21 August 1964, Volume 145, Number 3634 **SCIENCE**

The Chemistry of Noble Gas Compounds

The synthesis of simple fluorides, oxyfluorides, oxides, and xenates and perxenates is discussed.

Herbert H. Hyman

In 1962 it was established that the family of elements in the periodic table formerly described as the inert gases had a rather rich chemistry (*1*). This discovery and the proliferating research resulting from the publication of these observations have been reported and discussed at three symposiums, the first held specifically for this purpose at Argonne National Laboratory on 22 and 23 April 1963 (*2*). A session on the chemistry of noble gas compounds was included in the symposium on inorganic fluorine chemistry at the Argonne Laboratory, held from 4 to 6 September 1963, and another such session, sponsored by the American Chemical Society's division of inorganic chemistry, was part of the Society's national meeting in New York the following week. In view of this extensive and well-reported research, it is possible to discuss the chemistry of this group in the periodic table with considerable confidence and generality.

As in any rapidly developing area, preliminary speculation about the nature and structure, and even the formula, of particular xenon compounds has often been erroneous. The iconoclastic aspects of the discoveries of noble gas compounds encouraged premature publication of such guesses, and a reviewer must accept responsibility for correcting the record wherever possible.

It hardly need be emphasized that even the simple xenon compounds have not been exhaustively investigated. Unresolved differences of both observation and interpretation are easily noted. Several such disagreements were aired at each of the aforementioned conferences and, while some have been resolved, a number of significant controversies remain.

The difficulties encountered in explaining the properties of xenon hexafluoride, and some conflicting observations on the hydrolysis of the lower fluorides, are discussed here in some detail, but most of the material covered in this review is as certain and as soundly based as comparable chemical information of much older vintage.

Perhaps the initial generalization that can be drawn from the experimental observations is that chemical bonds are formed only between the heavy noble gases and the most electronegative elements, fluorine and oxygen. Since the most stable isotope of radon has a half-life of less than 4 days, the observations on the chemistry of radon are rather limited. Krypton fluorides are more difficult to make and harder to keep than their xenon analogs, so to some extent the chemistry of the noble gases refers primarily to observations on the chemistry of xenon and reasonable extrapolations to krypton and radon compounds.

Such extrapolations suggest very strongly that no compounds analogous to the fluorides of xenon will be found with argon or any lighter noble gas or with xenon and any element less electronegative than oxygen. Scientists have been understandably reluctant to report their failure in the attempt to make argon fluorides or new xenon compounds.

I am aware of a number of unsuccessful attempts involving argon and fluorine in which high and low temperatures, high pressure, and electric discharge were employed. Perhaps the most convincing published evidence for the nonexistence of an argon fluoride is found in the work of Turner and Pimentel (*3*). They deposited mixtures of argon and fluorine on a transparent window at 20°K and irradiated the frozen matrix with rather intense ultraviolet light. They found no evidence for an argon fluoride, although both a krypton fluoride and two xenon fluorides are easily produced and identified by their infrared absorption spectra when a little of either of the gases is mixed with the argon.

I know of only a few attempts to make xenon compounds with elements other than oxygen or fluorine bonded to the xenon, notably by the irradiation at low temperature of a xenon chlorine mixture. No success has been reported. With radon as the central atom, there may well be a somewhat greater chance of success.

Xenon exhibits every even oxidation number from 2 to 8, and stable compounds in massive amounts have been isolated for each of these. The characteristic compounds for xenon (II) and (IV) are the binary fluorides, xenon difluoride and tetrafluoride. For Xe (VIII), the perxenate anion is the most important species, while xenon (VI) has the most diversified chemical behavior.

Xenon compounds that cannot be readily fitted into this simple bonding scheme have been reported from time to time. Some of these compounds are

---

The author is a senior chemist at Argonne National Laboratory, operated by the University of Chicago for the U.S. Atomic Energy Commission at Argonne, Ill.

real, complex, and not yet thoroughly understood. Other reports of this nature have not been confirmed, and some data have been reinterpreted so as to remove the need for strained explanation.

The compounds of xenon may be conveniently grouped in three categories. The xenon-metal hexafluoride adducts, the xenon fluorides and oxyfluorides, and the xenon oxides, xenates, and perxenates.

The Xenon-Metal Hexafluoride Adducts

Although the compound formed between xenon and platinum hexafluoride provided the first evidence that xenon was not a truly inert gas, the nature of the products resulting from this reaction, as well as the similar xenon adducts formed with ruthenium and rhodium hexafluorides, has not been fully elucidated. The actual composition of these adducts is not reproducible. For example, in a single set of experiments, analyses show that from 0.86 to 2.2 moles of platinum hexafluoride are combined per mole of xenon (*4*). Most of the preparations contain some platinum (V), and thus presumably the PtF_6^- anion, but the evidence for any substantial concentration of the cation radical Xe^+ is weak. Bartlett decided to investigate the reaction of xenon and platinum hexafluorides, because he observed a red impurity in platinum hexafluoride; he determined its structure as $O_2^+PtF_6$, successfully predicted the synthesis of this red compound by the direct combination, at room temperature, of oxygen and platinum hexafluoride, and then successfully predicted an analogous reaction between xenon and platinum hexafluoride. The nature of the oxygen adducts with metal fluorides is also somewhat in doubt, since magnetic studies on such compounds as O_2BF_4 and O_2PF_6 show significant concentrations of unpaired electrons, but much lower concentrations than would be required for uniform distribution of the oxygens as O_2^+ cations (*5*).

Clifford (*6*) has suggested the presence of similar xenon (I) *cations* as a constituent of the complex xenon fluosilicates produced by electric discharge in mixtures of xenon and fluorine in silica equipment.

Morton and Falconer have exposed xenon tetrafluoride crystals to ionizing radiation at low temperatures (*7*) and have studied the formation and decay of the odd electron species XeF^+. In a xenon tetrafluoride lattice at room temperature a reasonable concentration of such cations would not be expected, but the possibility of finding such species in xenon metal hexafluoride adducts cannot be dismissed. However, it is likely that rearrangement to more stable configurations involving xenon (II) will be preferred, and that samples in which substantially all the xenon is present as a xenon (I) are probably rather difficult to prepare. No evidence has been suggested for the existence in the gas, or in solution, of an individual molecule containing such a cation.

Xenon compounds have been prepared as the mixed fluorides which contain group (V) metals surrounded by fluorine. $XeF_2\cdot(SbF_5)_2$ might be taken as a type compound (*8*). This might be formulated in a number of ways—for example, as the ionic $Xe^{++}(SbF_6^-)_2$ or as a bridged structure with Xe joining the two hexafluoroantimonate octahedrons. Peacock has argued persuasively in favor of the bridged structure. Arsenic or tantalum may take the place of antimony, but BF_3 does not seem to form adducts with the lower fluorides. Since the composition and the physical properties of these compounds also seem to vary somewhat, depending on the technique of preparation, xenon (I) has been postulated as a constituent in some of these preparations (*6*), but on the basis of little supporting evidence.

Table 1. Xenon fluoride, oxyfluoride, and oxides: some thermochemical data. The values given are estimates, by me, for the crystalline state at 298°C; they are based on selected averaging of data discussed in the text.

Oxidation No.	Compound	ΔH_f (kcal/mole)	ΔH_v (kcal/mole)	Comments*
2	XeF_2	−30	12.3	
2	XeO			Observed in emission spectrum
4	XeF_4	−68	15.3	
4	$XeOF_2$			Probably prepared but never adequately purified and characterized
4	XeO_2			Never observed as independent species
6	XeF_6	−96	13	
6	$XeOF_4$		10	
6	XeO_2F_2			Observed only in mass spectrometer.
6	XeO_3	96		A sensitive and violent explosive; easily prepared.

* All the species listed, as well as a number of fragmentation products, have been observed in the mass spectrometer as positive ions. Correlation of such observations with the existence of stable independent species is often possible and has been made for each of the xenon compounds isolated in massive amounts, as well as for XeO_2F_2 (*19*).

Table 2. Vibrational spectra of XeF_2.

Vibration	Description	Spectral region (waves/cm)*	
		Vapor	Solid
ν_1	Symmetric stretching	IR (~513)† R 515	R 496
ν_2	Bending	IR 213.2	
ν_3	Asymmetric stretching	IR 550 IR 564 } 557	
$\nu_1 + \nu_3$	Combination	IR 1070	
	Libration		R 108

* IR, infrared; R, Raman. † Value obtained by subtraction: 1070 − 557.

Xenon hexafluoride forms solid adducts with a number of electron pair acceptors (Lewis acids), including boron trifluoride and arsenic pentafluoride (*9*). The boron trifluoride adduct seems to sublime in vacuum without decomposition, but the structure of these complexes has not yet been established in either gaseous or solid phase.

