CHEMISTRY OF THE NOBLE GASES*

By Professor N. N. GREENWOOD, M.SC., SC.D., F.R.I.C.
University of Newcastle upon Tyne

The inert gases, or noble gases as they are now more appropriately called, are a remarkable group of elements. The lightest, helium, was recognized in the gases of the sun before it was isolated on earth as its name (ἥλιος) implies. The first inert gas was isolated in 1895 by Ramsay and Rayleigh; it was named argon (ἀργός, inert) and occurs to the extent of 0·93% in the earth's atmosphere. The other gases were all isolated before the turn of the century and were named neon (νέον, new), krypton (κρυπτόν, hidden), xenon ξένον, stranger) and radon (radioactive emanation). Though they occur much less abundantly than argon they cannot strictly be called rare gases; this can be illustrated by calculating the volumes occupied at s.t.p. by the gases in this lecture theatre (volume $\simeq 10^6$ litres): helium 5·24 l, neon 18·3 l, argon 9,340 l, krypton 1·14 l and xenon 87 ml.

A few characteristic properties are listed in Table I, which shows that the inert-gas atoms have complete *s* and *p* subshells. For this reason there are only weak van der Waals interactions between the individual atoms and this leads to the very low boiling points and heats of vaporization shown. The ionization potentials (energy required to remove one electron from an atom to give a cation, M^+) are very high compared with those of the alkali metals (90–124 kcal/mole). In fact, all attempts to prepare well-defined stoichiometric chemical compounds of these elements were unsuccessful, and for over 60 years they epitomized chemical inertness. Indeed, their electron configuration, s^2p^6, became known as 'the stable octet,' and this formed the basis of the first electronic theory of valency in 1916. Despite this, many people felt that it should be possible to induce the inert gases to form compounds, and many of the early experiments directed to this end have recently been reviewed.[1]

TABLE I
SOME PROPERTIES OF THE NOBLE GASES

At. No.	Electron config.	Ionization potential (kcal/mole)	Boiling point (°C)	ΔH_{vap} (kcal/ mole)
He 2	$1s^2$	567	−269	0·022
Ne 10	$2s^22p^6$	497	−246	0·44
Ar 18	$3s^23p^6$	363	−186	1·50
Kr 36	$4s^24p^6$	323	−153	2·31
Xe 54	$5s^25p^6$	280	−107	3·27
Rn 86	$6s^26p^6$	247	−65	4·3

There were several reasons why chemists believed that the inert gases might form chemical compounds under the correct conditions. For example, the ionization potential of xenon is actually lower than those of hydrogen, nitrogen, oxygen, fluorine and chlorine, all of which readily form covalent compounds (Xe 280, H 313, N 335, O 314, F 402, Cl 300 kcal/mole). Furthermore, the ionization potential of radon is very similar to that of mercury, which readily forms cationic species (Rn 247, Hg 240 kcal/mole). There were also suggestive experimental observations. Thus, we are all familiar with the fact that iodine is virtually insoluble in water but dissolves freely in the presence of potassium iodide to give the brown I_3^- anion. The iodide ion I^- has exactly the same number of electrons as xenon, which might therefore be expected to behave very similarly; apparently it does not. The existence of stable interhalogen compounds, such as BrF_3, IF_5 and IF_7, also indicates that more electrons than are allowed by the classical octet theory can be involved in bonding and that the isoelectronic species, such as KrF_2, XeF_4 and XeF_6, might be capable of independent existence.

Finally, there was the possibility of forming co-ordination complexes by donating a pair of electrons from an inert-gas atom to another atom. After all, the inert gases are bristling

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with lone-pairs and their ionization potentials are often no greater than those of ammonia, water, ethylene and other well-known ligands. However, recent detailed studies of the interaction of xenon and krypton with powerful electron-pair acceptors, such as boron trifluoride and trichloride, indicated that there is no specific donor–acceptor bond-formation even at very low temperatures.

This was the position at the beginning of 1962. Then, in June of that year, N. Bartlett announced[2] that when xenon was placed in contact with gaseous platinum hexafluoride at room temperature an immediate reaction occurred to give an orange-yellow solid:

$$\mathrm{Xe\ (g) + PtF_6\ (g) = XePtF_6\ (s)}$$

Xenon hexafluoroplatinate(v) was the first authentic compound of a noble gas. The idea was taken up by dozens of different laboratories throughout the world, and within 18 months a 400-page book on the subject had been published.[3] This gives some idea of the speed at which modern advances in chemistry are made.

