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NOBLE-GAS CHEMISTRY AND ITS SIGNIFICANCE

Neil Bartlett

November 1971

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THE DANNIE-HEINEMAN PRIZE ADDRESS

Göttingen, Germany
November 26, 1971

"Noble-Gas Chemistry and Its Significance"

By Neil Bartlett

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When, in 1962, chemists were informed that a compound of a noble-gas had been prepared¹, there was much expression of surprize and initially even disbelief.

Faith in the chemical inertness of the noble gases had been fostered in part by previous failures to prepare compounds. The greatest prejudice, however, derived from the electronic theories of the chemical bond, which stressed the noble-gas electron arrangement as the ideal to which all other atoms tended.

Although, when the noble gases were discovered², in the last years of the 19th Century, they were unexpected, they were quickly recognized as a new Group of elements of Mendeliev's Table of The Elements. This new Group of elements fitted naturally into the "Table", each noble-gas being located between a halogen and an alkali metal. Since the Halogens included the most strongly oxidizing elements, whereas the Alkali Metals were the most strongly reducing elements of the Periodic Table, it was appropriate, for the intervening group of elements, to exhibit neither oxidizing nor reducing properties, i.e., to be chemically unreactive. All efforts to oxidize or reduce helium and argon (i.e., to bring them into chemical combination with other elements) failed², perhaps the most significant failure being Moissan's attempt in 1895 to prepare an argon fluoride³. The rarer noble gases were not subjected to the same intensive chemical investigation, and no claim for chemical activity of the gases was sustained prior to 1962.

When the electronic theories of chemical bonding were developed it was natural that the chemical inertness of the noble gases should be expressed in the theory. In their pioneering papers of 1916, both

W. Kossel⁴ and G. N. Lewis⁵ emphasized the ideality of the noble-gas configuration. An atom of an element other than a noble-gas was represented as gaining or losing electrons until its electron arrangement resembled that of a neighbouring noble-gas atom. Thus, as may be seen from Table I, Kossel suggested⁴ that the elements of Groups I, II,

Table I (from W. Kossel⁴)

Gruppen													von Elek- tronen (Funktion)
IV	V	VI	VII	I	II	III	IV	V	VI	VIII			
Aufnahme (negative)					Abgabe (positive)								
- 4	- 3	- 2	- 1	0	+ 1	+ 2	+ 3	+ 4	+ 5	+ 6	+ 7	+ 8	
				He	H ₂ (H ₂ O)	Be (BeO)	B (B ₂ O ₃)	C (CO ₂)	N (N ₂ O ₅)	O (—)	F (—)		
C (CH ₄)	N (NH ₃)	O (OH ₂)	Fl (FlH)	Ne	Li (Li ₂ O)	Mg (MgO)	Al (Al ₂ O ₃)	Si (SiO ₂)	P (P ₂ O ₅)	S (SO ₂)	Cl (Cl ₂ O ₇)		
Si (SiH ₄)	P (PH ₃)	S (SH ₂)	Cl (ClH)	Ar	K (K ₂ O)	Ca (CaO)	Sc (Sc ₂ O ₃)	Ti (TiO ₂)	V (V ₂ O ₅)	Cr (CrO ₃)	Mn (Mn ₂ O ₇)		
Ge (GeH ₄ ?)	As (AsH ₃)	Se (SeH ₂)	Br (BrH)	Kr	Rb (Rb ₂ O)	Sr (SrO)	Y (Y ₂ O ₃)	Zr (ZrO ₂)	Nb (Nb ₂ O ₅)	Mo (MO ₃)	unbe- kannt	Ru (RuO ₄)	
	Sb (SbH ₃)	Te (TeH ₂)	J (JH)	X	Cs (Cs ₂ O)	Ba (BaO)	La (La ₂ O ₃)	Ce (CeO ₂)	Pr (Pr ₂ O ₃)?	Nd (Nd ₂ O ₃)?			
				Eman.	—	Ra (RaCl ₂)	—	Th (Th ₁ O ₃)	—	Ur (UrO ₃)			