Xenon hexafluoride appears to be absorbed on sodium fluoride, and it seems likely that compounds are formed analogous to Na_2UF_8, which has been identified in the complex formed by absorbing uranium hexafluoride on sodium fluoride. Xenon hexafluoride is less strongly absorbed than uranium hexafluoride (or hydrogen fluoride) but much more strongly absorbed than xenon tetrafluoride or molybdenum hexafluoride (*10*).

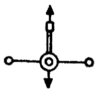
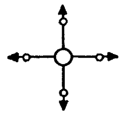
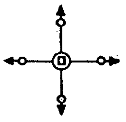
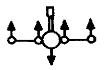
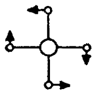
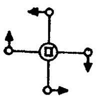
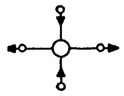
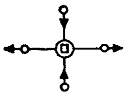
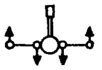
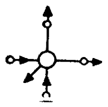
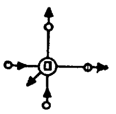
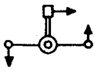
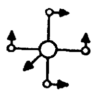
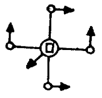
Xenon Fluorides and Oxyfluorides

The fluorides and oxyfluorides are probably the most studied and the best-understood group of noble gas compounds. Xenon fluorides may be synthesized from the elements by virtually any process which exposes xenon to fluorine atoms. These processes include the use of high temperature, of ultraviolet or other ionizing radiation, and of electrical discharge in either fluorine gas or reactive fluorides. With low concentrations of fluorine atoms, the difluoride is formed first, and rather pure fractions may be removed from the system. Continued exposure yields the tetrafluoride; xenon hexafluoride has so far been produced only under conditions where it is in equilibrium with the tetrafluoride, and a considerable excess of fluorine is required to obtain substantial yields.

At a total pressure of about 30 atmospheres, an equimolar mixture of xenon and fluorine reacts spontaneously at room temperature to yield xenon difluoride. At 8 to 12 atmospheres the reaction rate becomes negligibly slow at room temperature (*11*).

The reaction of xenon with fluorine is an exothermic reaction. After some preliminary measurements of the heat of reaction of xenon fluorides with hydrogen, the heat of formation, ΔH_f, of

Table 3. Vibrational spectra of xenon tetrafluoride and xenon oxide tetrafluoride. All reported infrared bands are for the vapor. Raman bands for $XeOF_4$ and for the liquid, and for XeF_4 are for the solid. The ν_1 and ν_5 Raman bands for XEF_4 have been observed in the vapor at, respectively, 549 and 513 waves per centimeter.

Xenon tetrafluoride (XeF_4)					Xenon oxide tetrafluoride ($XeOF_4$)				
Mode of atomic motion	Symmetry*	Vibration number†	Where observed‡	Wave number§ (cm^{-1})	Mode of atomic motion	Symmetry*	Vibration number†	Where observed‡	Wave number§ (cm^{-1})
						a_1	ν_1	R, p	919 (s)
								IR	928.2(s)
	a_{1g}	ν_1	R	543 (vs)		a_1	ν_2	R, p	566 (vs)
								IR	578? (vw)
	a_{2u}	ν_2	IR	291 (s)		a_1	ν_3	R	286 (vw)
								IR	288 (s)
	b_{1g}	ν_3	R	235 (w)		b_1	ν_4	R	231 (w)
	b_{2g}	ν_5	R	502 (vs)		b_2	ν_5	R	530 (s)
	b_{1u}	ν_4	Inactive	221 ?		b_2	ν_6	R	N.o.
	e_u	ν_6	IR	586 (vs)		e	ν_7	R	N.o.
								IR	609 (vs)
						e	ν_8	R	364 (mw)
								IR	362 (ms)
	e_u	ν_7	IR	N.o.		e	ν_9	R	161 (vw)
								IR	N.o.
		$\nu_5 + \nu_6$	IR	1105 (w)			$\nu_2 + \nu_7$	IR	1186 (w)
		$\nu_1 + \nu_6$	IR	1136 (w)			$2\nu_2$	IR	1156 (w)
							$2\nu_8$ and/or $\nu_7 + \nu_9$ and/or $\nu_5 + \nu_6$	IR	735 (w)
							$\nu_3 + \nu_5$	R	818 (w)

---

* The designations (a_1, b_2, e) are group theoretical notations that designate the symmetry of vibration. They are related to the alteration in electric moment and polarizability associated with the modes of atomic motion given in the diagrams. † The numbering of each vibration band is somewhat arbitrary, but is needed to permit the simple designation of combination bands. ‡ Some bands can be observed only in the Raman, others only in the infrared, some in both. R, Raman; IR, infrared; p, polarized. § While infrared and Raman bands are usually measured as wavelengths in air, the parameter which is important for theoretical calculations is the frequency, which is conventionally divided by the velocity of light and expressed as the wave number (waves/cm). This is equal to the reciprocal of the wavelength in a vacuum. vs, Very strong; s, strong; m, moderate (or moderately); w, weak; vw, very weak. Some bands, which, while weak, should be observable for the given structures, have not yet been observed; these are labeled N.o. ‖A 123-cm^{-1} line as reported in the literature (*25*) has now been reinterpreted as an HF rotation; the ν_7 line has not yet been observed.

XeF_4 and XeF_6 were reported as −54.8 and −78.7 kcal/mole, respectively, at 398°K (*12*). After recalculation with a revised value of the ΔH_f for hydrogen fluoride (*13*), these results become −57.6 and −82.9, respectively. This suggests a bond strength of about 33 kcal/mole for the xenon fluorine bond.

The equilibrium constant for the formation of XeF_2 (200 ± 20 atm) at 250°C may be combined with a calculated entropy based on the vibrational spectrum [$\Delta S°$ (the standard entropy change for the formation of XeF_2) at 250°C = −27 cal/mole deg] to yield a ΔH_f for gaseous XeF_2 of −19.4 kcal/mole (*14*), or about 28 kcal/mole for the xenon fluorine bond.

A measurement of the heat liberated on hydrolysis of xenon tetrafluoride in an aqueous iodide solution (*15*), when corrected through recalculation with the improved value for heat of formation of hydrogen fluoride yielded −63 kcal/mole for the ΔH_f^{298} (the heat of formation at 25°C) of XeF_4. A measurement of the heat of combustion of solid XeF_2 in NH_3 in a standard combustion calorimeter gave 28.8 kcal/mole for ΔH_f^{298} of that compound (*16*). These measurements correspond to xenon fluorine bond energies of about 30 kcal/mole in XeF_4 and 27 kcal/mole in XeF_2.

An estimate of the bond energies and heats of formation has been based on appearance potentials in a mass spectrometer (*17*). The results for XeF_4 and XeF_2 are in the same range (~ 30 kcal/mole for the bond energy). There seems to be good evidence that in XeF_4 the second set of fluorines are harder to remove in the mass spectrometer than the first set. Svec and Flesch (*17*) believe this finding would correspond to greater bond strength in XeF_2 and, although the actual observations are rather approximate, their summary suggests −53 ± 5 and −37 ± 10 kcal/mole, respectively, for the heat of formation, at about 400°C, for xenon tetrafluoride and xenon difluoride.

The general relationship between bond energy and interatomic distance leads to an independent estimate of relative bond strength. For xenon difluoride and tetrafluoride the bond distances are rather accurately known from diffraction data. The lesser distance (and therefore the greater bond strength) is associated with higher oxidation number. The opposite conclusions, derived from results with the mass spectrometer, may arise from the uncertainties surrounding the determination of bond energies from appearance potentials. A reasonable estimate of the average xenon-fluorine bond energy in the three xenon fluorides might be 28, 32, and 34 kcal/mole, respectively, for the difluoride, tetrafluoride, and hexafluoride.

In general, one oxygen atom may be written for two fluorine atoms in any of the xenon fluorides. The resulting compounds are listed in Table 1. The heat of formation (of the solid) has been determined for the explosively unstable XeO_3 as about 96 kcal/mole (*18*). This positive heat of formation is expected, in view of the great stability of molecular oxygen, and the strength of the xenon oxygen double bond is near 25 kcal/mole. But since molecular oxygen is not easily dissociated, the production of massive amounts of oxygen-containing compounds from the elements has not yet been demonstrated, and the substitution of oxygen for fluorine requires a metathetical reaction. Hydrolysis is probably the most convenient procedure for producing oxygen compounds of xenon (VI).

$$\begin{aligned} XeF_6 + H_2O &\rightarrow XeOF_4 + 2HF \\ + 2H_2O &\rightarrow XeO_2F_2 + 4HF \\ + 3H_2O &\rightarrow XeO_3 + 6HF \end{aligned}$$

As may be noted in Table 1, xenon oxide tetrafluoride, $XeOF_4$, is a thermodynamically stable species, and gram amounts of this liquid have been isolated and studied. Xenon dioxide difluoride, XeO_2F_2, has been observed in the mass spectrometer as an independent species resulting from the hydrolysis of xenon hexafluoride (*19*). Significant quantities of this thermodynamically unstable compound have not yet been isolated.

