

# NOBLE-GAS COMPOUNDS

by Neil Bartlett

**The noble gases, long regarded as inert,  
turn out to have a chemistry after all.  
Furthermore, this new-found reactivity  
throws new light on chemical bonding**

**IN BRIEF:** Two years have now passed since the announcement that the noble gases, so named because of their reluctance to associate themselves with any other elements in compounds, were really not so noble after all. A dozen or more compounds of xenon, krypton, and radon now sit in bottles on laboratory shelves all around the world, while scientists by the hundred probe the chemical, physical, and theoretical peculiarities of these newest of molecules.

Oddly enough, the peculiarities are few; the structures and reactivities of noble-gas compounds seem, on hindsight, to be perfectly straightforward and predictable. Even the classical laws of valence bonding still stand. Only one compound, xenon hexafluoride, now appears to be a troublemaker; its structure, as yet undetermined, may prove whether the valence-bond theory or the molecular-orbital theory of bonding is correct. No other test case has shown as great divergence in predicted structure between the two methods.

The unexpected has been assimilated, the patient still lives.—H.W.M.

■ The discovery in late 1962 that the heavier noble gases have a chemistry, albeit limited, was greeted with incredulity by some chemists and with astonishment by the majority. The reasons for this surprise, and for the continued reluctance in some quarters to accept the idea that chemical bonding in noble-gas compounds is similar to that in "normal" compounds, are rooted in history and ingrained tradition.

Throughout that history, the noble elements have played a central role in the development of a theory of chemical bonding. And the significant thing, in most minds, about the discovery that they can form bonds is the new light it may throw on bonding.

Although there was almost universal surprise at the announcement, there was little actual disbelief. Such was not the case in 1894 when Lord Rayleigh and William Ramsay announced their discovery of a new element, argon, present in air in a concentration of almost 1%.

An element like argon had not been predicted by Mendeleev's periodic table, formulated 25 years earlier, and many saw no place for it in the table. Even Mendeleev maintained

that the new gas must be another molecular form of nitrogen,  $N_3$ , and predicted that it would be very stable.

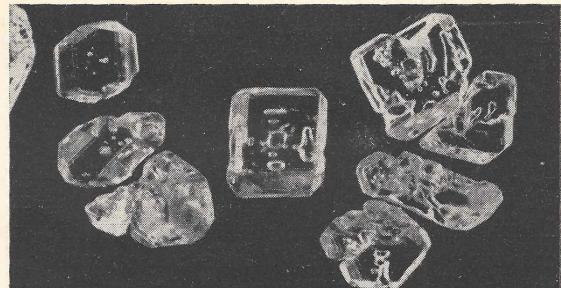
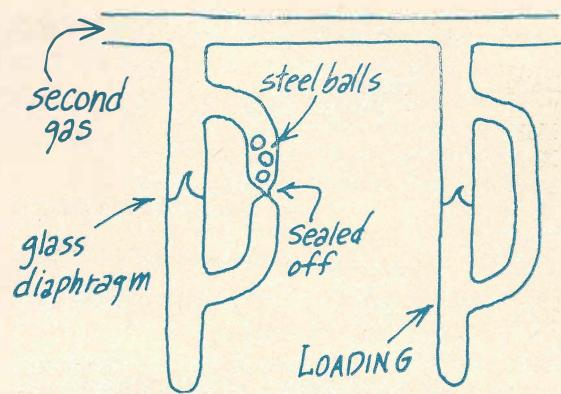
Ultimately, of course, argon was established as a new element, and as a member of a new group in the periodic table, with its relatives helium, neon, krypton, and xenon. As Ramsay had proposed early in the argon work, the new group was placed between the highly oxidizing halogens and the strongly reducing alkali metals. This location indicated that the new gases might well be neither oxidizing nor reducing, and hence chemically inert. Rayleigh and Ramsay conducted numerous experiments on argon, endeavoring to produce compounds of the element, but they were uniformly unsuccessful. They thus concluded, "It is a most astonishingly indifferent body, inasmuch as it is unattacked by elements of very opposite character. . . . It will be interesting to see if fluorine is also without action. . . ."

To follow up this speculation, Ramsay supplied argon to his friend Henri Moissan, who discovered fluorine in 1886, but nothing came of the experiments (see FLUORINE CHEMISTRY, November 1962).

The other gases were subjected to a much less searching chemical investigation than ar-

Noble Gas	Shell Number. <i>n</i>						Total
	1	2	3	4	5	6	
Helium	2						2
Neon	2	8					10
Argon	2	8	8				18
Krypton	2	8	18	8			36
Xenon	2	8	18	18	8		54
Radon	2	8	18	32	18	8	86

Fig. 1. The electronic configuration of the elements produces an eight-electron highest energy shell in all noble gases heavier than helium.



*Fig. 2. Historic apparatus—these glass reaction tubes were used in the first experiments to show actual chemical bonding in noble gases; glass diaphragms in drawing were broken to allow xenon and platinum hexafluoride vapor to mix, producing  $XePtF_6$ . Crystals below are xenon tetrafluoride.*

gon, and no evidence of chemical reactivity was revealed by their discoverers. Since krypton and xenon were so rare, they were the least investigated of the group.

#### **Anatomy of a misconception**

In the midst of this chemical ferment, J. J. Thompson discovered the electron in 1897, and correlated his speculative atomic model with the periodic table by arranging the electrons in concentric rings of eight. This tied in beautifully with the new group of apparently zero valent elements.

Moseley's discovery in 1913 that elements bombarded with cathode rays emitted x rays provided the tool which helped establish the atomic numbers of the noble gases as 2, 10, 18, 36, 54, and 86, and thus their position in Mendeleev's scheme.

Bohr's atomic theory, postulated the same year, restricted the energy of the orbiting electrons to an integral number of quanta, and limited the maximum number of electrons in a given energy level. In this model, the noble gases always contained eight electrons in their highest occupied energy level.