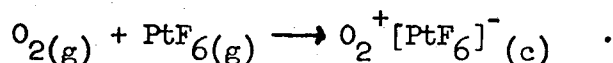
III, IV and V of the Periodic Table, in their oxides, lose 1, 2, 3, 4 and 5 electrons respectively, to the oxygen atoms. Each element, in its highest oxide, thereby diminished its electron complement to that of the immediately preceding noble gas. On the other hand, for the

hydrides of the elements of groups IV, V, VI and VII, Kossel proposed that each atom of these groups, acquire 4, 3, 2 or 1 electron respectively. Each atom of these groups thus increased its electron complement to that of the succeeding noble-gas. Kossel, in his theory, visualized complete electron transfer between the bonded atoms, whereas Lewis⁵, although allowing the appropriateness of complete electron transfer in some cases, stressed a sharing of electrons between the chemically bound atoms. By suitably sharing electrons, Lewis demonstrated that the great majority of the known chemical compounds could be rationalized in terms of each atom attaining a noble-gas electron arrangement. Thus he represented the diatomic molecule of hydrogen, H₂, as H:H, the symbol, :, implying the pair of electrons for the combined molecule. This pair of electrons, placed between the positively charged kernels (nuclei, in this case) accounted for the binding of the molecule, and, being shared equally between the two atoms, provided each atom of the molecule with an approximation to a helium configuration. In like fashion, Lewis represented the water molecule as H:Ö:H, the symbol, Ö, being the Kernel, or chemically invariable part of the oxygen atom, and electronically equivalent to the helium atom. Thus, by sharing a pair of electrons with each hydrogen atom, the oxygen atom approximates its electron arrangement to that of the next noble-gas, which is neon. The hydrogen atoms again tend to a helium-like electron arrangement.

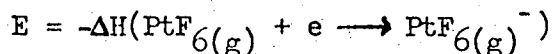
The Kossel and Lewis theories unified and correlated much of what was then known of the bonding capabilities of the chemical elements. The theories quickly had wide appeal. Since the electron arrangements of the noble gases were evidently the ideal arrangements, to which all

other atoms aspired, the chemical inertness of the gases was self evident, at least at a superficial level of inspection. Unfortunately in the inevitable shorthand of convenient description, the noble-gas electron arrangements were usually represented by the group term "octet", this being (except in helium, which possesses a "duet") the outermost set of electrons of the noble-gas atom. This common term helped to foster the illusion that all noble-gas electron configurations are essentially the same and of the same stability. They are not.

Of prime importance to the discovery of the chemical activity of the heavier noble gases was the discovery⁶ by Bartlett and Lohmann of the remarkable oxidizing properties of the gaseous compound platinum hexafluoride. In 1962 they had established that a red solid, prepared by burning platinum or platinum compounds in fluorine in glass apparatus, was the salt, dioxygenyl hexafluoroplatinate, $O_2^+[PtF_6]^-$. This salt was especially noteworthy for its cation, O_2^+ . The salt formulation implied that the free hexafluoride (which had previously been reported, in 1957, by Weinstock, et al⁷, of The Argonne National Laboratory) should be capable of spontaneously oxidizing molecular oxygen. This proved to be so:



The two gases combined immediately to provide the now familiar salt $O_2^+[PtF_6]^-$. Although the salt formulation had seemed appropriate much earlier in the investigation, it had posed the difficulty that in order for the oxidation of molecular oxygen to proceed spontaneously, the electron affinity for the platinum hexafluoride,



needed to be greater than $160 \text{ kcal/mole}^{-1}$ (that is, approximately twice the value for atomic fluorine or atomic chlorine. Now, with the spontaneous oxidation of oxygen and the salt formulation proved, it was clear that platinum hexafluoride was the most powerful oxidizer available hithertoo. At this point, Bartlett noted that the ionization potentials of the noble gases decreased markedly, with increasing atomic number as shown in Table II.