While an electric discharge in a mixture of xenon and oxygen produces an emission spectrum attributed to the XeO molecule (*20*), the hydrolysis of xenon difluoride yields only xenon and oxygen (*21*), and macro amounts of this compound have never been prepared.

The hydrolysis of xenon tetrafluoride in excess water leads to disproportionation and the liberation of two-thirds of the xenon (*21–23*). The resulting solution contains combined xenon (VI) and is probably identical with the solution obtained by the hydrolysis of a corresponding amount of xenon hexafluoride.

Solid oxyfluorides containing xenon (IV) have been reported as by-products of the reaction of xenon and fluorine (or oxygen difluoride) when oxygen or oxides were present (*8, 24*). Both electric discharge and thermal methods have been used. Xenon oxide difluoride is on the border line of thermal stability and should be characterized eventually, but suitable samples have not yet been available for study. No evidence for the existence of xenon dioxide is reported. If produced, it would probably be unstable, like the trioxide.

In terms of physical measurement and structural determination the greatest effort, in studies of the noble gas compounds, has been concentrated on the four stable species, XeF_2, XeF_4, $XeOF_4$, and XeF_6.

From the vibrational spectra alone, the structure of three of these molecules has been firmly established. Xenon hexafluoride continues to baffle the investigators and provide fertile ground for speculation and controversy.

The vibrational frequencies of XeF_2 (*25*) are given in Table 2; similar data for the XeF_4 (*26*) molecule and the $XeOF_4$ (*25, 26*) molecule are given in Table 3.

Xenon difluoride is a linear molecule, xenon tetrafluoride is a square planar molecule, and xenon oxide tetrafluoride is a square pyramid with the oxygen atom perched above the central xenon atom. The plane containing the xenon and four fluorine atoms in xenon tetrafluoride is remarkably well preserved in the xenon oxide tetrafluoride structure.

The lower fluorides of xenon are usually observed as large, colorless, sparkling crystals. The relatively high vapor pressure (a few torr for both XeF_2 and XeF_4 near ambient temperature) and high birefringence which led to those observations were among the first characteristics noted. Xenon-oxide tetrafluoride is a colorless, volatile liquid at room temperature.

Accurate x-ray diffraction and neutron diffraction data have revealed the structure of the solids with a precision available for relatively few compounds (*27–30*). The structure of the difluoride is shown in Fig. 1 (*30*), that of the tetrafluoride, in Fig. 2 (*29*); in addition, an initially baffling phase has been shown to be an intermolecular lattice compound $XeF_2 \cdot XeF_4$ in which both linear and square molecules are arranged in a regular array (Fig. 3) (*31*).

Table 4 summarizes the interatomic distances. For the solids these values include corrections for thermal motion, based on reasonable assumptions about the relative vibrations of the light fluorine atoms and the heavy central xenon atom.

A number of discussions of the nature of the xenon fluorine bonds have been published (*32*). As a starting point for such discussion it is worth

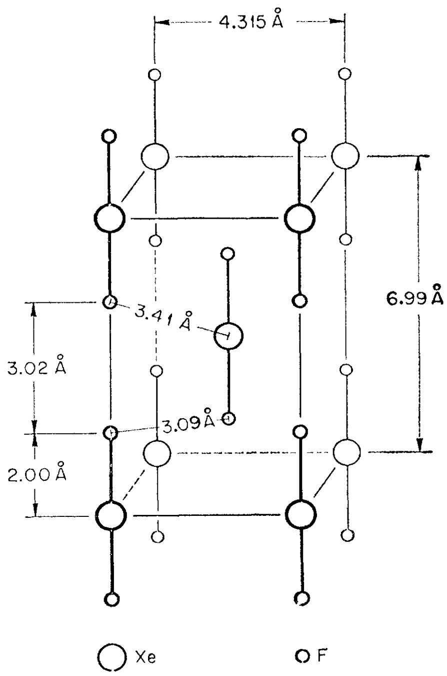


Fig. 1. Structure of xenon difluoride.

while to note both the similarities and the differences between the noble gas fluorides and the halogen fluorides. The similarities are basic in that bonding takes place between a heavier atom with an electron-rich outer shell and a strongly electronegative atom. The differences can mostly be explained in terms of the odd electron available with a central halogen atom in the halogen fluorides and with the fully paired xenon atom in xenon fluorides. As a result of the odd electron, halogen fluorides contain an odd number of fluorines and are unsymmetrical molecules. They show a long liquid range, and they readily undergo fluoride ion transfer to form symmetrical ionic species. The even-numbered and symmetrical xenon fluorides show none of these characteristics. An experimental chemist will find this analogy most helpful in describing and predicting the observed chemical behavior. The theoretician will attempt to explain both families of compounds.

In seeking to interpret and predict chemical bond formations, most theoreticians today employ molecular orbital calculations, with varying degrees of mathematical complexity, depending on the problem. The alternative, valence bond approach should lead to identical predictions. There is little doubt that a sufficiently detailed analysis from either point of view will account for the gross phenomena observed in dealing with the noble gas compounds. For xenon difluoride and xenon tetrafluoride the observed shape of the molecules can be derived rather unambiguously with either approach.

Molecular orbital calculations suggest that delocalized *p*-orbitals constructed from the xenon 5*p* and the fluorine 2*p* atomic orbitals contribute most to the ground-state description. Calculations by Lohr and Lipscomb (*33*) and Hinze and Pitzer (*34*) suggest that there is a relatively small contribution from the xenon *d*-orbitals. Rundle (*35*) has suggested that the xenon fluorides offer perfect examples of the four-electron three-center bond structure which he originally proposed to describe interhalogen bonds. An alternative description, in terms of resonance, cites contributions from the pair of ionic structures $F{-}Xe^{+}F^{-}$ and $F^{-}Xe^{+}{-}F$ and analogous structures for the tetrafluoride. Each of these formulations describes a rather polar bond and suggests a substantially ionic character for the bonds in xenon difluoride and xenon tetrafluoride.

Support for this interpretation has been sought not only in the shape of the fluoride molecules but also in some measurements of physical phenomena.

Figure 4 (*36*) summarizes a study of nuclear magnetic resonance and provides the chemical shielding values for a number of binary fluorides (*36, 37*). The line shape is asymmetrical in xenon tetrafluoride (*38*) (Fig. 5). These observations are readily interpreted as indicating a substantially ionic character for the xenon fluoride bonds.

An analysis of the nuclear magnetic resonance data by Jameson and Gutowsky (*39*) confirms this interpretation but favors a formulation in which a localized *spd* hybrid bond is used over one with delocalized, largely *p*, orbitals. The observed velocity spectrum associated with the Mössbauer effect for Xe^{129} in xenon fluorides (*40*) (Fig. 6) has also been interpreted as indicating a substantially ionic character for these bonds.

The electronic absorption spectra in the 1100- to 2500-angstrom region have been studied for both xenon difluoride and xenon tetrafluoride. A detailed analysis (*41*) suggests reasonable agreement between these observations and the molecular orbital calculations.