The first group to start work after the initial discovery was one at the Argonne National Laboratory in Chicago, and three months after Bartlett's paper they reported[4] that xenon combined directly with fluorine when the two gases were heated in a nickel vessel under pressure at 400°:

$$\mathrm{Xe\ (g) + 2F_2\ (g) = XeF_4\ (s)}$$

The compound can even be made simply by passing a mixture of xenon and fluorine diluted with nitrogen through a nickel tube heated with a bunsen burner; white crystals of xenon tetrafluoride sublime out—an experiment that could have been done at any time during the past 60 years!

TABLE II

PROPERTIES OF THE XENON FLUORIDES

Property	XeF_2	XeF_4	XeF_6
M.p. (°C)	140	114	46
Density (g/ml)	4·32	4·04	—
Sol. in liq. HF at 25° (g/100 g)	175	4	250
Heat of solution (kcal/mole)	2·5	6·7	18
Vap. press. (mm Hg at 25°) . .	3	4	30
Heat of sublimation (kcal/mole)	12·3	15·3	9·0
Bond length Xe–F (Å) . .	2·00	1·95	1·91

About 20 compounds of xenon have now been isolated and many more identified in reaction systems. Compounds of krypton and radon have also been made, and a systematic account of this new area of chemistry will now be given. Detailed references to the original literature are given in refs 1, 3, 5 and 6. It will be convenient to break up the discussion into three parts:

(1) Preparation, physical properties and structures;

(2) Chemical reactions;

(3) Stability and bonding theory.

PREPARATION, PHYSICAL PROPERTIES AND STRUCTURES

Xenon Difluoride

XeF_2 is a white crystalline compound which is most simply prepared by irradiating a mixture of xenon and excess fluorine for one day at 25° and $1\frac{1}{2}$ atm pressure with light from a high-pressure mercury arc. It is important to freeze out the product at $-78°$ as it forms, otherwise some xenon tetrafluoride is also formed, and these two compounds are very difficult to separate. Amounts up to 10 g can be prepared in this way in silica vessels or in nickel vessels with sapphire windows. The compound can also be prepared by irradiating a xenon–fluorine mixture with ^{60}Co γ-rays, or by circulating a 1:4 mixture of the gases through a heated nickel tube at 400° and trapping the product at $-50°$. Some properties of xenon difluoride are summarized in Table II. It can be seen that the melting point, 140°, is far above the m.p. of both xenon ($-111°$) and fluorine ($-223°$) and the density is also greater than that of solid xenon (3·1) or fluorine (1·3). Xenon difluoride has a very high solubility in anhydrous hydrogen fluoride, in which it is non-conducting.

The vapour pressure is sufficient to allow the compound to sublime readily when warmed under vacuum and it forms beautiful crystals in this way. The heat of vaporization (12·3 kcal/mole) suggests that there is appreciable separation of charge within the molecule, and this coulombic attraction contributes to the low volatility (cf. ΔH_{vap} Xe

3·27, F_2 1·64 kcal/mole). Xenon difluoride is diamagnetic, indicating that there are no unpaired electrons in the structure.

Neutron diffraction and X-ray diffraction have shown that xenon difluoride crystallizes in the tetragonal system with cell constants $a = 4{\cdot}315$ and $c = 6{\cdot}990 \pm 0{\cdot}004$ Å, and two molecules in the unit cell, as illustrated in Fig. 1. The XeF_2 molecule is linear and this is also consistent with the infra-red and Raman vibrational spectra (both band shapes and occurrence). The modes of vibration are shown in Fig. 2.