Table II
Atomic Radius and First Ionization Potential

Noble-Gas	For Each Noble-Gas					
	He	Ne	Ar	Kr	Xe	Rn
Radius (Å) ^(a)	1.3	1.6	1.92	1.98	2.18	--
First Ionization Potential (eV) ^(b)	24.586	21.563	15.759	13.999	12.129	10.747

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

b. Ref. (a) p. 237.

It was evident that the heavier gases should be more easily oxidizable than the lighter. ** Most importantly, the ionization potentials of xenon (12.2 eV) and radon (10.7 eV) were as low as, or lower than, molecular oxygen (12.2 eV). Radon being difficult to

handle as a consequence of the short life and α -particle activity of all of its isotopes, the oxidation of xenon appeared to be the easiest noble-gas oxidation to carry out.

Xenon gas proved to be as easy to oxidize as molecular oxygen. An orange-yellow solid formed rapidly in the spontaneous gas-gas reaction and was designated xenon hexafluoroplatinate $\text{Xe}^+[\text{PtF}_6]^-$.[†] Clearly, the xenon electron arrangement was not chemically inviolate!

When this oxidation of xenon by platinum hexafluoride was reported¹ it was immediately repeated at the Argonne National Laboratory and, there, similar studies were also carried out with the related hexafluorides ruthenium hexafluoride and plutonium hexafluoride⁹. The products of the ruthenium hexafluoride-xenon reaction appeared to contain ruthenium

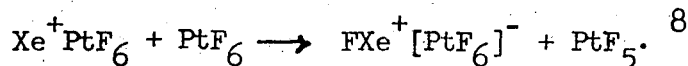
Although the greater sizes of the more easily ionizable gases is somewhat disadvantageous to bond formation, this adverse size effect is much less significant than the ionization potential influence.

†

Subsequent investigation showed that the product of the xenon/ PtF_6 reaction is more complex. Two reactions occur, the first being:



followed by interaction of any excess PtF_6 with the first product:



pentafluoride and this observation suggested that xenon fluorides should exist.

The first xenon fluoride to be reported¹⁰ was the tetrafluoride prepared by Claassen, Selig and Malm of the Argonne National Laboratory. Independent study of the xenon-fluorine system by Hoppe and his coworkers¹¹ in Giessen, Germany, led to the isolation of a difluoride. Within a few weeks the fluorides XeF_2 , XeF_4 , XeF_6 and the oxyfluoride XeOF_4 were known and within nine months, of the first report, the first conference on Noble-Gas Chemistry was called and met at The Argonne National Laboratory. More than fifty papers were contributed in the two day meeting and the proceedings subsequently appeared as a 400 page volume¹². (Figure 1 provides the properties of some of the known compounds of the noble gases.)

(Figure 1)

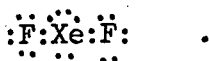
During the April 1963 meeting the range of noble-gas chemistry was rather well defined. As might have been expected, the nature of the bonding in the new compounds evoked the greatest interest and discussion. Since that time important physical details of the properties of the compounds have been accumulated and the nature of the bonding is now rather well defined.

To appreciate the nature of the bonding in the noble-gas compounds it should be noted that the following conditions apply to compound formation: (1) only the heavier, more easily ionized gases form compounds, and (2) only the most strongly electron withdrawing atoms or groups make bonds to the noble-gas atoms.

It is clear that compound formation depends upon electron removal from the noble-gas atom. Table II gives the first ionization potential and the atomic radius for each of the noble-gas atoms. It should be noted that the bigger the atom the further are its outermost electrons from the positively charged nucleus (which is virtually a point charge). The bigger atoms therefore lose their electrons more readily than the smaller.