The simple valence bond approach has been decribed most completely by Gillespie (*42*). In his version the eight electrons from the xenon atom outer (O) shell and one electron from each fluorine atom, or two from an oxygen atom, are distributed in pairs which either form bonds between atoms or occur as lone pairs in the outer molecular shell. The shape of the molecule then depends on the relative repulsion of (i) lone pairs and (ii) fluorine atoms and oxygen double bonds. For xenon difluoride, xenon tetrafluoride, and xenon oxide tetrafluoride, the distribution of ten electrons (in two bonds and three lone pairs), 12 electrons (in four bonds and two lone pairs), and 14 electrons (in four bonds, one double bond, and one lone pair) may be easily reconciled

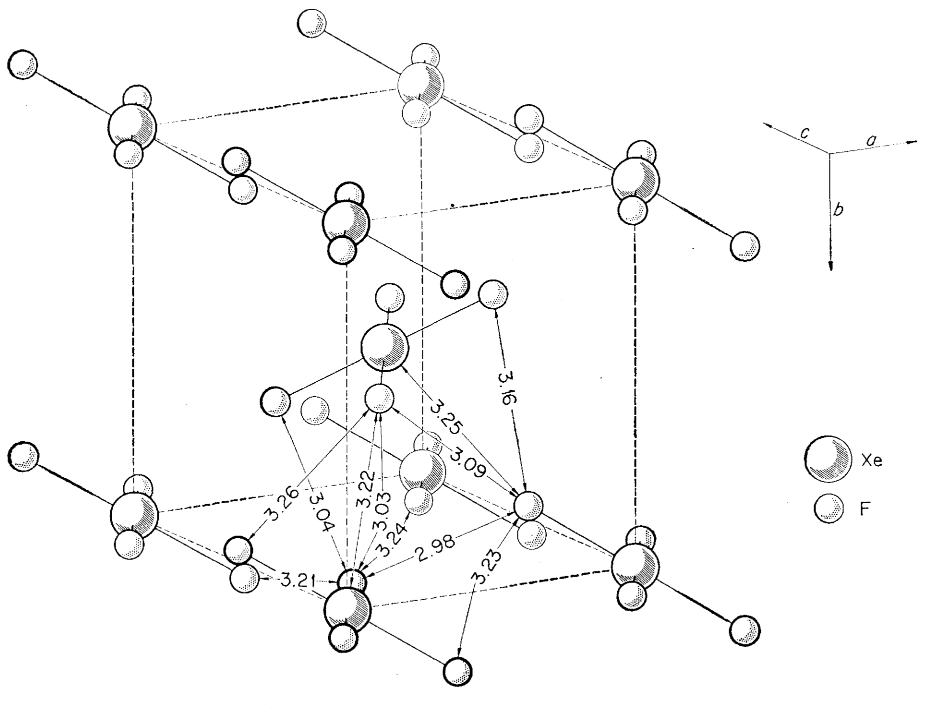


Fig. 2. Structure of xenon tetrafluoride.

with the established symmetry. No assumptions about the nature of the bond are needed other than the basic assumption that a pair of electrons is associated with a single bond.

Similar conclusions minimizing the ionic character of the xenon fluorine bond have been reached by Smith, on the basis of an analysis of the vibration spectra (*25*). He has argued that the ratio of the interaction stretching constant to the principal stretching constant is substantially less for xenon difluoride and tetrafluoride than for the ICl_2^- ion. The latter ion has been used as the prototype example for the four-electron three-center bond structure, and the observed spectra have been interpreted as indicating bonding of substantially ionic character. Smith, therefore, suggests that covalent bonding is important for the xenon fluorides. He believes that the *d*-orbitals are more involved in the resulting hybrid orbitals than Rundle (*35*) or Pimentel (*43*) believed, and probably of more importance than is consistent with the molecular orbital calculations cited above.

With respect to chemical behavior, we have little in the way of evidence. Both xenon difluoride and tetrafluoride dissolve in hydrogen fluoride with little or no ionization, dissociation, or interaction of any kind (see Fig. 7) (*44*). The difluoride is very soluble, and at room temperature there may be appreciable exchange of fluorines. The tetrafluoride is much less soluble, and there is no evidence of even a slight tendency toward fluorine transfer. In hydrogen fluoride solution all the halogen fluorides show extensive ionization and transfer of fluoride ion to the hydrogen fluoride molecule. However, in this case part of the driving force must be derived from the increased symmetry associated with the ionic species, as compared to the neutral molecules, whereas for the xenon fluorides this factor would have the opposite effect.

Smith's arguments have not been generally accepted. The spectra and magnetic properties, or similar evidence, cited above cannot really be used as a means of deciding between the contributions of bonding of ionic character and the effect of *d*-orbital hybridization, since as yet there is no agreement on the experimental results to be expected in the two cases. It is probable that most of the scientists who have considered the problem would attach most weight to the molecular orbital calculations. But since these calculations all allow for some *d*-orbital hybridization and no approach excludes a significant ionic contribution, the details of this discussion would have aroused little interest were it not for the case of xenon hexafluoride.

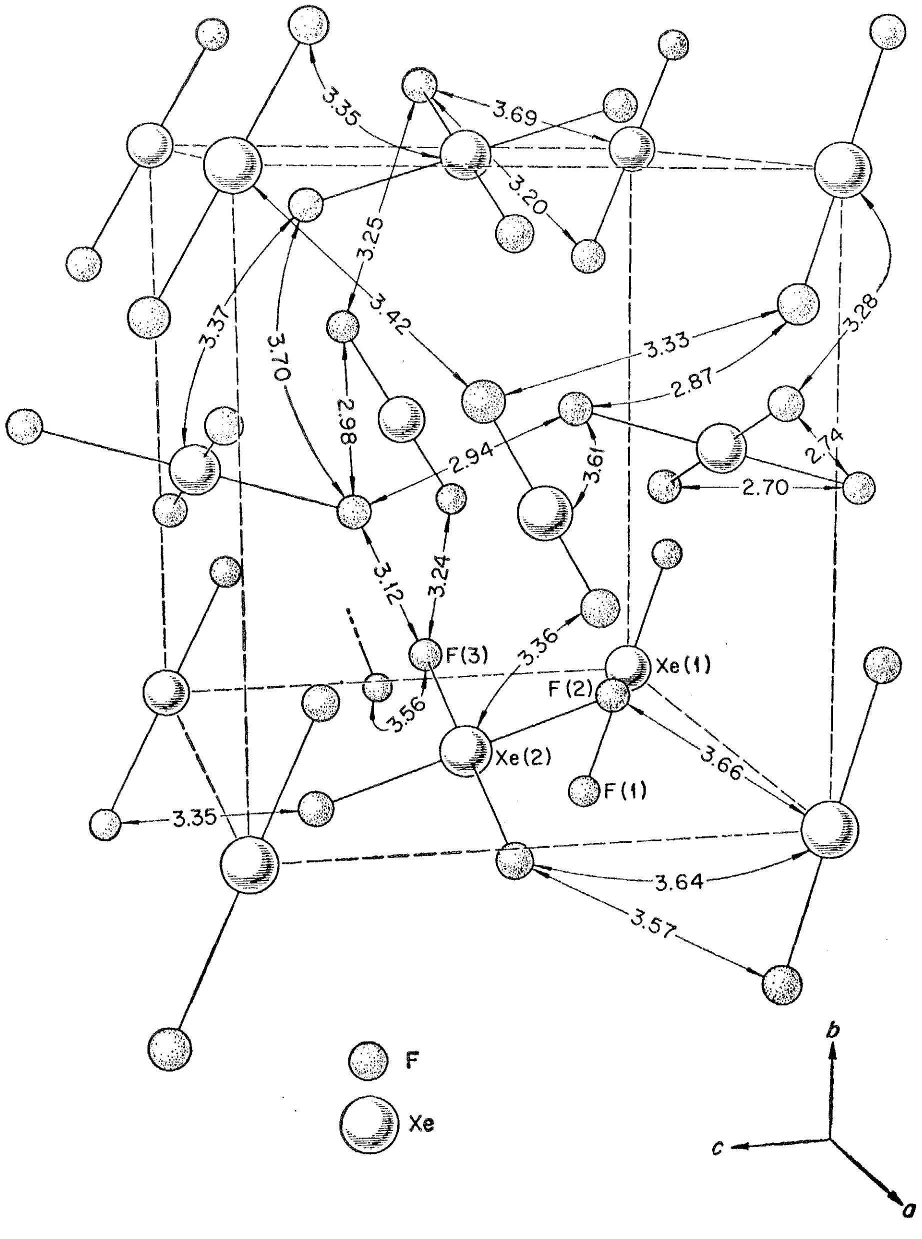


Fig. 3. Structure of the complex crystal XeF_2-XeF_4.