All the various pieces of physical evidence seemed to define the concept that the electronic configuration of the noble gases was the "ideal" toward which an anthropomorphic element might "strive" when undergoing reac-

tion with another. This concept was formalized in 1916 into two hypotheses, put forward by Lewis and Kossel working independently. Kossel pointed out, for example, that those elements that immediately preceded the noble gases in the periodic table, the halogens, attracted electrons strongly and were univalent. The alkali metals following the noble gases in the table, on the other hand, gave up electrons easily and were also univalent. Thus each group seemed to strive to attain an outside shell of eight electrons, like the noble gases, even if it had to become an electrically charged ion to do so. A similar situation held for the groups of divalent elements removed one additional step in each direction.

According to Kossel, this gave rise to mutual attraction between oppositely charged ions, and hence to chemical bonding. The then new technique of x-ray crystallography confirmed that this theory must be approximately true, at least for those elements adjacent to the noble gases.

Kossel's theory was somewhat less plausible in nonionizable molecules such as methane,  $CH_4$ . Here, Lewis showed another way that an atom could achieve a noble-gas structure—by sharing its electrons. He represented the diatomic hydrogen molecule,  $H_2$ , with each of the electrons of the two participating atoms

Compound	Form	Melting point, °C	Vapor pressure, mm at 25°C
XeF <sub>2</sub>	colorless crystal	140	3.8
XeF <sub>4</sub>	"	114	3
XeF <sub>6</sub>	"	46	29
KrF <sub>4</sub>	"	60 (dec.)	115
XeOF <sub>2</sub>	"	?	?
XeOF <sub>3</sub>	"	?	?
XeOF <sub>4</sub>	colorless liquid	-28	29
XeO <sub>3</sub>	white solid	exploses	
XeO <sub>6</sub> <sup>-4</sup>	exists as salt of barium (Ba <sub>3</sub> XeO <sub>6</sub> ) and sodium (Na <sub>2</sub> XeO <sub>6</sub> • 8H <sub>2</sub> O)		

Table 1. Simple known compounds of noble gases with fluorine and oxygen.

hydrogen atom was visualized as approaching the ideal noble-gas configuration of helium. In methane and ammonia, NH<sub>3</sub>, the carbon and nitrogen approach the neon configuration, the hydrogen atoms approach that of helium.

The twin theories were so successful in correlating the body of chemical facts that working chemists tended to overemphasize them, and to ignore the numerous cases where the so-called octet rule did not apply.

#### The ever-present skeptic

Not everyone was convinced of the nobleness of the group, however. For instance, even the discoverers of argon made use of argon's high solubility in water, by extracting it from rain water, which proved to contain twice as much dissolved argon as nitrogen. The French chemist Villard showed that the element formed a crystalline hydrate with water, and later, hydrates of krypton and xenon were also prepared. Structural studies have since shown that these "compounds" are really clathrates, in which the noble-gas atoms are physically caged in holes in frameworks composed of hydrogen-bonded water molecules.

Water is not the only substance to enclathrate the heavier noble gases either; β-hydroquinone and phenol also form clathrates involving some other molecules in the cage besides the noble-gas atoms. Neon and helium do not form clathrates; presumably the attractive forces between the caged species and the cage are too weak in such small, poorly polarizable atoms. The existence of clathrates, we should note, doesn't involve the valence electrons in any chemical bonding. The octet remains intact.

However, there was one class of noble-gas compounds which grew up in the literature which did involve valence bonding. These were the compounds of noble gases, particularly helium, with metals. In 1924 Manley described the first such compound, a helide of mercury, produced by interacting low-pressure helium

with mercury in a glow discharge. Later workers claimed helides of tungsten, phosphorus, iodine, and sulfur.

Unfortunately, none of the work can be said to have conclusively established the existence of definite chemical compounds of the gases with other elements. Waller, after unsuccessfully attempting to repeat a number of preparations in 1960 asserted, "... it may be concluded that the inert gases are truly inert."

In 1935, Booth and Wilson claimed to have evidence of compound formation between boron trifluoride and argon, but Wiberg and Karbe were unable to confirm these findings, nor to detect any evidence of compound formation between boron trifluoride and either krypton or xenon.

Although Oddo must be credited as one of the first to predict reactivity of the heavier noble gases—he suggested in a letter to Ramsay that krypton and xenon should form halides—he was deterred by Ramsay's pessimism. Von Antropoff, coming to the same conclusion as Oddo, even predicted octavalence for the heavier elements in 1924. In 1932 he and his co-workers thought they had isolated a red krypton chloride; a year later he showed it to be a compound formed from nitrous oxide and hydrogen chloride, both impurities in the reaction mix.

Pauling made the most accurate predictions of all in 1933: From considerations of ionic radii and periodic table relationships, he predicted the formation of xenon hexafluoride, XeF<sub>6</sub>, and krypton hexafluoride, KrF<sub>6</sub>, and the possible existence of xenon octafluoride, XeF<sub>8</sub>. He also suggested that xenic acid, H<sub>4</sub>XeO<sub>6</sub>, should exist, and that salts such as silver xenate, AgXeO<sub>6</sub>, should be preparable.

Unfortunately, the experimental difficulties of working with fluorine in 1933 were great. For example, when Yost and Kaye took Pauling's cue and studied the xenon-fluoride reaction at CalTech in 1933, they had to generate their own fluorine from a sometimes-balky cell. Their total supply of xenon, "borrowed" from Allen of Purdue, was 200 cc at less than half an atmosphere of pressure. The reaction was carried out in quartz apparatus, which (we now know) doomed it to failure. All they got for their pains was etched quartz, in all probability a result of interaction with the fluorine. Had their apparatus been sufficiently cooled, or constructed of fluorite or alumina instead of quartz, the xenon fluorides would have been discovered thirty years earlier.