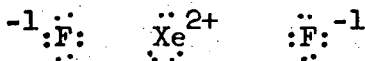
If fluorine atoms bond to a noble-gas atom it is essential that the latter should give some of its electrons to the fluorine atoms. If we apply either of the classical models (either that of Kossel or that of Lewis) we recognize that the fluorine atom, by acquiring an electron, or a share in an electron, attains a neon-like electron arrangement. The electron arrangement of the noble-gas atom, in such a bonding situation, must, simultaneously, become less perfect. A detailed appraisal of the bonding in xenon difluoride is illustrative.

If we insist on each fluorine atom, in xenon difluoride, being bound to the xenon atom by an electron-pair bond, the Lewis dot formula would be:



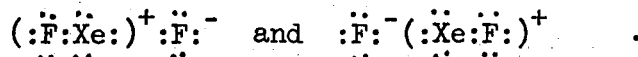
With this model, we see that the xenon atom possesses an electron arrangement (including shared electrons) amounting to 10 in number. But a xenon atom has no affinity for electrons. Furthermore, the criteria, previously mentioned, for bond formation in noble-gas compounds, indicate that the noble-gas atom, as a result of bonding, should suffer a net loss in its electron complement. The classical Lewis electron pair model must therefore be judged to be unsatisfactory.*

It should also be appreciated that the classical Kossel representation of bonding in XeF_2 , would be:



This leaves the xenon atom two electrons short of the noble-gas configuration. Since the noble-gas electron arrangement is evidently such a favourable one elsewhere in chemistry, it is disturbing to have to abandon it completely at this point.

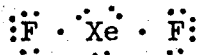
It is a happy but perhaps not too unexpected finding, that the best model for the bonding in the noble-gas compounds is essentially a mixture of aspects of both the Lewis and Kassel models. Thus, as first pointed out by Coulson¹⁴, we can write XeF_2 as a fusion of equal weights of the two (canonical) forms:



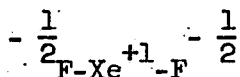
The cation is a classical Lewis electron pair species. The anion has attained its neon-electron arrangement by complete electron acquisition, as in a Kossel description. The new ingredient in the bonding description is the canonical-form-fusion, called resonance.¹⁵ We can, however, represent the bonding in an equivalent manner and avoid the concept of resonance, if we adapt the classical Lewis electron dot representation

* The success of valence electron pair repulsion theory¹³ in accounting for the molecular geometry of each of the known noble-gas compounds, has led many to the erroneous conclusion that the halogen-noble-gas bonds (e.g., Xe-F) are electron pair bonds. Similarly the oxygen-noble-gas bonds have erroneously been visualized as four electron bonds.

as first suggested by Bilham and Linnet¹⁶:

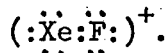


This implies that each fluorine atom acquires a share in one xenon electron and it thus becomes approximately neon-like. At the same time the xenon atom, although no longer having a perfect noble-gas electron arrangement, does retain the form of such a configuration. We note that if each of the single, bonding electrons, is equally shared between the xenon atom and the fluorine atom, the molecule will have a net charge distribution:



This bond polarity is in harmony with the known enthalpy of sublimation of the difluoride^{17,18} and with its other physical properties¹⁹. In this last description of XeF₂ we have used the Lewis concept of shared electrons, for the generation of noble-gas electron arrangements. It should be noted, however, that the xenon-fluorine bonds in XeF₂ are, in effect, single-electron bonds.