One would expect a hexafluoride molecule to have a symmetrical octahedral structure. Fifteen other hexafluoride molecules do indeed have this structure. Systematic study of the physical and chemical properties of the hexafluoride has provided an opportunity to project trends for a set of molecules of uniform and well-defined shape. These projections have been so fully and frequently borne out that the likelihood of the existence of a nonoctahedral hexafluoride seemed remote. Further, the concepts used in the molecular orbital treatment of the lower fluorides seem to lead only to the octahedral structure. It is not surprising that when the infrared absorption spectrum of xenon hexafluoride was first observed, an attempt was made to fit the structure to the octahedral pattern. Impurity bands were attributed to XeF_6, and extra bands, to impurities. One group of workers carefully excluded a number of possible impurities and attributed a remaining extraneous infrared absorption band at wave number of 520 cm^{-1} to xenon pentafluoride (*14*). They later showed that no such compound did exist in their system. A number of reliable observations are now available; they are summarized in Tables 5 and 6 and in Fig. 8 (*25, 45*). The study of the Raman spectra of xenon hexafluo-

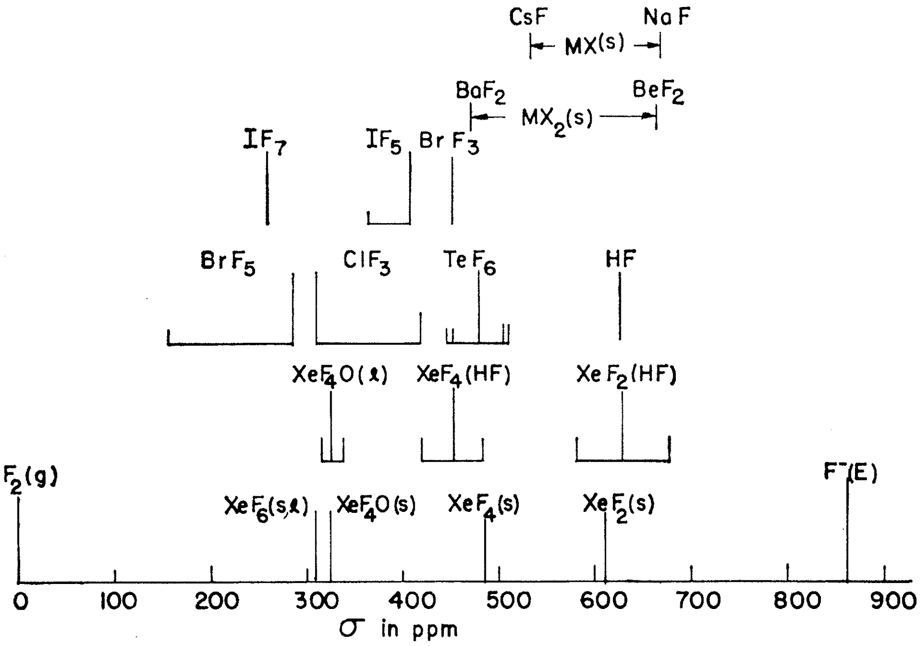


Fig. 4. Shielding values for a number of binary fluorides.

ride in hydrogen fluoride solution is still incomplete, but the preliminary results are interesting (*44*).

The structure of XeF$_6$ is one of the few established points of divergence between Rundle's approach and Gillespie's approach to bonding in the xenon fluoride.

Three four-electron three-center bonds define an octahedrally symmetrical molecule. No molecular orbital formulation yet attempted has led to any other conclusion. But the valence bond approach in its simplest form leaves room for a lower symmetry and an appreciably polar molecule. The lower symmetry is also compatible with the formulation involving substantial *d*-orbital hybridization.

In discussion of the structure of xenon hexafluoride a number of significant observations are now available.

Table 4. Interatomic distances in xenon fluorides and krypton tetrafluoride.

Compound	Xenon fluorine distance (Å)	
	Solid	Gas
XeF$_2$	2.00 (*30*)	1.9* (*25*)
XeF$_4$	1.95 (*29*)	1.94 (*71*)
XeF$_2$-XeF$_4$	2.01 1.94, 1.97† (*31*)	
XeF$_6$		1.95 (*46*)
KrF$_4$		1.89 (*68*)

* Value obtained from separation of *P–R* peaks in the 557 waves per centimeter band in the infrared. This value is regarded as in good agreement with the precise data for the solid. † In the tetrafluoride part of this complex crystal, the square is slightly distorted to give this pair of distances.

Xenon hexafluoride has the lowest vapor pressure of any known hexafluoride. Unlike most hexafluorides, the melting point (~48°C) (*10*) is well below the normal boiling point (~76°C). High volatility and short liquid range are readily attributed in the octahedral hexafluorides to their high symmetry and low dipole interactions.

The electron diffraction data seem incompatible with a symmetrical gaseous molecule (*46*).

This physical evidence supporting a less symmetrical structure is reinforced by the scattered chemical evidence now available. Unlike the typical symmetrical molecule, such as uranium hexafluoride, xenon hexafluoride is very soluble in anhydrous hydrogen fluoride and is extensively ionized. As noted above, xenon hexafluoride forms reasonably stable compounds with Lewis acids, such as antimony pentafluoride or even boron trifluoride. While the structure of these compounds and the nature of the ionic species in solution has not been established, such behavior is quite compatible with the Gillespie suggestion of a lone pair and is not reported for the other hexafluorides.

Xenon hexafluoride is a white solid which not only melts to a yellow liquid but indeed turns yellow at about 42°C while still solid. The solid appears to turn yellow at an even lower temperature under ultraviolet irradiation.

Goodman (*47*) has studied this phenomenon and, in attempting to explain it, has made an effort to preserve the concept of an octahedrally symmetrical ground state. He first suggested that both the electronic transitions associated with the yellow color and the superfluous infrared absorption bands involve the same low-lying state. The infrared spectrum is not easily explained on this basis, and Goodman has alternatively suggested a low barrier to rotation of the fluorine bonds, comparable to the barrier to free rotation in ethane. The absence of a strong Raman line associated with the octahedrally symmetrical vibration would argue against this interpretation, but xenon hexafluoride is yellow both as pure liquid and as vapor, and in any concentrated solution. The available equipment for obtaining Raman spectra uses the 4358-angstrom line of mercury and is not really suitable for studying yellow substances, and the values reported for solutions in Tables 5 and 6 have not been adequately confirmed. The apparent absence of the octahedral structure in the solid might be attributable to lattice distortions.

The evidence presented by Goodman and favoring a low-lying triplet state permits either a symmetrical or an unsymmetrical ground state. The evidence for a structure differing in a substantive way from that of the other hexafluorides is overwhelming. It is not clear (to me) that the evidence observed so far for such an unsymmetrical structure is incompatible with a symmetrical ground state and a low energy barrier to transformation to a less symmetrical configuration.

The high reactivity of xenon hexafluoride as a fluorinating agent has been hinted at, though never extensively explored (*44*). This high reactivity throws little light on the symmetry. The symmetrical hexafluorides include the extremely inert compound formed with

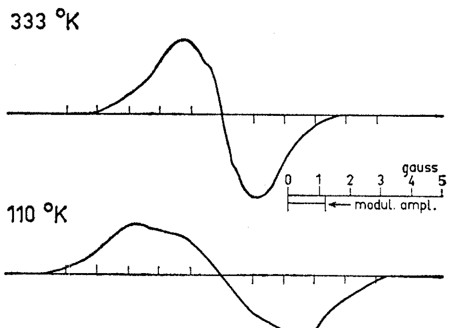
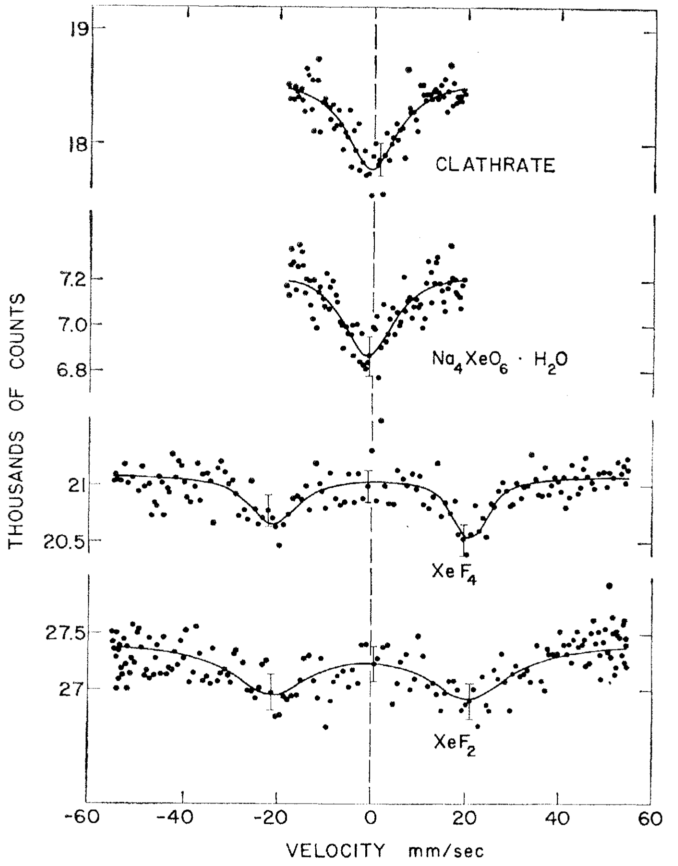
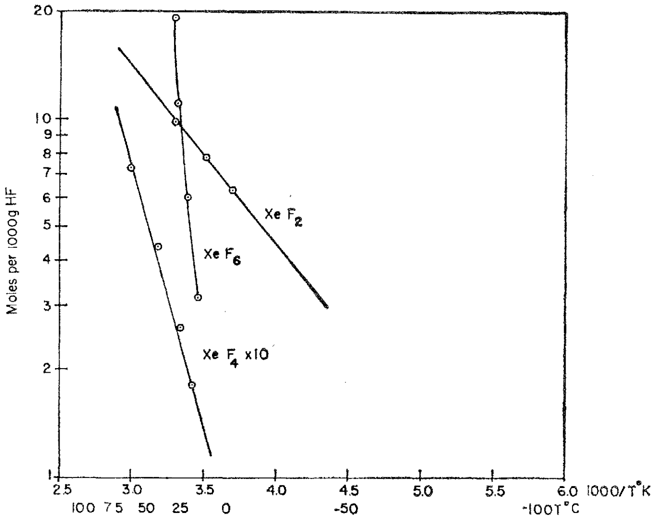


Fig. 5. The line shapes of fluorine magnetic resonance in XeF$_4$ at 29 megacycles per second.