The failure of all attempts to establish conclusively the existence of any compounds of the noble gases in which the elements were either oxidized or reduced had, by the late thirties, entrenched the belief that the noble-gas electronic configuration would apparently withstand all chemical assaults.

The chain of events that was to shatter the belief in this invulnerability began in 1961.

D. H. Lohmann and I were fluorinating platinum and platinum compounds at the University of British Columbia, working in glass apparatus. One of the compounds we obtained was a red solid, which (after three man-years of analysis) turned out to have the empirical formula  $\text{PtO}_2\text{F}_6$ . Depending on the conditions of preparation, it resembled  $\text{K}[\text{PtF}_6]$  or  $\text{K}[\text{SbF}_6]$ ; the potassium (K) ions in both compounds, of course, are univalent, and the platinum (Pt) and antimony (Sb) ions pentavalent. Weinstock, Claassen, and Malm (keep those names in mind) had reported making platinum hexafluoride,  $\text{PtF}_6$ , a volatile red solid, four years earlier at Argonne National Lab, but monovalent ions of molecular oxygen ( $\text{O}_2^+$ ) were unknown—molecular oxygen holds its electrons so firmly it takes 281 kcal to remove the first electron from 32 g (1 mole).

The confirming test of the existence of monovalent dioxygenyl ions would be if  $\text{PtF}_6$  would oxidize oxygen itself to yield the compound we had found. In brief, it did;  $\text{PtF}_6$  and oxygen reacted rapidly, and the ionic formula,  $\text{O}_2^+[\text{PtF}_6]^-$ , took the place of the simple empirical formula.

From calculations of the heat cycle involved in the reaction, it was apparent that platinum hexafluoride was the most powerful oxidizing agent ever known; it obviously had such a powerful electron affinity that it could create cations never before attained, from compounds normally considered stable. I was turning over in my mind various possibilities to try, when quite by chance I ran across a chart of ionization potential plotted against atomic number in a book I was checking for another matter entirely.

Now ionization potential, the energy required to strip away an electron from an atom or molecule in oxidation, rises and falls through the periodic table (see Fig. 3) with maxima at the noble gases and minima at the alkali metals. The maxima, however, gradually decrease as you go up in atomic number. Then the thought: We had contemplated the oxidation of relatively inert chemical species; why not the “inert” noble gases?

The first ionization potential of xenon was the same as that of molecular oxygen, about 12.2 electron volts; radon was also possibly within range, with a first ionization potential of 10.7 Ev. Although other factors tend to affect these energy calculations, we decided to try to confirm experimentally the predicted reaction with xenon.

#### **And then it happened**

It turned out to be a simple and dramatic experiment. A container of deep red platinum hexafluoride vapor of known pressure was separated by a glass diaphragm from a second flask containing the same volume of xenon at a greater pressure. When we broke the diaphragm, the two gases immediately combined to produce a yellow solid at room temperature; the quantity of xenon remaining was commensurate with a combining ratio of 1:1. The yellow solid sublimed when heated under vacuum, and the sublimate yielded xenon when treated with water. Clearly the xenon was bound tightly enough for it to persist in a vapor state species. The compound was formulated as  $\text{Xe}^+[\text{PtF}_6]^-$ , the first known noble-gas compound in which valence electrons actually entered into the bonding.

We published these results immediately, and Claassen, Selig, and Malm, at Argonne, quickly confirmed the reaction. They then went on to study the interaction of xenon with ruthenium hexafluoride,  $\text{RuF}_6$ . They noted that roughly three molecules of  $\text{RuF}_6$  were consumed per atom of xenon and that some reduction of the ruthenium seemed to occur. This suggested that  $\text{RuF}_6$  was, at least in part, acting simply as a fluorinating agent, producing fluorides of xenon.

To check this heretical idea, the group ran a quick, qualitative test in which they mixed essentially equal parts (by pressure) of xenon and fluorine in a metal can and heated them for an hour at  $400^\circ\text{C}$ , then cooled to  $-195^\circ\text{C}$ . When the reaction mix was warmed to room temperature, there was not a sign of the xenon gas! In spite of the fact that they had hoped for direct reaction, Claassen wrote in

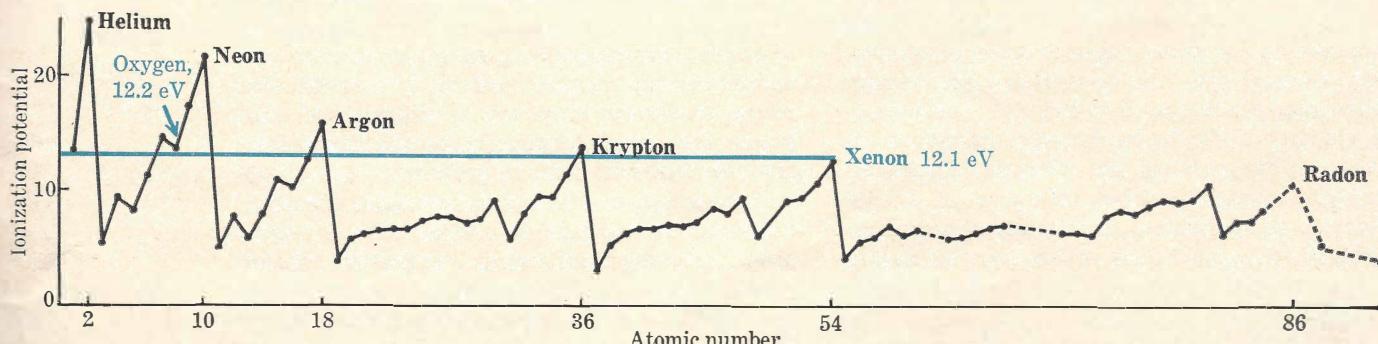


Fig. 3. Chart of ionization potential against atomic number shows regular increase to a noble gas, then drops. Xenon and oxygen have same value.

