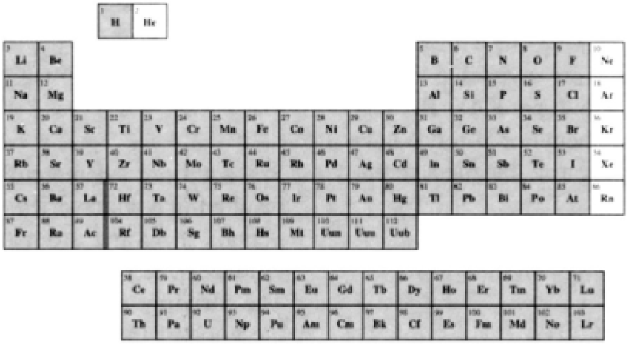


18

The Noble Gases: Helium, Neon, Argon, Krypton, Xenon and Radon

18.1 Introduction

In 1785 H. Cavendish in his classic work on the composition of air (p. 406) noted that, after repeatedly sparking a sample of air with an excess of O_2, there was a small residue of gas which he was unable to remove by chemical means and which he estimated with astonishing accuracy to be "not more than $\frac{1}{120}$th part of the whole". He could not further characterize this component of air, and its identification as argon had to wait for more than a century. But first came the discovery of helium, which is unique in being the only element discovered extraterrestrially before being found on earth. During the solar eclipse of 18 August 1868, a new yellow line was observed close to the sodium D lines in the spectrum of the sun's chromosphere. This led J. N. Lockyer (founder in 1869 of the journal *Nature*) and E. Frankland to suggest the existence of a new element which, appropriately, they named helium (Greek ἥλιος, the sun). The same line was observed by L. Palmieri in 1881 in the spectrum of volcanic gas from Mount Vesuvius, and the terrestrial existence of helium was finally confirmed by W. Ramsay$^{(1)}$ in the course of his intensive study of atmospheric gases which led to the recognition of a new group in the periodic table. This work was initiated by the physicist, Lord Rayleigh, and was recognized in 1904 by the award of the Nobel Prizes for Chemistry and Physics to Ramsay and Rayleigh respectively.

In order to test Prout's hypothesis (that the atomic weights of all elements are multiples of that of hydrogen) Rayleigh made accurate measurements of the densities of common gases and found, to his surprise, that the density of nitrogen obtained from air by the removal of O_2, CO_2 and H_2O was consistently about 0.5% higher than that of nitrogen obtained chemically from ammonia. Ramsay then treated "atmospheric nitrogen" with heated magnesium ($3Mg + N_2 \longrightarrow Mg_3N_2$), and was left with a small amount of a much

---

[1] M. W. Travers, *Life of Sir William Ramsay*, E. Arnold, London, 1956.

denser, monatomic gas[†] which, in a joint paper [*Proc. R. Soc.* **57**, 265 (1895)], was identified as a new element which was named *argon* (Greek ἀργόν, idle or lazy) because of its inert nature. Unfortunately there was no space for a new and unreactive, gaseous, element in the periodic table (p. 20), which led to Ramsay's audacious suggestion that a whole new group might be accommodated. By 1898 Ramsay and M. W. Travers had isolated three further new elements by the low-temperature distillation of liquid air (which had only recently become available) and characterized them by spectroscopic analysis: krypton (Greek κρυπτόν, hidden, concealed), neon (Greek νέον, new) and xenon (Greek ξένον, strange).

In 1895 Ramsay also identified helium as the gas previously found occluded in uranium minerals and mistakenly reported as nitrogen. Five years later he and Travers isolated helium from samples of atmospheric neon.

Element 86, the final member of the group, is a short-lived, radioactive element, formerly known as radium-emanation or niton or, depending on which radioactive series it originates in (i.e. which isotope) as radon, thoron, or actinon. It was first isolated and studied in 1902 by E. Rutherford and F. Soddy and is now universally known as radon (from radium and the termination-on adopted for the noble gases; Latin *radius*, ray).

Once the existence of the new group had been established it was apparent that it not only fitted into the periodic table but actually improved it by providing a bridge between the strongly electronegative halogens and strongly electropositive alkali metals. The elements became known as "inert gases" comprising Group 0, though A. von Antropoff suggested that a maximum valency of eight might be attainable and designated them as Group VIIIB. They have also been described as the "rare gases" but, since the lighter members are by no means rare and the heavier ones are not entirely inert, "noble" gases seems a more appropriate name and has come into general use during the past three decades as has their designation as Group 18 of the periodic table.

The apparent inertness of the noble gases gave them a key position in the electronic theories of valency as developed by G. N. Lewis (1916) and W. Kossel (1916) and the attainment of a "stable octet" was regarded as a prime criterion for bond formation between atoms (p. 21). Their monatomic, non-polar nature makes them the most nearly "perfect" gases known, and has led to continuous interest in their physical properties.

18.2 The Elements

18.2.1 Distribution, production and uses (2,3)

Helium is the second most abundant element in the universe (76% H, 23% He) as a result of its synthesis from hydrogen (p. 9) but, being too light to be retained by the earth's gravitational field, all primordial helium has been lost and terrestrial helium, like argon, is the result of radioactive decay (^{4}He from α-decay of heavier elements, ^{40}Ar from electron capture by ^{40}K (p. 18).

The noble gases make up about 1% of the earth's atmosphere in which their major component is Ar. Smaller concentrations are occluded in igneous rocks, but the atmosphere is the principal commercial source of Ne, Ar, Kr and Xe, which are obtained as by-products of the liquefaction and separation of air (p. 604). Some Ar is also obtained from synthetic ammonia plants in which it accumulates after entering as impurity in the N_2 and H_2 feeds. World production of

---

[†] The molecular weight (mean relative molecular mass) was obtained by determination of density but, in order to determine that the gas was monatomic and its atomic and molecular weights identical, it was necessary to measure the velocity of sound in the gas and to derive from this the ratio of its specific heats: kinetic theory predicts that $C_p/C_v = 1.67$ for a monatomic and 1.40 for a diatomic gas.

[2] Helium group gases, in *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th edn, Vol. 13, pp. 1–53. Wiley-Interscience, New York, 1995.

[3] W. J. GRANT and S. L. REDFEARN, Industrial gases, in R. THOMPSON (ed.), *The Modern Inorganic Chemicals Industry*, pp. 273–301. The Chemical Society, London, 1977.

Ar in 1975 was 700 000 tonnes for use mainly as an inert atmosphere in high-temperature metallurgical processes and, in smaller amounts, for filling incandescent lamps. By 1993, production had increased considerably and 716 000 tonnes ($427 \times 10^6\ m^3$) were produced in the USA alone. The price was $\$0.76/m^3$ for bulk supplies and $\$2.6-8.5/m^3$ for laboratory quantities, depending on purity. Along with Ne, Kr and Xe, which are produced on a much smaller scale, Ar is also used in discharge tubes — the so-called neon lights for advertisements — (the colour produced depending on the particular mixture of gases used). They are also used in fluorescent tubes, though here the colour produced depends not on the gas but on the phosphor which is coated on the inside walls of the tube. Lasers are another important application, though the actual amount of gas required for this use is minute compared with the other uses.

Although the concentration of He in the atmosphere is five times that of Kr and sixty times that of Xe (see Table 18.1), its recovery from this source is uneconomical compared to that from natural gas if more than 0.4% He is present. This concentration is attained in a number of gases in the USA (concentrations as high as 7% are known) and in eastern Europe (mainly Poland). Some $99 \times 10^6\ m^3$ (16 800 tonnes) of He was produced in the USA in 1993, the bulk price being $\$1.77/m^3$ ($\$2.30\,m^3$ for liquid He). Laboratory quantities were in the range $\$5.00-45.00/m^3$ depending on purity. The former use of He as a non-flammable gas (it has a lifting power of approximately 1 kg per m^3) in airships is no longer important, though it is still employed in meteorological balloons. The primary domestic use of He (30%) in as a cryogenic fluid for temperatures at or below 4.2 K; as much as two-thirds of this is for magnetic resonance imaging and other nmr instruments. Other major uses are in arc welding (21%), pressurizing and purging (11%). The choice between Ar and He for these purposes is determined by cost and, except in the USA, this generally favours Ar. Smaller, but important, uses for He are:

(a) as a substitute for N_2 in synthetic breathing gas for deep-sea diving (its low solubility in blood minimizes the degassing which occurs with N_2 when divers are depressurized and which produces the sometimes fatal "bends");
(b) as a leak detector;
(c) as a coolant in HTR nuclear reactors (p. 1258);
(d) as a flow-gas in gas-liquid chromatography;
(e) for deaeration of solutions and as a general inert diluent or inert atmosphere.