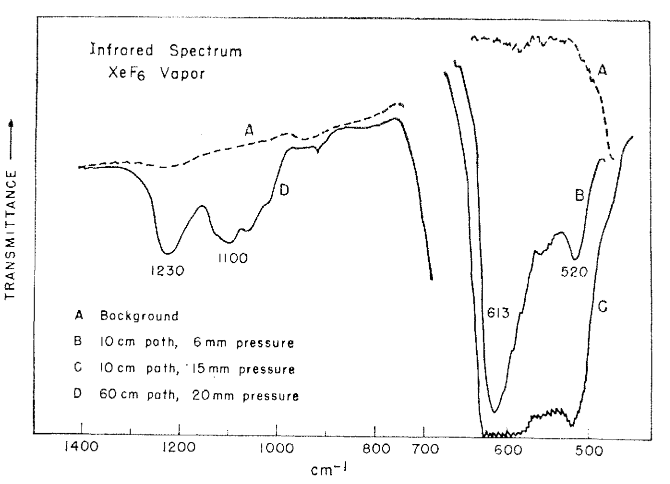


Fig. 6 (above). Mössbauer effect velocity spectra of xenon compounds in studies in which a NaI^{129} source was used. Fig. 7 (top right). Solubility of xenon fluorides in hydrogen fluoride. The abscissa is chosen to yield the straight line predicted from consideration of elementary thermodynamics. It is the reciprocal of the absolute temperature in degrees Kevlin, and the 1000 is introduced to give simple numerical values. The lower scale gives the corresponding values in degrees Celsius. Thus, the value 25°C corresponds to 298°K and 3.3 for (1000/T). Fig. 8 (bottom right). Infrared absorption spectrum of xenon hexafluoride vapor.

sulfur and the very reactive platinum hexafluoride. The properties of xenon hexafluoride have posed a challenge to both theoretician and experimentalist. A great deal of work seems to be needed before either can be satisfied with the state of our understanding.

Up to this point I have refrained from discussing xenon octafluoride. Experiments suggesting formation of this compound at high excess fluorine pressure were reported by Slivnik *et al.* (*48*) at the Argonne conference. Results of a study of the kinetics of F^{18} exchange between xenon hexafluoride and fluorine have been interpreted as indicating addition to xenon hexafluoride rather than dissociation (*49*). A number of samples prepared in this study have shown fluorine-to-xenon ratios in excess of 6. Yet the most careful work under conditions of excess fluorine pressure well above that reported to yield higher fluorides has in fact yielded only xenon hexafluoride (*14, 50, 51*).

There seems to be no theoretical study which excludes the possibility that a xenon octafluoride comparable in stability to the lower fluorides exists, but its existence has not yet been adequately demonstrated, and it seems futile at present to attempt to extrapolate the properties of the lower fluorides so as to predict the behavior of this compound.

Xenon Oxides, Xenates, and Perxenates

The finding that reasonably stable aqueous solutions of xenon compounds exist was in some ways most surprising, although here too the analogy with halogen compounds is useful in understanding the properties of the xenon compounds. A number of these compounds have proved amenable to detailed study, and many have been isolated in ponderable amounts. The first member of the group characterized was xenon trioxide, which, while easily prepared, is a sensitive and powerful explosive (*52*). As noted above, this compound has a positive heat of formation, largely because of the great strength of the bond in molecular oxygen. This factor has prevented the synthesis of xenon oxygen bonds from the elements, and as yet all of the xenates, perxenates and oxides are prepared from the fluorides.

Xenon trioxide may be isolated after the hydrolysis in acid or neutral solutions of either xenon tetrafluoride (*53*) or xenon hexafluoride (*52*). The structure of solid xenon trioxide is based on a regular array of XeO_3 molecules and is closely related to that of the isoelectronic IO_3^- in HIO_3 (*54*). The XeO_3 molecule is a trigonal pyramid with an average XeO bond length of 1.76 angstroms and an O–XeO bond angle of 103 degrees. The trioxide, perhaps unexpectedly, has no measurable vapor pressure at room temperature.

Xenon trioxide appears to be reasonably stable in aqueous acid or neutral solution, and the Raman spectrum of such solutions is most readily interpreted as the spectrum of individual XeO_3 molecules similar to those found in the solid crystal (*55*). It is not easy to determine the extent to which water molecules are attached to the xenon trioxide molecules in such aqueous solutions, but it doesn't seem particularly helpful to discuss the chemistry of the xenon species in terms of a "xenic acid" with a formula such as $Xe(OH)_6$, though the term *xenic acid,* without mention, necessarily, of any single formula, has often been used in describing the solution produced by hydrolysis of either xenon tetrafluoride (*24, 56*) or hexafluoride (*50*).

A controversy about the nature of "xenic acid" solution has now been partially resolved (*56*). When pure xenon tetrafluoride is hydrolyzed in water or dilute acid, the major product, and perhaps the only isolable product, appears to be xenon trioxide, as in the hydrolysis of xenon hexafluoride (*21, 23*).

The somewhat different behavior described by Grosse has now been shown to be associated with the presence of XeF_2 (*57, 58*).

Xenon difluoride has a significant solubility in water. In solution it decomposes at a reasonable rate which appears to increase with increase in *p*H and temperature. The half-time of decomposition is about ½ day at 0°C in dilute hydrogen fluoride. Unreacted xenon difluoride can be recovered from this solution.

Table 5. Vibrational spectra of XeF_6: absorption bands observed in the infrared.

Waves per centimeter	Density in vapor*	Comments
520	m	Disappeared in solid
565	vw	Somewhat stronger in solid
612	s	Strongest band
1100	m	Very broad band
1230	m	Very broad band

* m, Moderate; vw, very weak; s, strong.

A number of intermediate species in the hydrolysis of each of the xenon fluorides have been postulated. Both tetrahedrally coordinated and octahedrally coordinated species are possible. Every even oxidation number from 2 to 8 may be considered, as may a judicious mixture of F, O, and OH ligands arranged around the central xenon.

At this stage, any guess as to the nature of such intermediate species as might exist would be highly speculative. In my opinion the term *xenic acid* is likely to be misleading in most cases.

When solutions containing XeO_3 are made alkaline by the addition of sodium hydroxide, a slow disproportionation takes place, with evolution of xenon gas and formation of sodium perxenate. In the presence of ozone, no xenon is liberated, and the xenon is quantitatively oxidized to xenon (VIII) (*21, 22*).

Sodium perxenate usually precipitates as a hydrate. At room temperature the octahydrate $Na_4XeO_6 \cdot 8H_2O$ has been characterized and its structure has been determined by x-ray analysis (*59*). At 5°C the hexahydrate seems to be the form isolated. The structure of this compound has also been established (*60*). A number of other phases have been found, both by dehydration in a recording thermal gravimetric system (*61*) and by x-ray analysis (*27*). The anhydrous material decomposes at elevated temperatures, with loss of xenon and oxygen.

The XeO_6^{4-} ion appears to be octahedrally symmetrical. Both molecular orbital and valence bond formulations appear to predict this symmetry.

In acid solution the perxenate loses oxygen and reverts back to a stable solution of xenon trioxide. Solids containing the perxenate anion and a variety of cations have been prepared. Sodium perxenate is relatively stable with respect to thermal decomposition, but some of these perxenates are much less stable, silver perxenate decomposing violently at 150°C (*62*). All perxenates show an intense absorption band in the region of 650 to 680 waves per centimeter; the position of the band is insensitive to the nature of the cation. This band has been attributed to a ν_3 fundamental of the octahedral XeO_6 group, comparable to bands found in the spectra of compounds containing SbO_6, TeO_6, and IO_6 groups.

