

NOBLE-GAS COMPOUNDS

1. Introduction

The noble gases had been characterized for many years as inert and incapable of forming compounds with other elements. Failed attempts to induce chemical reactivity led to assumptions of chemical inertness and inviolability of the noble-gas valence shell octet of electrons, the so-called octet rule (1). The discovery of the reactivity of the noble gases (qv) was first reported by Bartlett (2) in 1962. Deep red-brown PtF_6 vapor in the presence of xenon gas at room temperature produced a yellow-orange compound, then formulated as $\text{Xe}^+\text{PtF}_6^-$. Within a few months of this discovery, xenon tetrafluoride (3) and xenon difluoride (4) were prepared. A number of other xenon compounds, krypton difluoride and radon difluoride followed (5).

The heavier noble gases, krypton, xenon and radon, are shown to react with fluorine (qv) and other powerful oxidants to form a number of stable products. Although a compound of argon has been isolated in a low temperature matrix and several argon species are known in the gas phase (see the section **Prospects for Compounds of the Lighter Noble Gases**), no stable compounds of the lighter noble gases, helium, neon, and argon, have been isolated in macroscopic amounts as of this writing. Additional surveys of noble-gas compounds are provided in (5–12). Some of the properties of the fluorides, oxides, and oxide fluorides of noble-gas compounds are given in Table 1. Prior to the discovery of these compounds, hydrates and other clathrate compounds of the noble gases were known. A discussion of clathrates may be found in the literature (6,34) (see INCLUSION COMPOUNDS).

2. Xenon Compounds

2.1. Halides. The xenon fluorides xenon difluoride, XeF_2 [13709-36-9], xenon tetrafluoride, XeF_4 [13709-61-0], and xenon hexafluoride, XeF_6 [13693-09-9], as well as xenon oxide tetrafluoride, XeOF_4 [13774-85-1], are thermodynamically stable. The xenon fluorides are colorless, crystalline solids that can be sublimed under vacuum at 25°C. The mean thermochemical bond energies for the binary fluorides are XeF_2 , 132.3 ± 0.7 kJ/mol (31.6 ± 0.2 kcal/mol); XeF_4 , 130.3 ± 0.5 kJ/mol (31.1 ± 0.1 kcal/mol) and XeF_6 , 125.3 ± 0.7 kJ/mol (29.9 ± 0.2 kcal/mol) (16). Xenon hexafluoride is yellow-green as a liquid or gas and colorless as a solid. Reports of xenon octafluoride, XeF_8 [17457-75-9], remain unsubstantiated. Xenon difluoride is a linear symmetrical molecule having an Xe-F distance of 197.73(15) pm (35), and XeF_4 is a square planar molecule [Xe–F, 195.3(4) pm] (36). Experimental evidence is consistent with a distorted octahedral structure for gaseous XeF_6 (37) arising from the presence of an extra pair of nonbonding electrons in the xenon valence shell. Solid XeF_6 exists in at least four crystal morphologies that consist of tetrameric and hexameric rings of virtually undistorted square pyramidal XeF_5^+ cations linked together by fluoride ion bridges (24,38).

Xenon dichloride, XeCl_2 [13780-38-6], and xenon(II) chlorofluoride, XeClF [73378-52-6], have been prepared by photochemical and electric discharge

methods and have been examined at low temperatures by matrix-isolation techniques (39,40). Like XeF_2 , the dichloride has a linear structure. Evidence for the existence of XeCl_2 , xenon dibromide, XeBr_2 [73378-57-1], and xenon tetrachloride, XeCl_4 [14989-42-5], have been obtained from Mössbauer studies (41,42). Owing to their thermochemical instabilities, no neutral halides other than the binary fluorides have been prepared in macroscopic amounts. A cationic species, the monochloroxenon(II) cation, XeCl^+ [398508-13-9], has recently been isolated as $\text{XeCl}^+\text{Sb}_2\text{F}_{11}^-$, and possesses a xenon-chlorine bond length of 230.9(2) pm (43). Other species containing Xe(II)-Cl bonds include $(\text{C}_6\text{F}_5)\text{XeCl}$ [249733-81-1] and $[(\text{C}_6\text{F}_5)\text{Xe}]_2\text{Cl}^+\text{AsF}_6^-$ [249733-78-6] (see also the section Xenon Bonded to Carbon) (44).

Unstable monohalides of xenon, XeF [16757-14-5], XeCl [55130-03-5], XeBr [55130-04-6], and XeI [55130-05-7]), have been produced in the gas phase by electron bombardment methods (45,46) and in solid matrices by gamma and ultraviolet (uv) irradiation methods (47,48). Although short lived in the gas phase, these halides are of considerable importance as light-emitting species in gas lasers (qv).

2.2. Oxides. Two oxides of xenon are known: xenon trioxide, XeO_3 [13776-58-4], and xenon tetroxide, XeO_4 [12340-14-6] (Table 1). Xenon trioxide is most efficiently prepared by the controlled hydrolysis of XeF_6 (49) or by the reaction of XeF_6 with HOPOF_2 (50). Xenon tetroxide is prepared by the interaction of concentrated sulfuric acid with sodium or barium perxenate, Na_4XeO_6 , Ba_2XeO_6 (33,51). The XeO_3 molecule has a trigonal pyramidal shape with an Xe-O bond length of 176(3) pm (52), while XeO_4 has a tetrahedral shape with Xe-O equal to 173.6(2) pm (53). Xenon tetroxide has also been characterized in solution by low temperature ^{17}O , ^{129}Xe , and ^{131}Xe NMR spectroscopy (51). Both oxides are thermodynamically unstable, explosive solids that must be handled with the greatest care. On decomposing to the elements, solid XeO_3 and gaseous XeO_4 release 402 and 642 kJ/mol (96.1 and 153 kcal/mol), respectively (29). Xenon trioxide has a negligible vapor pressure at room temperature and readily dissolves in water to give stable solutions containing mainly molecular XeO_3 and hydrogen xenate, HXeO_4^- . The concentration of HXeO_4^- is vanishingly small [$K \approx 3 \times 10^{-11}$ for $\text{XeO}_3(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HXeO}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$], except in basic solution [$K \approx 1.5 \times 10^3$ for $\text{XeO}_3(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{HXeO}_4^-(\text{aq})$]. Xenon tetroxide is volatile at 25°C, but frequently decomposes violently before this temperature is reached.

2.3. Oxide Fluorides. The oxide fluoride of xenon(II), $\text{O}(\text{XeF})_2$, is pale yellow in color, and is formed by the low temperature displacement of XeF_2 from $\text{FXeOXe}-\text{FXeF}^+\text{AsF}_6^-$ using the fluoride ion donor NOF (54). The $\text{O}(\text{XeF})_2$ molecule possesses a V-shaped geometry and is isoelectronic with $\text{F}(\text{XeF})_2^+$ (also written as Xe_2F_3^+). Xenon oxide tetrafluoride, XeOF_4 , is a colorless liquid (Table 1) and has a square pyramidal geometry with the oxygen atom trans to the electron lone pair; the Xe-F distance is 170.3(15) pm, while the Xe-O distance is 190.0(5) pm (55). It is a volatile colorless liquid. The XeO_2F_2 molecule is based on a trigonal bipyramidal valence shell electron-pair repulsion (VSEPR) arrangement (56) of oxygen and fluorine bonding electron pairs and a single valence electron lone pair. Both oxygen atoms and the lone pair of electrons are in the equatorial plane, while the fluorine atoms are in the axial posi-

tions, resulting in a distorted tetrahedral geometry. The Xe-F distance is 171.4(4) pm, while the Xe-O distance is 189.9(3) pm (57). It is a colorless solid (Table 1). Xenon oxide tetrafluoride is formed by the interaction of XeF_6 with equimolar amounts of water (58) or NaNO_3 (59). The reaction of stoichiometric amounts of N_2O_5 and XeOF_4 affords XeO_2F_2 (60). Xenon oxide difluoride, XeOF_2 [13780-64-8], is formed as an unstable yellow solid by the interaction of XeF_4 with a stoichiometric amount of water (26,27). Two thermally unstable oxide fluorides of xenon(VIII) are known; xenon trioxide difluoride, XeO_3F_2 [15192-14-0] (61), and xenon dioxide hexafluoride, XeO_2F_4 [15195-51-4] (62). The structure of XeO_3F_2 has been verified by vibrational spectroscopy and by ^{19}F and ^{129}Xe NMR spectroscopy, while XeO_2F_4 has only been characterized by mass spectrometry.