It will be recognized that if a fluoride ion is removed from the XeF₂ molecule: XeF₂ — XeF⁺ + F⁻, the resulting cation is an electron pair bound species



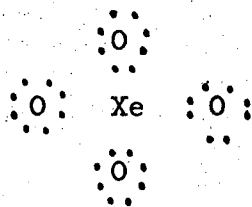
If therefore, the single electron bond representations for the XeF₂ molecule are valid, the XeF⁺ salts should exhibit shorter stronger bonds than in XeF₂ itself. We have particularly addressed ourselves to this question in recent years. Vibrational spectroscopic⁸ and crystallographic studies^{20,21} have confirmed that the removal of a fluoride ion from the

XeF₂ molecule leaves a residual bond which is much shorter and stronger than in XeF₂ itself. The structural and vibrational spectroscopic findings are given in Figure 2. It is persuasive that if we accept a

(Figure 2)

bond order of 0.5 (a one electron bond) as appropriate for the bond length of 2.01 Å reported²² for XeF₂, the bond length predicted, from an empirical Pauling equation,²³ for the cation XeF⁺ (bond order one) is 1.83 Å. This is very close to the bond length of 1.84 Å given²¹ for the residual XeF species in the structure of FXeSb₂F₁₁, as reported by Peacock and his coworkers.

Similar bonding models apply to the other noble-gas compounds. Thus XeF₄ can be represented in terms of the XeF₂²⁺(F⁻)₂ canonical forms and XeF₆ in terms of XeF₃³⁺(F⁻)₃ forms, or, equivalently, as Xe(·F)₄ and Xe(·F)₆. The oxides on the other hand are electron-pair bound. Thus xenon tetroxide may be represented simply by the Lewis formula:



This automatically implies an appreciable positive charge on the xenon atom (+4 for equal sharing of the electron pairs). Since the Xe-O bond is an electron-pair bond we expect a shorter stronger bond than in the fluorides. It is impressive that the Xe-F bond length in XeF₆ is 1.89 Å²⁴ whereas in XeO₃ the Xe-O bond length is 1.76 Å²⁵.

We can conclude that it remains true that the noble-gas electron arrangement is a peculiarly stable arrangement, which all non-transition-element atoms attain, or retain. The heavier noble gases are not

exceptional to this rule. Of crucial importance to the understanding of noble-gas chemistry, however, is the lower stability of the electron arrangements of the heavier gases relative to the greater stability of the lighter-gas electron configuration (particularly that of neon). The octet is of paramount importance, the electron-pair bond is not.

It is a tribute to the great insight of W. Kossel that, in his 1916 paper⁴, he recognized the inequality of the noble-gas electron arrangements, which, we have seen, underlies noble-gas chemistry. After pointing to the ionization potential data then available for the noble gases, he remarked: "Für die Beurteilung der exzeptionellen Stellung der Edelgase wäre es demnach von höchster Wichtigkeit, zu wissen, ob analog etwa zum Jodfluorid auch ein Xenon- oder vielleicht auch Kryptonfluorid existenzfähig ist, oder deren Existenz mit Schärfe ausschliessen zu können — auf jeden Fall ist eine solche Bindung durch das negativste Element für diejenige Form zu halten, in der sich am ehesten ein Edelgas in eigentlicher Valenzbetätigung in ein binäres Molekül mass einfügen lassen."

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Figure 1

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Figure 1

Some Simple Noble-Gas Compounds
(Interatomic distances in Angstrom Units)

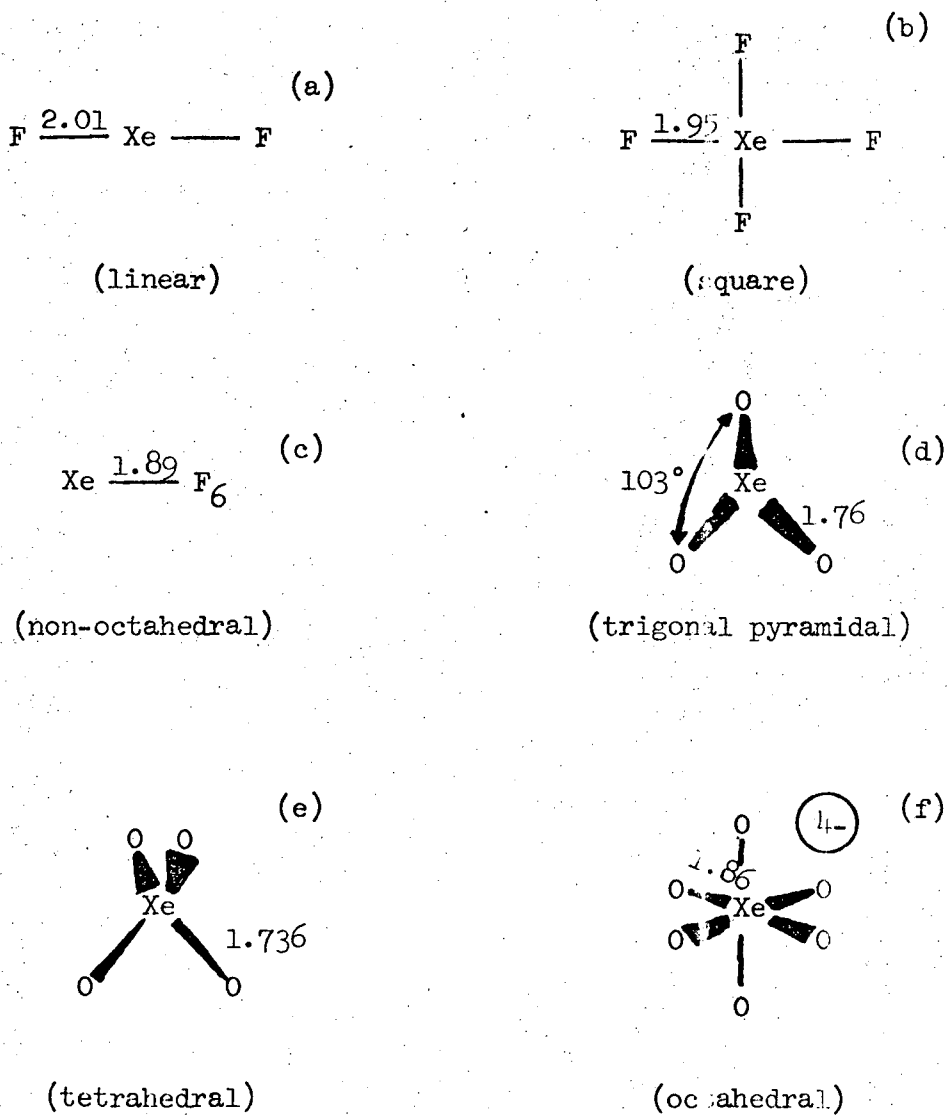
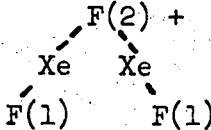


Figure 2
The Xe^{II}-F Bond

<u>Species</u>	<u>Bond Lengths (Å)</u>		<u>Bond Order*</u>		<u>Stretching</u> <u>Frequency (cm⁻¹)</u>
	<u>Xe-F(1)</u>	<u>Xe...F(2)</u>	<u>Xe-F(1)</u>	<u>Xe-F(2)</u>	<u>Xe-F(1)</u>
F(1)-Xe-F(1)	2.01	--- (a)	0.5 [†]		497
	1.90	2.14 (b)	0.7 ₆	0.3	588
F(1)Xe..F(2)RuF ₅	1.88	2.2 (c)	0.8 ₃	0.2	604
F(1)Xe..F(2)SbF ₄ FSbF ₅	1.84	2.35 (d)	0.9 ₆	0.1 ₃	621
XeF ⁺	1.83		1.0		

* From the Pauling equation^(e): $(n/2) = r(1) - 0.60 \log n/2$, where n is the bond order and r is the bond length (Å).

[†] Assumed value.

(a) Ref. 22; (b) F. O. Sladky, P. A. Bulliner, N. Bartlett, B. G. DeBoer, and A. Zalkin, Chem. Commun., 1968, 1048 and Ref. 8; (c) Ref. 20; (d) Ref. 21;

(e) Ref. 23.

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