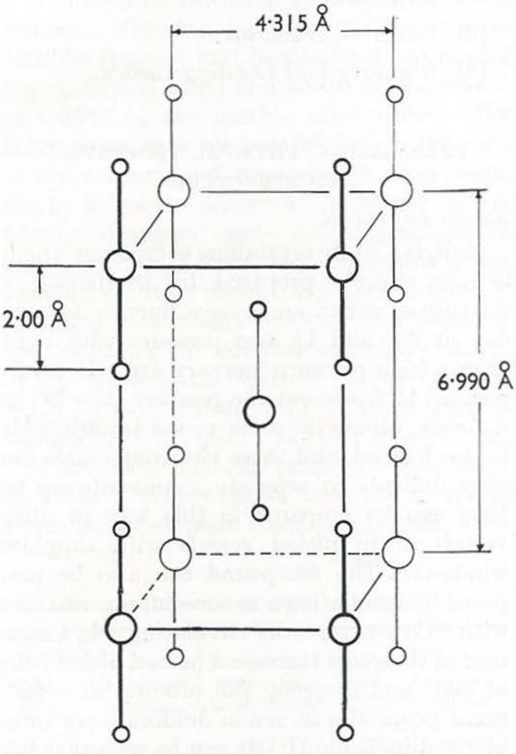


Fig. 1. Crystal structure of XeF_2

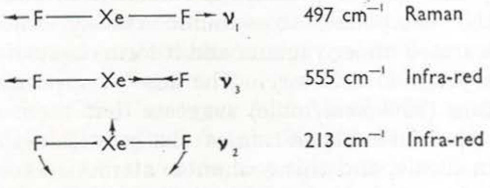


Fig. 2. Vibrational spectrum of XeF_2

Xenon Tetrafluoride

XeF_4 is best prepared by heating xenon and fluorine in an atom ratio of 1 : 5 at 13 atm and 400° in a nickel weighing-can for 1 hr. Up to 50 g can be handled and the yield is quantitative. Flow methods through a nickel tube, electrial discharge methods and γ-irradiation have also been used. The compound sublimes readily under reduced pressure and is obtained as beautifully-formed colourless crystals.

The properties of xenon tetrafluoride are summarized in Table II. Comparison with xenon difluoride shows that the tetrafluoride has a lower m.p. and density, and a considerably lower solubility in anhydrous hydrogen fluoride; the heat of vaporization, however, is 25 per cent higher. Neutron diffraction and X-ray diffraction results indicate that the tetrafluoride crystallizes in the monoclinic system with two molecules in the unit cell, as shown in Fig. 3. The molecule is square-planar with the F–Xe–F bond angle 90°, and the Xe–F bond distance slightly less than that for the difluoride. The molecules pack in a body-centred array, and the angle between the planes of the two sets of molecules is 55·2°.

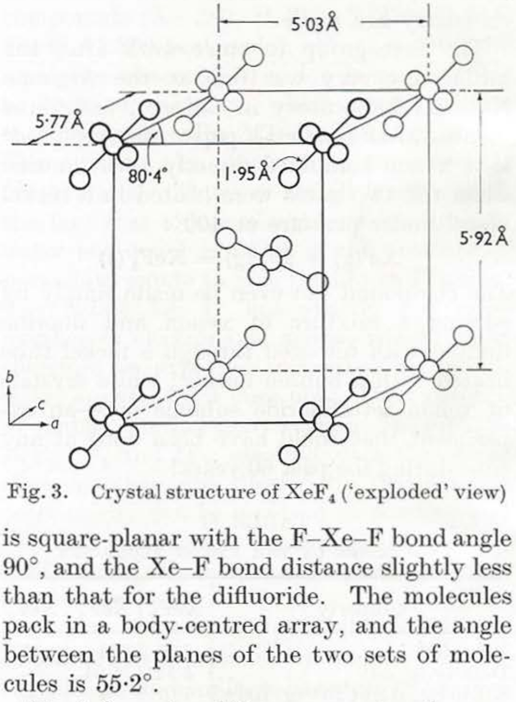
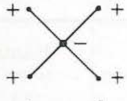
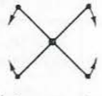
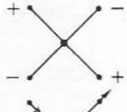
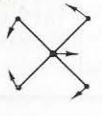


Fig. 3. Crystal structure of XeF_4 ('exploded' view)

The infra-red and Raman spectra of xenon tetrafluoride are also best interpreted on the basis of a square-planar model. Details are given in Table III. A molecule containing five atoms should have nine (*i.e.* $3n-6$) modes of vibration, but if it has square-planar symmetry two pairs of these should be doubly degenerate, that is, have the same energy; ν_6 represents one of these pairs and ν_7 the other, so that only seven fundamental modes are expected, of which one, ν_4, is inactive in both infra-red and Raman and can only be observed as an overtone. It will also be seen that no fundamental vibration in the infra-red appears in the Raman spectrum and vice versa. This 'rule of mutual exclusion' indicates that the molecule has a centre of symmetry and confirms that it is not tetrahedral. (A tetrahedral molecule gives rise to only four fundamental modes, all of which give Raman lines and two of which also give lines in the infra-red; the infra-red modes are triply degenerate and one of the Raman modes is doubly degenerate, making a total of nine modes in all, as required for a pentatomic molecule.)