2.4. Xenates and Perxenates. Alkali metal xenates of composition $\text{MXeO}_4 \cdot 1.5 \text{H}_2\text{O}$, where M is sodium, potassium, rubidium or cesium, have been prepared by freeze drying mixtures of xenon trioxide and the corresponding metal hydroxides in 1:1 molar ratios. The xenates are unstable, explosive solids (63).

When XeF_6 is hydrolyzed in a strongly alkaline solution, part of the xenon is evolved as gas, but a large fraction precipitates as a perxenate salt (XeO_6^{4-}), where xenon is in the +8 oxidation state (7). Among the salts that have been prepared in this manner, or by alternative procedures, are $\text{Na}_4\text{XeO}_6 \cdot 6 \text{H}_2\text{O}$ [30970-85-5], $\text{K}_4\text{XeO}_6 \cdot 9 \text{H}_2\text{O}$ [60763-18-0], $\text{Li}_4\text{XeO}_6 \cdot 2 \text{H}_2\text{O}$ [34901-38-7], and $\text{Ba}_2\text{XeO}_6 \cdot 1.5 \text{H}_2\text{O}$ [15842-32-7]. The average Xe-O bond length is 185(2) pm (7). The salts are kinetically very stable, losing water gradually when heated; eg, $\text{Na}_4\text{XeO}_6 \cdot 6 \text{H}_2\text{O}$ becomes anhydrous at 100°C and decomposes at 360°C. A number of transition metal and actinide perxenates have been prepared but are not thoroughly characterized and include those of copper, lead, silver, zinc, thorium, and uranium. Perxenate solutions are powerful oxidants in aqueous solution and are capable of oxidizing iodate ion to periodate and manganous ion to permanganate. The aqueous chemistries of perxenates and other xenon compounds have been fully described (63).

2.5. Complex Salts and Molecular Adducts. The majority of the known complexes of xenon can be classified as cation or anion derivatives of binary fluorides, oxide fluorides and XeO_3 . Gross geometries are in accord with the VSEPR model (56) of molecular geometry and are listed in Table 2 along with those of the parent compounds. Although complex compounds derived by the interaction of a xenon fluoride or oxide fluoride with a strong fluoride ion acceptor are generally written as ionic formulations, the cations and anions interact with one another by means of weak covalent interactions of the cation with one or more fluorine atoms on the anion—an interaction that is termed fluorine bridging (10).

Xenon difluoride behaves as a fluoride ion donor toward many metal pentafluorides to form complex salts containing the XeF^+ and Xe_2F_3^+ cations (10), the latter possessing a V-shaped structure. In reactions with the pentafluorides of arsenic, antimony, and ruthenium, eg, XeF_2 forms the salts $\text{Xe}_2\text{F}_3^+\text{AsF}_6^-$ [21308-45-2], $\text{XeF}^+\text{AsF}_6^-$ [26024-71-5], $\text{Xe}_2\text{F}_3^+\text{SbF}_6^-$ [12528-47-1], $\text{XeF}^+\text{SbF}_6^-$ [36539-18-1], [17679-45-7], $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ [15364-10-0], [36539-19-2], $\text{Xe}_2\text{F}_3^+\text{RuF}_6^-$ [26297-25-6], $\text{XeF}^+\text{RuF}_6^-$ [22527-13-5], [26500-06-1] and $\text{XeF}^+\text{Ru}_2\text{F}_{11}^-$

[22527-14-6]. The bonding in these structures can be illustrated using the known structures $\text{XeF}^+\text{AsF}_6^-$, where xenon bonds to one terminal fluorine atom and weakly interacts with one fluorine atom of the anion ($\text{Xe}-\text{F}_{\text{terminal}}$, 187.3(6); $\text{Xe}-\text{F}_{\text{bridge}}$, 212(5) pm), and $\text{Xe}_2\text{F}_3^+\text{AsF}_6^-$, where the two XeF^+ units of Xe_2F_3^+ are joined by a bridging fluorine atom through the xenon atoms ($\text{Xe}-\text{F}_{\text{terminal}}$, 190.8(6), 192.9(6); $\text{Xe}-\text{F}_{\text{bridge}}$, 214.2(7), 215.7(3) pm) (81,82). Bartlett's original compound, $\text{Xe}^+\text{PtF}_6^-$, appears to be $\text{XeF}^+\text{PtF}_5^-$ [86275-65-2], and the products of further oxidation by PtF_6 gave $\text{XeF}^+\text{PtF}_6^-$ [26024-75-9], PtF_5 and $\text{XeF}^+\text{Pt}_2\text{F}_{11}^-$ [267410-30-0] (83). Adducts containing the weak fluoride ion acceptors MF_4 ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), MoOF_4 and WOF_4 are known in which XeF_2 interacts with the metal by formation of asymmetric $\text{Xe}-\text{F}-\text{M}$ bridges, eg, $\text{FXe}-\text{F}-\text{CrF}_4$ [143852-09-9] (84), $\text{FXe}-\text{F}-\text{MoOF}_4$ [74080-83-4], $\text{FXe}-\text{F}-\text{WOF}_4$ [55888-4-7] and $\text{FXe}-\text{F}-\text{MoOF}_4(\text{MoOF}_4)_2$ [65622-63-1] (85,86). A crystal structure of $\text{XeF}_2\cdot\text{WOF}_4$ [55888-48-7] exhibits the bond lengths, $\text{Xe}-\text{F}_{\text{bridge}}$, 204(3) pm; $\text{W}-\text{F}_{\text{bridge}}$, 218(3) pm; and $\text{Xe}-\text{F}_{\text{terminal}}$, 189(3) pm (87). Xenon difluoride interacts weakly with the Ag^+ and BrO_2^+ cations to give $\text{FXe}-\text{F}-\text{Ag}-\text{F}-\text{XeF}^+$ [136952-28-8] and $\text{FXe}-\text{F}-\text{BrOF}_2^+$ [77071-47-7], in the compounds $2\text{XeF}_2\cdot\text{Ag}^+\text{AsF}_6^-$ (88) and $\text{XeF}_2\cdot\text{BrOF}_2^+\text{AsF}_6^-$ (89). Xenon difluoride also forms a number of molecular complexes in which the molecular parameters are essentially the same as in the pure compound; these include $\text{XeF}_2\cdot\text{IF}_5$ [21992-39-2] (90), $\text{XeF}_2\cdot\text{XeOF}_4$ [34166-84-2] (91) and $\text{XeF}_2\cdot\text{XeF}_4$ [12337-03-0] (92).

Xenon difluoride reacts with hydronium ion salts, $\text{H}_3\text{O}^+\text{MF}_6^-$ ($\text{M} = \text{As}, \text{Sb}$) in HF to give the novel salt, $\text{FXeOXeFXeF}^+\text{MF}_6^-$, which is deep red to magenta in color. The only example of xenon in a fractional oxidation state, $+1/2$, is the bright emerald green paramagnetic dioxenon cation, Xe_2^+ [12185-20-5]. Mixtures of xenon and fluorine gases react spontaneously with liquid antimony pentafluoride in the dark to form solutions of $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$, in which Xe_2^+ is formed as an intermediate product that is subsequently oxidized by fluorine to the XeF^+ cation (93). Spectroscopic studies have shown that xenon is oxidized at room temperature by solutions of XeF^+ in SbF_5 solvent to give the Xe_2^+ cation (94). An X-ray crystal structure of $\text{Xe}_2^+\text{Sb}_4\text{F}_{21}^-$ [188070-38-4] has subsequently shown that the Xe-Xe bond length is 308.7(1) pm (95).

Xenon tetrafluoride is a much weaker fluoride ion donor and only forms stable complex salts with the strongest fluoride ion acceptors: $\text{XeF}_3^+\text{SbF}_6^-$ [39797-63-2] (64), $\text{XeF}_3^+\text{Sb}_2\text{F}_{11}^-$ [35718-37-7] (65), and $\text{XeF}_3^+\text{BiF}_6^-$ [66121-33-3] (66). Xenon tetrafluoride has also been shown to behave as a weak fluoride ion acceptor toward alkali metal fluorides and the naked fluoride ion source $\text{N}(\text{CH}_3)_4^+\text{F}^-$ to give salts of the novel pentagonal planar XeF_5^- [133042-38-3] anion (67). Xenon oxide difluoride is a fluoride ion acceptor, forming the only other anion containing xenon in the +4 oxidation state; the XeOF_3^- anion in $\text{Cs}^+\text{XeOF}_3^-$ [65014-02-0] (27).

Xenon hexafluoride is both a strong fluoride ion donor and acceptor. Examples of salts containing the XeF_5^+ cation are numerous (10,11). A representative crystal structure is that of $\text{XeF}_5^+\text{PtF}_6^-$ [18533-64-7] (68). There are several examples of salts that contain the fluoride-bridged $\text{F}(\text{XeF}_5)_2^+$ cation (usually denoted as $\text{Xe}_2\text{F}_{11}^+$) that have a number of counteranions in common with those of the XeF_5^+ salts (10,11). The structure of the $\text{Xe}_2\text{F}_{11}^+$ cation is exemplified in the crystal structure of $\text{Xe}_2\text{F}_{11}^+\text{AuF}_6^-$ [39043-77-1] (70). Xenon(VI) fluorometalates(III) and

(IV) of the rare earth elements are also known, and exist as $6\text{XeF}_6 \cdot \text{LnF}_3$ ($\text{Ln} = \text{Y}, \text{Tm}, \text{Yb}, \text{Lu}, \text{Ho}, \text{Er}$), $3\text{XeF}_6 \cdot \text{DyF}_3$ [160095-01-2], $\text{XeF}_6 \cdot 2\text{LnF}_4$ ($\text{Ln} = \text{Tb}, \text{Ce}$), and $\text{XeF}_6 \cdot 4\text{PrF}_4$ [160179-01-1] (96). A number of salts in which XeF_6 behaves as a fluoride-ion acceptor toward alkali metal fluorides are known which likely contain the XeF_7^- and XeF_8^{2-} anions (97). Several nonalkali metal salts have been shown by X-ray crystallography and vibrational spectroscopy to contain the XeF_7^- and XeF_8^{2-} anions and include $\text{NF}_4^+ \text{XeF}_7^-$ [82963-12-0] (69,98), $[\text{NF}_4^+]_2 \text{XeF}_8^{2-}$ [82963-15-3] (69), $\text{Cs}^+ \text{XeF}_7^-$ [179237-50-4] (69,70), and $[\text{NO}^+]_2 \text{XeF}_8^{2-}$ [17501-82-5] (69). Reaction of XeF_6 with the fluoride ion donor NO_2F (2:1 mol ratio) gives $\text{NO}_2^+ \text{Xe}_2\text{F}_{13}^-$ [179089-23-7]; the structure is that of an XeF_6 molecule fluorine bridged through two $\text{Xe}-\text{F}$ bonds to an XeF_7^- anion (70).

The oxide fluorides of xenon(VI) exhibit analogous fluoride ion donor and acceptor properties. Salts of both the XeOF_3^+ and XeO_2F^+ cations are known, as well as a salt of the fluoride-bridged cation $\text{FO}_2\text{Xe}-\text{F}-\text{XeO}_2\text{F}^+$, and include $\text{XeOF}_3^+ \text{SbF}_6^-$ [42861-25-6], $\text{XeOF}_3^+ \text{Sb}_2\text{F}_{11}^-$ [15600-67-6], $\text{XeO}_2\text{F}^+ \text{Sb}_2\text{F}_{11}^-$ [52078-91-8], $\text{XeO}_2\text{F}^+ \text{AsF}_6^-$ [115117-21-0] and $\text{FO}_2\text{Xe}-\text{F}-\text{XeO}_2\text{F}^+ \text{AsF}_6^-$ [13875-06-4] (73,77–79). Several ionic fluoride complexes with XeOF_4 are known, such as $3\text{KF} \cdot \text{XeOF}_4$ [12186-19-5], $3\text{RbF} \cdot 2\text{XeOF}_4$ [12186-23-1], $\text{CsF} \cdot \text{XeOF}_4$ [12191-01-4], $\text{CsF} \cdot 3\text{XeOF}_4$ [76077-76-4], $\text{NOF} \cdot \text{XeOF}_4$ [13996-09-1] and $\text{NH}_4\text{F} \cdot \text{XeOF}_4$ [161535-97-3]. Structural studies show that the CsF complexes are best formulated as $\text{M}^+ \text{XeOF}_5^-$ [12191-01-4] [$\text{M} = \text{Cs}, \text{NO}, \text{N}(\text{CH}_3)_4$] (72–74) and $\text{Cs}^+(\text{XeOF}_4)_3\text{F}^-$ [76077-76-4] (74). The XeOF_5^- unit has all five fluorine atoms in the equatorial plane with the oxygen atom in an axial position trans to the lone pair. The only complexes formed between XeO_2F_2 and a strong fluoride ion donor are the salts $\text{Cs}^+ \text{XeO}_2\text{F}_3^-$ [65014-03-1] and $\text{NO}_2^+ \text{XeO}_2\text{F}_3^- \cdot n\text{XeO}_2\text{F}_2$ [116025-38-8] (27,60).

Alkali metal fluoroxenates KXeO_3F [23525-88-4, 27002-68-2], RbXeO_3F [12434-32-1, 33572-57-5], and CsXeO_3F [12443-46-8, 33572-58-6], which decompose above 200°C , and a chloroxenate, CsXeO_3Cl [26283-13-6, 27002-67-1], which decomposes $>150^\circ\text{C}$, have been prepared by evaporating aqueous solutions of XeO_3 and the corresponding alkali metal fluorides and chloride. The alkali metal fluoroxenates are the most stable solid oxygenated compounds of xenon(VI) known. X-ray crystallography shows that $\text{K}^+ \text{XeO}_3\text{F}^-$ is an open-chain polymeric structure where each XeO_3 group is bonded to two fluorine atoms, which bridge adjacent XeO_3 groups (80). Similarly, the X-ray crystal structures of the compounds $2.25 \text{MCl} \cdot \text{XeO}_3$ ($\text{M} = \text{Rb}, \text{Cs}$) feature infinite chains of XeO_3Cl^- anions linked by nearly linear chlorine bridges (99). The CsXeO_3Br compound is unstable even at room temperature (100).

3. Derivatives in Which Xenon is Bonded to Polyatomic Groups

3.1. Xenon Bonded to Oxygen. The greatest variety of polyatomic ligand groups bonded to xenon occur for xenon in its +2 oxidation state, and those bonded through oxygen are most plentiful. Both mono- and disubstituted derivatives having the formulations FXeL and XeL_2 are known where $\text{L} = \text{OTeF}_5, \text{OSeF}_5, \text{OSO}_2\text{F}, \text{OP}(\text{O})\text{F}_2, \text{OClO}_3, \text{ONO}_2, \text{OC}(\text{O})\text{CH}_3, \text{OC}(\text{O})\text{CF}_3, \text{OSO}_2\text{CH}_3, \text{OSO}_2\text{CF}_3$, and OIOF_4 . With the exception of OIOF_4 and $\text{OP}(\text{O})\text{F}_2$, the syntheses involve HF elimination reactions of the parent acid HL with XeF_2

(eg, $\text{XeF}_2 + x\text{HL} \rightarrow \text{F}_{2-x}\text{XeL}_x + x\text{HF}$; $x = 1, 2$) (9,101). The highly electronegative $-\text{OTeF}_5$ group is the only ligand known to completely replace fluorine in compounds of xenon in the +4 and +6 oxidation states. The derivative, $\text{Xe}(\text{OTeF}_5)_4$ [66255-64-9], is the only example known where xenon in the +4 oxidation state is coordinated exclusively to oxygen atoms (102–104); the average Xe–O length is 203.2(5) pm (105). The mixed ligand derivatives $\text{F}_x\text{Xe}(\text{OTeF}_5)_{4-x}$ ($x = 0–3$) result from the ligand redistribution upon mixing XeF_4 and $\text{Xe}(\text{OTeF}_5)_4$ (106). Reaction of $\text{Xe}(\text{OTeF}_5)_4$ with SbF_5 results in the formation of the mixed cations $\text{F}_x\text{Xe}(\text{OTeF}_5)_{3-x}^+$ ($x = 0–2$) (107). The known $-\text{OTeF}_5$ derivatives of xenon in the +6 oxidation state include $\text{Xe}(\text{OTeF}_5)_6$ [68854-31-9] (101), $\text{O}_2\text{Xe}(\text{OTeF}_5)_2$ (105,106), and $\text{O}=\text{XeF}(\text{OTeF}_5)_4$ [68854-32-0] (108). Unlike its fluorine analogue, XeF_6 , $\text{Xe}(\text{OTeF}_5)_6$ is monomeric in the solid state. In addition, the mixed ligand derivatives, $\text{O}_2\text{XeF}(\text{OTeF}_5)$ [91002-54-9] (106) and $\text{O}=\text{XeF}_x(\text{OTeF}_5)_{3-x}^+$ ($x = 0–3$) (103,106), are known, as well as the $\text{O}_2\text{XeOTeF}_5^+$ [142533-95-7] (107) and $\text{O}=\text{XeF}_x(\text{OTeF}_5)_{3-x}^+$ ($x = 0–2$) cations (107). Xenon difluoride and $\text{Xe}(\text{OTeF}_5)_2$ react in stoichiometric quantities to give FXeOTeF_5 [25599-15-9] (109). The selenium analogue, FXeOSeF_5 [38167-25-8], is prepared from the reaction of XeF_2 and SeO_2F_2 (110). Both FXeOTeF_5 and FXeOSeF_5 act as fluoride ion donors, reacting with AsF_5 to form $\text{XeOTeF}_5^+\text{AsF}_6^-$ [27680-14-4] (111) and $\text{XeOSeF}_5^+\text{AsF}_6^-$ [374778-61-7] (112), respectively. The crystal structures of both compounds have been determined; the Xe–O bond length in $\text{XeOSeF}_5^+\text{AsF}_6^-$ is 204(4) pm and 196(4) pm in $\text{XeOTeF}_5^+\text{AsF}_6^-$ (112).

3.2. Xenon Bonded to Nitrogen. Several ligand groups form compounds containing xenon–nitrogen bonds (12). The first xenon–nitrogen bonded compound synthesized, $\text{FXeN}(\text{SO}_2\text{F})_2$ [53719-78-1], was prepared by reaction of $\text{HN}(\text{SO}_2\text{F})_2$ and XeF_2 at 0°C in CF_2Cl_2 solvent (113). Proof for Xe–N bonding was established by X-ray crystallography (114). The Xe–N and Xe–F bond distances are 220.0(3) pm and 196.7(3) pm, with trigonal planar coordination around the nitrogen atom. Compounds containing N–Xe–N linkages are also known, viz, $\text{XeN}(\text{SO}_2\text{F})_2$ [85883-06-3] (115,116) and $\text{Xe}[\text{N}(\text{SO}_2\text{CF}_3)_2]$ [82113-64-2] (117). The fluoride ion donor properties of $\text{FXeN}(\text{SO}_2\text{F})_2$ have been studied, leading to the characterization of the salts $\text{XeN}(\text{SO}_2\text{F})_2^+\text{Sb}_3\text{F}_{16}^-$, [99665-06-2] (118), and $(\text{FO}_2\text{S})_2\text{NXe}—\text{F}—\text{XeN}(\text{SO}_2\text{F})_2^+\text{AsF}_6^-$ (115,116). The Xe–N bond length in the $\text{XeN}(\text{SO}_2\text{F})_2^+$ cation in $\text{XeN}(\text{SO}_2\text{F})_2^+\text{Sb}_3\text{F}_{16}^-$ is 202(1) pm (118).

The XeF^+ cation forms Lewis acid–base adduct cations containing N–Xe–F linkages with nitrogen bases that are resistant to oxidation by the strongly oxidizing XeF^+ cation, which has an estimated electron affinity of 10.9 eV (12). The thermally unstable, colorless salt, $\text{HC}\equiv\text{NXeF}^+\text{AsF}_6^-$ [112144-23-7], is prepared by reaction of $\text{HC}\equiv\text{N}$ with $\text{Xe}_2\text{F}_3^+\text{AsF}_6^-$ or $\text{XeF}^+\text{AsF}_6^-$ in anhydrous HF solvent or by reaction of $\text{HC}\equiv\text{NH}^+\text{AsF}_6^-$ with XeF_2 in BrF_5 solvent (119,120). Other nitriles, $\text{RC}\equiv\text{N}$, forming the white solids $\text{RC}\equiv\text{NXeF}^+\text{AsF}_6^-$ ($\text{R} = \text{CH}_3$ [112144-25-9], CH_2F [112144-27-1], CF_3 [119127-10-5], C_2H_5 [112144-29-3], C_2F_5 [112144-31-7], C_3F_7 [112144-33-9], C_6F_5 [112154-24-2]), have been prepared using methods similar to those used for the preparation of $\text{HC}\equiv\text{NXeF}^+\text{AsF}_6^-$ and are generally less stable than $\text{HC}\equiv\text{NXeF}^+\text{AsF}_6^-$ (119,121). The fluoro(perfluoropyridine)xenon(II) cations $4\text{-RC}_5\text{F}_4\text{NXeF}^+$ ($\text{R} = \text{F}$ [114481-54-8], CF_3 [114481-56-0]) (122) and the $s\text{-C}_3\text{F}_3\text{N}_2\text{NXeF}^+\text{AsF}_6^-$ cation (121) have been prepared as colorless AsF_6^- salts and are planar cations in which the xenon atom

is bonded to the ring through the lone pair of electrons on a nitrogen atom. The salt, $s\text{-C}_3\text{F}_3\text{N}_2\text{NXeF}^+\text{AsF}_6^-$ [119127-04-7], is the only salt in this series that is stable at room temperature (121) and is prepared by the reaction of $\text{XeF}^+\text{AsF}_6^-$ with liquid s -trifluorotriazine, $s\text{-C}_3\text{F}_3\text{N}_3$, at room temperature (12).

Xenon(II) also forms bonds to inorganic nitrogen bases, including $\text{F}_3\text{S}=\text{NXeF}^+\text{AsF}_6^-$, $\text{F}_3\text{S}=\text{NXeOTeF}_5^+\text{AsF}_6^-$ and $\text{F}_3\text{S}=\text{NXeOSeF}_5^+\text{AsF}_6^-$, and are formed by reaction of the corresponding xenon cation, XeL^+ , with liquid $\text{F}_3\text{S}=\text{N}$ at -20°C or in HF solvent (12). Reaction of $\text{F}_3\text{S}=\text{NXeOSeF}_5^+\text{AsF}_6^-$ in HF leads to $\text{F}_4\text{S}=\text{NXe}^+\text{AsF}_6^-$ and $\text{F}_5\text{SN}(\text{H})\text{Xe}^+$. The $\text{F}_5\text{TeN}(\text{H})\text{Xe}^+$ cation can be obtained by the reaction of F_5TeNH_2 with $\text{XeF}^+\text{AsF}_6^-$ or $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ with XeF_2 in HF or BrF_5 at low temperatures (12).

3.3. Xenon Bonded to Carbon. A number of structurally well-characterized compounds containing Xe-C bonds are known. In all cases, they occur as colorless salts of xenonium cations, RXe^+ , where R is a fluorophenyl or alkynyl group. The formation of the pentafluorophenylxenon(II) cation, $\text{C}_6\text{F}_5\text{Xe}^+$, [121850-39-3] in CH_2Cl_2 (-30°C) and $\text{CH}_3\text{C}\equiv\text{N}$ (0°C) solutions with the anions $\text{B}(\text{C}_6\text{F}_5)_3\text{F}^-$ [121850-40-6], $\text{B}(\text{C}_6\text{F}_5)_2\text{F}_2^-$ [123168-25-2], and $\text{B}(\text{C}_6\text{F}_5)_3\text{F}_3^-$ [124302-51-8] has been established (123–127). The salts are formed by the reaction of XeF_2 with the ligand transfer reagent $\text{B}(\text{C}_6\text{F}_5)_3$. The X-ray crystal structure of $\text{CH}_3\text{C}\equiv\text{NXeC}_6\text{F}_5^+(\text{C}_6\text{F}_5)_2\text{BF}_2^-$ shows that the xenon atom is weakly coordinated to the nitrogen atom of a $\text{CH}_3\text{C}\equiv\text{N}$ molecule, with an Xe-N bond length of 268.1(8) pm, and a Xe-C bond length of 209.2(8) pm (128). The neutral compound, $(\text{C}_6\text{F}_5)\text{XeF}$ [328379-53-9], has also been synthesized and characterized by ^{13}C , ^{19}F , and ^{129}Xe NMR spectroscopy (129). Xenon also forms bonds to two ligands through carbon; $\text{Xe}(\text{C}_6\text{F}_5)_2$ [328379-54-0] (130) has been prepared where the two xenon-carbon bond lengths in the crystal structure are 235(1) and 239.4(9) pm (131). A perfluoroalkenyl complex of xenon(II) has also been prepared: $\text{F}_2\text{C}=\text{C}(\text{F})\text{Xe}^+\text{BF}_4^-$ [229493-86-1], which has been characterized by ^{13}C , ^{19}F , and ^{129}Xe NMR spectroscopy (132). Alkynyl complexes have also been synthesized, including $(\text{CH}_3)_3\text{CC}\equiv\text{CXe}^+\text{BF}_4^-$ [141624-78-4], $(\text{CH}_3)_3\text{SiC}\equiv\text{CXe}^+\text{BF}_4^-$ [141643-91-6], $\text{CH}_3\text{CH}_2\text{CC}\equiv\text{CXe}^+\text{BF}_4^-$ [141624-76-2] and $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CXe}^+\text{BF}_4^-$ [141624-74-0] (133). Examples of xenon(II) bonded to carbon and chlorine have also been synthesized, and include $(\text{C}_6\text{F}_5)\text{XeCl}$ [249733-81-1] and $[(\text{C}_6\text{F}_5)\text{Xe}]_2\text{Cl}^+\text{AsF}_6^-$ [249733-78-6] (see the section **Xenon Compounds; Halides**) (44).

Only one Xe(IV)-C species has been synthesized to date: $(\text{C}_6\text{F}_5)\text{XeF}_2^+\text{BF}_4^-$ [260405-6-1] is a yellow solid, which has been prepared by the reaction of $\text{C}_6\text{F}_5\text{BF}_2$ with XeF_4 in CH_2Cl_2 at -55°C (134).

The existence of the XeCH_3^+ [34176-86-8] cation has been established in the gas phase. The Xe-C bond energy of the XeCH_3^+ cation has been estimated to be 180 ± 33 kJ/mol (135) and 231 ± 10 kJ/mol (136) by ion cyclotron resonance spectroscopy. The compound, bis(trifluoromethyl) xenon(II) [72599-34-9], $\text{Xe}(\text{CF}_3)_2$, is reported to be a waxy white solid having a half-life of ~ 30 min at room temperature (137). The synthesis involved the addition of XeF_2 to a trifluoromethyl plasma, but the characterization of this compound is limited and has not been independently confirmed. Xenon-carbon chemistry has been extensively reviewed elsewhere (138).

3.4. Xenon Bonded to Other Elements. An early report in the literature claims that FXeBF_2 [35788-52-4] had been prepared by the reaction of xenon gas with $\text{O}_2^+\text{BF}_4^-$ (139), however, the vibrational spectrum appears to be that of $\text{XeF}^+\text{BF}_4^-$ [22474-91-5], $\text{Xe}_2\text{F}_3^+\text{BF}_4^-$ [22474-92-6] or a mixture of both salts, and, as such, these results should be viewed with scepticism. An interesting series of xenon–gold cations have been synthesized, in which xenon acts as a ligand. The first compound to be isolated in this series, $\text{AuXe}_4^{2+}(\text{Sb}_2\text{F}_{11}^-)_2$ [312304-18-0], where the AuXe_4^{2+} cation is square planar about gold, and represents rare examples of gold in the +2 oxidation state and xenon in the 0 oxidation state. The compound was prepared by the reduction of AuF_3 with elemental xenon, and has Au–Xe bond lengths of 274 pm (140). Other cations containing Au^{2+} have been synthesized, namely *cis*- $\text{AuXe}_2^{2+}(\text{Sb}_2\text{F}_{11}^-)_2$ [412927-94-7], *trans*- AuXe_2^{2+} [412927-95-8] and $\text{XeAu}-\text{F}-\text{AuXe}^{3+}(\text{SbF}_6^-)_3$ [412927-97-0] with average Xe–Au bond lengths of 266.5(1), 270.9(1), and 264.7(1) pm, respectively (140). The first Au^{3+} -Xe complex, *trans*- $\text{AuXe}_2\text{F}^{2+}\text{SbF}_6^-\text{Sb}_2\text{F}_{11}^-$ [412928-02-0], has also been isolated, and shown to possess Au–Xe bond lengths of 259.3(1) and 261.9(1) pm, which are significantly shorter than bond lengths associated with Au^{2+} -Xe complexes (140).

A number of short-lived compounds containing xenon bonded to other elements have been studied by mass spectrometry or by matrix-isolation infrared spectroscopy. While these compounds have not been obtained in bulk quantities, their existence is of importance in extending the known chemistry of the noble gases. For example, the gaseous trifluorosilylxenon cation [164076-6-4], F_3SiXe^+ , has been synthesized by the displacement of HF from SiF_4H^+ by xenon gas; its structure has been verified by mass spectrometry (141). The F_3SiXe^+ cation has also been generated in a selected-ion flow tube by the direct reaction of SiF_3^+ with Xe in a helium atmosphere at room temperature (142). A number of xenon-hydride species have been isolated in matrices by uv irradiation of the precursors HX (X = F, Cl, Br, I, OH, SH, H, CN, NCO) in xenon matrices and have led to the formation of HXeF [79240-97-4] (143), HXeCl [117802-18-3] (143,144), HXeBr [163731-12-2] (143), HXeI [163731-12-3] (144), HXeOH [255059-18-8] (145), HXeSH [211797-16-9] (146), HXeH [12593-17-8] (143), HXeCN [211098-99-6] (147) and HXeNCO [252896-93-8] (148). Noble gas–actinide compounds of the general type $\text{CUO}(\text{Ar})_{4-n}(\text{Xe})_n$ ($n = 1-4$) have been isolated in low temperature argon matrices (149). Their existence has been inferred from infrared spectroscopy by the weakening of the U–O and U–C bonds, indicating that xenon and argon are directly bound to the uranium center. Calculations predict a pseudo-octahedral geometry about the uranium atom.

4. Krypton Compounds

4.1. Krypton Difluoride. Krypton difluoride, KrF_2 [13773-81-4], is a colorless crystalline solid that can be sublimed under vacuum at 0°C but is thermodynamically unstable and slowly decomposes to the elements at ambient temperatures (Table 1). It can, however, be stored for indefinite periods of time at -78°C . The KrF_2 molecule has been shown, like XeF_2 , to be linear in the gas phase and in the solid state. The standard enthalpy of formation, derived from

calorimetric measurements of the gaseous compound at 93°C, is 60.2 kJ/mol (14.4 kcal/mol) (15). Consistent with its thermodynamic instability, krypton difluoride is a powerful oxidative fluorinating agent, and is capable of oxidizing xenon to XeF₆ (150) and gold to AuF₅ (151). The heat of atomization for KrF₂ is only 97.8 kJ/mol (23.4 kcal/mol) (14,15), and is substantially less than that of F₂, which is reported to be 157.7 ± 0.4 kJ/mol (37.7 ± 0.1 kcal/mol) (152), making it a better low temperature source of fluorine atoms and an aggressive fluorinating agent even at low temperatures. Although the first krypton compound to be prepared was described as the tetrafluoride, the properties ascribed to this compound have been shown to be those of the difluoride. No other kinetically stable molecular fluoride of krypton is known, so that the chemistry of krypton is limited to that of krypton difluoride and its derivatives. Krypton monofluoride, KrF [34160-02-6], is short lived in the gas phase and is an important species in excimer laser systems (153; also see the section **Uses**).

4.2. Complex Salts. The cationic species KrF⁺ and Kr₂F₃⁺ are formed in reactions of KrF₂ with strong and weak fluoride ion acceptors to give complex salts that are analogous to those of XeF₂. Salts of the former type are formed with the pentafluorides of Group, (VB) metals and those of platinum and gold: KrF⁺BiF₆⁻ [76009-41-1], KrF⁺SbF₆⁻ [52708-44-8, 35289-40-8], KrF⁺Sb₂F₁₁⁻ [35140-44-4, 39578-36-4], Kr₂F₃⁺SbF₆⁻ [52708-43-7, 52721-22-9], KrF⁺PF₆⁻ [351198-01-1], KrF⁺AsF₆⁻ [50859-36-4], Kr₂F₃⁺AsF₆⁻ [52721-23-0], KrF⁺Nb₂F₁₁⁻ [58815-73-9], KrF⁺TaF₆⁻ [39438-53-4], KrF⁺Ta₂F₁₁⁻ [58815-72-8], KrF⁺PtF₆⁻ [52707-25-2] and KrF⁺AuF₆⁻ [57583-94-5] and KrF⁺AsF₆⁻·Kr₂F₃⁺AsF₆⁻ [351197-96-1] (10,154–156). As well, KrF₂ interacts weakly with Kr₂F₃⁺ salts in the solid state to give adducts which include Kr₂F₃⁺PF₆⁻·n KrF₂ [351198-00-0], Kr₂F₃⁺AsF₆⁻·n KrF₂, Kr₂F₃⁺SbF₆⁻·n KrF₂ [351197-97-2], Kr₂F₃⁺BF₄⁻·n KrF₂, and (Kr₂F₃⁺SbF₆⁻)₂·KrF₂ [13773-81-4] (156–158). The low temperature crystal structures of several krypton fluorocationic salts are now known, viz, KrF⁺MF₆⁻ (M = As, Sb, Bi, Au) (150–152), Kr₂F₃⁺SbF₆⁻·KrF₂, (Kr₂F₃⁺SbF₆⁻)₂·KrF₂, and Kr₂F₃⁺AsF₆⁻·KrF⁺AsF₆⁻ (159). The structures of the krypton salts are similar to their xenon analogues, as exemplified by the structures of KrF⁺AsF₆⁻ (Kr–F_{terminal}, 176.5(2) pm; Kr–F_{bridge}, 213.1(2) pm) and the V-shaped Kr₂F₃⁺ cation in Kr₂F₃⁺SbF₆⁻·KrF₂ (Kr–F_{terminal}, 180.0(5), 179.0(5) pm; Kr–F_{bridge}, 202.7(5), 204.6(5) pm) (156). Unlike their xenon analogues, the majority of these salts decompose below room temperature, however, several, including KrF⁺AsF₆⁻, KrF⁺SbF₆⁻, KrF⁺Sb₂F₁₁⁻, KrF⁺PtF₆⁻, and KrF⁺AuF₆⁻, are stable at room temperature for appreciable amounts of time. The KrF⁺ cation is among the most powerful chemical oxidants known (160) and is capable of oxidizing gaseous xenon to XeF₅⁺, gaseous oxygen to O₂⁺, NF₃ to NF₄⁺ (158) and chlorine, bromine and iodine pentafluorides to the ClF₆⁺, BrF₆⁺, and IF₆⁺, cations, respectively (158,161–163).

Adducts with the weak fluoride ion acceptors CrOF₄, MoOF₄, and WOF₄ are known in which KrF₂ interacts with the metal center by formation of asymmetric Kr–F–M bridges (M = Cr, Mo, W), eg, FKr–F–MOF₄ [102110-05-4], [77744-88-8], [77744-91-3], F–Kr–F–MoOF₄(MoOF₄)₂ [77744-90-2] (84,164).

4.3. Other Derivatives. Despite the strong oxidizing properties of the KrF⁺ cation, it has been shown to behave as a Lewis acid towards a limited number of Lewis bases at low temperatures. These bases are resistant to oxidation by the strongly oxidizing KrF⁺ cation and, as in the case of the XeF⁺ cation, they

have first adiabatic ionization potentials that are greater than or comparable with the estimated electron affinity of the KrF^+ cation (13.2 eV) (12). The Lewis acid–base cations are all thermally unstable above $\sim -40^\circ\text{C}$ and consist of $\text{HC}\equiv\text{NKrF}^+$ [117222-92-1], $\text{F}_3\text{CC}\equiv\text{NKrF}^+$ [119127-12-7], $\text{F}_3\text{CCF}_2\text{C}\equiv\text{NKrF}^+$ [119127-06-9] and $n\text{-F}_3\text{CF}_2\text{CF}_2\text{C}\equiv\text{NKrF}^+$ [119127-08-1], all having AsF_6^- as the counteranion (121,165). These cations comprise the only examples of krypton bonded to nitrogen. The compound, $\text{Kr}(\text{OTeF}_5)_2$ [68854-33-1], provides the only reported example in which krypton is bonded to oxygen (166). The existence of the KrCH_3^+ cation [109282-51-1] has been established in the gas phase by ion cyclotron resonance spectroscopy (167). The Kr–C bond energy of the KrCH_3^+ cation has been estimated to be 199.6 ± 10.5 kJ/mol (47.7 ± 2.5 kcal/mol), and is considerably more stable than the Kr–F bonds of KrF_2 (mean thermochemical bond energy of 48.9 kJ/mol (11.7 kcal/mol)) and KrF^+ [~ 155 kJ/mol (~ 37.0 kcal/mol)]. Three matrix-isolated hydrides of krypton, HKrF [163731-15-5] (168), HKrCl [163731-14-4] (169), and HKrCN [211099-00-2] (147), have been formed by the uv photolysis of HF, HCl, and HCN, respectively, in krypton matrices. No compounds in which krypton is in a higher formal oxidation state than +2 or bonded to elements other than fluorine, oxygen and nitrogen have been isolated in macroscopic amounts.

5. Radon Compounds

5.1. Radon Fluoride. When a mixture of trace amounts of radon-222 and fluorine gas are heated to approximately 400°C , an involatile fluoride is formed. The intense α -radiation provides the activation, allowing radon to react spontaneously with gaseous fluorine at room temperature and with liquid fluorine at -196°C . Radon is also oxidized by chlorine and bromine fluorides, IF_7 and NiF_6^{2-} in HF to give stable solutions of radon fluoride. The products of these fluorination reactions have not been analyzed because of their small masses and intense radioactivity. It has nevertheless been possible to deduce that radon difluoride [18976-85-7], RnF_2 is formed, as well as derivatives of the difluoride, by comparing reactions of radon with those of krypton and xenon. Electromigration and ion exchange (qv) studies show that ionic radon is present in many of these solutions and is believed to be RnF^+ and Rn^{2+} . The chemical behavior of radon is similar to that of an ionic fluoride and is consistent with its position in the Periodic Table (170). The chemistry of radon has been fully described elsewhere (170,171).

5.2. Complex Salts. Radon reacts at room temperature with solid oxidants, such as $\text{O}_2^+\text{SbF}_6^-$, $\text{O}_2^+\text{Sb}_2\text{F}_{11}^-$, $\text{N}_2\text{F}^+\text{SbF}_6^-$ and $\text{BrF}_2^+\text{BiF}_6^-$ to form involatile complex salts which are believed to be $\text{RnF}^+\text{SbF}_6^-$ [73384-63-1], $\text{RnF}^+\text{Sb}_2\text{F}_{11}^-$ [53851-50-6] and $\text{RnF}^+\text{BiF}_6^-$ [73384-62-0], by analogy with krypton and xenon, which also form the well-characterized products $\text{NgF}^+\text{SbF}_6^-$, $\text{NgF}^+\text{Sb}_2\text{F}_{11}^-$, and $\text{NgF}^+\text{BiF}_6^-$ (Ng = Kr, Xe) (170,171).

6. Prospects for Compounds of the Lighter Noble Gases

Theoretical calculations indicate that argon difluoride will be unstable but that the ArF^+ cation will be stable in the presence of a suitable oxidatively resistant anion (172). The corresponding HeF^+ [12336-97-9] and NeF^+ [12518-02-4] cations are predicted to be unstable (172). Experimental evidence for ArF^+ [11089-94-4] in the gas phase has been obtained, leading to $D_o(\text{ArF}^+) \geq 1.655$ eV and confirming the instability of HeF^+ and NeF^+ in their electronic ground states (173). The electronegativity values assigned to the compound-forming noble gases (Ar, 3.2; Kr, 2.9; Xe, 2.3; and Rn, 2.1) and those predicted for the noble gases that do not appear to form compounds (He, 5.2; and Ne, 4.5) suggest that the values for argon and krypton are rather close, and that efforts to synthesize an ArF^+ salt are realistic. The ArF^+ cation is expected to be an even stronger oxidant than KrF^+ , making it an oxidizer of unprecedented strength (160,172). However, unlike KrF^+ , which can only be synthesized from KrF_2 , any synthesis of an ArF^+ salt apparently cannot rely upon synthesis from the difluoride precursor because ArF_2 is expected to be unbound [$\Delta H[\text{ArF}^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{Ar}(\text{g}) + 2\text{F} \cdot(\text{g})] = -983$ kJ/mol (-235 kcal/mol)] (172). The anion that will be used to stabilize the ArF^+ cation must be capable of withstanding oxidation by ArF^+ . Theoretical calculations also suggest that $\text{HC}\equiv\text{NArF}^+$ [124354-45-6] may be stable (174).

Low temperature, matrix-isolation techniques have helped to further the chemistry of the lighter noble-gas compounds; however, these compounds have not been isolated in macroscopic amounts. The photolysis of HF in a solid argon matrix has afforded the argon fluorohydride, HArF [163731-16-6], which has been characterized by infrared spectroscopy (175). Theoretical calculations confirm that HArF has a stable configuration with properties similar to HKrF and HXeF (176). Theoretical calculations also suggest that HHeF [283595-31-3] may form a metastable compound, while HNeF [274264-38-9] is predicted to be unstable (177).

7. Methods of Preparation of Binary Fluorides

All noble-gas chemistry conducted on a macroscopic scale originates with the binary fluorides. Amounts of the binary xenon fluorides suitable for synthetic work are generally prepared by heating mixtures of xenon and fluorine to 250–400°C in nickel or Monel vessels (178–180). Although all three xenon fluorides coexist in equilibrium under such synthetic conditions, suitable adjustments of temperature, pressure and Xe/F_2 ratio can be made to yield primarily XeF_2 , XeF_4 , or XeF_6 . Xenon difluoride can be prepared photochemically by exposing xenon and fluorine, contained in a Pyrex flask, to either direct sunlight or to uv light from a mercury arc (181–183). Other methods, including electric discharges, proton and electron beams, and γ -rays have been employed for the preparation of xenon fluorides but are rarely used. Both XeF_2 and XeF_4 can be manipulated in glass vacuum systems, but XeF_6 must be handled in either fluorine-passivated metal or fluoroplastic vacuum systems. Safety measures, such as the use of protective glasses, face shields, and other personal protective covering, are essential

for work involving the tetrafluoride and hexafluoride, which react with atmospheric moisture and liquid water to form explosive XeO_3 ; XeF_4 disproportionates in water according to the reaction, $6 \text{XeF}_4(\text{s}) + 12 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{XeO}_3(\text{s}) + 4 \text{Xe}(\text{g}) + 3 \text{O}_2(\text{g}) + 24 \text{HF}(\text{aq})$.

Krypton difluoride cannot be synthesized by the standard high pressure–high temperature means used to prepare xenon fluorides because of its low thermal stability. There are three low temperature methods that have proven practical for the preparation of gram and greater amounts of KrF_2 , viz, hotwire generation of F^\cdot radicals, electric glow discharge, and uv photolysis (184–187). Radon fluoride is most conveniently prepared by reaction of radon gas with a liquid halogen fluoride (ClF , ClF_3 , ClF_5 , BrF_3 , or IF_7) at room temperature (188,189).

8. Uses

Stable noble-gas compounds have no industrial uses as of this writing but are frequently utilized in laboratories as fluorinating and oxidizing agents. Xenon difluoride and xenon tetrafluoride are relatively strong oxidative fluorinating agents and have been used for the preparation of phosphorus, sulfur, tellurium, and silicon derivatives (190,191). Xenon difluoride has proven to be a versatile and stable fluorinating agent for use in synthetic organic chemistry (192), and an intermediate for the syntheses of ^{18}F -labeled radiopharmaceuticals [eg, ^{18}F]2-fluoro-2-deoxy-D-glucose and L- ^{18}F]6-fluorodopa] for use in medical imaging (positron emission tomography) (193). It has been used for the fluorination of alkenes, in fluorodecarboxylation and for the fluorination of thioethers, aromatic and aliphatic compounds. Xenon hexafluoride has been used to synthesize transition metal fluorides and oxide fluorides where the metal is in its highest oxidation state, eg, $\text{Xe}_2\text{F}_{11}^+\text{AuF}_6^-$ (70) and TcO_2F_3 (194). Krypton difluoride and its complex salts are extremely powerful oxidative fluorinating agents and can be used to oxidatively fluorinate gold, silver and halogen fluorides to their highest oxidation states, eg, AuF_5 (151), AgF_4^- (195), ClF_6^+ (158), and BrF_6^+ (154). Krypton species can also be used to fluorinate oxocompounds of elements that are already in their highest attainable oxidation states as is exemplified by the fluorination of OsO_4 to *cis*- OsO_2F_4 (196) and TcO_2F_3 to TcOF_5 (197) by KrF_2 and XeOF_4 to XeF_5^+ by KrF^+ (151). Aqueous solutions of sodium perxenate and of xenon trioxide are useful for analyzing manganese (198) and alcohols and carboxylic acids (199,200), respectively. Radon-222, an air contaminant in uranium mines and basements, can be analyzed by means of oxidants that form involatile radon salts (201).

A particularly important use for unstable noble gas halides is as the gain medium in excimer lasers, which are employed as high power sources of tunable laser light in the uv and visible spectral regions (202). The diatomic halides are used for this purpose because they are readily formed in their excited states by electron-beam pumping or by discharge pumping of suitable gas mixtures. Compared with other laser systems, high gains can be achieved because the ground states are generally dissociative. Consequently, these lasers provide the only sources of high energy pulses (up to several joules of typically 10–100-ns

duration) in the uv. The laser systems include ArCl [54635-29-9] (175 nm), ArF [56617-31-3] (193 nm), KrCl [56617-29-9] (222 nm), KrF [34160-02-6] (249 nm), XeBr [55130-04-6] (282 nm), XeCl [55130-03-5] (308 nm), and XeF [16757-14-5] (350 nm). Of these, XeCl is especially useful because of the capability for long operating lifetime. Most applications of excimer lasers are based on the removal of material. Unlike longer wavelength lasers that heat and vaporize, excimer lasers remove material by ablation, which results in much finer detail and much less damage to surrounding areas. Applications include medical uses, processing of integrated solid-state devices, and use in photochemistry, isotope separation, mineral exploration and studies of nuclear fusion. Medical applications include laser keratectomy and laser angioplasty.

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Table 1. Some Physical and Thermodynamic Properties of Parent Noble Gas Fluorides, Oxide fluorides and Oxides

Compound	CAS Registry no.	Melting point, °C	Color	ΔH_{sub}^a kJ/mol ^a	ΔH_f^a kJ/mol ^a	ΔG_f^a kJ/mol ^a	S_r J/mol K ^a	C_p J/mol K ^a	Density g/cm ³	References
KrF ₂	[13773-81-4]	dec. 25 ^b	colorless	41	60.2				3.24	13–15
XeF ₂	[13709-36-9]	129.03 ^c	colorless	55.71	–162.8	–86.08	115.09	75.60	4.32	16–20
XeF ₄	[13709-61-0]	117.10 ^c	colorless	60.92	–267.1	–145.5	167.00	118.39	4.04	16,18,21,22
XeF ₆	[13693-09-9]	49.48	colorless ^d or yellow- green ^h	59.12 ^e	–338.2 ^e	–169.0 ^e	210.38 ^f	171.59 ^e	3.56 ^g	16,23–25
XeOF ₂	[13780-64-8]	dec. ~ 0 ⁱ	yellow							26,27
XeOF ₄	[13774-85-1]	–46.2	colorless		–25 ^j				3.11 ^k	28,29
XeO ₂ F ₂	[13875-06-4]	30.8 ⁱ	colorless		234 ^j				4.10	29,30
XeO ₃	[13776-58-4]	dec. ~ 25 ⁱ	white	100 ⁱ	402		287		4.55	29,31,32
XeO ₄	[12340-14-6]	dec. < 0 ⁱ	yellow solid at (–196°C)		642					29,33

^aTo convert J to cal, divide by 4.184.

^bDecomposes at ~10%/h.

^cTriple point.

^dSolid.

^eLiquid.

^fVapor.

^gPhase I.

^hPhase II has a density of 3.71 g/cm³, Phase II, 3.82 g/cm³, and Phase IV, 3.73 g/cm³.

ⁱExplosive.

^jEstimated.

^kLiquid at 22.5°C.

Table 2. Fluoro- and Oxofluoro Cations and Anions of Xenon, Their Parent Compounds and Geometries

Parent compound	Structure ^a	Cation(s)	Structure ^a	References	Anion(s)	Structure ^a	References
XeF ₂	linear (<i>D</i> _{∞h})	XeF ⁺ ₂	linear (<i>C</i> _{∞v})	1			
O(XeF) ₂	V-shape (<i>C</i> _{2v})	FXe—F—XeF ⁺	V-shape (<i>C</i> _{2v}) ^b	1			
XeF ₄	square plane (<i>D</i> _{4h})	FXeOXe—F—XeF ⁺	zig-zag shape (<i>C</i> _s)	1,64–6	XeF ₅ [−]	pentagonal planar (<i>D</i> _{5h})	6
XeOF ₂	T-shape (<i>C</i> _{2v})	XeF ₃ ⁺	T-shape (<i>C</i> _{2v})			planar (<i>C</i> _{2v})	2
XeF ₆	monocapped octahedron (<i>C</i> _{3v})	XeF ₅ ⁺	square pyramid (<i>C</i> _{4v})	1,1,6	XeOF ₃ [−] XeF ₇ [−]	capped octahedron	6,7
		F ₅ Xe—F—XeF ₅ ⁺	^b	1,1,7	XeF _s ^{2−}	square antiprism (<i>D</i> _{4d})	6,7,7
XeOF ₄	square pyramid (<i>C</i> _{4v})	XeOF ₃ ⁺	disphenoid (<i>C</i> _s)	7	Xe ₂ F ₁₃ [−] XeOF ₅ [−]	pentagonal pyramid (<i>C</i> _{5v}) ^d	7 74–7
XeO ₂ F ₂	disphenoid	XeO ₂ F ⁺	trigonal pyramid (<i>C</i> _{2v})	7,7	(XeOF ₄) ₃ F [−] XeO ₂ F ₃ [−]	square pyramid (<i>C</i> _s) ^e	2,6 7
XeO ₃	trigonal pyramid (<i>C</i> _{3v})	FO ₂ Xe—F—XeO ₂ F ⁺	^f	7	XeO ₃ F [−]	^g	8

^aPoint group is given in parentheses.

^bCations that are mononuclear in xenon and the F₅Xe—F—XeF₅⁺(Xe₂F₁₁⁺) cation interact with their fluoro-anions through one or more fluorine bridges. The XeF₅-groups in Xe₂F₁₁⁺ have essentially square pyramidal geometries.

^cThe Xe₂F₁₃[−] anion structure is that of an XeF₆ molecule fluorine bridged through two Xe—F bonds to an XeF₇[−] anion.

^dPoint symmetry determined by vibrational spectroscopy (7).

^eThree XeOF₄ molecules, having essentially square pyramidal geometries, are coordinated through the xenon atoms to a single fluoride ion to give a trigonal pyramidal arrangement about the fluoride ion.

^fThe FO₂Xe—F—XeO₂F⁺ cation is bent at the bridge fluorine atom and the geometry at each xenon atom is a disphenoid in which the oxygen atoms are in equatorial positions, along with the valence electron pair, and the bridging and terminal fluorine atoms are in axial positions.

^gThe structure consists of open polymeric chains, [XeO₃F[−]]_n, with two fluorine bridges to each xenon atom.