The price per m^3 of the other noble gases is considerably higher (Ne \$70, Kr \$350 and Xe \$3500, and this tends to restrict their usage to specialist applications only. Radon has been used in the treatment of cancer and as a radioactive source in testing metal castings but, because of its short half-life (3.824 days) it has been superseded by more convenient materials. Such small quantities as are required are obtained as a decay product of ^{226}Ra (1 g of which yields $0.64\,cm^3$ in 30 days).

18.2.2 Atomic and physical properties of the elements (2-4)

Some of the important properties of the elements are given in Table 18.1. The imprecision of the atomic weights of Kr and Xe reflects the natural occurrence of several isotopes of these elements. For He, however, and to a lesser extent Ar, a single isotope predominates (^4He, 99.999 863%; ^{40}Ar, 99.600%) and much greater precision is possible. The natural preponderance of ^{40}Ar is indeed responsible for the well-known inversion of atomic weight order of Ar and K in the periodic table, and the position of Ar in front of K was only finally accepted when it was shown that the atomic weight of He placed it in front of Li. The second isotope of helium, ^3He, has only been available in significant amounts since

---

[4] A. H. COCKETT and K. C. SMITH, Chap. 5 in *Comprehensive Inorganic Chemistry*, Vol. 1, pp. 139–211, Pergamon Press, Oxford, 1973. G. A. COOK (ed.), *Argon, Helium and the Rare Gases*, 2 vols, Interscience, New York, 1961, 818 pp.

Table 18.1 Some properties of the noble gases

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Number of naturally occurring isotopes	2	3[a]	3	6	9	(1)
Atomic weight	4.002 602(2)	20.179 7(6)	39.948(1)	83.80(1)	131.29(2)	(222)[b]
Abundance in dry air/ppm by vol	5.24	18.21	9340	1.14	0.087	Variable traces[c]
Abundance in igneous rocks/ppm by wt	3×10^{-3}	7×10^{-5}	4×10^{-2}	—	—	1.7×10^{-10}
Outer shell electronic configuration	$1s^2$	$2s^22p^6$	$3s^23p^6$	$4s^24p^6$	$5s^25p^6$	$6s^26p^6$
First ionization energy/kJ mol^{-1}	2372	2080	1520	1351	1170	1037
BP/K	4.215	27.09	87.28	119.80	165.03	211
/°C	−268.93	−246.06	−185.86	−153.35	−108.13	−62
MP/K	—[d]	24.56	83.80	115.76	161.37	202
/°C	—	−248.61	−189.37	−157.20	−111.80	−71
ΔH_{vap}/kJ mol^{-1}	0.08	1.74	6.52	9.05	12.65	18.1
Density at STP/mg cm^{-3}	0.178 50	0.899 94	1.7838	3.7493	5.8971	9.73
Thermal conductivity at 0°C/J s^{-1} m^{-1} K^{-1}	0.1418	0.0461	0.0169	0.008 74	0.005 06	
Solubility in water at 20°C/cm^3 kg^{-1}	8.61	10.5	33.6	59.4	108.1	230

[a] In the pioneering work of J. J. Thomson and F. W. Aston on mass-spectrometry, neon was the first non-radioactive element shown to exist in different isotopic forms.

[b] The relative atomic mass of this nuclide is 222.0176.

[c] Mean value $\sim 6 \times 10^{-14}$.

[d] Helium is the only liquid which cannot be frozen by the reduction of temperature alone. Pressure must also be applied. It is also the only substance lacking a "triple point", i.e. a combination of temperature and pressure at which solid, liquid and gas coexist in equilibrium.

the 1950s when it began to accumulate as a β-decay product of tritium stored for thermonuclear weapons.

All the elements have stable electronic configurations ($1s^2$ or ns^2np^6) and, under normal circumstances are colourless, odourless and tasteless monatomic gases. The non-polar, spherical nature of the atoms which this implies, leads to physical properties which vary regularly with atomic number. The only interatomic interactions are weak van der Waals forces. These increase in magnitude as the polarizabilities of the atoms increase and the ionization energies decrease, the effect of both factors therefore being to increase the interactions as the sizes of the atoms increase. This is shown most directly by the enthalpy of vaporization, which is a measure of the energy required to overcome the interactions, and increases from He to Rn by a factor of over 200. However, ΔH_{vap} is in all cases small and bps are correspondingly low, that of He being the lowest of any substance.

The stability of the electronic configuration is indicated by the fact that each element has the highest ionization energy in its period, though the value decreases down the group as a result of increasing size of the atoms. For the heavier elements is it actually smaller than for first-row elements such as O and F with consequences for the chemical reactivities of the noble gases which will be considered in the next section. Nuclear properties, particularly for xenon, have been exploited for nmr spectroscopy$^{(5)}$ and Mössbauer

---

[5] C. J. JAMESON in J. MASON (ed.), *Multinuclear NMR*, Plenum Press, New York, 1987, pp. 463–77.

spectroscopy⁽⁶⁾ (p. 896). The environmental health hazard posed by the natural generation of radioactive radon gas should also be noted.⁽⁷⁾

As the first member of this unusual group He has, of course, a number of unique properties. Among these is the astonishing transition from so-called HeI to HeII which occurs around 2.2 K (the λ-point temperature) when liquid He (^{4}He to be precise, since ^{3}He does not behave in this way until 1–3 millikelvin) is cooled by continuous pumping. The transition is clearly seen as the sudden cessation of turbulent boiling, even though evaporation continues. HeI is a normal liquid but at the transition the specific heat increases abruptly by a factor of 10, the thermal conductivity by the order of 10^6, and the viscosity, as measured by its flow through a fine capillary, becomes effectively zero (hence its description as a "superfluid"). HeII also has the curious ability to cover, with a film a few hundred atoms thick, all solid surfaces which are connected to it and are below the λ point. This can be spectacularly demonstrated by dipping the bottom of a suitable container into a bath of HeII. Once the vessel has cooled, liquid He flows, apparently without friction, up and over the edge of the container until the levels inside and outside are equal. These phenomena are evidently the result of quantum effects on a macroscopic scale, and HeII is believed to consist of two components: a true superfluid with zero viscosity and entropy, together with a normal fluid, the fraction of the former increasing to 1 at absolute zero. No completely satisfactory explanation of these phenomena is yet available.

Finally, a property of practical importance which may be noted is the ability of noble gases, especially He, to diffuse through many materials commonly used in laboratories. Rubber and PVC are cases in point, and He will even diffuse through most glasses so that glass Dewar vessels cannot be used in cryoscopic work involving liquid He.

18.3 Chemistry of the Noble Gases⁽⁸⁻¹²⁾

The discovery of the noble gases was a direct result of their unreactive nature, and early unsuccessful attempts to induce chemical reactions reinforced the belief in their inertness. Nevertheless, attempts were made to make the heavier gases react, and in 1933 Linus Pauling, from a consideration of ionic radii, suggested that KrF_6 and XeF_6 should be preparable. D. M. Yost and A. L. Kaye attempted to prepare the latter by passing an electric discharge through a mixture of Xe and F_2 but failed[†] and, until "$XePtF_6$" was prepared in 1962, the only compounds of the noble gases which could be prepared were clathrates.

While investigating the chemistry of PtF_6, N. Bartlett noticed that its accidental exposure to air produced a change in colour, and with D. H. Lohmann he later showed this to be $O_2{}^+$-$[PtF_6]^-$.⁽¹³⁾ Recognizing that PtF_6 must therefore be an oxidizing agent of unprecedented power, he noted that Rn and Xe should similarly be oxidizable by this reagent since the first ionization energy of Rn is less than, and that of

---

[6] N. N. Greenwood and T. C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall, London 1971, ^{83}Kr pp. 437–41; ^{129}Xe, ^{131}Xe pp. 482–6.

[7] P. K. Hopke (ed.), *Radon and its Decay Products: Occurrence, Properties and Health Effects* ACS Symposium Series No. 331, 1986, 586 pp. D. J. Hanson, *Chem. & Eng. News*, Feb. 6, 1989, pp. 7–13. A. F. Gardner, R. S. Gillett and P. S. Phillips, *Chem. in Britain*, April 1992, pp. 344–8.

[8] N. Bartlett and F. E. Sladky, Chap. 6, in *Comprehensive Inorganic Chemistry*, Vol. 1, pp. 213–330, Pergamon Press, Oxford. 1973.

[9] D. T. Hawkins, W. E. Falconer and N. Bartlett, *Noble Gas Compounds, A Bibliography 1962–1976*. Plenum Press, New York, 1978.

[10] J. H. Holloway, *Noble-gas Chemistry*, Methuen, London, 1968, 213 pp. See also *Chem. in Britain*, July 1987, pp. 658–64.

[11] K. Seppelt and D. Lentz, *Progr. Inorg. Chem.* **29**, 167–202 (1982).

[12] pp. 38–53 of ref. 2.

[13] N. Bartlett and D. H. Lohmann, *Proc. Chem. Soc.* 1962, 115–6.

[†] By what must have seemed to these workers a cruel irony, essentially the same method, but using sunlight instead of a discharge, when tried 30 years later produced XeF_2.

Xe is comparable to, that of molecular oxygen (1175 kJ mol^{-1} for $O_2 \rightarrow O_2{}^+ + e^-$). He quickly proceeded to show that deep-red PtF_6 vapour spontaneously oxidized Xe to produce an orange-yellow solid and announced this in a brief note.$^{(14)}$ Within a few months XeF_4 and XeF_2 had been synthesized in other laboratories.$^{(15,16)}$ Noble-gas chemistry had begun.

Isolable compounds are obtained only with the heavier noble gases Kr and Xe; radon also reacts with F_2 but isolation and characterization of products is hampered by its intense radioactivity which is not only hazardous but also decomposes the reagents involved. The compounds usually involve bonds to F or O, in most cases exclusively so. However, a growing number of compounds involving bonds to Cl, N and even C are becoming known (p. 901). Chemical combinations involving the lighter noble gases have been observed but are very unstable, and frequently occur only as transient species (p. 903).

18.3.1 Clathrates

Probably the most familiar of all clathrates are those formed by Ar, Kr and Xe with quinol, 1,4-$C_6H_4(OH)_2$, and with water. The former are obtained by crystallizing quinol from aqueous or other convenient solution in the presence of the noble gas at a pressure of 10–40 atm. The quinol crystallizes in the less-common β-form, the lattice of which is held together by hydrogen bonds in such a way as to produce cavities in the ratio 1 cavity: 3 molecules of quinol. Molecules of gas (G) are physically trapped in these cavities, there being only weak van der Waals interactions between "guest" and "host" molecules. The clathrates are therefore nonstoichiometric but have an "ideal" or "limiting" composition of $[G\{C_6H_4(OH)_2\}_3]$. Once formed they have considerable stability but the gas is released on dissolution or melting. Similar clathrates are obtained with numerous other gases of comparable size, such as O_2, N_2, CO and SO_2 (the first clathrate to be fully characterized, by H. M. Powell in 1947) but not He or Ne, which are too small or insufficiently polarizable to be retained.

Noble gas hydrates are formed similarly when water is frozen under a high pressure of gas (p. 626). They have the ideal composition, $[G_8(H_2O)_{46}]$, and again are formed by Ar, Kr and Xe but not by He or Ne. A comparable phenomenon occurs when synthetic zeolites (molecular sieves) are cooled under a high pressure of gas, and Ar and Kr have been encapsulated in this way (p. 358). Samples containing up to 20% by weight of Ar have been obtained.

Clathrates provide a means of storing noble gases and of handling the various radioactive isotopes of Kr and Xe which are produced in nuclear reactors.

18.3.2 Compounds of xenon

The chemistry of Xe is much the most extensive in this group and the known oxidation states of Xe range from +2 to +8. Details of some of the more important compounds are given in Table 18.2. There is clearly a rich variety of stereochemistries, though the description of these depends on whether only nearest-neighbour atoms are considered or whether the supposed disposition of lone-pairs of electrons is also included. Weaker secondary interactions in crystalline compounds also tend to increase the number of atoms surrounding a central Xe atom. For example, $[XeF_5]^+[AsF_6]^-$ has 5 F at 179–182 pm and *three* further F at 265–281 pm, whereas $[XeF_5]^+[RuF_6]^-$ has 5 F at 179–184 pm and *four* further F at 255–292 pm. If only the most closely bonded atoms are counted, then Xe is known with all coordination numbers from 0 to 8 as shown schematically in Table 18.3.

---

[14] N. Bartlett, *Proc. Chem. Soc.* 1962, 218.

[15] H. H. Claassen, H. Selig and J. G. Malm, *J. Am. Chem. Soc.* **84**, 3593 (1962). See also P. Lazlo and G. J. Schrobilgen, *Angew. Chem. Int. Edn. Engl.* **28**, 636 (1989) for further detailed chronology of the first synthesis of XeF_4.

[16] R. Hoppe, W. Dähne, H. Mattauch and K. H. Rödder, *Angew. Chem.* **74**, 903 (1962). See also note on priorities by W. Klemm, *Nachr. Chem. Tech. Lab.* **30**, 963 (1982).

Table 18.2 Some compounds of xenon with fluorine and oxygen

			Stereochemistry of Xe	
Oxidation State	Compound	MP/°C	Actual	Pseudo, i.e. with electron lone-pairs (in parentheses) included
+2	XeF_2	129	$D_{\infty h}$, linear	Trigonal bipyramidal (3)
+4	XeF_4	117.1	D_{4h}, square planar	Octahedral (2)
+6	XeF_6	49.5	Distorted octahedral (fluxional)	Pentagonal bipyramidal or capped octahedral (1)
	$[XeF_5]^+[AsF_6]^-$	130.5	C_{4v}, square pyramidal	Octahedral (1)
	$CsXeF_7$	dec > 50		
	$[NO]^+{}_2[XeF_8]^{2-}$		D_{4d}, square antiprismatic	(Lone-pair inactive)
	$XeOF_4$	(−46)	C_{4v}, square pyramidal	Octahedral (1)
	XeO_2F_2	30.8	C_{2v}, "see-saw"	Trigonal bipyramidal (1)
	$CsXeOF_5$		Distorted octahedral	Capped octahedral (1)
	$KXeO_3F$		Square pyramidal (chain)	Octahedral (1)
	XeO_3	explodes	C_{3v}, pyramidal	Tetrahedral (1)
+8	XeO_4	−35.9	T_d, tetrahedral	(No lone-pairs on Xe)
	XeO_3F_2	−54.1	D_{3h}, trigonal bipyramidal	Trigonal bipyramidal
	Ba_2XeO_6	dec > 300	O_h, octahedral	(No lone-pairs on Xe)

The three fluorides of Xe can be obtained by direct reaction but conditions need to be carefully controlled if these are to be produced individually in pure form. XeF_2 can be prepared by heating F_2 with an excess of Xe to 400°C in a sealed nickel vessel or by irradiating mixtures of Xe and F_2 with sunlight. The product is a white, crystalline solid consisting of parallel linear XeF_2 units (Fig. 18.1). It is sublimable and its infrared and Raman spectra show that the linear molecular structure is retained in the vapour. XeF_2 is a versatile mild fluorinating agent and will, for instance, difluorinate olefins (alkenes). Oxidative fluorination of MeI yields $MeIF_2$, and similar reactions yield Me_2EF_2 (E = S, Se, Te) and Me_3EF_2 (E = P, As, Sb).(17) A related reaction was used to prepare the organotellurium(VI) compound *mer*-Ph_3TeF_3:(18)

$$Ph_3TeF + XeF_2 \xrightarrow[\text{r.t.}]{CHCl_3} Ph_3TeF_3 + Xe$$

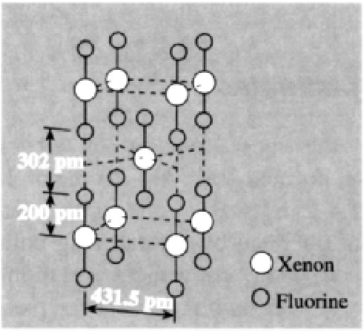


Figure 18.1 The until cell of crystalline XeF_2.

Reductive fluorination is exemplified by the high-yield synthesis of crystalline $CrOF_3$ at 275°C:(19)

$$2CrO_2F_2 + XeF_2 \longrightarrow 2CrOF_3 + Xe + O_2$$

XeF_2 sequentially fluorinates $Ir_4(CO)_{12}$ dissolved in anhydrous HF yielding, initially, the novel neutral complexes *mer*- and *fac*-$[Ir(CO)_3F_3]$.(20)

---

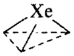
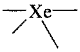
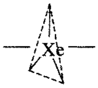
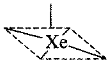
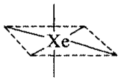
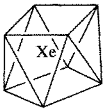
[17] A. M. Forster and A. J. Downs, *Polyhedron* **4**, 1625-35 (1985).

[18] A. S. Secco, K. Alam, B. J. Blackburn and A. F. Janzen, *Inorg. Chem.* **25** 2125-9 (1986).

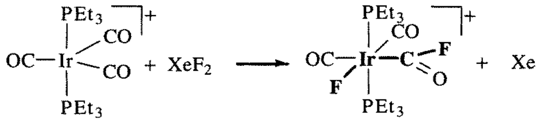
[19] M. McHughes, R. D. Willett, H. B. Davis and G. L. Gard, *Inorg. Chem.* **25**, 426-7 (1986).

[20] S. A. Brewer, J. H. Holloway, E. G. Hope and P. G. Watson, *J. Chem. Soc., Chem. Commun.*, 1577-8 (1992).

Table 18.3 Stereochemistry of xenon

CN	Stereochemistry	Examples	Structure
0	—	Xe(g)	Xe
1	—	$[XeF]^+$, $[XeOTeF_5]^-$	Xe—
2	Linear	XeF_2, $[FXeFXeF]^+$, $FXeOSO_2F$	—Xe—
3	Pyramidal	XeO_3	
	T-shaped	$[XeF_3]^+$, $XeOF_2$	
4	Tetrahedral	XeO_4	
	Square	XeF_4	
	C_{2v}, "see-saw"	XeO_2F_2	
5	Trigonal bipyramidal	XeO_3F_2	
	Square pyramidal	$XeOF_4$, $[XeF_5]^+$	
6	Octahedral Distorted octahedral	$[XeO_6]^{4-}$ $XeF_6(g)$, $[XeOF_5]^-$	
7	(?)	$CsXeF_7$	
8	Square antiprismatic	$[XeF_8]^{2-}$	

By contrast, reaction of XeF_2 with the iridium carbonyl complex cation $[Ir(CO)_3(PEt_3)_2]^+$ in CH_2Cl_2 results in addition across one of the Ir–CO bonds to give the first example of a metal fluoroacyl complex:(21)



The product was isolated as white, air-sensitive crystals of the BF_4^- and PF_6^- salts.

XeF_2 dissolves in water to the extent of $25\,g\,dm^{-3}$ at 0°C, the solution being fairly stable (half-life ~7 h at 0°C) unless base is present, in which case almost instantaneous decomposition takes place:

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

The aqueous solutions are powerful oxidizing agents, converting $2Cl^-$ to Cl_2, Ce^{III} to Ce^{IV}, Cr^{III} to Cr^{VI}, Ag^I to Ag^{II}, and even BrO_3^- to BrO_4^- (p. 871).

---

[21] A. J. Blake, R. W. Cockman, E. A. V. Ebsworth and J. H. Holloway, *J. Chem. Soc., Chem. Commun.*, 529–30 (1988).

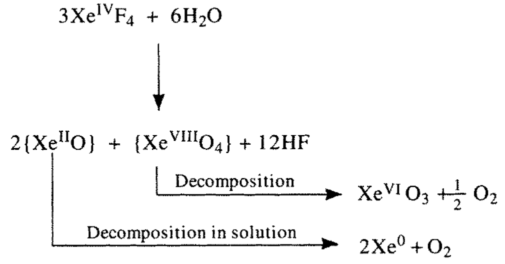
XeF_4 is best prepared by heating a 1:5 volume mixture of Xe and F_2 to 400°C under 6 atm pressure in a nickel vessel. It also is a white, crystalline, easily sublimed solid; the molecular shape is square planar (Xe–F 195.2 pm) and is essentially the same in both the solid and gaseous phases. Its properties are similar to those of XeF_2 except that it is a rather stronger fluorinating agent, as shown by the reactions:

$$2Hg + XeF_4 \longrightarrow Xe + 2HgF_2$$
$$Pt + XeF_4 \longrightarrow Xe + PtF_4$$
$$2SF_4 + XeF_4 \longrightarrow Xe + 2SF_6$$

It is also hydrolysed instantly by water, yielding a variety of products which include XeO_3:

$$XeF_4 + 2H_2O \longrightarrow \tfrac{1}{3}XeO_3 + \tfrac{2}{3}Xe + \tfrac{1}{2}O_2 + 4HF$$

This reaction is indeed a major hazard in Xe/F chemistry, since XeO_3 is highly explosive, and the complete exclusion of moisture is therefore essential (see p. 165 of ref. 10). Interestingly, the maximum yield of XeO_3 is 33% rather than the 50% that would be expected from a simple disproportionation of $2Xe^{IV} \rightarrow Xe^{VI} + Xe^{II}$, and the following reaction sequence has been suggested to explain this:



The stoichiometry of the reaction also depends sensitively on the precise conditions of hydrolysis.[22]

XeF_6 is produced by the prolonged heating of 1:20 volume mixtures of Xe and F_2 at 250–300°C under 50–60 atm pressure in a nickel vessel. It is a crystalline solid, even more volatile than XeF_2 and XeF_4, and although colourless in the solid it is yellow in the liquid and gaseous phases. It is also more reactive than the other fluorides, being both a stronger oxidizing and a stronger fluorinating agent. Hydrolysis occurs with great vigour and the compound cannot be handled in glass or quartz apparatus because of a stepwise reaction which finally produces the dangerous XeO_3:

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$
$$2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$$
$$2XeO_2F_2 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$$

The structure of XeF_6 was the source of some controversy for more than a decade after its discovery in 1963. This was partly a result of the obvious problems associated with a substance which attacks most of the materials used to construct apparatus for structural determinations. It is now clear that in the gaseous phase this seemingly simple molecule is not a regular octahedron; it appears to be a non-rigid, distorted octahedron although, in spite of numerous theoretical studies, the precise nature of the distortion is uncertain (see, for instance, p. 299 of ref. 8). In the crystalline state at least four different forms of XeF_6 are known comprising square-pyramidal XeF_5^+ ions bridged by F^- ions. Three of these forms are tetramers, $[(XeF_5^+)F^-]_4$, while in the fourth and best-characterized cubic form,[(23)] the unit cell comprises 24 tetramers and 8 hexamers, $[(XeF_5^+)F^-]_6$ (Fig. 18.2).

The nature of the bonding in these xenon fluorides is discussed in the Panel opposite.

Apart from XeF, which is the light-emitting species in certain Xe/F_2 lasers, there is no evidence for the existence of any odd-valent fluorides. Reports of XeF_8 have not been confirmed. Of the other halides, $XeCl_2$, $XeBr_2$ and $XeCl_4$ have been detected by Mössbauer spectroscopy as products of the β-decay of their $^{129}_{53}I$

---

[22] J. L. HUSTON, *Inorg. Chem.* **21**, 685–8 (1982).

[23] R. D. BURBANK and G. R. JONES, *J. Am. Chem. Soc.* **96**, 43–8 (1974).

Bonding in Noble Gas Compounds

As it was widely believed, prior to 1962, that the noble gases were chemically inert because of the stability, if not inviolability, of their electronic configurations, the discovery that compounds could in fact be prepared, immediately necessitated a description of the bonding involved. A variety of approaches has been suggested,[(24)] none of which is universally applicable. The simplest molecular-orbital description is that of the 3-centre, 4-electron σ bond in XeF_2, which involves only valence shell p orbitals and eschews the use of higher energy d orbitals. The orbitals involved are the colinear set comprising the $5p_x$ orbital of Xe, which contains 2 electrons, and the $2p_x$ orbitals from each of the F atoms, each containing 1 electron. The possible combinations of these orbitals are shown in Fig. A and yield 1 bonding, 1 nonbonding, and 1 antibonding orbital. A single bonding pair of electrons is responsible for binding all 3 atoms, and the occupation of the nonbonding orbital, situated largely on the F atoms, implies significant ionic character. The scheme should be compared with the 3-centre, 2-electron bonding proposed for boron hydrides (p. 158).

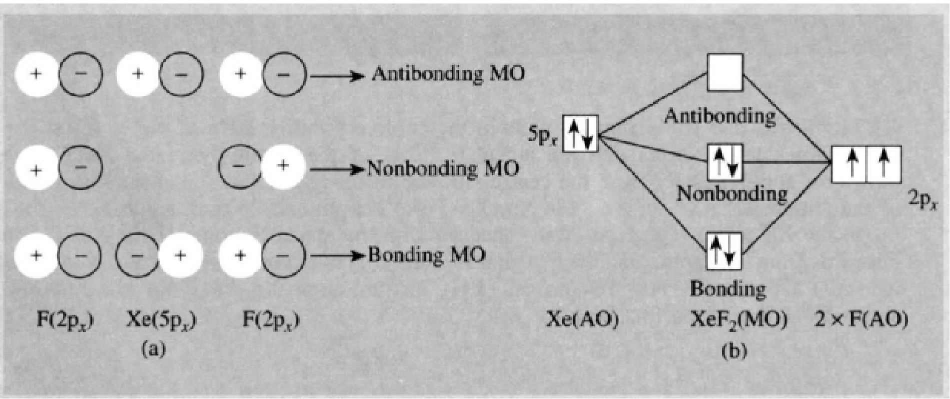


Fig. A. Molecular-orbital representation of the 3-centre F–Xe–F bond. (a) The possible combinations of colinear p_x atomic orbitals, and (b) the energies of the resulting MOs (schematic).

A similar treatment, involving two 3-centre bonds accounts satisfactorily for the planar structure of XeF_4 but fails when applied to XeF_6 since three 3-centre bonds would produce a regular octahedron instead of the distorted structure actually found. An improvement is possible if involvement of the Xe 5d orbitals is invoked,[(25)] since this produces a triplet level which would be subject to a Jahn-Teller distortion (p. 1021). However, the approach which has most consistently rationalized the stereochemistries of noble-gas compounds (as distinct from their bonding) is the electron-pair repulsion theory of Gillespie and Nyholm.[(26)] This assumes that stereochemistry is determined by the repulsions between valence-shell electron-pairs, both nonbonding and bonding, and that the former exert the stronger effect. Thus, in XeF_2 the Xe is surrounded by 10 electrons (8 from Xe and 1 from each F) distributed in 5 pairs; 2 bonding and 3 nonbonding. The 5 pairs are directed to the corners of a trigonal bipyramid and, because of their greater mutual repulsions, the 3 nonbonding pairs are situated in the equatorial plane at 120° to each other, leaving the 2 bonding pairs perpendicular to the plane and so producing a linear F–Xe–F molecule.

In the same way XeF_4, with 6 electron-pairs, is considered as pseudo-octahedral with its 2 nonbonding pairs trans to each other, leaving the 4 F atoms in a plane around the Xe. More distinctively, the 7 electron-pairs of XeF_6 suggest the possibility of a non-regular octahedral geometry and imply a distorted structure based on either a monocapped octahedral or a pentagonal pyramidal arrangement of electron-pairs, with the Xe–F bonds bending away from the projecting nonbonding pair.

It is an instructive exercise to devise similar rationalizations for the xenon oxides and oxofluorides listed in Table 18.3.

---

[24] C. A. Coulson, *J. Chem. Soc.* 1442–54 (1964). J. G. Malm, H. Selig, J. Jortner and S. A. Rice, *Chem. Revs.* **65**, 199–236 (1965)

[25] G. L. Goodman, *J. Chem. Phys.* **56**, 5038–41 (1972).

[26] R. J. Gillespie, *Molecular Geometry*, van Nostrand Rheinhold, London, 1972, 228 pp.

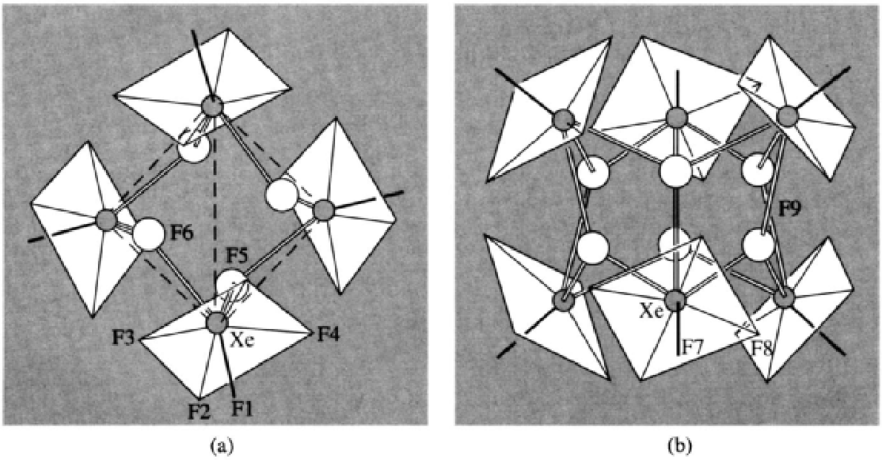


Figure 18.2 (a) Tetrameric, and (b) hexameric units in the cubic crystalline form of XeF_6. In (a) the Xe atoms (●) form a tetrahedron, with the apical F atoms of the square-pyramidal $XeF_5{}^+$ ions pointing outwards, approximately from the centre, and the bridging F^- ions (○) near four of the six edges of the tetrahedron: Xe–F(1–5) 184 pm, Xe–F(6), 223 pm and 260 pm, angle Xe–F(6)–Xe 120.7°. In (b) the Xe atoms (●) form an octahedron with the apical F atoms of the $XeF_5{}^+$ ions pointing outwards from the centre, and the bridging F^- ions (○) over six of the eight faces of the octahedron: Xe–F(7) 175 pm, Xe–F(8) 188 pm, Xe–F(9) 256 pm, angle Xe–F(9)–Xe 118.8°. $XeF_5{}^+$ ions are shown in skeletal form for clarity.

analogues, for instance:

$$^{129}_{53}ICl_2{}^- \xrightarrow{-\beta^-} {}^{129}_{54}XeCl_2$$

$XeCl_2$ has also been trapped in a matrix of solid Xe after Xe/Cl_2 mixtures had been passed through a microwave discharge, but these halides are too unstable to be chemically characterized.

It is from the binary fluorides that other compounds of xenon are invariably prepared, by reactions which fall mostly into four classes:

(a) with F^- acceptors, yielding fluorocations of xenon;
(b) with F^- donors, yielding fluoroanions of xenon;
(c) F/H metathesis between XeF_2 and an anhydrous acid;
(d) hydrolysis, yielding oxofluorides, oxides and xenates.

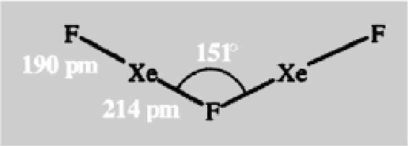
(a) *Reactions with F^- acceptors.* XeF_2 has a more extensive F^- donor chemistry than has XeF_4; it reacts with the pentafluorides of P, As, Sb, I, as well as with metal pentafluorides, to form salts of the types $[XeF]^+[MF_6]^-$, $[XeF]^+[M_2F_{11}]^-$ and $[Xe_2F_3]^+[MF_6]^-$. The $[XeF]^+$ ions are apparently always weakly attached to the counter-anion forming linear F–Xe···F–M units with one short and one long Xe–F bond, while the $[Xe_2F_3]^+$ ions are V-shaped (see p. 899; cf. isoelectronic $I_5{}^-$ with central angle 95°, p. 837). With SbF_5 the bright-green paramagnetic $Xe_2{}^+$ cation has been identified as a further product.[27] MOF_4 (M = W, Mo) are also weak F^- acceptors and form $[XeF]^+[MOF_5]^-$, which again contain linear F–Xe···F–M units.[28] The XeF^+ cation is an excellent Lewis acid and this property has been used to prepare a range of compounds featuring Xe–N bonds[29] (see also p. 902).

---

[27] L. Stein and W. H. Henderson, *J. Am. Chem. Soc.* **102**, 2856–7 (1980).

[28] J. H. Holloway and G. J. Schrobilgen, *Inorg. Chem.* **19**, 2632–40 (1980).

[29] G. J. Schrobilgen, Chap. 1 in G. A. Olah, R. D. Chambers and G. K. S. Prakash (eds.), *Synthetic Fluorine Chemistry*, John Wiley, New York, 1992, pp. 1–30.



Although the orange-yellow solid prepared by Bartlett (p. 892) was originally formulated as $Xe^+[PtF_6]^-$, it was subsequently found to have the variable composition $Xe(PtF_6)_x$, x lying between 1 and 2. The material has still not been fully characterized but probably contains both $[XeF]^+[PtF_6]^-$ and $[XeF]^+[Pt_2F_{11}]^-$.

XeF_4 forms comparable complexes only with the strongest F^- acceptors such as SbF_5 and BiF_5, but XeF_6 combines with a variety of pentafluorides to yield 1:1 adducts. In view of the structure of XeF_6 (see Fig. 18.2) it is not surprising that these adducts contain $XeF_5{}^+$ cations, as for instance in $[XeF_5]^+[AsF_6]^-$ and $[XeF_5]^+[PtF_6]^-$. In a similar manner, reactions with FeF_3 and CoF_3 yield $[XeF_5][MF_4]$ in which layers of corner-sharing FeF_6 octahedra are separated by $[XeF_5]^+$ ions.[30]

(b) *Reactions with F^- donors.* F^- acceptor behaviour of xenon fluorides is evidently confined to XeF_6 which reacts with alkali metal fluorides to form $MXeF_7$ (M = Rb, Cs) and M_2XeF_8 (M = Na, K, Rb, Cs). These compounds lose XeF_6 when heated:

$$2MXeF_7 \longrightarrow M_2XeF_8 + XeF_6$$
$$M_2XeF_8 \longrightarrow 2MF + XeF_6$$

Their thermal stability increases with molecular weight. Thus the Cs and Rb octafluoro complexes only decompose above 400°C, whereas the Na complex decomposes below 100°C. NaF can therefore conveniently be used to separate XeF_6 from XeF_2 and XeF_4, with which it does not react, the purified XeF_6 being regenerated on heating.

A similar product, $[NO]^+{}_2[XeF_8]^{2-}$, is formed with NOF and its anion has been shown by X-ray crystallography to be a slightly distorted square antiprism[31] (probably due to weak $F\cdots NO^+$ interactions). The absence of any clearly defined ninth coordination position for the lone-pair of valence electrons which is present, implies that this must be stereochemically inactive.

(c) *F/H metathesis between XeF_2 and an anhydrous acid:*

$$XeF_2 + nHL \longrightarrow F_{2-n}XeL_n + nHF \quad (n = 1, 2)$$

where L = $OTeF_5$, $OSeF_5$, OSO_2F, $OClO_3$, ONO_2, OC(O)Me, $OC(O)CF_3$, OSO_2Me and OSO_2CF_3 (see also p. 902 for an analogous reaction with $HN(OSO_2F)_2$). The compounds are colourless or pale yellow and many are thermodynamically unstable. The perchlorate (mp 16.5°) is dangerously explosive. The fluorosulfate (mp 36.6°) can be stored for many weeks at 0° but decomposes with a half-life of a few days at 20°.

$$2FXeOSO_2F \longrightarrow XeF_2 + Xe + S_2O_6F_2$$

The molecular structure of $FXeOSO_2F$ is in Fig. 18.3a. Many other such compounds have been made by similar routes e.g. $O_2Xe(F)(OTeF_5)$, $O_2Xe(OTeF_5)_2$, $OXeF_{4-n}(OTeF_5)_n$ (n = 1–4) and $XeF_{4-n}(OTeF_5)_n$ (n = 1–4);[32] $FXeOI(O)F_4$ and $Xe\{OI(O)F_4\}_2$;[33] $FXeOP(O)F_2$ and $Xe\{OP(O)F_2\}_2$ etc. Typical reactions are:

$$3O_2XeF_2 + 2B(OTeF_5)_3 \longrightarrow 3O_2Xe(OTeF_5)_2 + 2BF_3{}^{(32)}$$

$$OXe(OTeF_5)_4 \longrightarrow O_2Xe(OTeF_5)_2 + O(TeF_5)_2{}^{(34)}$$

$$XeF_2 + (IO_2F_3)_2 \longrightarrow FXeOI(O)F_4 + OIF_3 + \tfrac{1}{2}O_2{}^{(33)}$$

---

[30] J. Slivnik, B. Zemva, M. Bohinc, D. Hanzel, J. Grannec and P. Hagenmuller, *J. Inorg. Nucl. Chem.* **38**, 997–1000 (1976).

[31] S. W. Peterson, J. H. Holloway, B. A. Coyle and J. M. Williams, *Science*, **173**, 1238–9 (1971).

[32] G. A. Schumacher and G. J. Schrobilgen, *Inorg. Chem.* **23**, 2923–9 (1984).

[33] R. G. Styret and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 1529–30 (1985).

[34] L. Turowsky and K. Seppelt, *Z. anorg. allg. Chem.* **609**, 153–6 (1992).

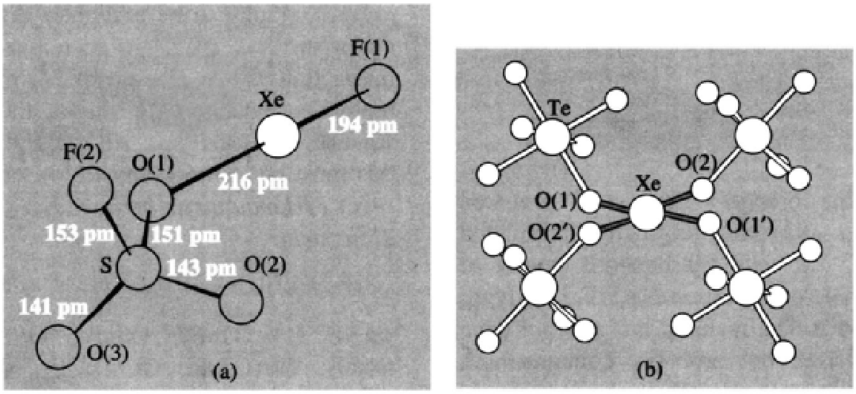


Figure 18.3 (a) The molecular structure of $FXeOSO_2F$. Precision of bond lengths is *ca.* 1 pm (uncorrected for thermal motion). The angle F(1)–Xe–O(1) is $177.5 \pm 0.4°$ and angle Xe–O(1)–S is $123.4 \pm 0.6°$. (b) The molecular structure of $Xe(OTeF_5)_4$ (see text)

$$FXeOI(O)F_4 + (IO_2F_3)_2 \longrightarrow Xe\{OI(O)F_4\}_2 + OIF_3 + \tfrac{1}{2}O_2 \text{ (33)}$$

$$Xe(OTeF_5)_2 + 2HOI(O)F_4 \longrightarrow Xe\{OI(O)F_4\}_2 + 2HOTeF_5 \text{ (33)}$$

$$3XeF_2 + B(OSO_2CF_3)_3 \longrightarrow 3FXe(OSO_2CF_3) + BF_3 \text{ (35)}$$

$$3XeF_2 + 2B(OCOCF_3)_3 \longrightarrow 3Xe(OCOCF_3)_2 + 2BF_3 \text{ (35)}$$

The molecular structure of yellow crystalline $Xe(OTeF_5)_4$ has been determined by X-ray analysis (see Fig. 18.3b);(34) the Xe atom is surrounded by a square-planar array of four O atoms, with the adjacent TeF_5 groups pointing, curiously, pair-wise up and down from this plane (Xe–O 203.9(5) and 202.6(5) pm, Te–O 188.5 pm).

(d) *Hydrolysis and related reactions.* Two Xe^{VI} oxofluorides, $XeOF_4$ and XeO_2F_2, have been characterized, and the Xe^{VIII} derivative XeO_3F_2 (mp. $-54.1°C$)(22) is also known (see below). $XeOF_4$ is a colourless volatile liquid with a square-pyramidal molecular structure, the O atom being at the apex. It can be prepared by the controlled hydrolysis of XeF_6:

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

Its most pronounced chemical characteristic is its propensity to hydrolyse further to XeO_2F_2 and then XeO_3 (p. 901). This reaction is difficult to control, and the low-melting, colourless solid, XeO_2F_2, is more reliably obtained by the reaction:

$$XeO_3 + XeOF_4 \longrightarrow 2XeO_2F_2$$

An analogous reaction with XeO_4 (see p. 901) is:

$$XeO_4 + XeF_6 \longrightarrow XeO_3F_2 + XeOF_4$$

Indeed, many of the reactions of the xenon oxides, fluorides and oxofluorides can be systematized in terms of generalized acid-base theory in which any acid (here defined as an oxide acceptor) can react with any base (oxide donor) lying beneath it in the sequence of descending acidity: $XeF_6 > XeO_2F_4 > XeO_3F_2 > XeO_4 > XeOF_4 > XeF_4 > XeO_2F_2 > XeO_3 \approx XeF_2$.(22)

In addition, oxofluoro anions may be produced by treating hydrolysis products with F^-. Thus aqueous XeO_3 and MF (M = K, Cs) yield the stable white solids $M[XeO_3F]$ in which the anion consists of chains of pseudo-octahedral Xe atoms (the lone-pair of valence electrons occupying one of the six positions) linked by angular F bridges.

---

[35] B. Cremer-Lober, H. Butler, D. Naumann and W. Tyrra, *Z. anorg. allg. Chem.* **607**, 34–40 (1992).

Again, the reaction of $XeOF_4$ and dry CsF has been shown to yield the labile $Cs[(XeOF_4)_3F]$ in which the anion consists of three equivalent $XeOF_4$ groups attached to a central F^- ion.(36) The ready loss of $2XeOF_4$ produces the more stable $CsXeOF_5$, the anion of which has a distorted octahedral geometry, the lone-pair of electrons again being stereochemically active and apparently occupying an octahedral face.

Complete hydrolysis of XeF_6 is the route to XeO_3. The most effective control of this potentially violent reaction is achieved by using a current of dry N_2 to sweep XeF_6 vapour into water:(37)

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

The HF may then be removed by adding MgO to precipitate MgF_2 and the colourless deliquescent solid XeO_3 obtained by evaporation. The aqueous solution known as "xenic acid" is quite stable if all oxidizable material is excluded, but the solid is a most dangerous explosive (reported to be comparable to TNT) which is easily detonated. The X-ray analysis, made even more difficult by the tendency of the crystals to disintegrate in an X-ray beam, shows the solid to consist of trigonal pyramidal XeO_3 units, with the xenon atom at the apex(38) (cf. the isoelectronic iodate ion IO_3^-; p. 863).

In aqueous solution XeO_3 is an extremely strong oxidizing agent (for $XeO_3 + 6H^+ + 6e^- \rightleftharpoons Xe + 3H_2O; E^\circ = 2.10$ V), but may be kinetically slow; the oxidation of Mn^{II} takes hours to produce MnO_2 and days before MnO_4^- is obtained. Treatment of aqueous XeO_3 with alkali produces xenate ions:

$$XeO_3 + OH^- \rightleftharpoons HXeO_4^-; \quad K = 1.5 \times 10^3$$

However, although some salts have been isolated, alkaline solutions are not stable and immediately, if slowly, begin to disproportionate into Xe^{VIII} (perxenates) and Xe gas by routes such as:

$$2HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O$$

Similar results are obtained by the alkaline hydrolysis of XeF_6:

$$2XeF_6 + 16OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 12F^- + 8H_2O$$

The most efficient production of perxenate is the treatment of XeO_3 in aqueous NaOH with ozone, when $Na_4XeO_6.2\frac{1}{5}H_2O$ precipitates almost quantitatively. The crystal structures of $Na_4XeO_6.6H_2O$ and $Na_4XeO_6.8H_2O$ show them to contain octahedral XeO_6^{4-} units with Xe–O 184 pm and 186.4 pm respectively. Perxenates of other alkali metals (Li^+, K^+) and of several divalent and trivalent cations (e.g. (Ba^{2+}, Am^{3+}) have also been prepared. They are colourless solids, thermally stable to over 200°C, and contain octahedral XeO_6^{4-} ions. They are powerful oxidizing agents, the reduction of Xe^{VIII} to Xe^{VI} in aqueous acid solution being very rapid. The oxidation of Mn^{II} to MnO_4^- by perxenates, unlike that by XeO_3, is thus immediate and is accompanied by evolution of O_2:

$$2H_2XeO_6^{2-} + 2H^+ \longrightarrow 2HXeO_4^- + O_2 + 2H_2O$$

The addition of solid Ba_2XeO_6 to cold conc H_2SO_4 produces the second known oxide of xenon, XeO_4. This is an explosively unstable gas which may be condensed in a liquid nitrogen trap. The solid tends to detonate when melted but small sublimed crystals have been shown to melt sharply at −35.9°C.(22) XeO_4 has only been incompletely studied, but electron diffraction and infrared evidence show the molecule to be tetrahedral.

Whilst the great bulk of noble-gas chemistry concerns Xe–F or Xe–O bonds, attempts to bond Xe to certain other atoms have also been successful. Compounds containing Xe–N bonds have been produced by the replacement of F

---

[36] G. J. SCHROBILGEN, D. MARTIN-ROVET, P. CHARPIN and M. LANCE, *J. Chem. Soc., Chem. Commun.*, 894–7 (1980). J. H. HOLLOWAY, V. KAUČIČ, D. MARTIN-ROVET, D. R. RUSSELL, G. J. SCHROBILGEN and H. SELIG, *Inorg. Chem.* **24**, 678–83 (1985).

[37] B. JASELSKIS, T. M. SPITTLER and J. L. HUSTON, *J. Am. Chem. Soc.* **88**, 2149–50 (1966).

[38] D. H. TEMPLETON, A. ZALKIN, J. D. FORRESTER and S. M. WILLIAMSON, *J. Am. Chem. Soc.* **85**, 817 (1963).

atoms by $-N(SO_2F)_2$ groups.$^{(39)}$ The relevant reactions may be represented as:

$$\begin{tikzcd}
2XeF_2 + 2HN(SO_2F)_2 \arrow[r, "\text{in } CF_2Cl_2", "0^\circ C, 4\text{ days}"'] & \begin{array}{c}2F{-}Xe{-}N(SO_2F)_2\\ \text{white solid}\end{array} \arrow[dl, "2AsF_3", "-10^\circ C"'] \\
\begin{array}{c}2[FXe(NSO_2F)_2\cdot AsF_5]\\ \text{unstable, bright yellow solid}\end{array} \arrow[d, "-AsF_5"', "22^\circ C, \text{vacuum}"] & \\
\begin{array}{c}[F\{Xe{-}N(SO_2F)_2\}_2]^+ AsF_6^-\\ \text{pale yellow solid}\end{array} &
\end{tikzcd}$$

The first (white) product has been characterized by X-ray diffraction at −55° and features a linear F–Xe–N group and a planar N atom (Fig. 18.4).$^{(40)}$ On the basis of Raman and ^{19}F nmr data, the cation of the final (pale yellow) product is believed to be essentially like the V-shaped $[Xe_2F_3]^+$ cation but with the 2 terminal F atoms replaced by $-N(SO_2F)_2$ groups.$^{(40)}$ The related compound $[Xe\{N(SO_2F)_2\}_2]$ was the first to feature an Xe atom bonded to two N atoms.$^{(41)}$ The cations $[XeN(SO_2F)_2]^+$ and $[F\{XeN(SO_2F)_2\}_2]^+$ have also been characterized and the X-ray structure of $[XeN(SO_2F)_2]^+[Sb_3F_{16}]^-$ determined.$^{(42)}$ An important new synthetic strategy was introduced by G. J. Schrobilgen who exploited the Lewis acid (electron-pair acceptor) properties of the XeF^+ cation to prepare a wide range of stable nitrile adducts featuring Xe–N bonds, e.g. $[RC{\equiv}NXeF]^+AsF_6^-$ (R = H, Me, CH_2F, Et, C_2F_5, C_3F_7, C_6F_5).$^{(43)}$ Similarly, perfluoropyridine ligands have been used to prepare $[4\text{-}RC_5F_4NXeF]^+$ cations (R = F, CF_3) in HF or BrF_5 solutions at temperatures below −30°C.$^{(44)}$ Other cationic species involving Xe–N bonds include $[F_3S{\equiv}NXeF]^+$, $[F_4S{=}NXe]^+$, $[F_5SN(H)Xe]^+$, $[F_5TeN(H)Xe]^+$, $[s\text{-}C_3F_3N_2NXeF]^+$, $[MeC{\equiv}NXeOTeF_5]^+$, $[C_5F_5NXeOTeF_5]^+$ and $[F_3S{\equiv}NXeOSeF_5]^+$. Over three dozen such compounds are now known and The field has been recently reviewed.$^{(29)}$

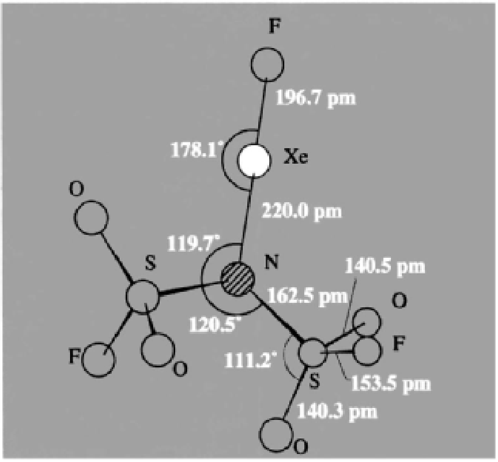


Figure 18.4 The structure of $FXeN(SO_2F)_2$ (C_2 symmetry) showing essentially linear Xe and planar N. Other bond angles are OSO 122.6°, OSF 106.3°, NSO 107.2° and 111.2°, NSF 101.2°.

Fewer compounds with Xe–C bonds have been characterized. The first to be claimed was synthesized by the plasma reaction of XeF_2 with $CF_3^{\bullet}$ radicals; the volatile waxy white solid produced, $Xe(CF_3)_2$, decomposed at room temperature with a half-life of about 30 min.$^{(45)}$

$$XeF_2 + C_2F_6 \xrightarrow{\text{plasma}} Xe(CF_3)_2 + F_2$$

$$Xe(CF_3)_2 \xrightarrow[t_{\frac{1}{2}}\ 30\,\text{min}]{20^\circ} XeF_2 + C_nF_m$$

---

[39] D. D. DesMarteau, *J. Am. Chem. Soc.* **100**, 6270–1 (1978). D. D. DesMarteau, R. D. LeBlond, S. F. Hossain and D. Nothe, *J. Am. Chem. Soc.* **103**, 7734–9 (1981).

[40] J. F. Sawyer, G. J. Schrobilgen and S. J. Sutherland, *J. Chem. Soc., Chem. Commun.*, 210–11 (1982).

[41] G. A. Schumacher and G. J. Schrobilgen, *Inorg. Chem.* **22**, 2178–83 (1983).

[42] R. Faggiani, D. K. Kennepohl, C. J. L. Lock and G. J. Schrobilgen, *Inorg. Chem.* **25**, 563–71 (1986).

[43] A. A. A. Emara and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 1644–6 (1987).

[44] A. A. A. Emara and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 257–9 (1988).

[45] L. J. Turbini, R. E. Aikman and R. J. Lagow, *J. Am. Chem. Soc.* **101**, 5833–4 (1979).

However, the first compound to have a stable Xe–C bond was reported independently by two groups in 1989:(46) reaction of XeF_2 with an excess of $B(C_6F_5)_3$ in MeCN or CH_2Cl_2 yielded $[XeC_6F_5]^+[B(C_6F_5)_3F]^-$ which was characterized by its chemical reactions and by ^{129}Xe and ^{19}F nmr spectroscopy. The compound can be isolated as a colourless solid. Several other similar compounds have since been synthesized at temperatures below −40°C, e.g. $[XeC_6H_4R]^+[B(C_6H_4R)_nF_{4-n}]^-$ ($R = m$-F, p-F, m-CF_3, p-CF_3), ($n = 0, 1, 2$).(47) An X-ray structure analysis of the adduct, $[MeC{\equiv}N{\rightarrow}Xe{-}C_6F_5]^+[(C_6F_5)_2BF_2]^-$ at −123°C established the Xe–C distance as 209.2(8) pm and the coordinate link N→Xe as 268.1(8) pm (substantially longer than the Xe–N distance in Fig. 18.4; the angle C–Xe–N is 174.5(3)°.(48) The alkynyl xenonium compound $[Bu^tC{\equiv}C{-}Xe]^+BF_4^-$ has also been characterized.(49)

The most recent extension of xenon chemistry is the formation of a compound containing a Xe–Xe bond.(49a) Thus, when the yellow compound $XeF^+Sb_2F_{11}^-$ was reacted with Xe in "magic acid" (HF/SbF_5), dark-green crystals of $Xe_2^+Sb_4F_{21}^-$ were formed at −30°C. An X-ray structure analysis at −143°C revealed that the $Xe{-}Xe^+$ bond length was 308.7(1) pm, making it the longest element–element bond yet known [cf. 304.1(1) pm for Re–Re in $Re_2(CO)_{10}$].

18.3.3 Compounds of other noble gases

No stable compounds of He, Ne or Ar are known. Radon apparently forms a difluoride and some complexes such as $[RnF]^+X^-$ ($X^- = SbF_6^-$, TaF_6^-, BiF_6^-), but the evidence is based solely on radiochemical tracer techniques since Rn has no stable isotopes.(50) The remaining noble gas, Kr, has an emerging chemistry though this is less extensive than that of Xe.

Apart from the violet free radical KrF, which has been generated in minute amounts by γ-radiation of KrF_2 and exists only below −153°C, the chemistry of Kr was for some time confined to the difluoride and its derivatives. An early claim for KrF_4 remains unsubstantiated. The volatile, colourless solid, KrF_2, is produced when mixtures of Kr and F_2 are cooled to temperatures near −196°C and then subjected to electric discharge, or irradiated with high-energy electrons or X-rays. It is a thermally (and thermodynamically) unstable compound which slowly decomposes even at room temperature. It has the same linear molecular structure as XeF_2 (Kr–F 188.9 pm) but, consistent with its lower stability, is a stronger fluorinating agent and is rapidly decomposed by water without requiring the addition of a base. KrF_2 has been used as a specialist reagent to prepare high oxidation state fluorides. Reaction with Ag or AgF in HF gave the new fluoride AgF_3;(51) high-purity MnF_4 was prepared from MnF_2/HF via the adducts $2KrF_2.MnF_4$ and $KrF_2.MnF_4$;(52) the square-pyramidal CrF_4O (mp. 55°C) was obtained by an improved route from CrO_2F_2/HF.(53) KrF_2 also affords an unusual and extremely useful room-temperature route to NpF_6 and PuF_6, thus avoiding the necessity of using F_2 at high temperatures, the compound O_2F_2 being the only other reagent known to do this.(54)

Complexes of KrF_2 are analogous to those of XeF_2 and are confined to cationic species

---

[46] D. Naumann and W. Tyrra, *J. Chem. Soc., Chem. Commun.*, 47–50 (1989). H. J. Frohn and S. Jakobs, *J. Chem. Soc., Chem. Commun.*, 625–7 (1989).

[47] H. J. Frohn and C. Rossbach, *Z. anorg. allg. Chem.* **619**, 1672–8 (1993).

[48] H. J. Frohn, S. Jacobs and G. Henkel, *Angew. Chem. Int. Edn. Engl.* **28**, 1506–7 (1989).

[49] V. V. Zhdankin, P. J. Stang and N. S. Zefirov, *J. Chem. Soc., Chem. Commun.*, 578–9 (1992).

[49a] T. Drews and K. Seppelt, *Angew. Chem. Int. Edn. Engl.* **36**, 273–4 (1997), and references cited therein.

[50] L. Stein, *Inorg. Chem.* **23**, 3670–1 (1984).

[51] R. Bougon, T. B. Huy, M. Lance and H. Abazli, *Inorg. Chem.* **23**, 3667–8 (1984).

[52] K. Lutar, A. Jesih and B. Žemva, *Polyhedron* **7**, 1217–9 (1988).

[53] K. O. Christe, W. W. Wilson and R. A. Bougon, *Inorg. Chem.* **25**, 2163–9 (1986).

[54] L. B. Asprey, P. G. Eller and S. A. Kinkead, *Inorg. Chem.* **25**, 670–2 (1986).

which can be generated by reaction with F^- acceptors. Thus, such compounds as $[KrF]^+[MF_6]^-$, $[Kr_2F_3]^+[MF_6]^+$ (M = As, Sb) are known, and also $[KrF]^+[MoOF_5]^-$ and $[KrF]^+[WOF_5]^-$ which have been prepared and characterized by ^{19}F nmr and Raman spectroscopy.[55] In addition, adducts of KrF^+ with nitrile donors have been synthesized, analogous to those of XeF^+ described in the preceding section, e.g. $[RC{\equiv}NKrF]^+$ (R = Me, CF_3, C_2F_5, *n*-C_3F_5).(29,56)

The formation of the first compound having Kr–O bonds has been documented by using ^{19}F and ^{17}O nmr spectroscopy of ^{17}O-enriched samples to follow the synthesis and decomposition of the thermally unstable compound, $[Kr(OTeF_5)_2]$, according to the reactions:(57)

$$3KrF_2 + 2B(OTeF_5)_3 \longrightarrow 3Kr(OTeF_5)_2 + 2BF_3$$

$$Kr(OTeF_5)_2 \longrightarrow Kr + F_5TeOOTeF_5$$

---

[55] J. H. HOLLOWAY and G. J. SCHROBILGEN, *Inorg. Chem.* **20**, 3363–8 (1981).

[56] G. J. SCHROBILGEN, *J. Chem. Soc., Chem. Commun.*, 863–5 and 1506–8 (1988).

[57] J. C. P. SAUNDERS and G. J. SCHROBILGEN, *J. Chem. Soc., Chem. Commun.*, 1576–8 (1989).