FLUORIDES OF XENON AND RADON

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Until recently it was universally considered that the so-called inert, or noble gases — helium, neon, argon, krypton, xenon, and radon — differ sharply from all the other elements in that they do not react chemically, either with one another, or with any other substance. By virtue of this peculiarity they occupy a special place in the Periodic System — Group 0.

Experiments to disprove the hypothesis of the inertness of the Group 0 elements have been undertaken more than once. Thus, there have been papers on the existence of "compounds" of helium with certain metals (mercury, tungsten, platinum, palladium, bismuth, iron, etc.), but it is improbable that chemical reaction occurred in these cases.

Clathrate compounds of argon, krypton, and xenon with β-hydroquinone, phenol, and water have been obtained[1-4]. It is known that in such compounds there is no chemical reaction between the crystal lattice of the clathrate-forming compound and the gas molecules occluded in the lattice vacancies[5].

Claims concerning the preparation of compounds of the inert gases with molecules having strong electron-acceptor properties, such as BF_3 or $B(CH_3)_3$, have not been confirmed subsequently[6].

Band spectra observed in an electric discharge were ascribed to XeO and KrO molecules but corresponding stable compounds were not isolated[7].

Very recently it has been claimed that at least two inert gases — xenon and radon — are able to form chemical compounds.

Bartlett[8] first published an account of the preparation of a complex which contained xenon, $XePtF_6$. This complex, obtained by direct reaction of xenon and platinum hexafluoride in the gas phase, is an orange-yellow solid, insoluble in carbon tetrachloride and having a negligibly small vapour pressure at room temperature. The compound sublimes on heating in a vacuum; on exposure of the sublimate to water vapour it is rapidly hydrolysed with liberation of xenon and oxygen (the composition of the liberated gas was established by mass spectroscopy) and precipitation of hydrated platinum dioxide:

$$2XePtF_6 + 6H_2O \longrightarrow 2Xe + O_2 + 2PtO_2 + 12HF.$$

By analogy with the complex $O_2^+[PtF_6]^-$ obtained earlier by Bartlett and Lohmann[9] the xenon compound was given the structure $Xe^+[PtF_6]^-$. The basis for such an analogy was provided, firstly, by the identical method of making both compounds and the similarity in their formulae, and secondly by the closeness of the ionisation potentials of the oxygen (12.2 eV)[10] and xenon (12.13 eV)[10] molecules, which makes it plausible that xenon is oxidised by the platinum hexafluoride to form the positive ion Xe^+.

Calculation of the lattice energy of $Xe^+[PtF_6]^-$ by Kapustinskii's equation[11] gave the value of ~100 kcal mole^{-1}, *i.e.* in all, ~10 kcal mole^{-1} less than for $O_2^+[PtF_6]^-$. Hence, assuming the compound to be ionic, a minimum value of 170 kcal mole^{-1} was found for the electron affinity of the hexafluoroplatinum, more than twice the corresponding value for the fluorine atom (~83 kcal g-atom^{-1})[12].

Somewhat later, Bartlett's experiments were reproduced, and furthermore it was shown that xenon reacts at room temperature with RuF_6 and PuF_6, but not with the hexafluorides of uranium, neptunium, or iridium[13].

Recently Claassen *et al.*[14] reported the production of xenon tetrafluoride XeF_4, a stable solid at room temperature, and gave preliminary results of the investigation of certain chemical and physical properties of this compound. Somewhat more detailed information concerning the physicochemical properties of XeF_4 and the possibility of existence of other fluorides of xenon was published soon afterwards by a group of investigators which include the authors mentioned.

To prepare xenon tetrafluoride, one part of xenon and about five parts of fluorine were mixed under pressure in a nickel vessel, the mixture of gases was heated to 400° for an hour and then rapidly cooled on the water-bath to room temperature. The atomic ratio of fluorine to xenon in the product was determined by weighing the nickel vessel before and after admitting the xenon and on finishing the reaction, and also by evacuating, freezing, and weighing the unreacted fluorine (with excess of fluorine all the xenon took part in the reaction). The F : Xe ratio in four experiments was 4.05, 3.92, 3.91, and 3.97, which closely corresponds to the formula XeF_4. Another method of finding the composition of the compound, leading to the same formula, was to reduce a weighed specimen of the substance with hydrogen at 400°. The reduction was found to take place by the reaction:

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF,$$

with formation of xenon and hydrogen fluoride.

Xenon tetrafluoride is a colourless solid with a vapour pressure negligibly small at -78° and equal to ~3 mm Hg at room temperature; it readily sublimes at ordinary temperatures. Specimens sealed under vacuum in a glass tube form coarse colourless crystals after a few hours.

Xenon tetrafluoride is stable at room temperature and can be stored for quite a long time in nickel or glass containers. No decomposition of the XeF_4 or reaction with the glass was observed during storage in a Pyrex vessel for more than six weeks. In a thin-walled capillary of Pyrex glass XeF_4 did not melt below 100°.

Dilute solutions of NaOH or water hydrolyse xenon tetrafluoride to form a yellow product, which slowly dissolves to form a transparent pale-yellow solution. Analyses for total fluorine support the following equation for the hydrolysis:

$$XeF_4 + 2H_2O \longrightarrow Xe + O_2 + 4HF,$$

but the quantity of gas evolved and the xenon : oxygen ratio did not agree with this equation.

The yellow alkaline solution can be evaporated to dryness without loss of xenon by use of a heater lamp. If the solution is previously acidified, then xenon is liberated during the evaporation. These results show that hydrolysis of XeF_4 proceeds by a complex mechanism and that in the aqueous solution there are xenon compounds, possibly in ionic form.

Xenon tetrafluoride does not dissolve in perfluoroheptane and does not react with it, but it dissolves with reaction in benzene. It dissolves readily in anhydrous hydrogen fluoride without reaction; at -78° the solubility is <1 mg ml^{-1} and at 60° exceeds 100 mg ml^{-1}. Such solutions do not decompose when stored for two weeks in poly(chlorotrifluoroethylene) vessels. The electrical conductivity of solutions of XeF_4 in HF is small. Since hydrogen fluoride is a good ionising solvent, the low conductivity of solutions of XeF_4 in it shows that there is little probability of ionic reactions occurring and excludes the possibility of an ionic mechanism for the fluorination reaction.

The absorption spectrum in the region from 50 000 to 400 cm^{-1} of a dilute (0.2 M) solution of XeF_4 in HF does not differ appreciably from the spectrum of pure hydrogen fluoride with the exception of the absorption in the ultraviolet region, which increases with decreasing wavelength.

A solution of XeF_4 in hydrogen fluoride is a moderately powerful fluorinating agent, in comparison with uranium hexafluoride. The action of such a solution on bright platinum forms PtF_4 and quantitatively releases xenon. Neither dry XeF_4 nor its solution in HF react with AgCl.

A preliminary investigation of the infrared absorption spectrum of xenon tetrafluoride vapour showed the presence of an intense band at 586 cm^{-1} (*i.e.* in the region in which the frequencies of the stretching vibrations of the fluorine–metal bonds usually lie), a weaker one at 290 cm^{-1} and very weak bands at 1100 and 1130 cm^{-1}. The Raman spectrum of solid XeF_4 contains two very intense bands at 502 and 543 cm^{-1} and probably one weak band at 235 cm^{-1}. These results agree with a square planar structure for xenon tetrafluoride and the previous results of X-ray structural analysis do not contradict this.

Direct determination of the molecular weight, confirming the correctness of the formula XeF_4 was accomplished by analysis of specimens of xenon tetrafluoride using a time-of-flight mass spectrometer; the results showed that other compounds of xenon and fluorine exist. Specimens for the mass spectrometric investigation were obtained by various methods. In one case xenon tetrafluoride was made using especially pure fluorine. The mass-spectrum of the vapour of the specimen taken at room temperature showed that in addition to XeF_4 there are XeF, XeF_2, and XeF_3. On slowly heating a specimen frozen at -78°, peaks appeared corresponding to XeF and XeF_2. It was concluded that XeF_2 exists as a stable compound, more volatile than XeF_4, whereas XeF and XeF_3 are probably fragments of XeF_2 and XeF_4 respectively.

Another specimen was made using ordinary fluorine containing a few tenths of one per cent of oxygen. Specimens were taken from the residue after removing almost all the xenon tetrafluoride. The spectrum, more complex than in the previous case, showed masses corresponding to the compounds XeF, XeF_2, XeF_3, XeF_4, XeO, XeOF, $XeOF_2$, $XeOF_3$, and $XeOF_4$. The authors consider that the compounds containing the group XeO are fragments of the oxide fluorides $XeOF_3$ and $XeOF_4$, whereas the latter exist as stable compounds comparable in volatility with xenon tetrafluoride.

The formation of xenon tetrafluoride during the reaction of gaseous xenon and fluorine was confirmed by Holloway and Peacock[15], who proposed a simple method of obtaining XeF_4 with a yield of 30–50% in a circulating system.

The reaction of xenon with fluorine (in molar ratio 1 : 2) also takes place when a mixture of these gases is illuminated at room temperature by a high-pressure quartz mercury lamp[13].

A colourless crystalline condensate with a composition near to XeF_4 is formed by the action of an electric discharge on a mixture of xenon and fluorine (in volumetric ratio 1 : 2) at room temperature in a quartz vessel[16].

Smith[17] succeeded in obtaining XeF_2 by reaction of xenon (partial pressure 60 mm Hg) and fluorine (240 mm Hg) in a circulating system (8 h circulation) at 400° and above. The compound was identified by its mass-spectrum.

Xenon difluoride is a colourless solid substance with a vapour pressure of ~3 mm Hg at room temperature, which readily sublimes under ordinary conditions with the formation of rhombohedral crystals. The infrared spectrum of XeF_2 has two branches: the *R*-branch with a maximum at 566 cm^{-1} and a *P*-branch with a maximum at 550 cm^{-1}. On the basis of the spectroscopic results conclusions were drawn concerning the linearity and symmetry of the XeF_2 molecule; the Xe–F distance was calculated as 1.7 Å.

This was soon followed by a report on the preparation of xenon hexafluoride[18,19] by reaction of the gaseous components at 300°–450° in nickel[18] and stainless steel[19] apparatus. The formula XeF_6 was established by chemical analysis. Mass-spectrometric investigation[18] showed the existence of XeF_6 and of certain of its fragments.

Xenon hexafluoride is a colourless solid stable at room temperature with a vapour pressure of 6–7.5 mm Hg at 0° and 27–30 mm Hg at 20°–25°. It reacts vigorously with water and hydrogen at room temperature, but dissolves without reaction in anhydrous hydrogen fluoride.

Its infrared spectrum contains an intense band at 610–612 cm^{-1}. It was concluded from the spectroscopic data that the XeF_6 molecule is symmetrical[19].

Following the reports on xenon compounds Fields *et al.*[20] described the reaction of traces of radon with fluorine. These authors found that radon forms a stable fluoride which is less volatile than XeF_4.

Gaseous radon (^{222}Rn) collected from an aqueous solution of radium chloride, was passed through a drying tube of magnesium perchlorate and a metallic vacuum line and frozen in a trap at -195°. On heating this trap to -78° the radon passed under vacuum into another part of the vacuum line, cooled to -195°. The position of the radon was determined by the 1.8 MeV gamma activity of the daughter ^{214}Bi isotope ($T_{\frac{1}{2}}$ = 19.7 min).

In the first experiments on the production of the fluoride, 5.1 μc of radon were condensed in a nickel vessel of capacity 5 cm^3, fluorine at a pressure of 300 mm Hg was introduced, and the mixture was heated at 400° for 30 min. Then the vessel was cooled to -78°, the excess of fluorine evacuated and cooled at -195°. During this operation it was noted that the volatility of the product was appreciably less than that of the initial radon: at 2×10^{-6} mm Hg and gradual heating to 150° radon was not released, but at 230°–250° part of the radon was removed from the vessel and condensed in the exit trap at ~100°.

To check whether the behaviour of radon in the presence of macroscopic amounts of a carrier is different, a mixture of xenon and radon was fluorinated: 87 μc radon were put in a 7 cm^3 nickel vessel, xenon (partial pressure 100 mm Hg) and fluorine (partial pressure 1200 mm Hg) were added,

and it was heated at 400° for 25 min. After cooling the vessel to -78° the excess of fluorine was evacuated and the vessel heated to 50° when xenon fluoride sublimed in the vacuum and passed into a trap at -195°. Less volatile radon fluoride remained in the vessel and was only removed on heating to 250°. It was shown by control experiments that pure radon does not react with the walls of the nickel vessel on heating to 400°.

The authors did not succeed in establishing the composition of the radon fluoride formed. As for its chemical properties, it is known only that it is quantitatively reduced by hydrogen to elemental radon. The reaction with hydrogen does not take place at 200°, but at 500° and a hydrogen pressure of 800 mm Hg reduction is complete after 15 min.

The experimental results described are of considerable interest but the available material unfortunately is insufficient to attempt to draw any definite conclusions concerning the structure of these compounds. To decide these questions it will be necessary to study further the physicochemical properties of the fluorides of xenon and radon, especially the magnetic properties and structure.

Reports on the preparation of compounds of the inert gases and fluorine show that there is evidently interest in even an approximate comparison of the inert gases and halogens according to their electronegativity, *i.e.* according to Mulliken[21], by the sum of the ionisation potentials and electron affinity.

The Table gives the appropriate data[12]. For the atoms of the inert gases the electron affinity has been taken as approximately zero; published results for helium, neon, and argon (respectively -0.53, -0.8, and -1.0 eV)[12] show that no substantial error is involved.

The Table shows that on passing from neon to argon there is a sharp change in ionisation potential and consequently in the electronegativity; starting with argon the inert gas is less electronegative than fluorine, chlorine, and bromine, and xenon and radon less even than iodine.

On the other hand it is known that starting from argon the atoms of the inert gases have incomplete *nd* electron shells (where $n = 3$ for argon, 4 for krypton, etc.) Both these circumstances favour the formation of chemical compounds of the inert gases under suitable conditions.

As noted above, in view of the lack of sufficient experimental evidence it is difficult to express any judgement concerning the nature of the fluorides of xenon and radon. Nevertheless the very fact of the appearance of reports on the preparation of these compounds cannot but favour the emergence of different hypotheses attempting to explain the formation of chemical bonds by atoms of the inert gases.

TABLE.

Element	Ionisation potential, eV	Electron affinity, eV	Electronegativity, eV
F	17.418	3.62	21.038
Cl	13.01	3.82	16.83
Br	11.84	3.54	15.38
I	10.44	3.23	13.67
He	24.58	~0	~24—25
Ne	21.559	~0	~21—22
Ar	15.755	~0	~15—16
Kr	13.996	~0	~13—14
Xe	12.127	~0	~12
Rn	10.745	~0	~10—11

Allen[22] took the first step in this direction, qualitatively considering the effect of correlation in pairs of electrons with antiparallel spins (α and β) on the geometric distribution of electron density in the xenon atom. Allen considered that correlation necessitates a certain spatial distribution of the clouds of the three p_α electrons and three p_β electrons with disturbance of spherical symmetry; through this there is a tendency to form an approximately octahedral relative distribution of the p electrons with alternation of the spins of four electrons about the equator and with antiparallel spins of two electrons on the polar axis (the two s electrons form an ellipse and are nearer to p electrons on the polar axis).

Four electrons (two with spin α and two with spin β) situated on the equator can, according to Allen, form bonds with halogen atoms. In the case of formation of xenon tetrafluoride two electrons of the fluorine atoms must have spin α and two spin β; as a result, the XeF molecule should be diamagnetic.

From Allen's ideas there results a square planar configuration for the XeF_4 molecule, which is consistent with the results of spectroscopic investigations on XeF_4.[13] Allen also briefly considered the possibility of the formation of XeF_2 and xenon oxide fluorides.

In another paper Allen and Horrocks[23] qualitatively described the fluorides and oxide fluorides of xenon using ideas expressed in electron pair terminology. For XeF_4 they considered a system of 12 electrons (the mechanism of formation of such a system is not discussed) which forms six pairs. From electrostatic concepts the authors propose the following model for the XeF_4 molecule: the molecule consists of a right octahedron at the centre of which is the Xe atom, with 4 F atoms at the corners of a square and two unshared electron pairs at the two other vertices. Such a structure corresponds to d^2sp^3 hybridisation. The Xe – F distance in XeF_4 was calculated to be 1.97 Å.

An analogous treatment for XeF_2 leads to a trigonal bipyramidal structure (dsp^3 or d^3sp hybridisation) with the Xe atom in the centre, three unshared pairs at the vertices of the triangle in the plane and two F atoms at the vertices above and below the plane of the triangle.

The formation of the oxide fluorides XeF_4O and XeF_4O_2 (in the case of XeF_4) and of XeF_2O, XeF_2O_2, and XeF_2O_3 (in the case of XeF_2) can be, according to Allen, accomplished as a result of completion of the electron clouds of the oxygen atoms by unshared electron pairs of the fluorides.

According to a recent paper of Rundle[24], which considered qualitatively the bond in the xenon fluorides from the aspect of molecular orbitals, a three-centred four-electron bond in which the d electrons would not take part is proposed for these compounds. By comparing XeF_4 and IF_5 Rundle calculated certain thermodynamic quantities for XeF_4 and found the Xe – F distance in XeF_4 to be ~1.96 Å.

With insufficient experimental data available it is difficult to say to what extent these hypotheses correspond with actuality. However, the intense development of the investigation of the compounds of the inert gases provides a basis for hoping that in the near future we will obtain sufficient data for a more detailed discussion of the structure of these interesting substances.

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