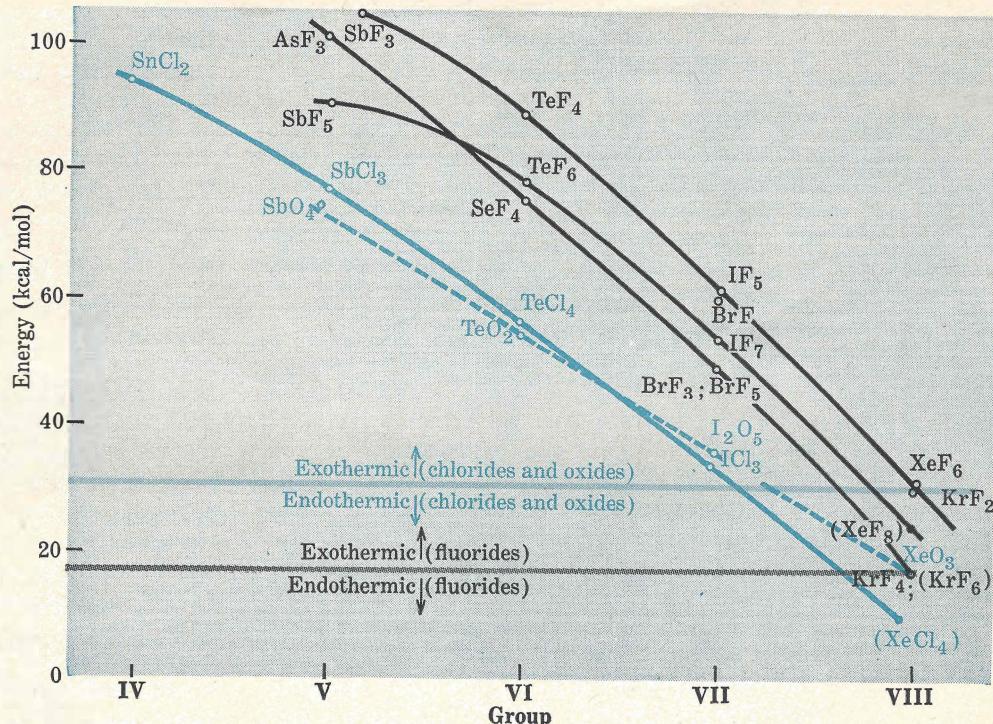


Fig. 4. Average bond energies of related compounds plotted against group in periodic table predict bond energies of hypothetical noble-gas compounds. Compounds in parentheses are not yet known; closed circles are predicted values, open circles are experimental.

his laboratory notebook that afternoon, "Go home somewhat puzzled. Where is the Xe?"

When the experiment was repeated quantitatively, they found that about four parts of fluorine combined with one part of xenon, to make colorless crystals of xenon tetrafluoride,  $\text{XeF}_4$ . Within a few weeks, they and their collaborators at Argonne had also prepared the difluoride and the hexafluoride, the difluoride by irradiating a xenon-fluorine mixture with light from a high-pressure mercury arc, the hexafluoride by heating xenon with a large excess of fluorine at  $300^\circ\text{C}$ .

A number of other xenon compounds have since been prepared; they are listed in Table 1 with their properties.

#### The rest of the nobility

Judging from the ionization potentials, radon should be easier to oxidize than xenon, and thus should have a more extensive chemistry. However, all the isotopes of the gas are short-lived radioactive species, and this causes considerable experimental difficulties. However, Field, Stein, and Zirin of Argonne have managed to establish the existence of a fluoride. Grosse and his co-workers at Temple University made the first krypton compound, which they claim to be krypton tetrafluoride ( $\text{KrF}_4$ ), by passing an electric discharge through krypton/fluorine mixtures at liquid nitrogen temperature. A colorless crystalline material, it is much less stable than its xenon analog; it decomposes rapidly into its elements at  $60^\circ\text{C}$ .

By analogy with  $\text{XeF}_4$ , you would expect  $\text{KrF}_4$  to yield kryptates when hydrolyzed, and indeed the Temple workers have found evi-

dence for an oxygen-containing salt of krypton derived in this way. They have not yet determined its formula, however.

Turner and Pimental at Berkeley irradiated a solid mixture of fluorine and krypton in an argon matrix at  $20^\circ\text{K}$  with an intense light flash, and obtained a chemical species which infrared evidence showed to be krypton difluoride ( $\text{KrF}_2$ ). This method gave no evidence for the formation of an argon fluoride when a solid argon/fluorine mixture was irradiated alone.

So far, no conclusive evidence has been found to support the existence of any argon, neon, or helium halides or oxides.

#### Some thermochemical considerations

What about the theoretical aspects of compound formation in these elements? From a thermodynamic standpoint, noble-gas chemistry turns out to be basically the same as other chemistries. In every reaction, two factors are important: the strength of the bonds formed in the product compared with the bonds broken in the reactants, and the change in disorder (entropy) as you go from the reactant system to the product system. If the bonds in the product are stronger than the bonds that must be broken in the reactants, the reaction will tend to proceed.

The change in entropy in reactions forming noble-gas compounds is almost always negative. Thus, the total energy (enthalpy) of the product system must be large enough to offset the loss, caused primarily by a reduction in the total number of molecules. For example, it requires 36.6 kcal/mole to split molecular fluorine ( $\text{F}_2$ ) into two atoms of fluorine ( $2\text{F}$ ).