TABLE III

VIBRATION SPECTRUM OF XENON TETRAFLUORIDE

ν_1 (R)	543 cm^{-1}	
ν_2 (I.R.)	291 cm^{-1}	
ν_3 (R)	235 cm^{-1}	
ν_4 inactive	(221 cm^{-1})	
ν_5 (R)	502 cm^{-1}	
ν_6 (I.R.)	586 cm^{-1}	
ν_7 (I.R.)	123 cm^{-1}	

(R) = Raman; (I.R.) = Infra-red

Xenon Hexafluoride

XeF_6 is less stable than the difluoride and tetrafluoride. It has been prepared in 10-g amounts by heating xenon in a large excess of fluorine at pressures up to 200 atm and temperatures of 300–400°. In a typical experiment a 95 per cent yield of xenon hexafluoride was obtained by heating $Xe + 20\ F_2$ for 16 hr at 300° and 60 atm. Electric-discharge methods have also been used. Some properties of xenon hexafluoride are listed in Table II. The low m.p. and high solubility in anhydrous hydrogen fluoride are noteworthy. Unlike solutions of the difluoride and tetrafluoride, these solutions are good conductors of electricity. The high vapour pressure and low heat of vaporization reflect the more symmetrical structure of this molecule. Xenon hexafluoride is thermochroic: the colourless crystals turn pale yellow at 42° and melt to a yellow liquid; the vapour is a pale yellow-green. All these changes are reversible and find explanation in terms of the detailed theory of bonding and the energy-level diagram for the compound.

X-ray and neutron-diffraction studies have proved difficult because of the reactivity of the hexafluoride. For example, glass, silicon and mercury are all rapidly attacked. However, the structure is certainly octahedral, though it is not yet certain whether all bond lengths are equal. The infra-red and Raman spectra have also only been partly elucidated; there appear to be no coincidences, indicating a centrosymmetrical molecule. The Xe–F symmetric stretching vibration occurs at 655 cm^{-1} in the Raman spectrum and the Xe–F antisymmetric stretching mode is at 612 cm^{-1} in the infra-red.

Other Xenon Fluorides

Irradiation of xenon tetrafluorides with ^{60}Co γ-rays at −196° yields xenon monofluoride radicals, XeF, trapped in the crystal lattice. This species, which is stable only at low temperatures, has one unpaired electron; it is paramagnetic and colours the host lattice bright blue.

Crystals of composition XeF_3 can be grown from the vapour of xenon tetrafluoride containing some difluoride. The compound is diamagnetic (no unpaired electrons) and colourless. X-ray crystallography shows that the lattice consists of equal numbers of XeF_2 and XeF_4 units packed so that the xenon atoms form a face-centred array. The crystals are monoclinic with cell dimensions $a = 6{\cdot}64$ Å, $b = 7{\cdot}33$ Å, $c = 6{\cdot}40$ Å, $\beta = 92^\circ 40'$. The density is 4·02 g/ml and all bond distances and bond angles are normal.

The preparation of xenon octafluoride has been claimed but not confirmed. Thus, when xenon was heated with 16 mole-equivalents of fluorine at 620° and 200 atm and the reaction vessel then chilled to −78°, yellow crystals of composition $XeF_{7\cdot9 \pm 0\cdot3}$ were said to be isolated. At room temperature the compound is apparently an unstable yellow gas.

Xenon Oxytetrafluoride

$XeOF_4$ is formed when xenon hexafluoride is kept in glass or silica vessels:

$$2XeF_6 + SiO_2 = 2XeOF_4 + SiF_4$$

Xenon hexafluoride reacts completely with quartz at 50° in two days. The stoichiometric amount of water vapour also hydrolyses the hexafluoride to this product:

$$XeF_6 + H_2O = XeOF_4 + 2HF$$

Xenon oxytetrafluoride is a clear, colourless liquid at room temperature. It freezes to a white solid at −40° (or −28°) and has a vapour pressure of 8 mm at 0° and 29 mm at 23°. The heat of vaporization is approximately 9 kcal/mole.

The infra-red and Raman spectra establish that the molecule is a square-based pyramid C_{4v} symmetry) as shown in Fig. 4. The detailed assignments are listed in Table IV, from which it can be seen that there are several coincidences in the Raman and infra-red spectra, consistent with the absence of a centre of symmetry. The spectra of the oxytetrafluoride should also be compared with those of xenon tetrafluoride in Table III; there is a marked similarity except for the two extra bands associated with the Xe–O stretching and wagging modes. Force-constant calculations clearly indicate the double-bond character of the Xe=O bond. Similarity with the isoelectronic interhalogen compound, bromine pentafluoride, is also noteworthy.

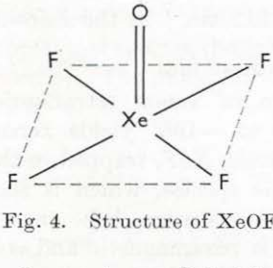


Fig. 4. Structure of $XeOF_4$

The molecular integrity of xenon oxytetrafluoride has been further demonstrated in a time-of-flight mass spectrometer which also indicated the presence of the species XeO_2F_2. In both these compounds xenon is in the oxidation state VI. Another oxyfluoride, $XeOF_2$, in which it is in the oxidation state IV, is formed when xenon reacts with oxygen difluoride in an electric discharge, but little is known of its properties.

$$Xe + F_2O = XeOF_2$$

Xenon Trioxide

XeO_3 was first prepared by an undergraduate at Berkeley University; it was

TABLE IV

VIBRATIONAL SPECTRUM OF XENON OXYTETRAFLUORIDE

Mode	Raman (liquid) cm^{-1}	I.R. (gas) cm^{-1}	Assignment
ν_1	919 (s, p)	928 (s)	Xe–O stretch
ν_2	566 (vs, p)	578 (w)	Xe–F_4 symmetric stretch
ν_3	286 (vw,p)	288 (s)	Xe–F_4 sym. out-of-plane deformation
ν_4	231 (w, dp)	inactive	Xe–F_4 sym. in-plane deformation
ν_5	530 (s, dp)	inactive	Xe–F_4 out-of-phase stretch
ν_6	not obs.	inactive	Xe–F_4 antisym. out-of-plane deformation
ν_7	not obs.	609 (vs)	Xe–F_4 antisym. stretch
ν_8	364 (mw, dp)	362 (ms)	Xe–O wag
ν_9	161 (vw, dp)	not obs.	Xe–F_4 antisym. in-plane deformation

vw, very weak; mw, medium-weak; w, weak; ms, medium-strong; s, strong; vs, very strong; p, polarized; dp, depolarized.

obtained as white, non-volatile, highly-explosive crystals by evaporating the aqueous acid hydrolysate of xenon tetrafluoride. During the hydrolysis about half of the Xe^{IV} disproportionates into Xe^0 and Xe^{VI}, and the other half oxidizes water to oxygen; the overall reaction can be represented approximately by the equation:

$$3XeF_4 + 6H_2O = 2Xe + \tfrac{3}{2}O_2 + XeO_3 + 12HF$$

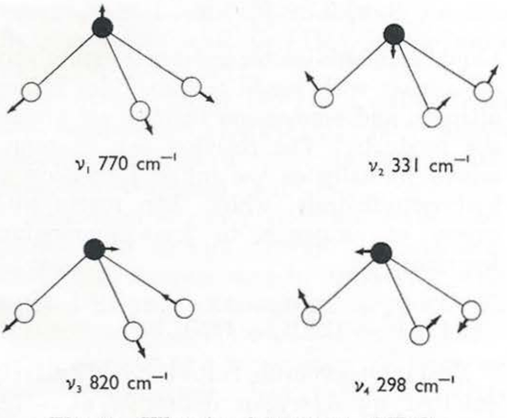
The trioxide can also be prepared by slow hydrolysis of the hexafluoride:

$$XeF_6 + 3H_2O = XeO_3 + 6HF$$

The degree of hydration of the trioxide is unknown but oxygen atoms can be exchanged by equilibration with ^{18}O-enriched water, and it seems probable that the reaction is

$$XeO_3 + 3H_2O \rightleftharpoons Xe(OH)_6$$

X-ray structural work on the crystals shows that xenon trioxide has an orthorhombic unit cell with $a = 6{\cdot}163 \pm 0{\cdot}008$ Å, $b = 8{\cdot}115 \pm 0{\cdot}010$ Å and $c = 5{\cdot}234 \pm 0{\cdot}008$ Å. There are four molecules in the unit cell and the density is 4·55 g/ml. XeO_3 is a trigonal pyramidal molecule as shown in Fig. 5. The bond length Xe–O is $1{\cdot}76 \pm 0{\cdot}04$ Å and the bond angle O–Xe–O is approximately 103°. The molecular symmetry and dimensions are very similar to those of the isoelectronic iodate ion, IO_3^-, for which the mean bond lengths and bond angles are 1·82 Å and 97°.



ν_1 770 cm^{-1} ν_2 331 cm^{-1}

ν_3 820 cm^{-1} ν_4 298 cm^{-1}

Fig. 5. Vibrational spectrum of XeO_3

Infra-red assignments are shown in Fig. 5. There is a marked similarity to the spectra of the ions ClO_3^-, BrO_3^- and IO_3^-, and the principal stretching-force constant indicates considerable double-bond character, consistent with the short Xe–O bond distance.

Xenon Tetroxide

XeO_4 is a volatile yellow solid, unstable at room temperature. It is prepared[7] by adding sodium or barium perxenate (*see* next section) to anhydrous sulphuric acid at −5°, the reaction being formally represented by the equation:

$$Ba_2XeO_6 + 2H_2SO_4 = XeO_4 + 2BaSO_4 + 2H_2O$$

Yields of up to 34 per cent (0·1 g) were obtained.

The xenon tetroxide molecule is tetrahedral (like osmium tetroxide and the periodate ion, IO_4^-) and has two infra-red active vibrations as expected: ν_3, 877 cm^{-1}; ν_4, 305·7 cm^{-1}. The vapour pressure is 3 mm at −35° and 25 mm at 0°, which corresponds to a heat of sublimation of 8·0 kcal/mole.

Compounds of Krypton and Radon

Compounds of krypton are less stable than those of xenon and this has limited the amount of attention they have received. Compounds of radon may well prove to be more stable, but difficulties of handling this highly radioactive element have also precluded extensive investigation.

Krypton, unlike xenon, does not react with platinum hexafluoride at temperatures up to 50° nor does it react when heated with fluorine. However, the species KrF_2 has been identified by matrix-isolation techniques. A mixture of fluorine and krypton with argon as the matrix was sprayed on to a caesium-iodide window at −253° and then irradiated with ultra-violet light. Bands appearing in the infra-red spectrum could be assigned to the linear molecule KrF_2: ν_3, 580 cm^{-1}; ν_2, 236 cm^{-1}.

Krypton tetrafluoride, KrF_4, is said to be formed as transparent, colourless crystals when an electric discharge is passed through a gaseous mixture of the elements. Thus, when a mixture of composition $Kr + 2F_2$ at 12 mm pressure was passed through an arc of approximately 1,000 V/30mA between copper electrodes and the products trapped out at −188°, a yield of 1·15 g KrF_4 was obtained in 4 hr. The compound has a vapour pressure of 4 mm at −30°, 30 mm at 0° and 90 mm at 20°, and a heat of sublimation of 8·8 kcal/mole. At 20° one-tenth of a sample of krypton tetrafluoride decomposed in one hour and decomposition was very rapid above 60°.

Hydrolysis of krypton tetrafluoride at room temperature results in the liberation of krypton and oxygen:

$$KrF_4 + 2H_2O = Kr + O_2 + 4HF$$

However, slow hydrolysis by ice at −30° to −60° gave 2–3 per cent of an acid whose stable barium salt could be isolated at room temperature.[8] Hydrolysis of krypton tetrafluoride with aqueous barium hydroxide at 0° gave a 7 per cent yield of a compound considered to be barium kryptate, $BaKrO_4$. The acid may be KrO_3,xH_2O, for example $Kr(OH)_6$; as the stoichiometric formula of the acid and the oxidation state of the krypton have not yet been established it is perhaps appropriate to call it kryptic acid.

Tracer experiments at the 10–100 μc level indicate that a radon fluoride, RnF_x, can be prepared from mixtures of the gases at 400° but the stoichiometry of the reaction has not yet been established. