1})
a_{1g}	ν_1 R	543 vs
a_{2u}	ν_2 IR	291 s
b_{1g}	ν_3 R	235 w
b_{2g}	ν_5 R	502 vs
b_{1u}	ν_4 inactive	221
e_u	ν_6 IR	586 vs
e_u	ν_7 IR	182 (calculated)

Force Constants

k	3.00 mdyn $Å^{-1}$	(q)
k_{rr}	0.12	
k'_{rr}	0.06	

Crystal Structure

X-ray Diffraction[j]

monoclinic

$P2_1/n$

a = 5.050 ± 0.003Å

b = 5.922 ± 0.003Å

c = 5.771 ± 0.003Å

β = 99.6 ± 0.1°

Z = 2

d = 4.04 g ml^{-1}

Xe-F = 1.93Å

∠ F-Xe-F 89.7° (σ = 0.9°)

90.3

Neutron-Diffraction [i][s][h]

Xe-F 1.953 ± 0.002Å

∠ FXeF 90.0 ± 0.1°

See Figure 3.3.2

^{19}F N.M.R. Data [t]

	Chemical Shift: σ_F (p.p.m.; σ_{F_2} = 0)	Coupling Constant: J (Hz)
Solid	482, 448	
Liquid	445	3836
HF Soln.	456, 452, 450	3860, 3864, 3860

Broad Line N.M.R. Findings:[u]

	XeF_4, microcrystalline solid	
	Experiment	Theory
$\underline{\sigma}_{ABS}$ ** (p.p.m.)	218 ± 5	168
$\underline{\sigma}_x$ §	0 ± 8	-33
$\underline{\sigma}_y$	261 ± 25 or 394 ± 25 ∂	-33
$\underline{\sigma}_z$	394 ± 25 or 261 ± 25	570

Rigid Lattice Second Moment

Exp. R.L.S.M. = $6.1_1 \pm 0.16$ G^2

Total Calc. R.L.S.M. = 5.6_2 G^2

(Intermolecular interactions account for 3.8_7 G^2 of the Total Calc. R.L.S.M.

Field Independent S.M. (300°K) = 1.8_3 G^2

** The absolute scale values for chemical shifts are referred to the bare ^{19}F nucleus.[w]

§ $\underline{\sigma}_x$ is the out of plane shielding ($\underline{D}_{4h}$ XeF_4), $\underline{\sigma}_z$ is the shielding ∥ Xe-F bond, and $\underline{\sigma}_y$ is the in plane shielding perpendicular to the Xe-F bond.

∂ If $\underline{\sigma}_z$ = 394 p.p.m. then $\underline{\sigma}_y$ = 261 p.p.m. or vice versa.

Mass Spectra [g]

Ion	XeF_4^+	XeF_3^+	XeF_2^+	XeF^+	Xe^+
Abundance	7	100	60	67	~800
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 $\Delta H°$ ($XeF_{4(g)} \longrightarrow XeF_3^+(g) + F^-(g)$) = 9.66 eV

Electron Diffraction:[y]

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

Mossbauer Spectrum: See Table 3.4.1.

Table 3.3.2

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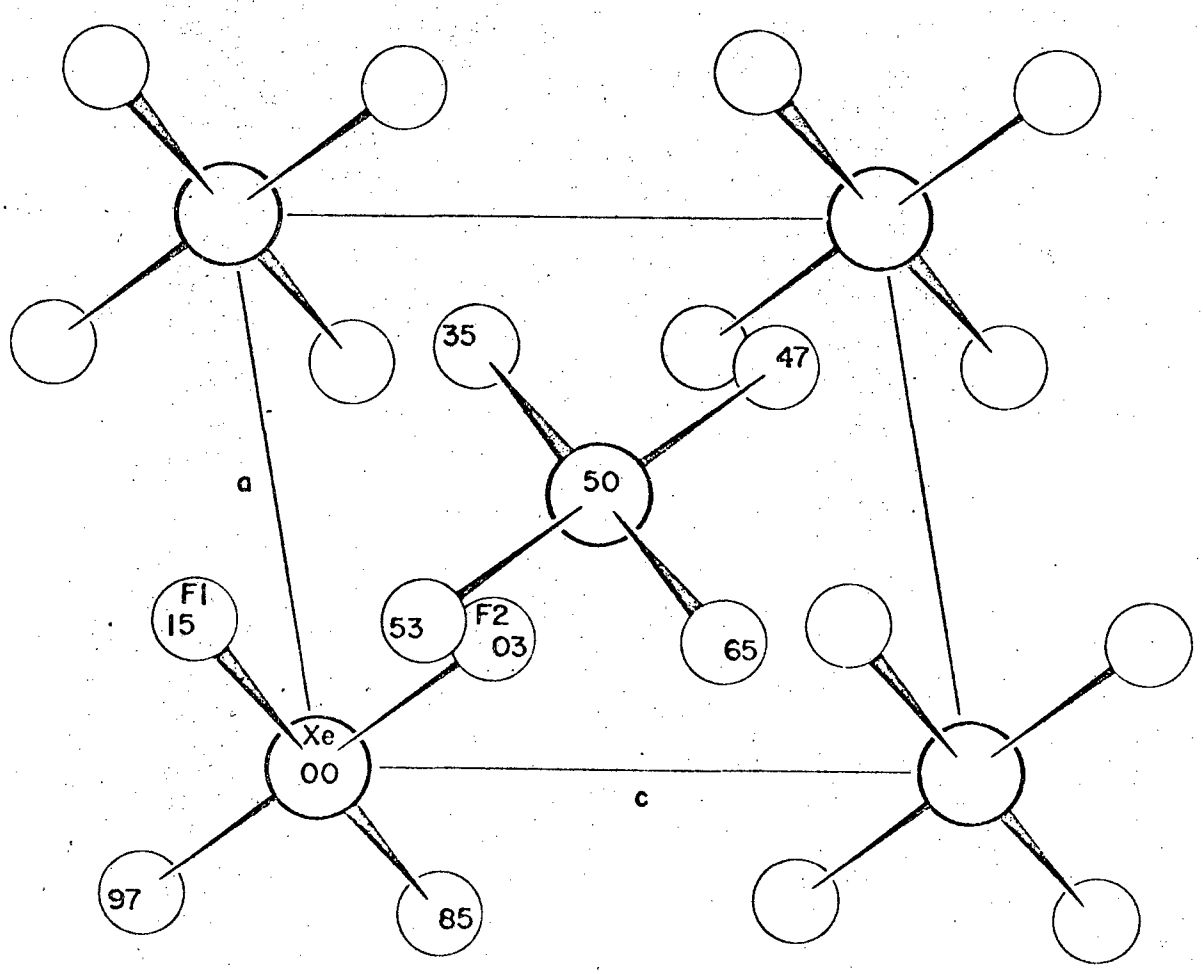
(y) See reference (c) p. 238.

Figure 3.3.2 (i)

(i) The view of the XeF_4 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.

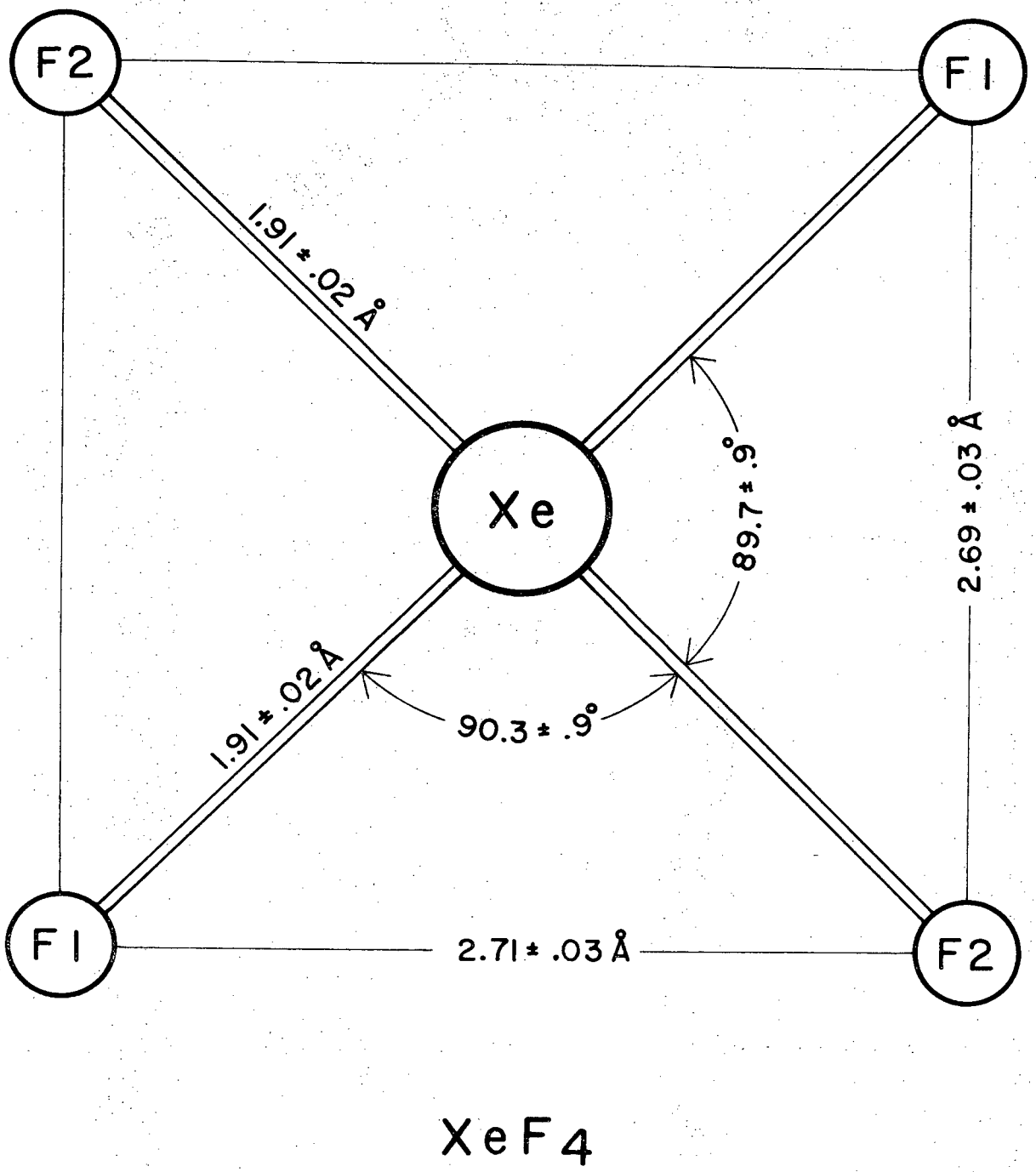
(a) See reference 17 b.



MUB-1522

Figure 3.3.2 (ii)

The Molecular Structure of XeF_4 as determined by X-ray diffraction[a].



[a] See reference 17 b.

Thus, for the disproportionation: $2XeF_{4(g)} \longrightarrow XeF_{2(g)} + XeF_{6(g)}$, $\Delta H° = +\ 5$ kcal mole^{-1} and $\Delta S \approx 0$ cal deg^{-1}mole^{-1} and for $3\ XeF_{4(g)} \longrightarrow Xe_{(g)} + 2XeF_6$, $\Delta H° = +\ 9$ kcal mole^{-1} and $\Delta S \approx -\ 9$ cal deg^{-1} mole^{-1}.

The enthalpy of vapourization of XeF_4, as in the case of XeF_2, is indicative of strong electrostatic interactions between XeF_4 molecules.[103]

Kinetic features. Since XeF_2 is an intermediate in the formation of XeF_4, the kinetics of formation of the former (see section 3.2.1) are relevant to the latter. From a study[178] of the thermally excited F_2 + Xe reactions, with F_2:Xe ratios of 16 or more and total pressures of 10 to 20 mm Hg, in the temperature range 190-250°, the XeF_2 formation was found to be zero order in F_2 and first order in Xe (the reverse of the findings for the conditions which favour exclusive XeF_2 formation - see 3.2.1) and the XeF_4 formation, zero order in F_2 and first order in XeF_2. The thermal reactions were shown to be heterogeneous and a mechanism involving absorption and dissociation of F_2 on the nickel fluoride surface of the container has been proposed. The activation energy for $F_2 + XeF_2 \longrightarrow XeF_4$ was deduced to be $\sim$ 13 kcal mole^{-1}.

Structural features. Vibrational spectroscopic[179, 180, 181] and electron diffraction data[182] have established the $XeF_{4(g)}$ molecule to be square planar (D_{4h}), the latter study giving Xe-F to be 1.94 ± 0.01Å. The crystallographic findings[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[17a] has shown the Xe-F bond length in the solid to be 1.953 (0.004)Å, the $\angle$ FXeF = 90.0 (0.02)°, 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}F n.m.r. studies.[177]

Figure 3.3.2.

The Crystal and Molecular Structure of XeF_4

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 [183, 121, 184] (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 [125] in terms of a F ligand charge of - 0.50. This evaluation assumed the bonding to involve primarily the F2p and Xe5p orbitals. On the other hand, Gutowsky and his coworkers [119] 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 [177] 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 [123, 124] of XeF_4, which is discussed further in section 3.3.2, has been interpreted [158] 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 [126] 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 [32] and Rundle [33] and generally emphasize the importance of the Xe 5p and F2p orbitals. Allen,[31b] Coulson[23] and Jortner and Rice [15] have reviewed the bonding models. Several authors have given [130, 185, 186, 187] 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.[25] (See sections 1.3.1 - 4 and 3.2.2).

Chemical Properties. A number of the earlier studies involving XeF_4 are suspect because of the likelihood that the samples were contaminated with XeF_2 or XeF_6 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.[188, 189] The latter has been trapped at -80° and, on the basis of infrared and e.s.r. examination,[190] formulated as $XeOF_2$ (see section 3.3.3). The ultimate products of hydrolysis are[188] Xe, O_2, HF and XeO_3 (see section 3.4.4). If the hydrolysis is carried out in strong base, perxenates are formed [151, 188, 155] (see section 3.5.5); and if the hydrolysis occurs in aqueous KI very little free O_2 is liberated,[172]

$$XeF_4 + 4I^- \longrightarrow Xe + 4F^- + 2I_2.$$

As with XeF_2, the low bond energy of XeF_4 causes it to be a strong oxidative fluorinator and it should compare with BrF_3 in oxidative capability. It seems, however, like XeF_2, to be kinetically rather inert. Solutions of XeF_4 in anhydrous HF (with which the fluoride does not undergo F-ligand exchange[183]) are strongly oxidizing and fluorinate Pt metal to PtF_4 [88, 173]. The neat compound oxidizes SF_4 to SF_6 [191], oxidizes NO to ONF, but does not interact, at a measurable rate, with NO_2.[85] The interaction of XeF_4 with H_2 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°.[192] The tetrafluoride, in contrast with XeF_2, fluorinates perfluoropropane at room temperature[145] but gives similar products to XeF_2 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 XeF_4 with BCl_3 at -78°[193] yields xenon and chlorine quantitatively: $3XeF_4 + 4BCl_3 \longrightarrow 4BF_4 + 3Xe + 6Cl_2$. There are indications, however, that (as in the XeF_2 case), the F-ligands may be substituted by other highly electronegative ligands, since XeF_4 dissolved in trifluoroacetic anhydride is reported to yield a crystalline compound considered[194] to be $Xe(OOCCF_3)_4$. Clearly, ligands such as $-O-ClO_3$, OSO_2F and $OTeF_5$ are possible but there is no certainty that the compounds will be stable to disproportionation or spontaneous reduction.

The fluoride ion donor ability of XeF_4 has been shown[169] to be less than that of XeF_2 or XeF_6 and this forms the basis of a chemical purification for XeF_4. These findings are in harmony with the enthalpies of ionization derived from photoionization studies by Berkowitz:[195]

Process	$\Delta H°$(eV)
$XeF_{2(g)} \longrightarrow XeF^+_{(g)} + F^-_{(g)}$,	= 9.45
$XeF_{4(g)} \longrightarrow XeF^+_{3(g)} + F^-_{(g)}$,	= 9.66
$XeF_{6(g)} \longrightarrow XeF^+_{5(g)} + F^-_{(g)}$,	= 9.24

The best fluoride ion acceptor (SbF_5) forms a crystalline solid[196, 197] (or solids) with XeF_4, probably containing XeF_3^+ and there is also evidence[197] for weaker fluoride ion acceptors (PF_5, AsF_5) forming compounds in BrF_3 solution. Reports that XeF_4 interacts with SbF_5 or TaF_5 to form XeF_2

derivatives,[163] or to yield $XeF_2, 2IF_5$ on dissolution[198] 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°) 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°:[192]

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$

A more convenient analytical technique involves reduction with mercury:

$$XeF_4 + 4Hg \longrightarrow Xe + 2Hg_2F_2 \text{ (or } 2HgF_2)$$

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 β decay of its ^{129}I analogues: $^{129}ICl_4^- \xrightarrow{-\beta} {}^{129}XeCl$. 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 $XeCl_4$ 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[200, 199]

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

the 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 $XeOF_2$ in the literature,[172, 191, 190] only one is supported with experimental evidence. The compound identified as $XeOF_2$ is the bright yellow solid formed by hydrolizing XeF_4 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 (ν_1, A_1, Xe-O str.), 520 (ν_2, A_1, Xe-F sym. str.) and 490 cm^{-1}

(ν_4, B_2, Xe-F asym. str.). It is argued that these data are compatible with a structure

$$\begin{array}{c} O \\ | \\ F - Xe - F \end{array}$$

with $\measuredangle$ F-Xe-O of about 90°, thus resembling ClF_3 and BrF_3 (see section 1.4.4). The Xe-O stretching force constant is 4.7 mdynes/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 $XeOF_4$ is 7.08 mdynes/Å (see section 3.4.2).

3.3.4 Xenon(IV) Oxide

Although XeO_2 has been postulated as an intermediate in the hydrolysis of XeF_4 (see section 3.4.4) there is no firm evidence for its existence.

3.3.5 F_{4-x} $Xe(OR)_x$ Compounds

Apart from the report[194] of the synthesis of $Xe(OOCCF_3)_4$ (see section 3.3.1), no other compounds in this class have yet been reported.

3.3.6 XeF_4 as a Fluoride Ion Donor and Acceptor

There is no evidence that XeF_4 can accept fluoride ion (or any other ion) and this provides for the ready removal of XeF_6 contaminant by absorption of the latter with alkali fluoride.[81]

Although XeF_4 is a poorer F^- donor than either XeF_2 or XeF_6 (see section 3.3.1) it does form compounds with the best F^- acceptor, SbF_5.[197] These may contain the XeF_3^+ 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 XeF_4

Only one molecular adduct of XeF_4 has been established, XeF_2, XeF_4.[170] 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 XeF_2, XeF_4 and their Components

	XeF_2, XeF_4[a]	XeF_2[b]	XeF_4[c]
Xe-F (Å) in XeF_2	(2) 2.010 (0.012)	(2) 2.00 (0.02)	
Xe-F (Å) in XeF_4	(2) 1.972 (0.014) (2) 1.945 (0.014)		1.953 (0.004)
F-Xe-F in XeF_4	(2) 89.1° (0.8)		90.0 (0.02)

(a) J. H. Burns, R. D. Ellison and H. A. Levy, Acta Cryst. 18 (1965) 11.

(b) H. A. Levy and P. A. Agron, J. Amer. Chem. Soc. 85 (1963) 241.

(c) J. H. Burns, P. A. Agron and H. A. Levy, Science 139, (1963) 1208.

- - - - - - - - - - - - - - - - - -

XeF_2, XeF_4 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.

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between positive charges on the Xe atoms and negative charges on the fluoride ligands of the surrounding molecules. The compound resembles other XeF_2 adducts (see section 3.2.8).

3.4 Xenon(VI) Compounds

The chemistry of Xe(VI) is limited to the fluoride XeF_6, the oxyfluorides $XeOF_4$ and XeO_2F_2, the oxide XeO_3, 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 XeO_2F_2. The oxide is a powerful explosive. The oxyfluoride $XeOF_4$ 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 XeF_6 was first described in four independent and almost simultaneous reports.[201, 202, 107, 203] All preparations are carried out in nickel or Monel vessels and, in general, high F_2 pressures and lower temperatures favour XeF_6 formation. A 95% conversion to XeF_6 is obtained with F_2/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[191] as a product of the electric discharge of a 3:1 F_2:Xe mixture, the product being trapped at -78°. Furthermore, O_2F_2 is reported[191] to oxidize XeF_4 to XeF_6 between -133 and -78°.

Laboratory Preparation. In order to obtain pure XeF_6 it is best[204] to form the $NaF.XeF_6$ adduct by mixing with NaF, the other xenon fluorides (XeF_2, XeF_4 and $XeOF_4$) likely to be present, being unable to form stable complexes with the NaF.

The apparatus and experimental procedures for XeF_6 synthesis[205] are essentially as given under XeF_2 and XeF_4 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° for 16 hours. Excess fluorine is removed under vacuum at -192° and the crude XeF_6 condensed onto NaF (previously fluorinated and in appreciable excess). This mixture is warmed to 50° 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°, to constant weight (an hour or so should suffice). The XeF_6 is then retrieved by heating to 125° under vacuum, when the gas is rapidly evolved and may be collected in cold traps (nickel, Monel or Kel-F at -196°).

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°, 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°K. The interpretation of these regions of anomalour 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 XeF_6

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] (°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. XeF_6, 245.3.

Vapour pressure (mm)[b]: 2.7 (0.04°); 23.43 (22.67°)

Vapour pressure equations: $\log P_{mm} = - X / T + Y$

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] $\log P_{mm} = - 6170.88\ T - 23.67815 \log T + 80.77778$

Second virial coefficient, B, $(PV = RT + BP)^{(c)} = - 955\ cm^3\ mole^{-1}$

Δ H sublim (kcal $mole^{-1}$) : 15.6 [b]; 13.2 [d] ΔH fus (kcal $mole^{-1}$): 1.37 [c]

Δ S vap (cal deg^{-1} $mole^{-1}$) : 32.74

C_p, solid (at 298.15 °K), (cal deg^{-1} $mole^{-1}$)[c]: 41.03

ΔH_f° (g) (kcal $mole^{-1}$)(298.15°K): 70.4[b]; 82.9[e]; 81[f]

ΔS_f° (g) (cal deg^{-1} $mole^{-1}$) : -97[b]

S° (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/F_2 equilibria, gas (298.15°K), 88.84 or 91.87

ΔH° $(XeF_{6(g)} \longrightarrow XeF_{5(g)}^{+} + F_{(g)}^{-})^{(f)}$: 9.24 ev (213 kcal $mole^{-1}$)

Solubility

Anhydrous HF:[g]

t(°C)	Moles XeF_6 / 1000 g HF	Moles HF / Mole XeF_6
15.8	3.16	15.8
21.7	6.06	8.25
28.5	11.2	4.46
30.25	19.45	2.57

Molar conductivity[g] of HF solutions (ohm^{-1} cm^2) in range 60-147 ohm^{-1} cm^2 (0.75 - 0.02 mole ℓ^{-1})

XeF_6 gives yellow-green solutions in WF_6, IF_5 and BrF_5[h]

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

Dipole Moment [j]:<0.03D

Magnetic Susceptibility:[k] $\chi_M = -(44.5 \pm 0.5) \times 10^{-6}$ cm^3 $mole^{-1}$

Specific Conductance[i](50°C): $1.45 \pm 0.05 \times 10^{-16}$ ohm^{-1} cm^{-2}

UV and Visible Absorption Spectrum[l]: 3300 Å, strong, half-width 580Å
very intense absorption below 2750Å

First Ionization Potential: $I(XeF_{6(g)})$[f] (1016Å) = 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 vw, 1075w, 1118 vw, 1238 w

R (cm^{-1}) (94°C)[m]: 520 s, 609 ms (P), also 206?

Electron Diffraction: Non octahedral molecular symmetry[o][p][q]
Xe-F bond length: 1.890Å[o]

Crystallographic Data:

Unit Cells:	Cubic[r] (stable between 103 and 301°K)[s]	Monoclinic
	a_o(-80°C) = 25.06 (0.05) Å	a_o 9.33 (0.03)Å
	Space group Fm3c; z = 144 XeF_6	b_o 10.96 (0.03)
	$d_{X\text{-ray}}$ (g cm^{-3}) (-80°C) = 3.73 (0.02)	c_o 8.95 (0.03)
	(See Figure 3.4.1)	β 91.9 (0.2)°

Density[c] ← solid → liquid

T°K	77.22	194.42	242.97	293.11	297.55	328.34
d(g cm^{-3})	3.848(0.006)	3.751(0.007)	3.668(0.014)	3.465(0.013)	3.411(0.015)	3.173(0.03)

Table 3.4.1

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indicative of polymerization in the liquid state. Two independent vapour density measurements[22, 209] show the hexafluoride to be predominantly monomeric in the gas phase. The hexafluoride is much more volatile than either XeF_2 or XeF_4, although much less volatile than other hexafluorides.

There is considerable disparity between the enthalpy of formation from the equilibrium studies (-70.4 kcal $mole^{-1}$) and the value (-82.9 kcal $mole^{-1}$) from the heat of combustion of XeF_6 ($XeF_6 + 3H_2 \longrightarrow Xe + 6HF$). Since the latter value is also in agreement with the value from photo-ionization studies[195], it is preferred. This infers a mean thermochemical bond energy for XeF_6 of 32 - 33 kcal $mole^{-1}$, which is, within the experimental uncertainty, the same as the values derived for XeF_2 and XeF_4.

Although equilibrium studies[22] showed no evidence of XeF_8 formation it is of interest that the rate of exchange of $^{18}F_2$ with XeF_6 at 150° was found to be a linear function of $^{18}F_2$ concentration, indicating an associative mechanism.[210]

Crystal and Molecular Structure. Although both a cubic and monoclinic form of crystalline XeF_6 have been identified[207] only the cubic structure has been described in detail.[211] (See Figure 3.4.1.) This structure indicates that XeF_6 is effectively $XeF_5^+F^-$, in the cubic phase. The

Figure 3.4.1

existence of both tetramers and hexamers in the same unit cell indicates that the way in which the XeF_5^+ ion is 'bridged' by the F^- ions is not of prime importance. It should be noted, however, that the 'bridging' F^- ions are not close to the four-fold axis of the XeF_5^+ groups. This is consistent with the location of the non-

Figure 3.4.1

The Structural Units of XeF_6(cubic)[a]

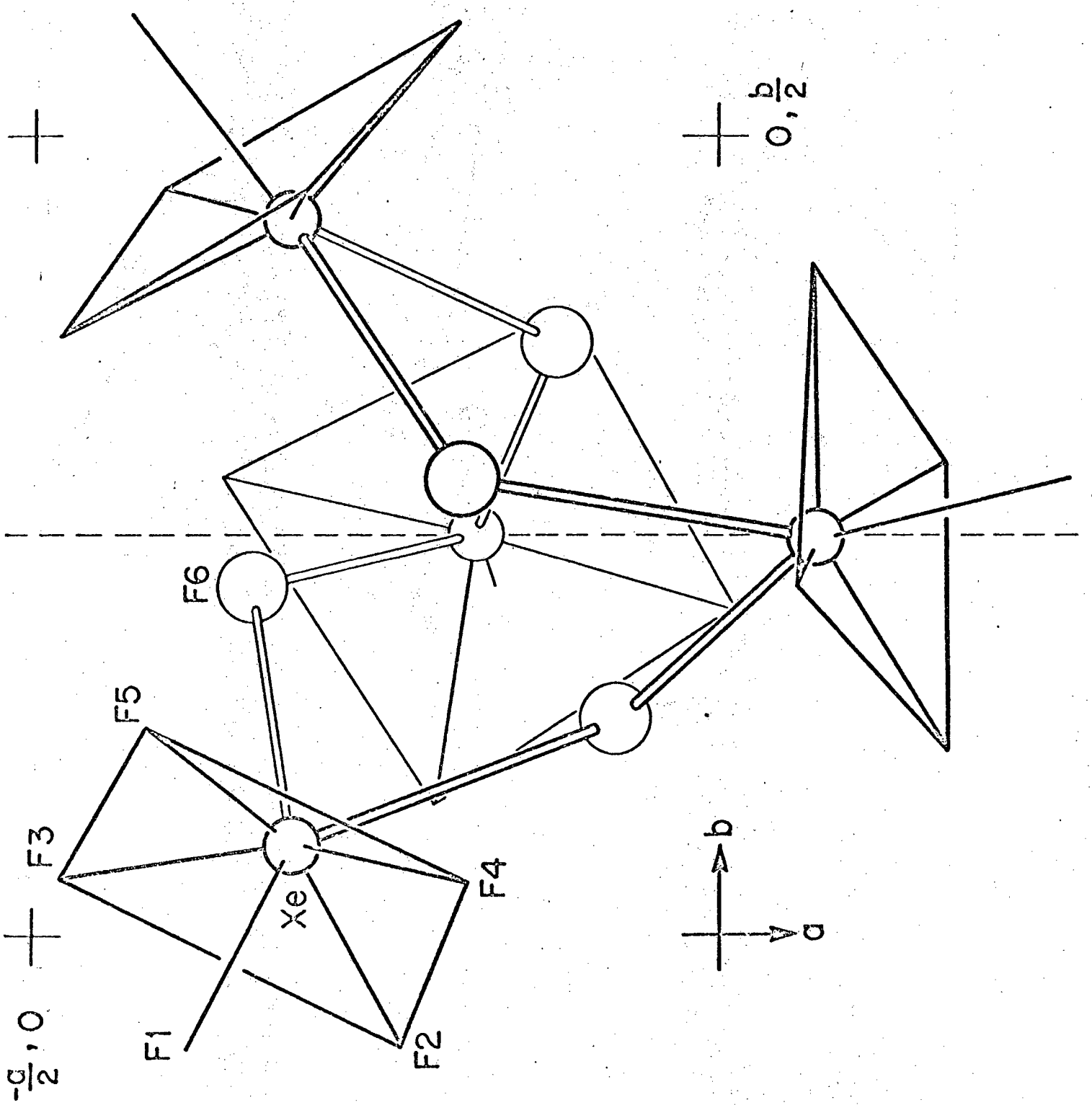
Caption. The cubic unit cell (space group Fm3c), a_o(-80°C) = 25.06 ± 0.05Å contains 144 'XeF_6 units.' Ions of XeF_5^+ and F^- are associated in tetrameric and hexameric units((a) and (b) in the figure). There are 24 tetramers and 8 hexamers in the unit cell. Both right and left handed conformations of both tetramers and hexamers occur.

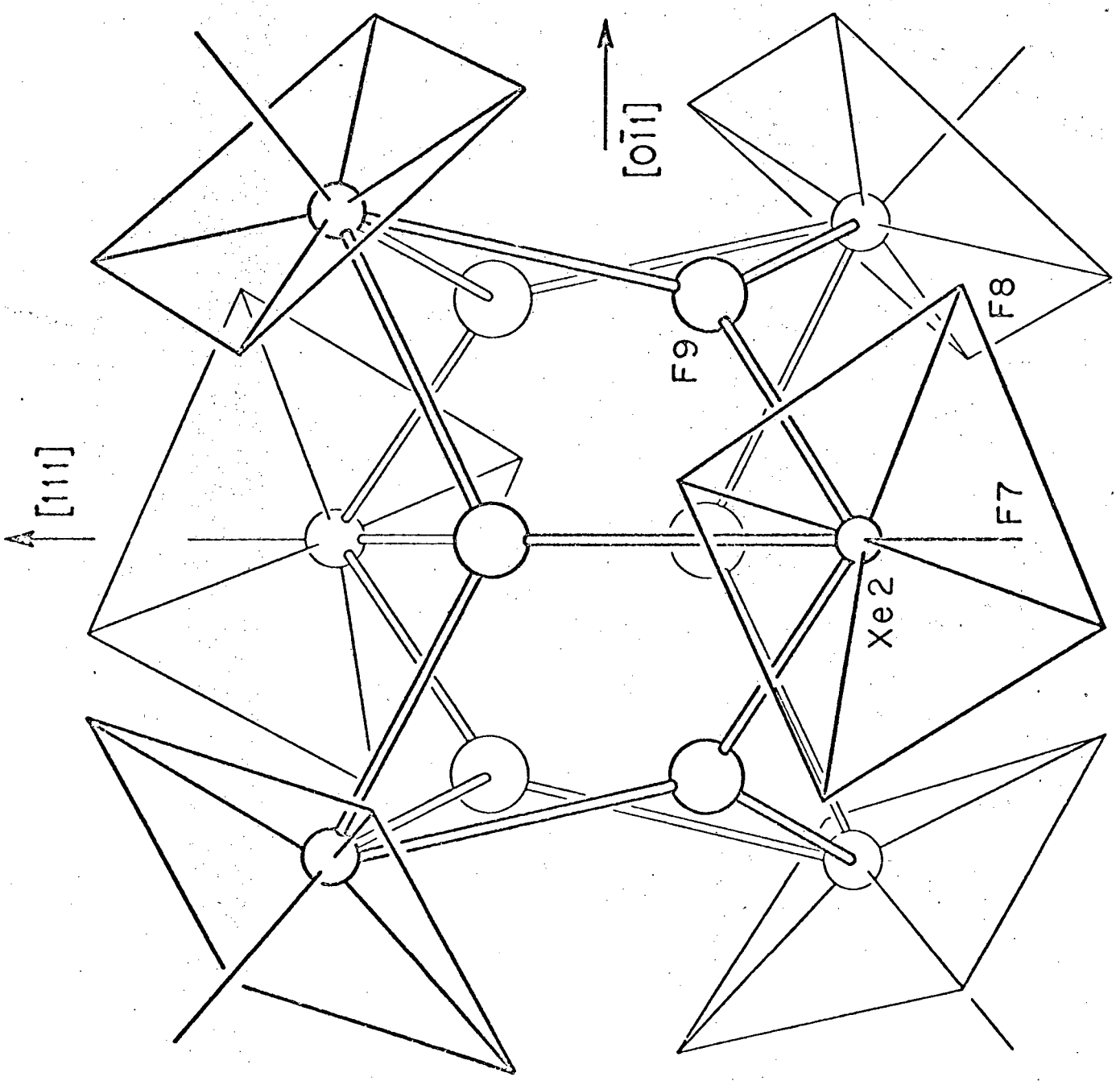
The XeF_5^+ ions have similar size and shape in the tetramers and hexamers. The F^- ions 'bridge' the XeF_5^+ ions in each cluster type. The $F_5Xe^+ - - F^- - - - XeF_5^+$ bridges are unsymmetrical in the tetramer but symmetrical in the hexamer, the chemically important bond lengths and angles are:

		Hexamer	Tetramer
XeF_5^+	Xe-F_{ap}(7,1)(Å)	1.76(3)	1.84(4)
	Xe-F_{bas}(8,3)(Å)	1.92(2)	1.86(3)
	F_{ap}-F_{bas} (Å)	2.33(3)	2.29(6)
	F_{bas}-F_{bas} (Å)	2.63(3)	2.54(13)
	∠ F_{ap}-Xe-F_{bas}	80.0(0.6)°	77.2(1.8)°av.
	∠ F_{bas}-Xe-F_{bas}	88.3(0.2)°	87.2(4.5)°av.
F_5Xe^+--F^- 'bridge' distance(Å)		2.56(2)	2.23(3) 2.60(3)
F_5Xe^+---F^----XeF_5^+ 'bridge angle		118.8(0.3)°	120.7(1.2)°

The F^- bridges $2XeF_5^+$ groups in the tetramer and 3 in the hexamer.

(a) R. D. Burbank and G. R. Jones, Science 168 (1970) 248.


0, b/2
F6
F5
F3
F4
Xe
F1
F2
-a/2, 0
b
a


[111]
[01$\bar{1}$1]
F9
F8
F7
Xe2

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:

$$XeF_{6(soln.)} + HF \longrightarrow XeF^+_{5(soln.)} + HF^-_{2(soln.)}$$

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 TeF_6 and the data[216, 217] have been interpreted[218, 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 C_{3v} 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 C_{2v}, C_{3v} and C_s 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 derives[217] 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 O_h ground state for XeF_6 would be separated by only very small energy from a triplet state of D_{3d} symmetry. Goodman predicts this triplet because his O_h structure has 2 electrons populating an antibonding a_{1g} 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 D_{4h} distortion is not compatible with the observed electron diffraction data, concludes that D_{3d} symmetry is appropriate. Bartell allows[218] that a D_{3d} species could be consistent with the electron diffraction findings. Unfortunately, a magnetic deflection molecular-beam experiment[221] has provided no evidence for a paramagentic XeF_6 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[222] has provided no evidence for a dipolar XeF_6 species. Indeed $\mu(XeF_6)$ must be < 0.03 D and this is difficult to reconcile with non-centric structures. Claassen and his coworkers,[223] from millimeter waveband studies, were unable to obtain evidence to support Bartell's inverting or pseudo rotator model.[224] Raman and infrared data[225] indicate that either the ground-state vapour molecules possess a symmetry lower than 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.

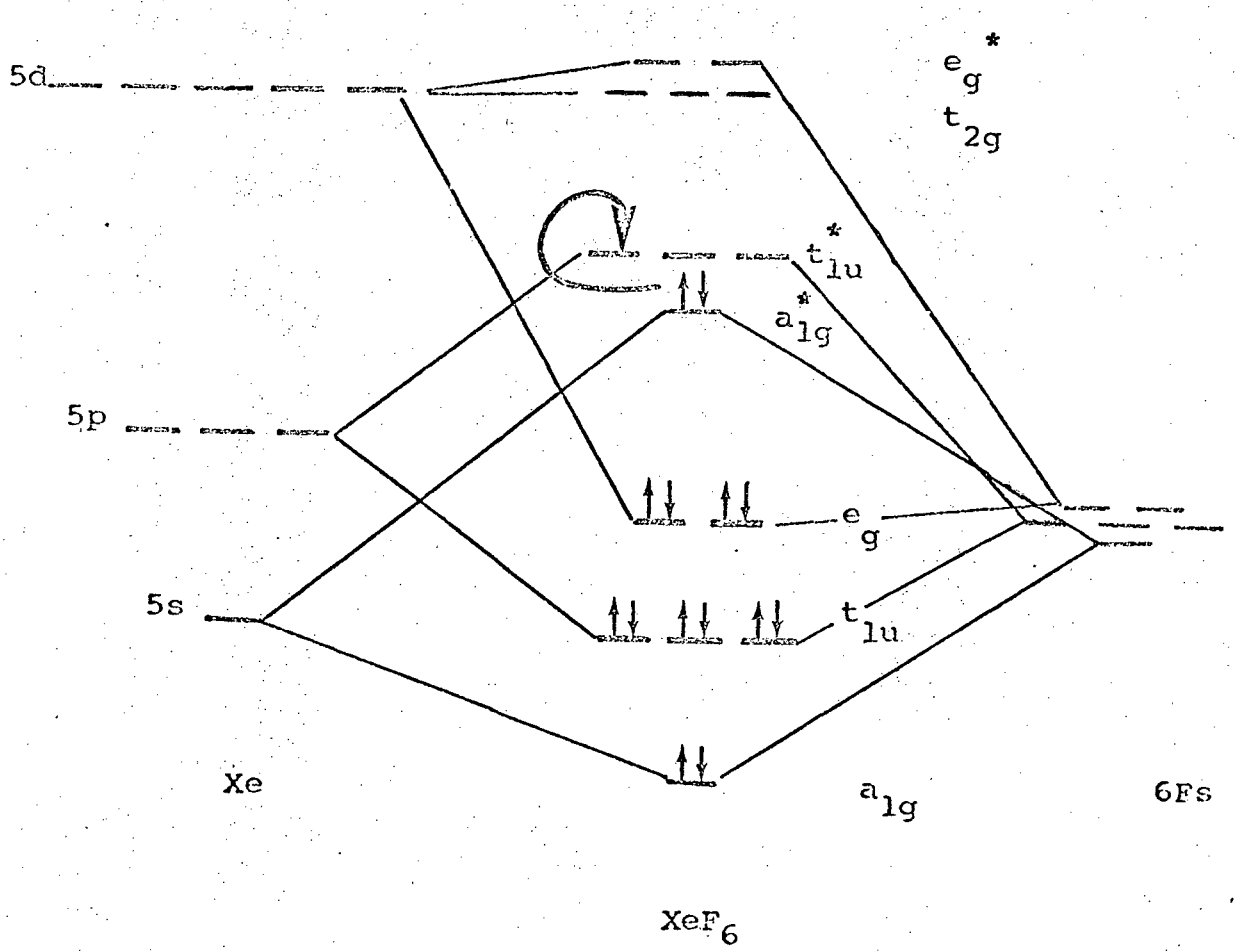
Bonding and Bond Polarity. Alone, of the first theoretical papers on the bonding in noble-gas compounds, the valence-shell-electron-pair-repulsion model predicted[39] that the XeF_6 molecule would be non-octahedral (see section 1.3.4). The 3-centre-4-electron 'molecular orbital' model predicted an octahedral molecule (see section 1.3.3). It now appears however, that the 'non-bonding-valence electron-pair' in $XeF_{6(g)}$ does not have the 'bulk' (or steric activity) usually associated with such a 'pair.'[218]

Evidently, even a Hückel molecular orbital model[218, 226] containing only Xe 5s, 5p atomic orbitals and a pσ 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 O_h symmetry than that observed.

The non-octahedral geometry and exceptional flexibility of the $XeF_{6(g)}$ molecule, implied by the electron diffraction findings, have been interpreted in terms of a pseudo-Jahn-Teller effect.[218] 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_h Molecule



bonding, the d orbital degeneracy having been removed by the ligand field. This model places a pair of electrons of the O_h symmetry 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 $XeF_6(O_h)$ 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 XeF_6 population should contain octahedral and D_{3d} symmetry species, the concentration of the latter increasing with increasing temperature.

As in the case of the other fluorides, the ^{19}F n.m.r. data has been interpreted on the basis of bond polarities approximating to Xe^{3+} $-(F^{0.5-})_6$. Both extreme theoretical approaches [119, 125] (one involving Xe5d orbitals, the other not) yielded this high bond polarity. Soft X-ray photoionization studies[126] (involving the ejection of core electrons from the Xe atom) have shown that the charge withdrawn

from the xenon atom in XeF_6 is a little less than 3 times the charge withdrawn in XeF_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[195]

$$XeF_6(g) \longrightarrow XeF_5^+(g) + F^-(g) \qquad \Delta H = 9.24 \text{ eV}$$

compared with XeF_4 and XeF_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_2 and XeF_4 data. This is compatible with the greater stability of XeF_5^+ salts compared with XeF_3^+ and even XeF^+ salts (see section 3.4.6). Evidently, the pseudo-octahedral geometry of the XeF_5^+ ion must be especially favourable. The IF_6^+ ion is also a very favourable species (thus IF_6^+ salts have greater stability than IF_4^+ salts[227], and IOF_5, which is nearly octahedral, is not known to form IOF_4^+ salts).[169]

As we have seen, the preference for the 'octahedral' geometry also shows up in the crystal structure of XeF_6(cubic). It is possible that even in the molecular state, XeF_6 and IF_7 are close to $XeF_5^+F^-$ and $IF_6^+F^-$ ion pairs.

Chemical Properties. As befits its higher oxidation state, XeF_6 is a much more powerful oxidizer and fluorinator than XeF_2 or XeF_4. It seems that XeF_6 has little of the kinetic stability noted in XeF_2 and XeF_4 chemical behaviour. Thus, unlike XeF_2 and XeF_4 it is not possible to store XeF_6 in glass or quartz. There is presumably a stepwise

interaction but these reactions are only effective for the formation of $XeOF_4$ and XeO_3 [228]:

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

$$2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_4 + SiF_4$$

$$2XeO_2F_4 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$$

The interaction with water [229, 230, 231, 232, 233, 203] similarly yields $XeOF_4$ and XeO_3 and the latter creates a hazard in XeF_6 handling. A large excess of water yields $XeO_{3(aq)}$ 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

$$2XeF_6 + 16NaOH \longrightarrow Na_4XeO_6 + Xe + O_2 + 12NaF + 8H_2O$$

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 H_2 to yield Xe and HF[202] and with mercury to give Xe and mercury fluorides.[107]

The greater reactivity of XeF_6 is illustrated by its interaction with perfluoropropene[145] which cleaves the molecule:

$$2XeF_6 + 3CF_3 \cdot CF = CF_2 \longrightarrow 3C_2F_6 + 3CF_4 + 2Xe$$

The tetrafluoride yields perfluoropropane and 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]

$$XeF_6 + 6HCl \longrightarrow Xe + 3Cl_2 + 6HF$$

$$XeF_6 + 8NH_3 \longrightarrow Xe + 6NH_4F + N_2$$

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_2XeF_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[204] 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 XeF_4, by using H_2 or Hg as the reducing agent.[202, 107] The latter is preferred.

3.4.2 Xenon Oxide Tetrafluoride

Preparation. The oxyfluoride, $XeOF_4$, was first detected by mass-spectroscopy,[88] among the xenon fluorides prepared by thermal excitation, and was soon isolated in macroscopic quantities by the partial hydrolysis of XeF_6.[229, 230]

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

Unreacted XeF_6 and HF are removed by treatment with NaF (which forms compounds with both) [231, 232]. The best reported procedure is that of Smith [229], 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 XeF_6 near its saturation vapour pressure, and the XeF_6 consumption is monotored by following the intensity of the XeF_6 band at 520 cm^{-1}. Yields of 80%, based on XeF_6 consumption, have been obtained.

The static methods, involving interaction of XeF_6 with H_2O or SiO_2[235, 112], 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 $Xe/F_2/O_2$ mixtures to 235 °, the $Xe:F_2$ ratio being $\sim$ 1:4 and the oxygen in considerable excess (5/2 times the F_2 content).[135] The last procedure yields XeF_4 as a major impurity, but the much greater volatility of

the $XeOF_4$ permits ready separation by vacuum distillation at ~ 0 °. 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°) 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°) 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 8.5×10^{-3} ohm^{-1} cm^{-2} at 24°[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[35] 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[239] 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 $XeOF_4$

Colourless solid, liquid and vapour[a]

m.p. (°C): -28[a]
-41[b]
-40[c]
-46.2[d]

Vapour pressure[b]

T°C	P_{mm}
0	7.0
0	8
23	29

Density ($g\ cm^{-3}$): $d = 3.168 - 0.0032T$[e]

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 4471Å). Temp. Coeff. of n: -0.00049

Molar refraction:[e] $R_D(25°C) = 18.24$ cc mole^{-1}

Dipole Moment[f] 0.65 ± 0.09 D ; Dielectric Constant (24°C) : 24.6 [d]

Volume Susceptibility[c] $-\chi_v = 0.82$

Infrared and Raman Spectra [g][h]

C_{4v} Symmetry		IR	R
a_1	ν_1	926 s	920 (2) P
	ν_2	576 m	567 (10) P
	ν_3	294 s	285 (0+) P
b_1	ν_4		527 (4)
	ν_5		230 (calc.)

b_2	$\underline{\nu}_6$		
e	$\underline{\nu}_7$	608 vs	
	$\underline{\nu}_8$	361 s	365 (2)
	$\underline{\nu}_9$		161 (0+)

Molecular dimensions

Microwave spectroscopy(f)(i)

Xe-O: 1.703 ± 0.015 Å

Xe-F: 1.900 ± 0.005

∠ O-Xe-F: 91.8 ± 0.5°(i)

N.M.R. Spectra

^{17}O Shift: $\underline{\sigma}_O$ = -313 ± 2 ppm ($\underline{\sigma}$, $H_2{}^{17}O$ = 0), J(^{129}Xe-^{17}O coupling) = + 692 ± 10 cps (j)

^{19}F Shift: $\underline{\sigma}_F$ = -100.27 ppm ($\underline{\sigma}_F$, CCl_3F = 0)(c); = 330 ppm (σ_F, $F_{2(g)}$ = 0)(k)(l)(m)

J(^{129}Xe - ^{19}F coupling) = 1127(l), 1124(c)

^{129}Xe Shift: $\underline{\sigma}_{Xe}$ = - 5511 ppm ($\underline{\sigma}_{Xe}$, $Xe_{(g)}$ = 0)(m)

Photoelectron Spectroscopy(n)

$\Delta E(XeOF_{4(g)})$ = 7.02 ± 0.13 eV (relative to $Xe_{(g)}$)

Electrical Conductivity(d)

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

RbF added: specific conductance (0.29M CsF soln. in $XeOF_4$): 8.5 x 10^{-3} $ohm^{-1}cm^{-2}$

Mass Spectrum[o]

Positive ions: all uni-positive ions observed but $XeOF_3^+$ / $XeOF_4^+$ ratio ~100:1

Negative ions: XeF^-, XeF_2^-, XeF_3^-, XeF_4^-, $XeOF_3^-$

Table 3.4.2

References

(a) C. L. Chernick,H. H. Claassen, J. G. Malm, and P. L. Plurien, in "Noble-Gas Compounds," H. H. Hyman, Ed., The University of Chicago Press, Chicago and London (1963) p.106.

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

(c) H. D. Frame, J. L. Huston and Irving Sheft, Inorg. Chem. 8 (1969) 1549.

(d) H. Selig, Inorg. Chem. 5 (1966) 183.

(e) H. Selig, C. L. Chernick, and C. W. Williams, Inorg. Nucl. Chem. Letters, 1 (1965 17.

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

(g) G. M. Begun, W. H. Fletcher and D. F. Smith, J. Chem. Phys 42 (1963) 2236.

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

(i) J Martins, and E. B. Wilson, Jr. J. Chem. Phys. 41 (1964) 570.

(j) J. Shamir, H. Selig , D. Samuel and J. Reuben, J. Amer. Chem. Soc. 87 (1965) 2359.

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

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

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

(n) S.E. Karlsson, K. Siegbahn and N. Bartlett, J. Amer. Chem. Soc. (1970) in press.

(o) See reference (a) p. 47.

4 F-ligands, are very nearly coplanar ($\measuredangle$ O-Xe-F = 91.8 ± 0.5°). The Xe-F bond length (1.900 ± 0.005Å)[239] is very similar to that found for XeF_6 (1.890Å)[217] and significantly shorter than for XeF_4 (1.95Å)[17a]. The Xe-O bond length (1.703 ± 0.015Å) is shorter than observed in either XeO_3 (1.76Å)[240] or XeO_4 (1.74Å)[241]. The force constants given in Table 3.4.3, derived from the vibration data, are consistent with these observations, the Xe-O bond evidently being stronger than

Table 3.4.3

Comparison of Bond Stretching Force Constants (mdynes $Å^{-1}$) of $XeOF_4$ with those of Related Molecules

	$XeOF_4$	XeF_4	XeO_3	XeO_4
k_r(Xe-F)	3.21[a], 3.26[c]	3.00[b]	- - -	- - -
k_r(Xe-O)	7.11[a], 7.08[c]	- - -	5.66[d]	5.75[e] (6.7)*

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

(b) H. H. Claassen, C. L. Chernick and J. G. Malm, J. Amer. Chem. Soc. 85 (1963) 1927.

(c) G. M. Begun, W. H. Fletcher and D. F. Smith, J. Chem. Phys. 42 (1963) 2236.

(d) D. F. Smith, in "Noble Gas Compounds," H. H. Hyman, Ed., The University of Chicago Press, Chicago and London (1963) p. 295.

(e) W. A. Yeranos, Bull. Soc. Chim. Belges 74 (1965) 414. This value was derived using a Urey-Bradley force field and an assumed value for ν_1.* Converting this to a valence-force-field value yields a k_r (Xe-O) of 6.7 mdynes $Å^{-1}$.

in XeO_3 or XeO_4.

Bonding and Bond Polarity. The observed geometry is as predicted by valence-electron-repulsion theory,[39] and by the three-centre-four-electron bond description[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 $XeOF_{4(g)}$ 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

Table 3.4.4.

X-ray Photo-Electron Chemical Shifts for XeM_V Core-Electrons in Gaseous Compounds(a)

	$Xe_{(g)}$	$XeF_{2(g)}$	$XeF_{4(g)}$	$XeOF_{4(g)}$	$XeF_{6(g)}$
XeM_V Chemical Shift (eV)	0	-2.95(13)	-5.47(18)	-7.02(13)	-7.88(18)
Shift/F atom	- - -	-1.48	-1.37	- - -	-1.31

(a) S.-E. Karlsson, K. Siegbahn, and N. Bartlett, J. Amer. Chem. Soc. (1970) in press.

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 $_{av}$ = 130°.

from the Xe atom. Thus, for $XeOF_4$

$$\Delta E_{XeOF_4} = -(q - q_o)\left(\frac{1}{r_v} - \frac{1}{R_F}\right) - q_o\left(\frac{1}{r_v} - \frac{1}{R_o}\right)$$

and by equating the first term with ΔE_{XeF_4} or $^2/_3\,\Delta E_{XeF_6}$

$$\Delta E_{XeOF_4} = \Delta E_{XeF_4} (\text{or } {}^2/_3\,\Delta E_{XeF_6}) - q_o\left(\frac{1}{r_v} - \frac{1}{R_o}\right) .$$

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

Xe valence shell radius (Å)	1.5	1.4	1.3	1.2	1.1	1.0	0.9
O-ligand charge q_o	1.5	0.91	0.64	0.47	0.36	0.28	0.22
F-ligand charge q_F*	0.63	0.48	0.37	0.30	0.20	0.16	0.13

(*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 $Xe^{+3}(F^{-\frac{1}{2}})_4\ O^{-1}$ for the oxyfluoride. In the latter view the Xe-O bond is a semi-ionic bond, $Xe^{+}{:}O^{-}$ The considerable polarity of the Xe-O bond predicts a large dipole moment for $XeOF_4$ ($> 4D$), if the non-bonding valence electron pair is sterically inactive

(i.e., in the Xe 5 s orbital). Since the observed dipole moment[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 ^{17}O n.m.r. spectrum of $^{17}OXeF_4$ shows a resonance (σ, -313 ppm relative to $H_2{}^{17}O$) down field from aqueous XeO_3 [242, 243] which has been interpreted[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, (σ, -500 to -600 ppm relative to $H_2{}^{17}O$).

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

Ligand Exchange in the System XeO_2F_2 / $XeOF_4$. A ^{19}F n.m.r. study and ^{18}F radiotracer investigation[228] in the system $XeO_2F_2/XeOF_4$ 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[235] :

$$XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2HF$$

$$XeO_2F_2 + H_2O \longrightarrow XeO_3 + 2HF$$

but it has not proved possible to control the hydrolysis to generate macroscopic yields of XeO_2F_2. The usual product is XeO_3.[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 [235] by interaction of $XeOF_4$ with H_2 in a nickel can at 300°:

$$XeOF_4 + 3H_2 \longrightarrow Xe + H_2O + 4HF$$

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_2F_2. It was subsequently prepared by Huston[244] 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_2F_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_2F_2. It is possible that chemical purification could be

Table 3.4.5

Some Physical Properties of XeO_2F_2

Colourless solid, liquid and vapour[a]

m.p. 30.8°C[a]

ΔH_f° ($XeO_2F_{2(g)}$) estimated[b]: + 56 kcal mole^{-1}

Volume Susceptibility $\chi_v = -0.86$[c]

Infrared and Raman (liquid and solid)[d]

Raman		Infrared	Assignment	
Solid	Liquid	(Ar matrix)	C_{2v} Symmetry	
205 ms	198 w		$\nu_4(a_1)$	
224 w	223 vw		$\nu_5(a_2)$	
315 vs	313 ms	317 ms	$\nu_9(b_2)$	
		324 s	$\nu_7(b_1)$	
350 ms	333 ms		$\nu_3(a_1)$	
537 vs	490 s		$\nu_2(a_1)$	
		537 vs	$\nu_5 + \nu_9$	$541(B_1)$
		550 w	$\nu_5 + \nu_7$	$547(B_2)$
		574 w	?	
	578 w	585 vs	$\nu_8(b_2)$	
769 w	788 vw			
814 w			?	
850 vs	845 vs	848 ms	$\nu_1(a_1)$	
882 s	905 w	905 s	$\nu_6(b_1)$	
		1023 w	?	
		1444 w	$\nu_1 + \nu_8$	$1433(B_2)$
		1496 vw	?	

Mass Spectra[a]

Positive ions : $XeO_2F_2^+$(0.89), XeO_2F^+(0.66), $XeOF_2^+$(4.8), XeO_2^+(1.6), XeF_2^+(3.3) $XeOF^+$(2.3), XeO^+(2.3), XeO^+(1.0), XeF^+(4.1).

Negative ions : XeF^-, XeF_2^-, $XeOF^-$ - no evidence for heavier ions.

(a) J. L. Huston, J. Phys. Chem., 71 (1967) 3339.

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

(c) H. D. Frame, J. L. Huston and I. Sheft, Inorg. Chem. 8 (1969) 1549.

(d) H. H. Claassen, E. L. Gasner and H. Kim, J. Chem. Phys. 49(1968)253.

achieved by complexing the XeF_2 with AsF_5 (see section 3.4.1) but this supposes that XeO_2F_2 does not form a salt or adduct with AsF_5.

Physical Properties. The solid, liquid and vapour are colourless and the solid low melting (29.5 - 30.5°). Although thermodynamically unstable, with respect to XeF_2 and O_2, 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 C_{2v} symmetry. Such an assignment is compatible with the observation that the isoelectronic species $IO_2F_2^-$ is of C_{2v} symmetry[245], being pseudo trigonal bipyramidal ($\measuredangle$ O-I-O = 180°; $\measuredangle$ F-I-F = 110°).

Chemical Properties. The compound interacts with XeF_6, with liquifaction, to yield $XeOF_4$:

$$XeF_6 + XeO_2F_2 \longrightarrow 2XeOF_4$$

It rapidly hydrolyses in moist air to yield XeO_3 but a faint ozone like odour, reminiscent of XeO_4, can be discerned.[244]

Analysis. The compound has been analyzed by decomposing it in a quartz container at 300°. The mixtures of Xe, O_2 and SiF_4 were

$$XeO_2F_2 \xrightarrow{SiO_2} 1.0\ Xe + 1.5\ O_2 + 0.45\ SiF_4 \quad \text{Found}$$

$$1.0\ Xe + 1.5\ O_2 + 0.5\ SiF_4 \quad \text{Calculated}$$

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[2] on the synthesis of XeF_4, Claassen, Selig and Malm noted that the hydrolysis of the solid yielded initially a yellow solid (now considered to be $XeOF_2$ see section 3.3.3) which dissolved to yield a clear, pale yellow solution. Cady and his coworkers, in their first report[203] of XeF_6, noted that the hydrolysis of the fluoride yielded a solution containing an oxidizing xenon species which they assumed to be xenic acid $Xe(OH)_6$. Simultaneous with the latter investigation, Smith[233] observed that XeF_6 exposed to moist air yielded a solid product, which proved to be xenon trioxide. Independently, Williamson and Koch discovered[188] that the solid recovered by evaporation of a hydrolysed XeF_4 solution was also XeO_3.[240]

Since XeO_3 is a powerful explosive, great care must be exercised in its preparation (and indeed in the handling of XeF_4 and XeF_6 since the oxide is formed when these interact with moisture). The oxide is most efficiently prepared from XeF_6 and two detailed procedures have been given[246, 247]. 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 XeF_6, 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:

$$XeF_{6(g)} + 3H_2O_{(\ell)} \longrightarrow 6HF_{(aq)} + XeO_{3(aq)}$$

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

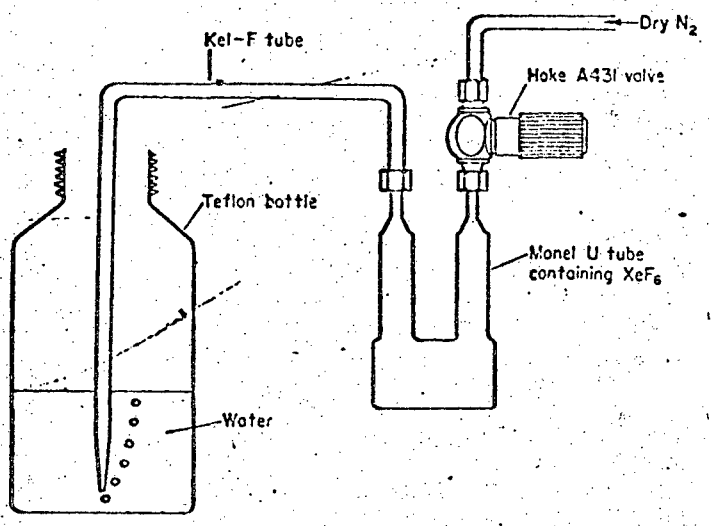


Figure 3.4.3

should not gain entrance to the XeF_6 container.

If it is necessary to remove the HF from the aqueous solution, this can be achieved by treating the solution with magnesium oxide ($MgO + 2HF \longrightarrow MgF_2 + H_2O$) 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 HNO_3.

The aqueous XeO_3 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 observations[238] to be 30 ± 10 kcal $mole^{-1}$. Calorimetry has given[248] ΔH_f° = + 96 kcal $mole^{-1}$ from which an Xe-O bond energy of ~17.5 kcal $mole^{-1}$ has been derived.

The XeO_3 molecule is pyramidal and almost identical in shape and size to the IO_3^- ion.[249, 240] The bond angles O-Xe-O are closer to T_d angles than right angles. The structure is shown in Figure 3.4.4.

Bonding and Bond Polarity. The pseudo-tetrahedral geometry of the XeO_3 molecule conforms to the representation of the bonding as Xe electron-pair donation, $Xe^+: \longrightarrow O^-$, the Xe orbitals being sp^3 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 XeO_3

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

Thermodynamic Features

ΔH sublimation (est): 30 ± 10 kcal $mole^{-1}$ (a)

ΔH_f° (298.15°K)(s): + 96 ± 2 kcal $mole^{-1}$ (b)

Mean thermochemical bond energy:

$27.5 - \frac{\Delta H \text{ sublim}}{3}$: 17.5 ± 4 kcal (a)

S°, $XeO_{3(g)}$ = 68.69 cal deg^{-1} $mole^{-1}$ (c)

Index of refraction: α = 1.79 (d)

Vibrational Spectra (e)

Infrared Spectrum (f)

(solid)		ν_1 (A)	770 cm^{-1}
		ν_2 (A)	311
		ν_3 (E)	820
		ν_4 (E)	298

Xe-O stretch force constant k_r: 5.66 mdyn/Å

Raman Spectrum (of 2.0 M aqu. soln.)

	C_{3v}		
ν_1		780 cm^{-1}	(p)
ν_2		344	
ν_3		833	
ν_4		317	

Crystal Structure (X-ray)[g]:

Orthorhombic

a = 6.163 ± 0.008 Å	z = 4
b = 8.115 ± 0.010	V = 262 Å^3
c = 5.234 ± 0.008	V_{mole} = 39.4 cm^3
$d_{X\text{-}ray}$: 4.55 g cm^{-3}	Space group: $P2_12_12_1$

Xe-O	1.74 ± 0.03Å	av. 1.76 Å
	1.76	
	1.77	
O-Xe-O	108 ± 2°	av. 103°
	100	
	101	

See Figure 3.4.4

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

(b) S. R. Gunn, in "Noble-Gas Compounds," H. H. Hyman, Ed., The University of Chicago Press, Chicago and London (1963) p. 149.

(c) G. Nagarajan, Bull. Soc. Chim. Belg., 73 (1964) 665.

(d) D. F. Smith, J. Amer. Chem. Soc. 85 (1963) 816.

(e) H. H. Claassen and G. Knapp, J. Amer. Chem. Soc. 86 (1964) 2341.

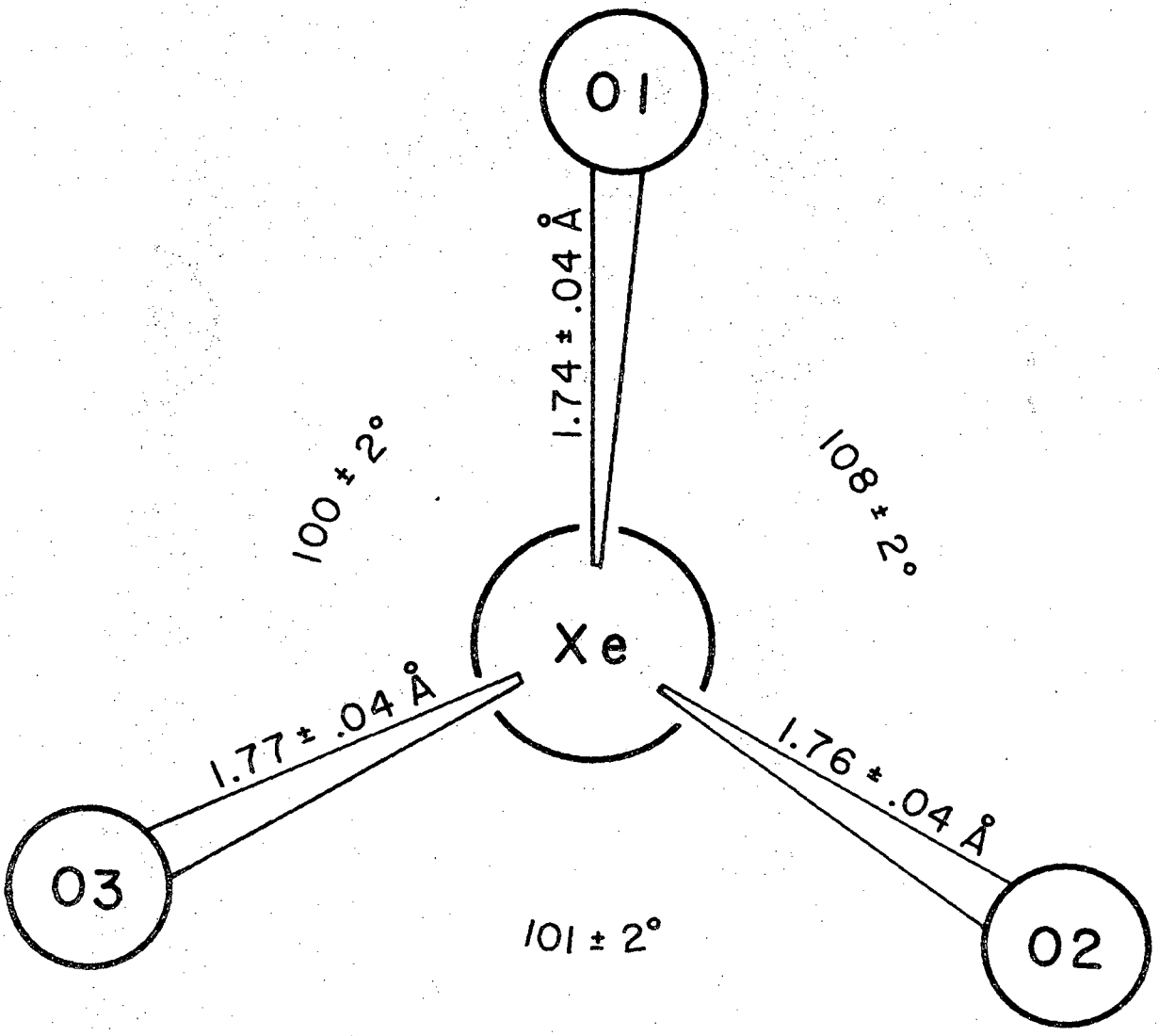
(f) See reference (b) p. 295.

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

Figure 3.4.4

The Molecular Shape and Packing In XeO_3(cryst)

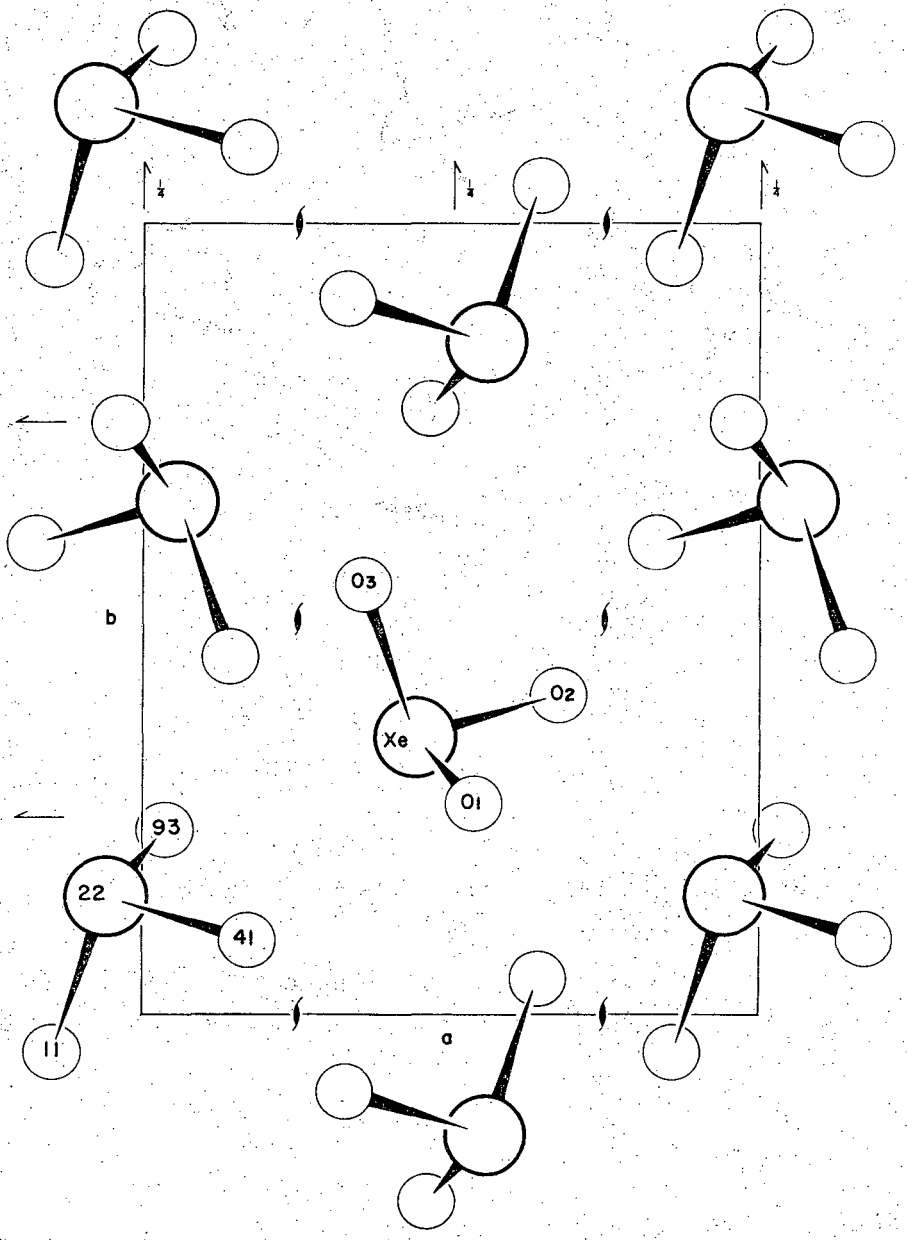
(See Table 3.4.5. for unit cell data)



XeO_3

MUB-1593

XeO_3



MUB-1594

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 affility 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:

There must be considerable polarity in the Xe-O bond and the 3 near-neighbour Xe---O distances of 2.8, 2.89 and 2.90Å must represent coulombic interactions $-Xe^{+x}---O-^{y-}$. 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 [200, 250] for ester like XeO_3— alcohol intermediates, in the oxidation of alcohols. A solution of XeO_3 in t-butyl alcohol[250] 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-XeO_2-OM.t-BuOH or $MHXeO_4$.2t-BuOH (M = K or Rb). Attempts to isolate a XeO_3-t butyl alcohol ester failed and XeO_3 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.[151] Excess sodium iodide is added to an aqueous acid: $XeO_3 + 6I^- + 6H^+ \longrightarrow Xe + 3H_2O + 3I_2$ solution. The liberated I_2 is titrated with standard thiosulphate to an amylose end point. It is of interest that if acid is added before the I^-, any perxenate decomposes to Xe(VI) and oxygen, whereas if I^- is added first, all of the oxidizing power is captured as triiodide.

3.4.5. Aqueous Xenon Trioxide ('Xenic Acid')

Preparation. Aqueous XeO_3 solutions are prepared[151, 247] as described under XeO_3. Solutions more concentrated than 2M in XeO_3 may be obtained. Solution calorimetric measurements have yielded[251] $\Delta H_f(XeO_3, \infty H_2O)$.

Physical Properties. The physical properties of aqueous XeO_3 are given in Table 3.4.7, at 298.15°K to be + 99.94 ± 0.24 kcal mole^{-1}. This implies $\Delta H_{soln.}$ = 3.9 ± 2 kcal mole^{-1}. The Xe/Xe(VI) redox potentials, derived from the aqueous solution calorimetric data, show XeO_3 to be one of the strongest oxidants in aqueous media:

$$\text{Acid,}\quad Xe_{(g)} + 3H_2O_{(l)} \longrightarrow XeO_{3(aq)} + 6H^+_{(aq)} + 6e^-,\ E^\circ_A = 2.10 \pm 0.01V$$

$$\text{Base,}\quad Xe_{(g)} + 7OH^-_{(aq)} \longrightarrow HXeO_4^-{}_{(aq)} + 3H_2O + 6e^-,\ E^\circ_B = 1.24 \pm 0.01V$$

Table 3.4.7

These potentials may be compared with those of the well known oxidizers Ce(IV) (E° = -1.61V) and O_3 (E° = - 2.07V). Xenic acid is reduced at the dropping mercury electrode in a single step to xenon.[252]

The Raman spectrum of 2M soln. of XeO_3 establishes[243] that the primary solution species is molecular XeO_3. This is further supported by the low electrical conductivity of the solution.[151] A ^{17}O n.m.r. study[242] shows that the oxygen ligands under fast exchange with the solvent, equilibrium being established within 3 min at 23 ± 10°. The ^{17}O chemical shift (-278 ± 2 p.p.m. with respect to water) is in the same range as those of perchloric acid (-288) and BrO_3^-, ClO_3^- and ClO_4^- (-297, -287, -288). This study also confirmed that XeO_3

Table 3.4.7

Some Physical Properties of Aqueous XeO_3

Solubility of XeO_3 in water: $\gg 2$ M[a]

Thermodynamic Features ΔH soln.[b] : 3.9 ± 2.0 kcal mole^{-1}

ΔH_f° ($XeO_3 \cdot \infty H_2O$, 298.15°K)[b]: 99.94 ± 0.24 kcal mole^{-1};

ΔS_f° = - 70 ± 4 cal deg^{-1} mole^{-1}

ΔG_f°($XeO_3 \cdot \infty H_2O$, 298.15°K): + 120.8 ± 1.2 kcal mole^{-1}

Electrode potentials of the Xe/XeO_3 couple:

Acid : E_A° ($Xe_{(g)} + 3H_2O_{(l)} \longrightarrow XeO_{3(aq)} + 6H^+_{(aq)} + 6e^-$) = 2.10 ± 0.01 V

Base : E_B° ($Xe_{(g)} + 7OH^-_{(aq)} \longrightarrow HXeO_4^-{}_{(aq)} + 3H_2O_{(l)} + 6e^-$) = 1.24 ± 0.01 V

Equilibrium constant[a] ($HXeO_4^-{}_{(aq)} \longrightarrow XeO_{3(aq)} + OH^-_{(aq)}$) = (6.7 ± 0.5) x 10^{-4}

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 ± 0.15°

(a) E. H. Appelman and J. G. Malm, J. Amer. Chem. Soc. 86 (1964) 2141.

(b) P.A. G. O'Hare, G. K. Johnson, and E. H. Appelman, Inorg. Chem. 9 (1970) 332.

may be extracted from aqueous solution with $CHCl_3$.[155]

An equilibrium constant, $6.7 \pm 0.5 \times 10^{-4}$, has been reported[151] for the process:

$$HXeO_4^-(aq) \longrightarrow XeO_{3(aq)} + OH^-(aq)$$

This accounts for the variation in the UV spectrum[151] as a function of pH. Shoulders at 210 and 250 m μ which are evident in acid media are presumably associated with XeO_3 and a shoulder which appears at 265 m μ in strong base may be associated with $HXeO_4^-$. The isolation of salts e.g., $CsHXeO_4$, (see section 3.4.11) support this rational.

Disproportionation. In strong base XeO_3 ($HXeO_4^-$?) disproportionates.[253, 151] The yield of perxenate at ~25° is ~33% for NaOH solutions of 0.25 ⟶ 4.2M and KOH solutions of 2 ⟶ 3.6M.[253] 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,[151] the reaction appeared to be: $4HXeO_4^- + 5OH^- \longrightarrow 3HXeO_6^{-3} + Xe + 3H_2O$. 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 $K_4XeO_6.2XeO_3$ has been isolated from the $KOH/XeO_{3(aq)}$ system[254] but other complexes probably occur. Evidence has been presented to show that these Xe(VI).Xe(VIII) complexes decompose predominently according to the equation:[253]

$$[Xe_{1+y}O_{4+3y}] \longrightarrow [XeO_4] + yXe + 1.5yO_2$$

It appears that the higher the perxenate concentration the less likely is the XeO_3 to disproportionate as follows:

$$2XeO_3 \longrightarrow [XeO_2] + [XeO_4]; \quad [XeO_2] \longrightarrow Xe + O_2$$

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 $XeO_3 + [XeO_2] \longrightarrow [XeO_4] + [XeO]; [XeO] \longrightarrow Xe + \frac{1}{2}O_2$, appears more likely than $XeO_3 + [XeO] \longrightarrow [XeO_4] + Xe$, since $XeF_{2(aq)}$ is known to reduce $XeO_{3(aq)}$.[147]

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]: $\Delta H(XeO_{3(aq)} + 9I^-_{(aq)} + 6H^+_{(aq)} \longrightarrow Xe_{(g)} + 3I_3^-{}_{(aq)} + 3H_2O_{(l)}) = -219.63 \pm 0.06$ 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:

$$6Pu(III) + XeO_3 + 6H^+ \longrightarrow 6Pu(IV) + Xe + 3H_2O \text{ (in } HClO_4 \text{ acid)}$$

and the rate law is $-d[Pu(III)]/dt = k[Pu(III)][XeO_3]$. 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;[256]

$$6Np(V) + Xe(VI) \longrightarrow 6Np(VI) + Xe$$

The reaction is first order in XeO_3, the rate expression being $-d[Np(V)]/dt = k_1[XeO_3]$ for which $k_1 \times 10^6$ (sec^{-1}) = 6.28 ± 0.58. The formation of excited XeO_3: $XeO_3 + h\nu$ UV $\longrightarrow XeO_3^*$, 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 $XeO_3 + H_2O \xrightarrow{h\nu}$ 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.[257] The XeO_3 solution interacts readily with vic-diols and primary alchols 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 [200] 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 CO_2 and H_2O.[258]

3.4.6. Complexes of XeF_6 with F^- Acceptors

A number of adducts involving XeF_6 in combination with recognized F^- acceptors have been reported. They include the following 1:1 adducts (m.p. (°C) given in parentheses): $XeF_6 \cdot AsF_5$ (130.5°) [259, 260, 261]; $XeF_6 \cdot BF_3$ (90°) [259]; $XeF_6 \cdot SbF_5$ [234]; $XeF_6 \cdot GeF_4$ (sub.) [262]; $XeF_6 \cdot PtF_5$ (~100°) [263, 264]; $XeF_6 \cdot IrF_5$ (116°) [169]; $XeF_6 \cdot RuF_5$ (118°) [227]. The X-ray structures of the 1:1 adducts with PtF_5 and AsF_5 have shown them to be XeF_5^+ salts [264, 265] (see Figure 3.4.5). The Ir and Ru compounds are isostructural with the Pt compound.[227] In view of the observation that the cubic form of XeF_6 is essentially $XeF_5^+ F^-$ (see Figure 3.4.1) it seems probable that all of the 1:1 adducts are XeF_5^+ salts. However, the following XeF_6 adducts (with F^- acceptors) may also contain XeF_5^+ ions, in clusters with bridging with F^- ions: $2XeF_6 \cdot AsF_5$ (110°)[261]; $2XeF_6 \cdot PF_5$ [261]; $2XeF_6 \cdot SbF_5$ [234]; $2XeF_6 \cdot PtF_5$ [263]; $2XeF_6 \cdot IrF_5$ (135°) [169]; $XeF_6 \cdot 2SbF_5$ (108°) [234]; $4XeF_6 \cdot GeF_4$; $2XeF_6 \cdot GeF_4$ [262]; $4XeF_6 \cdot SnF_4$ and $2XeF_6 \cdot SnF_4$.[266]

Preparation. The complexes may be prepared simply by fusing the neat components or by dissolving them in non-reductive solvents (e.g. BrF_5 or HF). Alternatively, XeF_6 may be formed *in situ*, thus, $XeF_5^+[PtF_6]^-$ and $2XeF_6 \cdot PtF_5$ have been isolated [263] from $Xe/F_2/PtF_5$ mixtures where the fluorine pressures and the reaction temperature favoured XeF_6 formation. The same mixtures yielded XeF^+ and $Xe_2F_3^+[PtF_6]^-$ salts (see section 3.2.6) at low fluorine concentrations.

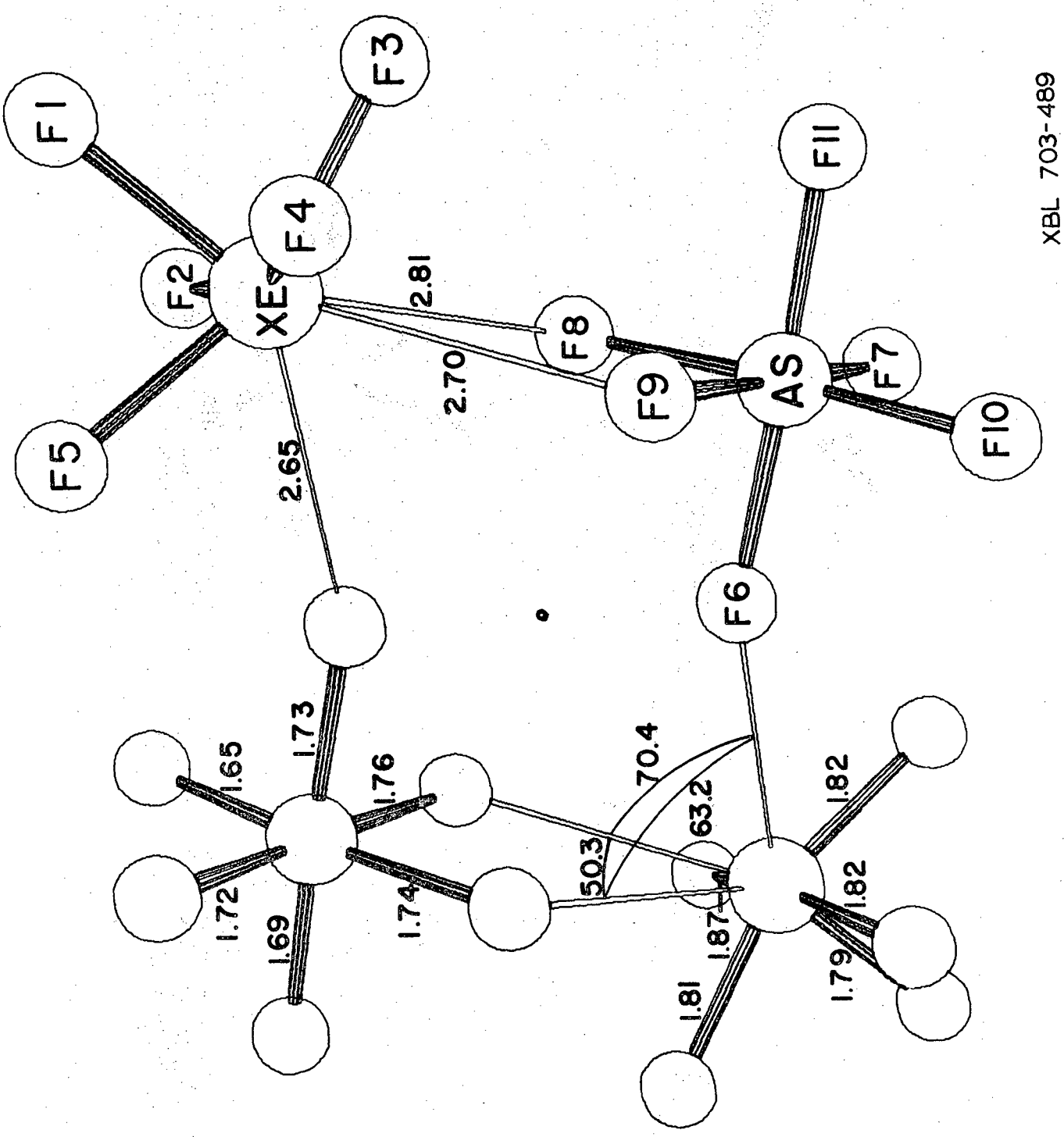


Figure 3.4.5
The Molecular Structure of $XeF_5^+[AsF_6]^-$.‡

‡ F. Hollander, D. Templeton, M. Wechsberg and N. Bartlett, unpublished observation.

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 $XeF_5^+[PtF_6]^-$ and $XeF_5^+[AsF_6]^-$ clearly indicate the ionic formulation they show the cation to possess considerable polarizing capability. The $XeF_5^+[AsF_6]^-$ structure, represented in Figure 3.4.5, shows the AsF_6^- ion appreciably distorted as a consequence

Figure 3.4.5

of those F-ligands of AsF_6^- near the xenon atoms, being attracted to the xenon. This is consistent with the charge of ~ +3 which the xenon(VI) atom is considered to bear.

Hydrolysis of these XeF_6 compounds occurs very readily. An almost quantitative yeild of 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 XeF_6 Adducts with F^- Donors

A number of compounds have been reported involving XeF_6 in combination with recognized fluoride ion donors. The following alkali fluoride compounds have been reported:[267, 268]

$CsF.XeF_6$ (yellow, ρ 4.72 g cm^{-3}) $\xrightarrow{\sim 50^\circ}$ $2CsF.XeF_6$ (cream coloured) $\xrightarrow{\sim 400^\circ}$ CsF

$RbF.XeF_6$ (colourless) $\xrightarrow{\sim 0^\circ}$ $2RbF.XeF_6$ (colourless) $\xrightarrow{\sim 400^\circ}$ RbF

$2KF.XeF_6$ (colourless) $\xrightarrow{\leq 250^\circ}$ KF

$2NaF.XeF_6$ (colourless) $\xrightarrow{\leq 250^\circ}$ NaF

Lithium compounds do not form. Other reports[204, 232] mention $NaF.XeF_6$ and give a decomposition temperature (under vacuum) of 125°. This decomposition temperature presumably applies to the $2NaF.XeF_6$ compound, since there is no evidence for a 1:1 compound.[268] As mentioned in section 3.4.1, the reversible compound formation of XeF_6 with NaF provides a convenient method for the purification of XeF_6, since XeF_2, XeF_4 and $XeOF_4$ (the common impurities in an XeF_6 preparation) do not complex with NaF.

The enthalpies of dissociation of the 1:1 adducts:

$$2Cs(Rb)F.XeF_6 \longrightarrow Cs_2(Rb_2)F_2.XeF_6 + XeF_6$$

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

A compound with nitrosyl fluoride[269], $2NOF.XeF_6$, is presumably closely related to the alkali fluoride compounds. The occurrence of infrared and Raman bands at 2310 and 2305 cm^{-1} indicate the presence of NO^+ cations. The band at 540 cm^{-1} is presumably associated with Xe-F stretch. This is the only structural information available for the F^- donor compounds. It does support the expectation that they are salts of general formulae $A^+[XeF_7]^-$ and $(A^+)_2[XeF_8]^{2-}$. Presumably, these anions, like XeF_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 $CsXeF_7$ in moist air yields $CsXeO_3F$ (see section 3.4.11). Dissolution of the latter yields $CsHXeO_4$.[268]

3.4.8 $XeOF_4$ Complexes with Fluoride Ion Acceptors

As in the case of XeF_6, antimony pentafluoride forms a complex[237] with $XeOF_4$ which is stable at room temperature. Excess SbF_5 yields a material of composition $XeOF_4.2SbF_5$ (m.p. ~ 70°). A complex, $2XeOF_4.VF_5$ is also reported.[270] Arsenic pentafluoride forms an adduct[237] with $XeOF_4$ at -78° but this does not exist at room temperature, even under pressures of one or two atmospheres of AsF_5. This contrasts with the XeF_6 behavior and it is clear that complex formation using AsF_5 may be used as a convenient chemical method for separating $XeOF_4$ and XeF_6. There is no firm structural information on the $XeOF_4$ complexes with the fluoride acceptors, but it is probable that they are salts of the $XeOF_3^+$ ion, which is presumably pseudo-trigonal bipyramidal (the oxygen ligand being in an equatorial position).

3.4.9 $XeOF_4$ Complexes with Fluoride Ion Donors

The oxide tetrafluoride complexes readily with CsF, RbF, KF[237] and NOF[269]. The trend in thermal stabilities of the alkali fluoride complexes is similar to that observed in the XeF_6 complexes, namely Cs > Rb > K. The NOF complex, $ONF.XeOF_4$, dissociated readily (m.p. 40°, v.p. 30 mm Hg at 23°)[269]. Thermogravimetric analysis[237] indicates the following stoichiometries:

$$CsF.XeOF_4 \xrightarrow{\sim 125^\circ} 3CsF.2XeOF_4 \xrightarrow{\sim 275^\circ} 3CsF.XeOF_4 \xrightarrow{\sim 400^\circ} CsF$$

$$3RbF.2XeOF_4 \xrightarrow{50^\circ} 3RbF.XeOF_4(?) \xrightarrow{\sim 400^\circ} RbF$$

$$3KF.XeOF_4 \xrightarrow{90^\circ} 6KF.XeOF_4 \xrightarrow{\sim 250^\circ} KF$$

The $MF.yXeOF_4$ 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 $MXeO_3F$ salts (see section 3.4.12) are formed.

The $XeOF_5^-$ ion may occur in these $XeOF_4$ complexes but it is more probable that polymeric species involving $XeOF_4$ molecules 'bridged' by F^- ions, like the XeF_6 tetramers and hexamers (see Figure 3.4.1) will be found.

3.4.10 XeO_2F_2 Adducts

Adducts of XeO_2F_2 have not been reported but it is possible that both XeO_2F^+ and $XeO_2F_3^-$ salts will be preparable. The cation should be structurally akin to XeO_3 and the anion pseudo-octahedral.

3.4.11 Xenates(VI)

Preparation. Mono alkali xenates of empirical formula $MHXeO_4.1.5\ H_2O$ (M = Na, K, Rb, Cs) have been prepared[271] by lyophilization of 0.1 M XeO_3 and alkali hydroxide in 1:1 ratio. The cesium salt has also been prepared by interaction of $XeO_{3(aq)}$ in the presence of 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 XeO_3, particularly when anhydrous. They are susceptible to detonation, particularly if they contain excess XeO_3. The salts are insoluble in methyl, ethyl and t-butyl alcohols, $CHCl_3$ and 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 Xe-O stretch.

Table 3.4.8

Table 3.4.8.

Infrared Spectra (cm^{-1}) of Monoalkali Xenates(VI)

Empirical Formula							
$NaHXeO_4$ [a]	3500w	1600w	1360m	770-800s	730sh	625s	469s	340-370m
$K(Rb)HXeO_4$ [a]	3500w	1600w	1360m	770-800s	730sh	~480s		340-370m
$CsHXeO_4$ [b]	3120vw	1430vw	783s	741s	721s	699s	386s	347s,316s

(a) T. M. Spittler and B. Jaselskis, J. Amer. Chem. Soc., 87 (1965) 3357.
(b) B. Jaselskis, T. M. Spittler and J. L. Huston, ibid, 88 (1966) 2149.

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.[271]

3.4.12 Complexes of XeO_3 with F^- and Cl^- and Br^- Donors

Alkali fluoro-xenates (VI) $MXeO_3F$[272], and chloro-xenates(VI)[273] have been prepared. Brief mention has also been made of $CsXeO_3Br$.[272]

Preparation. The $MXeO_3F$ 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. Evapouration 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 evapourating a solution prepared by mixing equal volumes of 0.5M $XeO_{3(aq)}$ and 1M $KF_{(aq)}$ and containing a few drops of HF.

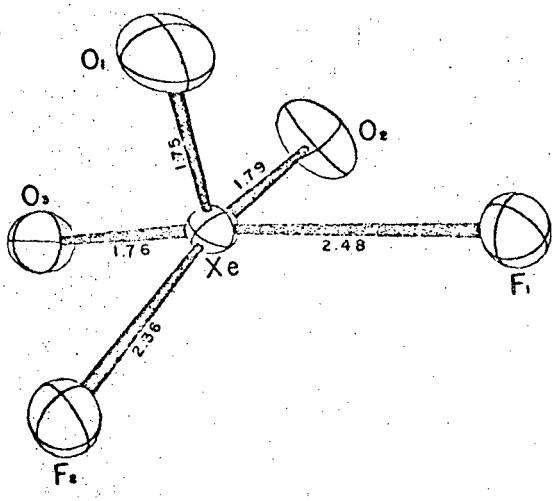
The chloro-xenate $CsXeO_3Cl$ is prepared[273] similarly although acetronitrile may be used as the solvent. A white crystalline precipitate is obtained after 3 hours following mixing of an ice-cold solution of ~2.0 ml of 1.5 M CsCl with 0.4 ml of 1.5M $XeO_{3(aq)}$.

Physical Properties. The fluoro-xenates(VI) are claimed to be[272] the most thermally stable of the solid oxygenated Xe(VI) compounds. Even the chloro-xenate[273] is considerably more stable than XeO_3.

The infrared spectra of the $MXeO_3F$ 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.[274] This structure shows XeO_3 units linked in infinite chains by bridging F atoms. The geometry of the XeO_3 moiety is very similar to that of XeO_3 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 $KXeO_3F$[274]



Angles	
O_1-Xe-O_2	101.1(8)°
O_3-Xe-O_2	97.8(7)°
O_1-Xe-O_3	100.5(1.2)°
O_3-Xe-F_2	85.3(5)°
O_2-Xe-F_1	77.2(6)°
F_2-Xe-F_1	98.7(2)°
O_1-Xe-F_1	87.6(1.1)°
O_1-Xe-F_2	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[273] 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 $KXeO_3F$.

Chemical Properties. The fluoro xenates do not decompose thermally below 200° but loose 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_2SO_4 to $CsXeO_3Cl$ 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 XeO_4 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, OsO_4 and OsO_3F_2 being known and OsF_8, $OsOF_6$ and OsO_2F_4 unknown.[275]

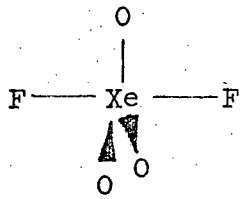
3.5.1 Xenon Octafluoride

Although, in an early report[276], a claim was made for the preparation of XeF_8, 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/F_2 system Weinstock et al[22] found no evidence for XeF_8, even at high F_2/Xe ratios and moderate temperatures (see section 1.2).

3.5.2. Xenon Trioxide Difluoride

Xenon trioxide difluoride has been prepared by interaction of XeF_6 with solid sodium perxenate contained in a Kel-F tube. This interaction produces a larger quantity of other xenon compounds, principally $XeOF_4$. The compound was detected mass spectrometrically, $XeO_3F_2^+$ being observed. Xenon tetroxide is formed in small quantities along with XeO_3F_2. These two compounds have comparable volatilities, both being sufficiently volatile at -78° to yield characteristic

mass spectra. Since XeO_3F_2 is more volatile than XeO_2F_2 (see section 3.4.3) the former is probably symmetrical and non-polar. This indicates that the $\underline{D_{3h}}$ 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, $XeOF_6$, at first sight, appears to be a thermodynamically favourable formulation, the low enthalpy of formation of IF_7 from IF_5 for the process: $IF_{5(g)} + F_{2(g)} \longrightarrow IF_{7(g)}$ (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 $OXeF_5^+$ ion and it may be that the parent oxyfluoride can be prepared from salts of this ion.

The oxyfluoride XeO_2F_4 may well be preparable. The ΔH_f° 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.[277, 278] Sodium or barium perxenate(Na_4XeO_6; Ba_2XeO_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'[277] and negligible XeO_4 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 XeO_4 are given in Table 3.5.1. The vapour pressure of XeO_4 is ~ 25mm at 0° and the volatility at -78° is sufficient to provide for mass spectrometric detection. Usually, decomposition to Xe and O_2 occurs before the sample reaches 0° and the decomposition can be violent - samples have exploded at -40°.[277] This instability is in accord with the heat of formation, obtained[238] by detonating several gaseous samples at ~25° : $\Delta H°(XeO_{4(g)} \longrightarrow Xe_{(g)} + 2O_{2(g)}) = -153.5$ kcal mole^{-1}. This enthalpy indicates a mean thermochemical bond energy of 21.1 kcal, which is a little greater than the value for XeO_3.

The infrared spectrum of gaseous samples were obtained using nickel cells having either silver chloride of 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.[241] The Xe-O stretching force constant is lower than in the case of $XeOF_4$ which suggests that the Xe-O bond in XeO_4 is weaker. This is supported by the bond

Table 3.5.1 :

Some Physical Properties of XeO_4

The solid is yellow.

Thermochemical Features

ΔH_f° (g) (298.15°K): + 153.5 kcal[a]; mean thermochemical bond energy: 21.1 kcal[a]

Vapour pressure, mm (°C) [b]: 3(-35°), 10(-16°), 25(0°)

Vibrational spectra

Infrared:		Obs.[b]	Calc.[c]
	ν_1		906
Supports T_d symmetry[b][c]	ν_2		301
	ν_3	877 (PQR) 870 885	876
	ν_4	306 (PQR) 298 314	305

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 T_d symmetry and gives Xe-O = 1.736 ± 0.002 Å

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

(b) H. Selig, H. H. Claassen, C. L. Chernick, J. G. Malm, and J. L. Huston, Science 143 (1964) 1322.

(c) W. A. Yeranos, Bull. Soc. Chim. Belges, 74 (1956) 414.

(d) G. Gunderson, K. Hedberg and J. Huston, Acta. Cryst. 25 (1969) 124; see also R. J. Gillespie, in "Noble Gas Compounds," H. H. Hyman, Ed., The University of Chicago Press, Chicago and London (1963) p. 333.

length of 1.736Å obtained from electron diffraction data, this being ~0.04 Å longer than the Xe-O bond in $XeOF_4$.[239]

Since the Xe-O bond strength in $XeOF_4$ appears to be greater than in XeO_4, it may be that the charge removal from the Xe atom by the 4 O-ligands in XeO_4 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: ⟶ $\ddot{O}$:) this would yield a central-atom charge of +4 for XeO_4 and only +3 for $XeOF_4$ (assuming 3 centre-4-electron bonds $^{-\frac{1}{2}}F\text{-}Xe^{+1}\text{-}F^{-\frac{1}{2}}$). However, the ligand repulsions for the oxide would be greater than for the oxyfluoride. The chemical shift derived from the Mössbauer spectrum of XeO_4 has been interpreted[158] as indicative of a charge of +1.7 on the xenon atom, whereas the same authors argue that the Xe-atom positive charge in XeF_4 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 spectra[278] show the typical isotope pattern of xenon repeated every 16 mass units up to XeO_4. Conventional analysis has been achieved[238] 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.

$$2XeF_6 + 4Na^+ + 16OH^- \longrightarrow Na_4XeO_6 + Xe + O_2 + 12F^- + 8H_2O$$

Evidently, the disproportionation of pure XeO_3 solution in base is much slower[151] and it is claimed[170] that only ~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[151] 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_2O per xenon atom, depending on the drying procedure. The preparation of the potassium salt, $K_4XeO_6 \cdot H_2O$, requires greater care,[279] since a mixed valence product $K_4XeO_6 \cdot 2XeO_3$ readily precipitates.[2, 254]

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;[151] a saturated solution at ~25° being only 2.3×10^{-5} M. The solubility of the perxenates decreases in the sequence $Na^+ > Li(1.0 \times 10^{-3}M) > Am^{3+}(6.1 \times 10^{-5}M) > Ba^{2+}(2.3 \times 10^{-5})$[280]. 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:

$$Na_4XeO_6 + H_2O \longrightarrow HXeO_6^{-3} + OH^- + 4Na^+$$

The ultraviolet spectra of the perxenate solutions are pH dependent. Isobestic points at 220 and 270 m μ indicate that two principle species contribute to the spectra. Potentiometric titrations suggest the following equilibria:

$$HXeO_6^{3-} + H^+ \rightleftharpoons H_2XeO_6^{2-} \quad (pK_A \sim 10.5)$$

$$H_2XeO_6^{2-} + H^+ \rightleftharpoons H_3XeO_6^- \quad (pK_A \sim 6)$$

Table 3.5.2

Some Physical Properties of Perxenates

Crystallographic Data

	$Na_4XeO_6 \cdot 6H_2O$ [a]	$Na_4XeO_6 \cdot 8H_2O$ [b] [c]	$K_4XeO_6 \cdot 9H_2O$ [d]
Space group	Pbca	Pbcn	$Pbc2_1$
a(Å)	18.44(1)	11.864 (5)	9.049 (4)
b	10.103(7)	10.426 (5)	10.924 (4)
c	5.873(5)	10.358 (5)	15.606 (6)
$d_{X\text{-ray}}$(g cm^{-3})	2.59	2.33 (5)	2.35
$d_{measured}$	> 2.17	2.38	- - -
z	4	4	4
Xe-O (Å)	(2) 1.86 (2) (2) 1.87 (2) (2) 1.80 (2) av. 1.840 (s)	(2) 1.88 (1) (2) 1.85 (1) (1) 1.84 (1) (1) 1.89 (1) av. 1.864 (12)	1.86 (1)
∠ O-Xe-O	89 (1)° 87 (1) 88 (1)	89.3 (8)° 89.0 (8) 87.4 (8)	88.8 to 91.2 (7)°

(See Figure 3.5.1)

Vibrational Data[e]

1.8 M cesium perxenate solution:

Raman bands (cm^{-1})	685 (vs)P	448 (mw)P	402(w)
Infrared bands (cm^{-1})	605(s)	443,425(s)	

$Na_4XeO_6 \cdot 0.4H_2O$ (solid):

Raman bands (cm^{-1})	683 (vs)	655(m)	470(mw)	390 (w)

Oxidation Potentials[f]

Xe(VIII) -Xe(VI), Acid: 3.0 V; Base: 0.9 V.

Table 3.5.2

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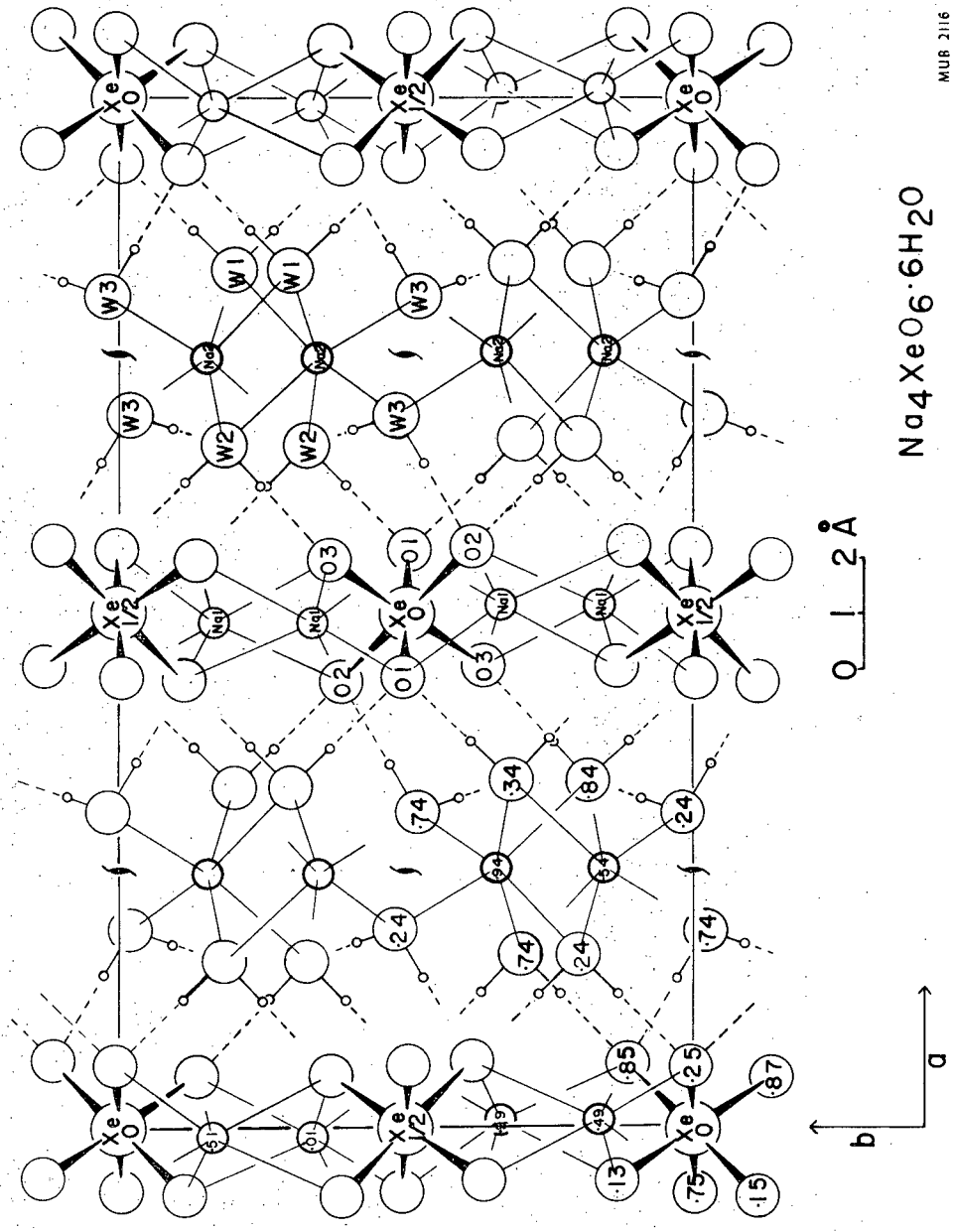
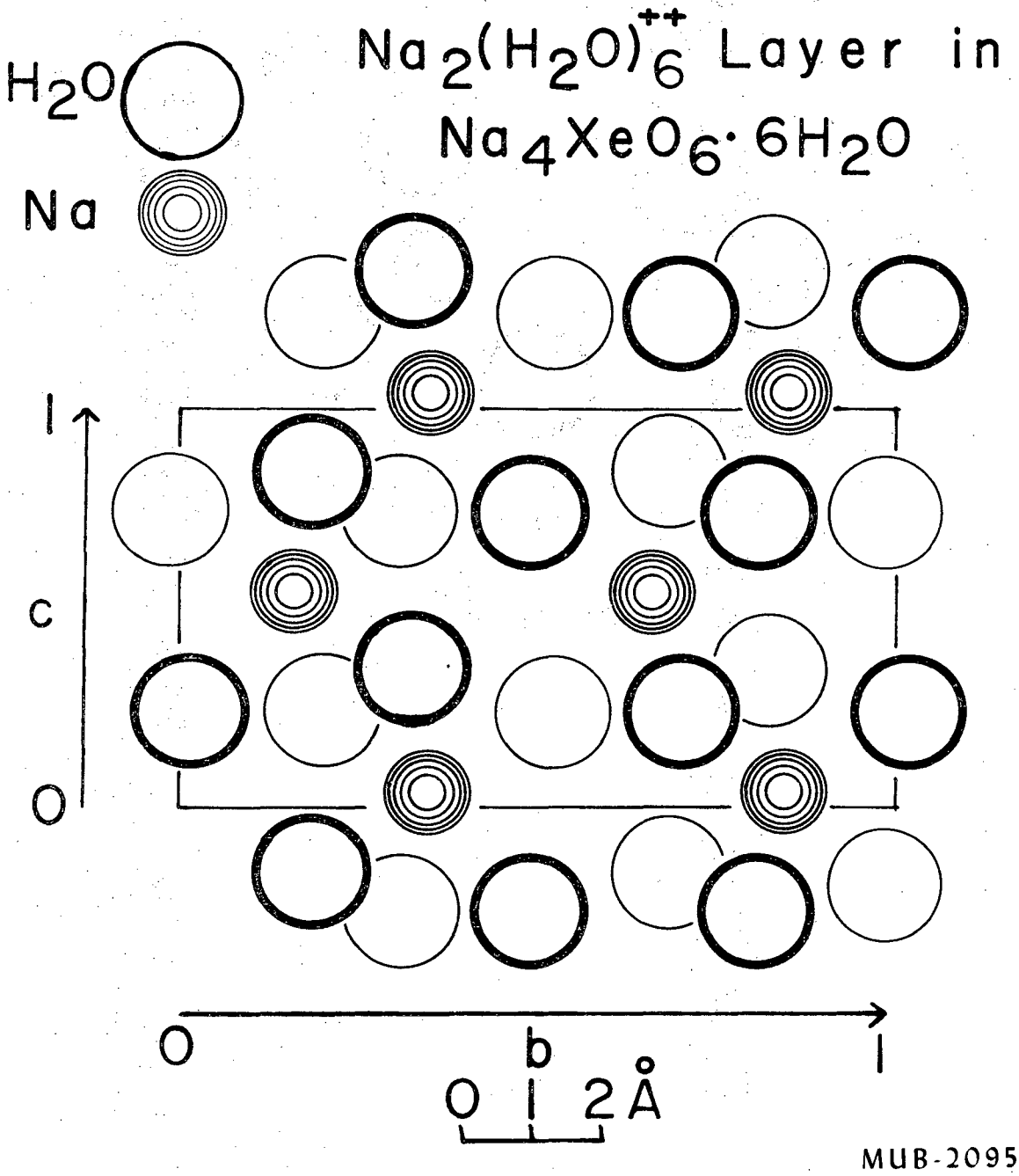
Figure 3.5.1

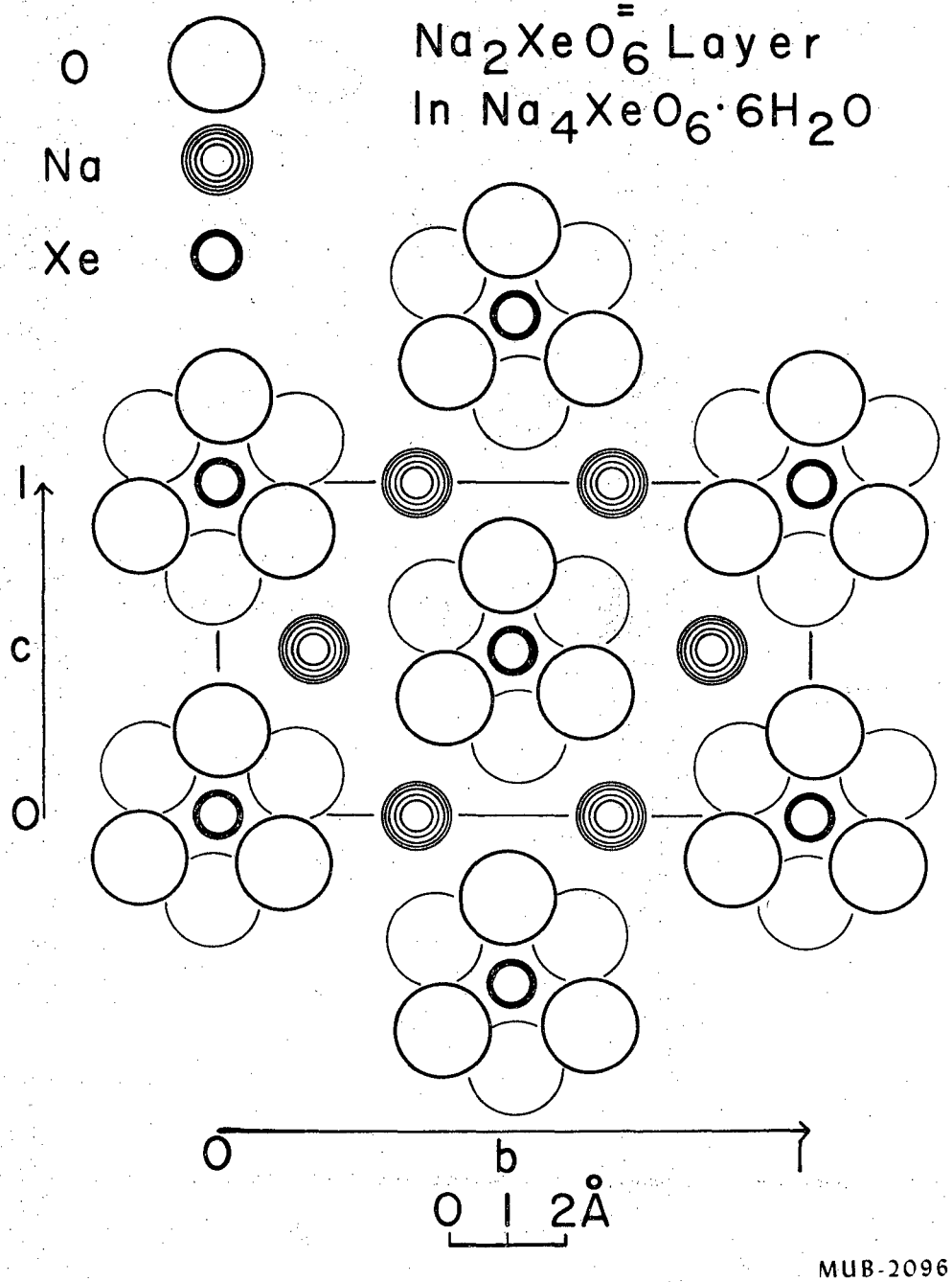
The Crystal Structure of $Na_4XeO_6.6H_2O$ ‡

‡Reproduced with permission from A. Zalkin, J. D. Forrester and D. H. Templeton, Inorg. Chem. 3 (1964) 1417.


Xe 0
Xe 1/2
W1
W2
W3
Na1
Na2
Na3
O1
O2
O3
.74
.34
.84
.24
.94
.85
.25
.87
.49
.13
.75
.15
.01
.51
0 1 2 Å
b
a
$Na_4XeO_6 \cdot 6H_2O$
MUB 2116



MUB-2095


O
Na
Xe
$Na_2XeO_6^{=}$ Layer
In $Na_4XeO_6 \cdot 6H_2O$
c
0
0
b
0 1 2Å
MUB-2096

The interpretation of the solution properties is also complicated by the reduction of Xe(VIII) to Xe(VI):

$$H_3XeO_6^- \longrightarrow HXeO_4^- + 0.5O_2 + H_2O$$

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,[281,282] octahydrate[283] and a nonahydrate[279] have been determined and the findings are summarized in Table 3.5.2. The structure of $Na_4XeO_6.6H_2O$ 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.[283, 279, 281] The Xe-O bond length, 1.84-1.88Å is slightly shorter than the Xe-F bond in XeF_6 (1.89Å) and much longer than in XeO_4 (1.74Å) and XeO_3 (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[284] suggest that a high concentration of symmetrical XeO_6^{4-} 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 $Na_4XeO_6.0.4H_2O$. It is very probably the totally symmetrical octahedral ν_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[158] of the perxenates imply chemical shifts which are very close to that of XeO_4, 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[32, 33], 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 O^- components, each 3-centre-4-electron bond arising from a linear array (see Figure 1.3.2):

$$^-O \qquad Xe^{2+} \qquad O^-$$

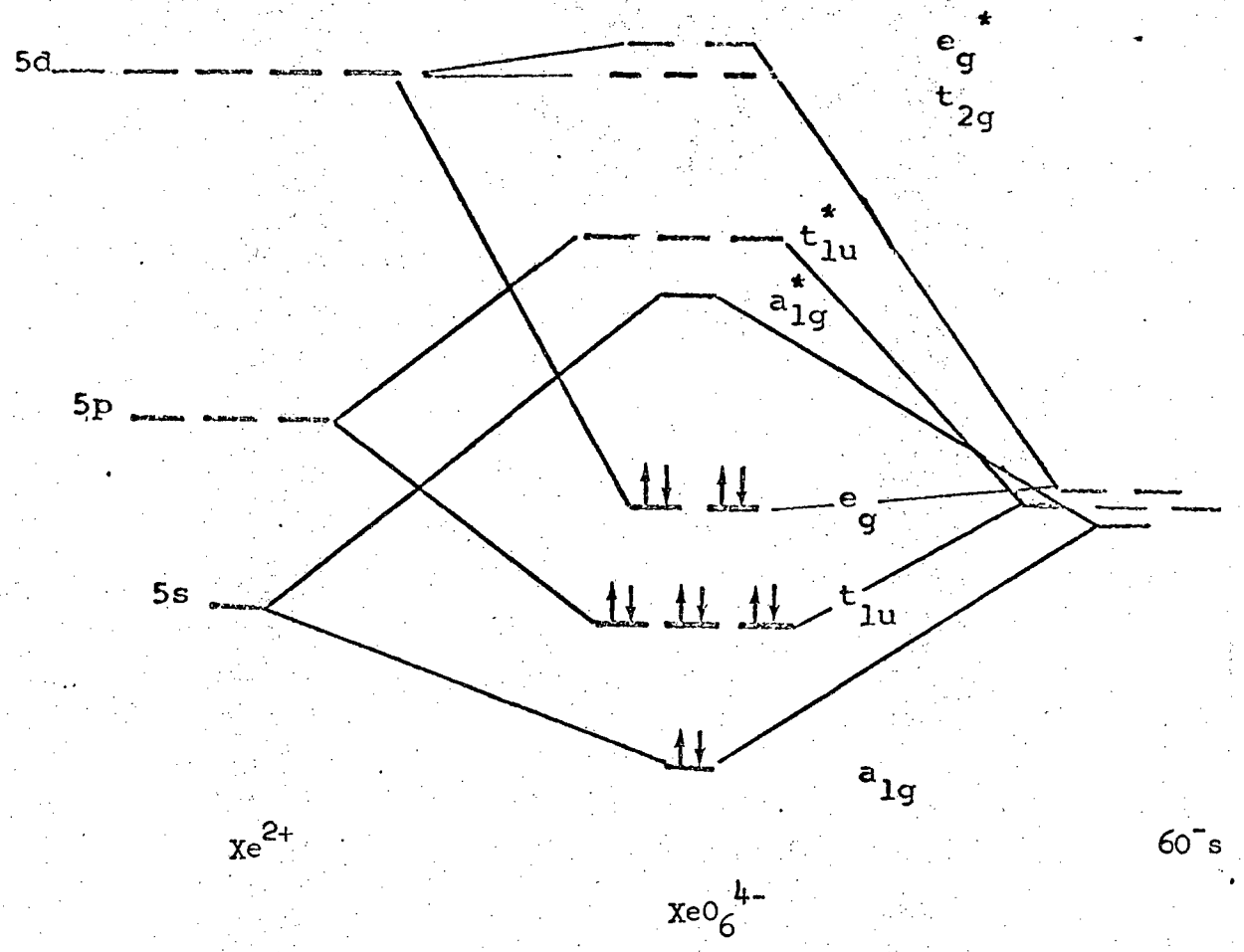
The high bond polarity of this model accounts for the greater intrinsic bond strength of Xe-O in $[XeO_6]^{4-}$ relative to XeF in $Xe-F_6$.

Alternatively, if d orbitals are involved in the bonding, the ion can be represented as an sp^3d^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 oribtals, 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 I_2, even in 1M base. Similarly Br^- is oxidized to Br_2 at pH 9 or less and Cl^- to Cl_2 in dilute acid.[151] Also in dilute acid perxenate immediately converts Mn^{2+} to MnO_4^-. Iodate is oxidized to IO_4^- 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, $Am_4(XeO_6)_3 \cdot 40\ H_2O$, prepared[280] from basic solutions of Am(III) is of low solubility in water (4.6×10^{-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.[151]

4. Radon Chemistry

4.1 Introduction

Prior to 1962, when Fields, Stein and Zirin reported a fluoride[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[286] that it did not react with metals and a large number of other substances. Nikitin was able[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}Rn, has a half-life of only 3.83 days. This isotope is derived from the decay of ^{226}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}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_6^{4-} etc.) would be thermodynamically more stable than in the case of their xenon counterparts. Evidently,[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[289] for the oxidation of Rn by strong aqueous oxidizers has been refuted[290] 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 - RnF_2 (?)

In their initial reports[285, 291] 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[288, 292] has shown that ^{222}Rn interacts spontaneously with fluorine and all of the stable interhalogen fluorides (e.g. $2BrF_3 + 3Rn \longrightarrow Br_2 + 3RnF_2(?)$) except IF_5 and is even oxidized by the $[NiF_6]^{2-}$ ion. In these experiments, gaseous ^{222}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 ^{222}Rn was found to be in the liquid phase. Removal of the excess reagent (BrF_5 or BrF_3 or ClF_3) in a vacuum at room temperature yielded, in all cases, a white solid containing all of the ^{222}Rn 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 RnF_2: $RnF_2 + H_2O \longrightarrow Rn + \frac{1}{2}O_2 + 2HF$. From the observation that AsF_5 will not oxidize Rn, whereas BrF_3 will, the standard free energy of formation of RnF_2 has been set between the limits of -29 and -51 kcal mole^{-1}.

Stein and his coworkers have shown[288] 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 $Rn_2F_3^+$ would seem more reasonable than Rn^{2+}. Presumably, the fluoride is ionic - both $Rn^{2+}(F^-)_2$ and $RnF^+(F^-)$ are consistent with the known properties.

Although complex salts containing RnF^+, $Rn_2F_3^+$ or even Rn^{2+} 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 PtF_6 should oxidize Rn (See section 3.1.2) and it seems likely that IrF_6 and possibly OsF_6 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[288] 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

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