Valence	GROUP (Group No. $\equiv G$ )				
	IVa	Va	VIa	VII	VIII
G	$\text{SnF}_4$ $\text{SnCl}_4$	$\text{SbF}_5$ $\text{SbCl}_5$	$\text{TeF}_6$	$\text{IF}_7$	$(\text{XeF}_8)?$
G-2	$\text{SnF}_2$ $\text{SnCl}_2$	$\text{SbF}_3$ $\text{SbCl}_3$	$\text{TeF}_4$ $\text{TeCl}_4$	$\text{IF}_5$	$\text{XeF}_6$
G-4			$\text{TeCl}_2$	$\text{IF}_3$ $\text{ICl}_3$	$\text{XeF}_4$
G-6				$\text{IF}$ $\text{ICl}$	$\text{XeF}_2$ ?

Valence	GROUP (Group No. $\equiv G$ )				
	IVa	Va	VIa	VII	VIII
G	$\text{GeF}_4$	$\text{AsF}_5$	$\text{SeF}_6$		
G-2	$\text{GeF}_2$	$\text{AsF}_3$	$\text{SeF}_4$	$\text{BrF}_5$	
G-4				$\text{BrF}_3$	$\text{KrF}_4$
G-6					$\text{KrF}_2$

Period	GROUP				
	IVa	Va	VIa	VII	VIII
3	Silicon (Si)	Phosphorus (P)	Sulfur (S)	Chlorine (Cl)	Argon (A)
4	Germanium (Ge)	Arsenic (As)	Selenium (Se)	Bromine (Br)	Krypton (Kr)
5	Tin (Sn)	Antimony (Sb)	Tellurium (Te)	Iodine (I)	Xenon (Xe)
6	Lead (Pb)	Bismuth (Bi)	Polonium (Po)	Astatine (At)	Radon (Rn)

Fig. 5. Plotting just the existence of compounds in groups ahead of the noble gases predicts the existence of those that we now know are real.

Thus, 18.3 kcal/mole can be designated the energy of formation of each fluorine atom. Experiments on both xenon tetrafluoride and hexafluoride show the energies per Xe-F bond to be about 32 kcal. This is about 14 kcal more than the enthalpy of formation of the fluorine (see margin); voila, fluorides form easily and are stable.

On the other hand, the average energy associated with each Xe-O bond in xenon trioxide is less than 28 kcal. This is 31 kcal less energy than is required to form atomic oxygen from molecular oxygen, and is in accord with the explosive nature of the trioxide. It also accounts for the lack of success in obtaining the compound from the elements.

Thermochemical calculations can be used to predict the stability of yet uninvestigated compounds. For example, calculations show that xenon oxide tetrafluoride,  $\text{XeOF}_4$ , should be an exothermic, stable compound with an enthalpy of -24 kcal/mole. Xenon dioxide difluoride,  $\text{XeO}_2\text{F}_2$ , on the other hand, should be endothermic and unstable, with an enthalpy of +35 kcal/mole. In fact, the first has already been found; the second has not.

Another method of estimating the average bond energies in unreported compounds is to extrapolate from values for related compounds. Thus, in Fig. 4, we have plotted average bond energies for compounds in the same period of the periodic table. From this it appears that the average bond energy in xenon octafluoride,  $\text{XeF}_8$ , should be about 24 kcal/mol. This would give a standard heat of formation of about -45 kcal/mole, which is certainly exothermic enough to be stable, although the entropy for this reaction is highly unfavorable. A group of Yugoslavian scientists headed by J. Slivnik, has already reported isolating this compound. Although the reported volatility is more than you would expect for an octafluoride.

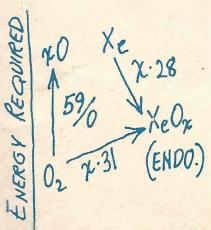
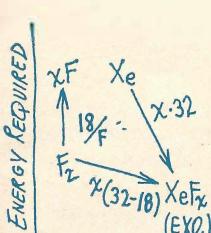
The difficulties of preparing  $\text{KrF}_4$  and its instability also coincide with the extrapolated curves. Krypton difluoride may be more stable than the tetrafluoride. Oxides and chlorides of xenon and krypton should be endothermic, and hence thermodynamically unstable. In fact, only the trioxide and tetroxide of xenon have been isolated.

We must assume that the combination of elements other than those discussed so far with the noble gases will be still less favorable. Only the more electronegative elements will form strong bonds, and only those elements with low heats of atomization will be favorable. Nitrogen, with its high heat of atomization, (113 kcal/mole) would almost certainly render a noble-gas compound endothermic and unstable.

#### Keeping up with the Joneses

Another approach which can supply information about noble-gas chemistry is comparing the chemistry of neighboring atoms within a given period of the periodic table. For example, if you chart the existing fluorides of the elements in the period containing xenon (tin, antimony, tellurium, iodine, and xenon) against their respective group numbers, the valence of the cation turns out to be numerically equal either to the group number, or to the group number minus an even number. Fluorides of xenon are a perfectly normal extension of this tradition, as shown in Fig. 5.

When you do the same thing with the chlorides, however, you get quite a different picture. Chlorine is less able to excite the higher valences; from the trend of the curve, the existence of any xenon chlorides appears un-



likely. A chart of the fluorides of the elements in the period containing krypton also indicates little likelihood of krypton fluorides higher than the tetrafluoride.

It is more difficult to attain valences as high as the group number in the radon period, and analogs of  $\text{XeF}_8$  and  $\text{XeO}_6^{-4}$  would be less likely. In spite of this, however, several compounds appear to be possible, including the fluorides  $\text{RnF}_2$ ,  $\text{RnF}_4$ , and  $\text{RnF}_6$ , as well as a chloride, perhaps  $\text{RnCl}_2$ , and an oxide,  $\text{RnO}_3$ .

### Shapes and more shapes

As far as their molecular shapes are known, the noble-gas compounds are identical to those observed in isoelectronic ions—those groups which on becoming ions gain or lose an electron or two and achieve an electronic configuration identical to those postulated for the noble-gas compounds. For example, the added electron in the iodine dichloride ion,  $\text{ICl}_2^-$ , compensates for iodine's having one less electron than xenon; thus the ion is isoelectronic with xenon difluoride.

Furthermore, the shapes may all be rationalized on the basis of the mutual repulsion of pairs of valence electrons, a useful rule of thumb in predicting shapes. One major point of this rule is that the pairs of electrons in a valency shell of an atom are always arranged basically in the same way, irrespective of whether they are shared with another atom (in which case they are bonding electrons) or not shared (nonbonding). Their basic arrangement depends only on their number. Second, the electrons of a double or triple bond are repelled as a set. Thus, they occupy only a single position in the arrangement, but since they embrace multiple electrons they repel more effectively than a single bond pair. Finally, the nonbonding electron pairs will be closer to the parent atom than the bonding electrons, and have a greater repulsive power.

In xenon difluoride, for example, one electron in each  $\text{Xe}-\text{F}$  bond is contributed by the xenon and one by the fluorine. Thus two xenon electrons of the valence set of eight are involved in bonding, while six are grouped in three nonbonding pairs. Minimum electron repulsion for such a set is achieved by placing the pairs at the points of a trigonal bipyramidal, as shown in Fig. 6. To minimize repulsion between nonbonding pairs, the nonbonding electrons take positions  $120^\circ$  apart, in an equilateral triangle array. The fluorines located above and below this plane each experience repulsion from the nonbonding electron pairs, which will lengthen the  $\text{XeF}$  bonds. This lengthened bond has been verified.

The other cases can be derived in a similar way, and it is noteworthy that the predictions are correct in all *known* cases. The one big problem that still exists is xenon hexafluoride, for which we do not yet know the structure. The electron-pair repulsion rule predicts a

### MOLECULE AND ION SHAPES

Compound	Shape	Configuration	Related Compounds	Bonds	Nonbonding pairs
$\text{XeF}_2$	linear		$\text{ICl}_2^-$	2	3
$\text{XeF}_4$	square planar		$\text{ICl}_4^-$	4	2
$\text{XeOF}_4$	square-base pyramid		$\text{IF}_5$	5	1
$\text{XeO}_4$	tetrahedral		$\text{IO}_4^-$	4	0
$\text{XeO}_3$	trigonal pyramidal		$\text{IO}_3^-$	3	1
$\text{XeO}_6^{4-}$	octahedral		$\text{IO}_6^{5-}; \text{TeO}_6^{6-}; \text{SbO}_6^{7-}$	6	0

● = xenon   ○ = fluorine   ● = oxygen

Fig. 6. Shapes of noble-gas compounds compared with those of neighboring elements, according to electron pair repulsion rule.

nonoctahedral structure, since the xenon will be surrounded by seven electron pairs (as in iodine heptafluoride,  $\text{IF}_7$ , which raised a few questions of its own when it was discovered in 1927), six bonding and one nonbonding.  $\text{XeF}_6$  is isoelectronic with  $\text{IF}_6^-$ , and there is evidence that indicates that this ion is non-octahedral. The infrared and Raman spectra which have been obtained for  $\text{XeF}_6$  cannot be interpreted in terms of an octahedral molecule. Even the lower volatility of the compound compared to  $\text{IF}_7$  is against such an interpretation. On balance, then, I believe that the available evidence favors nonoctahedral symmetry; evidently the compound crystallizes differently from the other hexafluorides, which are without exception octahedral.

### Theories of bonding

It should be obvious by now that the noble gas compounds must owe their existence to the same kind of chemical bonding found in compounds of other elements. Before we discuss the electronic bonding theories advanced, however, let's take a quick look at the basic concepts of atomic structure. The most significant difference between our present view and Bohr's is that electrons cannot be pinpointed, but have only a *probability* of being in a particular location at a given time. These probabilities are expressed as wave functions, which

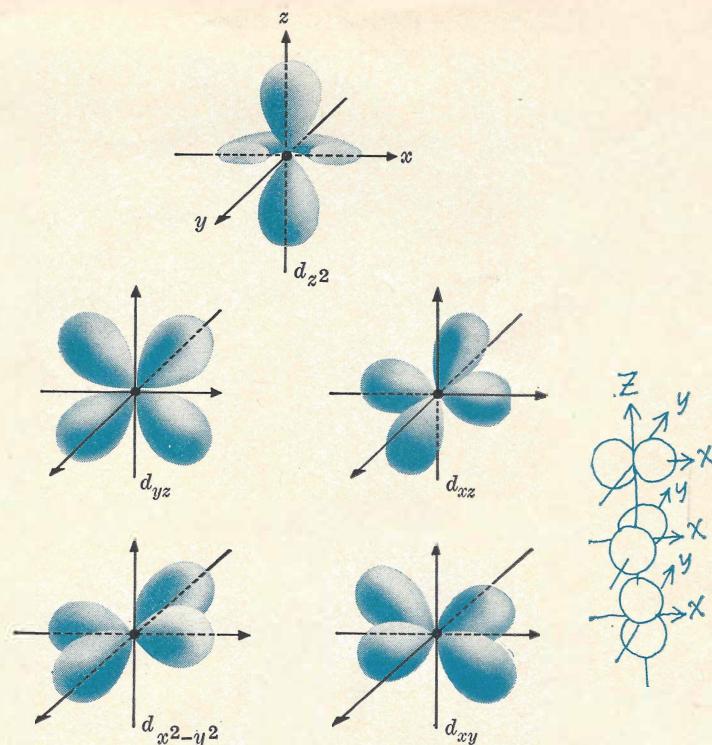
are usually characterized by four constants, the so-called quantum numbers. The principal quantum number,  $n$ , roughly defines the energy of an element,  $l$  defines the shape of the orbital described by the probability wave function, and  $m_l$  defines the orientation of the orbital in space. In addition,  $s$  gives the spin of the electron. Electrons having  $l = 0$  are often called  $s$ , electrons with  $l = 1$  are called  $p$ , while those with  $l = 2$  are called  $d$  electrons. For atoms in which  $n = 3$ ,  $l$  can equal 1, 2, or 3, and  $s$ ,  $p$ , and  $d$  orbitals are available; their shapes are shown in Fig. 7 and the sketch in the margin.

In the isolated hydrogen atom, these different orbitals have the same energy. In more complicated atoms, orbitals of like  $n$  but differing  $l$  are not equivalent. Indeed in xenon, where  $n = 5$ ,  $l$  has the values of 0, 1, 2, 3, and 4, but only the  $n = 5$ ,  $l = 0$  and 1 states are occupied. The eight electrons so contained constitute the outer octet of xenon. The next-highest energy level available to a promoted valence electron is not the  $n = 5$ ,  $l = 2$  orbital set, but the  $n = 6$ ,  $l = 0$ . This is why cesium, the element following xenon, is an alkali metal; its valence shell contains only one electron  $n = 6$ ,  $l = 0$ , which is readily lost.

All electronic theories of chemical bonding are based on these atomic orbitals, and all fall into one or the other of two different approaches. In the *valence-bond method*, chemical bonds are discussed in terms of the overlap of atomic orbitals. The greater the overlap, or interpenetration, of the electronic orbital "clouds" associated with the interacting orbitals, the higher the electron density between the nuclei, and the greater the attraction—the bond. Thus, a hydrogen molecule is formed from two spherical hydrogen atoms, whose orbitals overlap as shown in the margin.

In hydrogen, the interacting atoms use pure atomic orbitals; in other cases, however, experience demands that rather different orbitals should be used. For example, carbon contains one  $2s$  and two  $2p$  orbitals. Overlapping these orbitals, however, does not give the tetrahedral symmetry observed experimentally in carbon compounds. It is therefore necessary to postulate that the carbon orbitals are mixed, or hybridized, to give four equivalent orbitals, called  $sp^3$  hybrids. This involves the "promotion" of one  $s$  orbital electron.

A hybridization scheme may also be invoked to account for the octahedral molecule of sulfur hexafluoride,  $SF_6$ , which involves two high-energy  $3d$  orbitals to give the required hybrid set of  $sp^3d^2$  orbitals. Extending this approach to the noble gases, xenon difluoride, as a linear molecule, would use two  $sp$  hybrids of the xenon to overlap with  $p$  orbitals of the fluorine atoms. The six remaining nonbonding xenon electrons would then be housed in three "hybridized" xenon orbitals, involving either the  $6s$ ,  $4f$ , or  $5d$ .



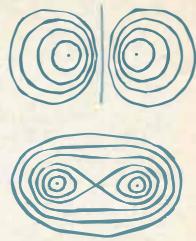
*Fig. 7. Three p orbitals (marginal) are equivalent in energy, except for orientation, as are the five d orbitals (above). Because of their directionality, however, they react differently in the presence of other atoms or molecules.*

Similarly in the tetrafluoride, which is square planar in structure, the valence-bond approach would allow the use of a high-energy  $d$  orbital to attain an  $sp^3d$  hybrid set of bonding orbitals; a second high-energy orbital and the remaining  $p$  orbitals of the valence set would house the four nonbonding electrons. Xenon hexafluoride, with six bonding electron pairs and one non-bonding electron pair, would involve three orbitals of higher energy than the valence set. If, as the electron-pair repulsion theory predicts, the nonbonding pair is effected by spatial or steric considerations, then the molecule would not be octahedral, and a hybridization scheme for the xenon orbitals such as  $sp^3d^3$  or  $sp^3f^3$  would be appropriate.

Many chemists are unhappy with the use of high-energy orbitals in bonding such molecules as  $SF_6$ , and lately a simple *molecular orbital* approach has found support. A molecular orbital, or M.O., is the molecular counterpart of an atomic orbital: true M.O.'s belong to the entire molecule. They are generally less precisely defined than atomic orbitals, and in fact are generated by a suitable linear combination of the mathematical expression for the atomic orbitals. The number of molecular orbitals is equal to the number of participating atomic orbitals.

In forming a hydrogen molecule, for example, the two  $1s$  orbitals give rise to two





molecular orbitals, one bonding (lower-energy configuration) and one antibonding (higher-energy) as shown in the margin. Since each molecular orbital, like each atomic orbital, can contain only two electrons, the two electrons of the hydrogen molecule reside in the bonding orbital. In contrast, the atom of helium contains two electrons already; thus both the bonding and antibonding orbitals are filled, and helium remains monatomic—forming an  $\text{He}_2$  molecule would offer no advantage in energy over two separate atoms.

Now a true M.O. extends over all atoms in a molecule; it is multicentered. A bonding M.O. containing two electrons will therefore tend to hold all of the atoms in a molecule together. The bonding stability will, however, depend on the number of such bonding M.O.'s in the molecule; if there should be only one bonding orbital in a molecule with  $n$  atoms, (and there is no filled antibonding orbital) the interatomic linkages will be only about  $1/n$  as strong as an electron-pair bond. In the linear iodine dichloride ion  $[\text{Cl}-\text{I}-\text{Cl}]^-$ , physical evidence shows that essentially only the  $p$  orbitals of the iodine can be involved in bonding. Similar evidence shows that  $p$  orbitals are also responsible for the bonding in the square planar  $[\text{ICl}_4]^-$  ion.

Molecular orbital theorists have widely assumed that similar situations will obtain in the molecules of  $\text{XeF}_2$  and  $\text{XeF}_4$ , which are pseudo-isoelectronic with the iodine chlorides, and have used the theory without significant modification to describe these compounds. In  $\text{XeF}_2$ , they assumed that a  $p$  orbital of the xenon valence set combines with two fluorine  $p$  orbitals to give rise to one bonding M.O., one nonbonding M.O., and one antibonding M.O. The two  $\text{XeF}$  bonds therefore are both dependent on a single bonding electron pair; consequently the bonds should be rather long and ionic. The electron pair repulsion theory also predicts a long bond. M.O. theory accounts for xenon tetrafluoride in the same way, with two xenon  $p$  orbitals interacting with pairs of fluorine atom orbitals.