Other alkaline solutions have been substituted for sodium hydroxide solutions in treating solutions containing XeO_3, but the results are not always analogous to those described above. Research is in progress at a number of laboratories aimed at sorting out the chemistry involved and the nature of the precipitates formed with potassium and other alkali hydroxides and other bases. With barium hydroxide, a precipitate formed immediately; this, when analyzed rapidly, was found to contain largely Xe (VI), but disproportionation appears to take place and, within minutes at room temperatures, only the relatively stable barium perxenate could be identified (*57a*).

Observations of a somewhat different nature are reported by the Temple University group (*56*). Barium hydroxide precipitates a white salt from the solution containing the volatile hydrolysis product of a xenon tetrafluoride, xenon difluoride system (XeF_2?). The compound is stable enough to permit characterization and analysis as barium xenate, although x-ray data are not yet available.

The solution chemistry of both xenon (VI) and xenon (VIII) has been studied in some detail. As noted above, for xenon (VI), the predominant species seems to be the trioxide molecule, and there is no evidence for hydrated species such as H_2XeO_4 that might be expected by analogy with other *M* (VI) oxy acids. (*M* is any element which exhibits a VI valence state). At high *p*H ($>$ 10.5) there does seem to be evidence of neutralization and therefore of some acidic character for xenon (VI) (*57a*). Presumably, the $HXeO_4^-$ ion is formed. However, at this point, disproportionation to the perxenate begins to play a role.

The perxenate ion, on the other hand, behaves as a basic substance and reacts readily with acids. In dilute acid the reaction is accompanied by reduction to xenon trioxide (*57a*). In concentrated sulfuric acid the very volatile xenon tetroxide is produced.

Xenon tetroxide was first identified

Table 6. Vibrational spectra of XeF_6: Raman bands.

Solid		Conc. HF solution		Dilute HF solution
$\Delta\nu$ (cm^{-1})	Intensity ratio	$\Delta\nu$ (cm^{-1})	Intensity ratio	$\Delta\nu$ (cm^{-1})
655	10	660	10	
635	8	600	8	620 vw*
582	4	550	3.5	

* vw, Very weak.

by mass spectrometric analysis in the vapor resulting from the reaction of sodium perxenate and sulfuric acid (*63*). In the preparation of larger samples (up to 100 mg) of this unstable species, barium perxenate has been reported to give somewhat higher yields. Though samples of xenon tetroxide often decomposed more or less violently during preparation, when samples condensed at low temperature were allowed to warm up, it was possible to measure some vapor pressures (3 torr at −35°C, 25 torr at 0°C), and the vapor was stable enough to permit analysis of the infrared spectrum. Two infrared active fundamentals were observed, with *P*, *Q*, and *R* branches at wave numbers of 298, 305.7, and 314 cm^{-1} and 870, 877, and 885 cm^{-1}, respectively (*64*). These data are consistent with tetrahedral symmetry for the XeO_4 molecules and an XeO bond distance of about 1.6 angstroms (*64*).

Perxenates may be employed as strong oxidizing agents. In dilute acid solution, manganous ion is oxidized to permanganate rapidly enough to compete effectively with the disappearance of perxenate by reaction with the water. Manganous ion may also be oxidized with hexavalent xenon, but the reaction with perxenate ion is much faster (*57*).

When aqueous solutions containing combined xenon became available, the pharmacology and toxicology were of obvious interest. Research along those lines, with radioactive xenon as a tracer, has shown that sodium perxenate in a solution administered intravenously to mice is rapidly metabolized, and xenon gas is removed by way of the respiratory tract, minutes after injection. Nevertheless, such solutions are moderately toxic; the median lethal dose is 15 to 30 mg/kg (*65*).

Other Noble Gas Compounds

Relatively little information is available as yet about either krypton or radon compounds. Both the difluoride and the tetrafluoride of krypton have been reported to be colorless crystals (*24, 66*). Observation of the infrared absorption spectrum of the difluoride (*3*), and nuclear magnetic resonance (*67*) and electron diffraction studies of the tetrafluoride (*68*), parallel similar studies with the xenon compounds and suggest similar structures.

All measurements on krypton tetrafluoride have been made on samples prepared and analyzed at the Research Institute of Temple University. At this writing no other laboratory has reported a similar preparation. The hydrolysis of krypton tetrafluoride and precipitation of a barium salt have been described (*69*). Detailed studies of the behavior of aqueous krypton will probably draw heavily on experience with the analogous xenon compounds.

Radon fluorides of moderate and low volatility have been noted. The low-volatility fluoride is probably one or more complex species; the moderately volatile fluoride is probably a species analogous to one of the simple xenon fluorides (or to a mixture of the simple fluorides) (*70*). A discussion of the chemistry of either of these elements must be highly speculative at this time.

References and Notes

1. N. Bartlett, *Proc. Chem. Soc.* **1962**, 218 (196→ H. H. Claassen, H. Selig, J. G. Malm, *J. Am. Chem. Soc.* **84**, 3593 (1962); C. L. Chernick, H. H. Claassen, P. R. Fields, H. H. Hyman, J. G. Malm, W. M. Manning, M. S. Matheson, L. A. Quarterman, F. Schreiner, H. H. Selig, I. Sheft, S. Siegel, E. N. Sloth, L. Stein, M. H. Studier, J. L. Weeks, M. H. Zirin, *Science* **138**, 136 (1962).
2. H. H. Hyman, *Science* **141**, 61 (1963); ———, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963).
3. J. J. Turner and G. C. Pimentel, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 101.
4. N. Bartlett and N. K. Jha, *ibid.*, p. 23.
5. I. J. Solomon, J. Keith, R. Uenishi, J. McDonough, paper presented at Symposium on Inorganic Fluorine Chemistry, Argonne National Laboratory, Sept. 1963; J. Hirata, S. S. Morrow, R. R. Young, paper presented at American Chemical Society meeting, New York, Sept. 1963 [see *Chem. Eng. News* **41**, No. 38, 40 (1963)].
6. A. F. Clifford and G. R. Zeilenga, *Science* **143**, 1431 (1964).
7. W. E. Falconer and J. R. Morton, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 245.
8. A. J. Edwards, J. H. Holloway, R. D. Peacock, *ibid.*, p. 71.
9. H. Selig, *Science* **144**, 537 (1964).
10. I. Sheft, T. Spittler, F. H. Martin, *ibid.* **145**, 701 (1964).
11. V. M. Khutorelskii and V. A. Shpanskii, *Dokl. Akad. Nauk SSSR* **155**, 379 (1964).
12. L. Stein and P. L. Plurien, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 144.
13. H. M. Feder, W. N. Hubbard, S. S. Wise, J. L. Margrave, *J. Phys. Chem.* **67**, 1148 (1963).
14. B. Weinstock, E. E. Weaver, C. P. Knop, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 50.
15. S. R. Gunn and S. M. Williamson, *ibid.*, p. 133.
16. W. V. Johnston, W. R. Bisbee, D. F. Sheehan, private communication.
17. H. J. Svec and G. D. Flesch, *Science* **142**, 954 (1963).
18. S. R. Gunn, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 149.
19. M. H. Studier and E. N. Sloth, *ibid.*, p. 47.
20. C. D. Cooper, G. C. Cobb, E. L. Tolnas, *J. Mol. Spectr.* **7**, 223 (1961).
21. J. G. Malm, B. D. Holt, R. W. Bane, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 167.
22. E. Appelman, *ibid.*, p. 185.
23. S. M. Williamson and C. W. Koch, *ibid.*, p. 158.
24. A. G. Streng, A. D. Kirshenbaum, L. V. Streng, A. V. Grosse, *ibid.*, p. 73.
25. D. F. Smith, *ibid.*, p. 295; P. A. Agron, G. M. Begun, H. A. Levy, A. A. Mason, C. G. Jones, D. F. Smith, *Science* **139**, 842 (1963).
26. H. H. Claassen, C. L. Chernick, J. G. Malm, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 287.
27. S. Siegel and E. Gebert, *ibid.*, p. 193.
28. W. C. Hamilton and J. A. Ibers, *ibid.*, p. 195; D. H. Templeton, A. Zalkin, J. D. Forrester, S. M. Williamson, *ibid.*, p. 203.
29. J. H. Burns, P. A. Agron, H. A. Levy, *ibid.*, p. 211.
30. H. A. Levy and P. A. Agron, *ibid.*, p. 221.
31. J. H. Burns, R. D. Ellison, H. A. Levy, *ibid.*, p. 226; *J. Chem. Phys.* **67**, 1569 (1963).
32. Many of these discussions are included in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), sect. 9, pp. 317–388. The reader is referred to this section for a more sophisticated treatment.
33. L. L. Lohr and W. N. Lipscomb, *ibid.*, p. 347.
34. J. Hinze and K. S. Pitzer, *ibid.*, p. 340.

→ R. E. Rundle, *J. Am. Chem. Soc.* **85**, 112 (1963).

36. J. C. Hindman and A. Svirmickas, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 251.
37. T. H. Brown, E. B. Whipple, P. H. Verdier, *ibid.*, p. 263.
38. R. Blinc, P. Podnar, J. Slivnik, B. Volavšek, S. Maričic, Z. Veksli, *ibid.*, p. 270.
39. C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.* **40**, 2285 (1964).
40. G. J. Perlow, C. E. Johnson, M. R. Perlow, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 279.
41. J. Jortner, E. G. Wilson, S. A. Rice, *ibid.*, p. 358; see also E. S. Pysh, J. Jortner, S. A. Rice, *J. Chem. Phys.* **40**, 2018 (1964).
42. R. J. Gillespie, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 333.
43. G. C. Pimentel and R. D. Spratley, *J. Am. Chem. Soc.* **85**, 826 (1963).
44. For preliminary data see H. H. Hyman and L. A. Quarterman, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 275; additional work is in progress.
45. H. H. Claassen, *ibid.*, p. 304.
46. R. K. Bohn, K. Katada, J. V. Martinez, S. H. Bauer, private commnication; preliminary results were reported at the New York meeting of the American Chemical Society, Sept. 1963.
47. G. L. Goodman, paper presented at Symposium on Inorganic Fluorine Chemistry, Argonne National Laboratory, Sept. 1963.
48. J. Slivnik, B. Volavšek, J. Marsel, V. Vrščaj, A. Smalc, B. Frlec, A. Zemljič, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 64.
49. I. Sheft and H. H. Hyman, *ibid.*, p. 68 (also unpublished observations).
50. F. B. Dudley, G. L. Gard, G. H. Cady, *ibid.*, p. 61.
51. C. L. Chernick, *ibid.*, p. 35.
52. D. F. Smith, *J. Am. Chem. Soc.* **85**, 816 (1963).
53. S. M. Williamson and C. W. Koch, *Science*, **139**, 1046 (1963).
54. D. H. Templeton, A. Zalkin, J. D. Forrester, S. M. Williamson, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 229.
55. H. H. Claassen and G. Knapp, *J. Am. Chem. Soc.* **86**, 2341 (1964).
56. A. D. Kirshenbaum and A. V. Grosse, *Science* **142**, 580 (1963). The aqueous chemistry of xenon and the somewhat discordant observations were discussed at the New York meeting of the American Chemical Society, Sept. 1963; the pertinent papers are those of A. V. Grosse, A. D. Kirshenbaum, A. G. Streng, and L. V. Streng; S. M. Williamson and C. W. Koch; and J. G. Malm and E. H. Appelman. Subsequent correspondence has resolved some of the discrepancies.
57. E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.* **86**, 2297 (1964).

57a. ———, *ibid.* **86**, p. 2141.

58. A. V. Grosse *et al.*, in preparation.

59. W. C. Hamilton, J. A. Ibers, D. R. Mackenzie, *Science* **141**, 532 (1963).
60. A. Zalkin, J. D. Forrester, D. H. Templeton, S. M. Williamson, C. W. Koch, *ibid.* **142**, 502 (1963).
61. H. Selig and L. Kreider, private communication.
62. D. M. Gruen, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 174.
63. J. L. Huston, M. H. Studier, E. N. Sloth, *Science* **143**, 1161 (1964).
64. H. Selig, H. H. Claassen, C. L. Chernick, J. G. Malm, J. L. Huston, *ibid.*, p. 1322. The infrared absorption bands corresponding to change in vibrational quantum number are made up of a number of closely spaced lines corresponding to changes in rotational quantum number. The three cases where the change in rotational quantum number is negative, zero, and positive, respectively, correspond to the *P*, *Q*, and *R* branches of the vibrational band.
65. A. J. Finkel, C. E. Miller, J. J. Katz, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 309.
66. D. R. Mackenzie, *Science* **141**, 1171 (1963).
67. T. H. Brown and P. H. Verdier, *J. Chem. Phys.* **40**, 2057 (1964).
68. R. K. Bohn and S. H. Bauer, private communication.
69. A. G. Streng and A. V. Grosse, *Science* **143**, 242 (1963).
70. P. R. Fields, L. Stein, M. H. Zirin, in *Noble-Gas Compounds*, H. H. Hyman, Ed. (Univ. of Chicago Press, Chicago, 1963), p. 113.
71. R. K. Bohn, K. Katada, J. V. Martinez, S. H. Bauer, *J. Chem. Phys.* **67**, 1569 (1963).
72. I am grateful to all those who have kept me informed of the progress of their work and have permitted me to quote from their observations prior to publication. A number of scientists, both at Argonne and elsewhere, have reviewed this article at various stages of preparation. I am grateful for their assistance, but I am reluctant to involve anyone by name. I cannot dilute my responsibility for errors of commission or omission.

Lipopolysaccharide of the Gram-Negative Cell Wall

Biosynthesis of a complex heteropolysaccharide occurs by successive addition of specific sugar residues.

M. J. Osborn, S. M. Rosen, L. Rothfield,
L. D. Zeleznick, B. L. Horecker

In recent years there have been rapid advances in our knowledge of the chemical composition and structure of the bacterial cell wall. Gram-negative as well as Gram-positive forms have been shown to contain a rigid polymer built up of units of *N*-acetylglucosamine and a muramic acid peptide (*1*). In addition to this basic structural unit, many Gram-positive species also contain teichoic acids, which are polymers of ribitol phosphate or glycerol phosphate carrying a variety of side chains (*2*). In contrast, Gram-negative organisms appear to contain little or no teichoic acid. The walls of most Gram-negative forms contain a complex lipopolysaccharide in addition to large amounts of protein and phospholipid. These components appear to overlie the rigid mucopeptide layer and may account for the difference in sensitivity of Gram-negative and Gram-positive species to attack by lysozyme. The lipopolysaccharide possesses many interesting biological properties and has, therefore, attracted the attention of large numbers of investigators. It is highly antigenic and contains the specific surface antigens, or O-antigens, which provide the basis for the Kauffmann-White scheme for the serological classification of the Enterobacteriaceae (*3*). The lipopolysaccharide is also an integral component of the endotoxin, a protein-lipid-lipopolysaccharide complex which is responsible for the physiological effects produced by injection of heat-killed bacteria. These effects include fever, shock, diarrhea, edema, and internal hemorrhage. As a result of the early classic work from the laboratories of Boivin (*4*), Raistrick (*5*), and Morgan (*6*), it became clear that antigenic and toxic properties of the endotoxin were both associated with the lipopolysaccharide and that the polysaccharide portion, which can be liberated from the complex by mild acid hydrolysis, carried the complete somatic or O-antigen specificity of the microorganism. The isolated polysaccharide is nontoxic, and the nature of the chemical structure or structures responsible for toxicity of the intact lipopolysaccharide is still uncertain. The lipid moiety of the lipopolysaccharide, lipid A, is a complex, phosphorylated lipid of unusual composition, which contains glucosamine instead of glycerol and is rich in β-hydroxymyristic acid (*7, 8*). Although toxicity can be recovered in isolated lipid A preparations (*9, 10*), it is not clear whether the lipid, as isolated, can account entirely for the toxicity of the original endotoxin.

The chemical basis of O-antigen specificity was firmly established by the monumental work of Kauffmann on the immunological classification of *Salmonella* and *Escherichia* (*3*) and by more recent structural and immunochemical studies in the laboratories of Westphal (*9–12*), Staub (*13, 14*), and Robbins (*15*). It is clear that the determinants for all O-antigen specificities of a given organism are located in a single polysaccharide molecule, and it has been possible in many cases to identify the monosaccharide or oligosaccharide groupings which determine individual specificities. It was early recognized (*16*) that mutation could result in complete loss of O-antigen specificity, and that the altered surface structure in these so-called "rough" mutants was accompanied by loss of virulence. Recent investigations of the chemistry (*12*), immunology (*17*), and genetics (*18*) of rough mutants have been of particular value in unraveling the structure of the lipopolysaccharide.

Our interest in biosynthesis of the lipopolysaccharide was stimulated by the potential value of the lipopolysaccharide as a model system for study of mechanisms of biosynthesis and control of structurally specific heteropolysaccharides. *Salmonella* lipopolysaccharides may contain as many as eight different sugars, and the high degree of antigenic specificity argues for an equivalent specificity in sugar sequence and linkage. In addition, the occurrence of

---

The authors are members of the department of molecular biology, Albert Einstein College of Medicine, Yeshiva University, New York, N.Y.