In the hexafluoride, all three xenon  $p$  orbitals are involved in creating three-center M.O.'s (two F, one Xe). The  $p$  orbitals are mutually at right angles; thus the theory predicts the tetrafluoride to be square planar and the hexafluoride to be octahedral.

The symmetries observed for the difluoride and the tetrafluoride confirm those predicted by *both* theoretical approaches. However, the hexafluoride, still unmeasured because of experimental difficulties, is indicated to be non-octahedral on the balance of experimental evidence. This would be compatible with valence bond theory and would, of course, imply the involvement of high-energy xenon orbitals. Experimental verification of the shape is thus being pressed with great interest.

From the preceding discussion, it should

be obvious that the range of stable compounds of the noble gases will probably never become extensive. In all probability the fluorides or fluorine-containing compounds of kryptons, xenon, and radon, and perhaps chlorides and oxides of the latter will be the only thermodynamically stable noble-gas compounds. We may be able to prepare kinetically stable oxygen-containing salts of radon and krypton, however, and as in the case of the xenates and perxenates, these should be powerful oxidizing agents.

#### Where to from here?

It is unlikely that the noble gases will form even metastable compounds with elements less electronegative than chlorine, but it may prove possible to link complex groups of high electronegativity to xenon atoms *already* linked to fluorine. Thus it will be worthwhile expending some effort to prepare compounds such as  $\text{F}_5\text{XeNF}_2$ ,  $\text{F}_5\text{XeCF}_3$ , and even  $\text{F}_5\text{XeSF}_6$ .

There appears to be no reason why xenon or the other noble gases should form compounds in which the noble gas acts as an electron acceptor, to become a negative ion. True helides, xenides, and the like, for example, seem most unlikely. However, in view of the claims by chemists, respected for their skill and veracity, for compounds of the gases with mercury and other metals, the whole subject should be reinvestigated.

Presumably the xenon fluorides will find use as fluorinating agents in preparing fluorides of other elements in high-valent states. Such reactions would be "clean"; the reduction product of the fluorinating agent will be relatively inert xenon, which would simply bubble off to be recovered. The explosive oxides may find an application where oxygen is needed rapidly in high concentration; decomposition products would be gases.

Much more certainly, a number of uses will be found for the easily stored, thermally stable alkali perxenates. They are strong oxidizing agents; their reduction products are merely the alkali oxides of hydroxides and xenon.

Radon compounds could be interesting as sources of alpha particles. They could be deposited at any site in a properly designed apparatus, and be built up in a probe to any desired level. When necessary, the radon could be easily removed from the site by chemically reducing the compound.

Undoubtedly the greatest immediate effect of the discovery of simple chemical compounds of the noble gases has been its effect on the attitude of the average chemist. It has removed inhibitions and has given an injection of healthy scepticism to a generation which had become overly theoretical in its approach to what is still very much an experimental science.

*For what little additional information there is on the subject, see To Dig Deeper, page 103.*

# DO SCIENTISTS NEED A COMPREHENSIVE INDEX TO ALL OF SCIENCE?

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found in "Magnetohydrodynamics—Future Power Process?" by Sporn and Kantrowitz, *Power*, Nov. 1959. To gage the enthusiasm of the Russians for MHD power generation, see the article "Power Stations of the Future" in *Svetskaya Litva*, Mar. 1961. The possible coupling of nuclear heat sources to MHD generators is discussed in "MHD Power Generation" by Gundson, Smith, Tsu, and Wright, *Nucleonics* 21, 7 (1963). A more detailed account of MHD work going on in the authors' laboratories is presented in Brogan's "MHD Power Generation," *IEEE Spectrum*, Feb. 1964. Readers interested in the process of nonequilibrium ionization should scan Rosa's "Nonequilibrium Ionization in MHD Generators," *Proc. IEEE* 51, 5 (1963).

The day-to-day literature of the field is heavy going, but recent papers may be found in *Proc. of the 5th Symposium on the Engineering Aspects of Magnetohydrodynamics* (April 1964 at MIT); write Prof. W. Heiser, Dept. of Mechanical Engineering, MIT, Cambridge 39, Mass. The world-wide interest in this field is well illustrated by papers given at the recent (July 6-11, 1964) International Symposium on Magnetohydrodynamic Electrical Power Generation in Paris. For a booklet of lengthy abstracts and the 20-page summary of this meeting prepared for ENEA by Satkowski of ONR write to H. B. Smets, Research Office, European Nuclear Energy Agency, OECD, 38 Blvd. Suchet, Paris 16.

There is, as yet, no single book on MHD power; however, two useful volumes are Cambel's *Plasma Physics and Magnetofluid-mechanics* (McGraw-Hill, 1963, \$11.50) and Spitzer's *Physics of Fully Ionized Gases* (Interscience, 1956, \$5).

## NOBLE-GAS COMPOUNDS 56

The literature of the reactions of these elements is naturally sparse, except in recent review articles, with one notable exception. A book called *Noble-Gas Compounds*, edited by Hyman, reproduces a symposium held at the Argonne National Labs about one year after the initial discoveries; and it's good (U. of Chicago Press, 1963, \$12.50).

A shorter review is by Chernick, "Chemical Compounds of the Noble Gases" (*Record of Chemical Progress* 24, No. 3, 1963). If you'd like to read about some frustrations accompanying the discovery and characterization of the noble gases, try *A Life of Sir William Ramsay* by Travers (Edward Arnold Publ., Ltd., London, 1956, \$10). It's complete and recent. Finally, a two-volume treatise on the gases themselves has recently come out, edited by Cook (Interscience, 2 vols., 1961, \$17.50 each).

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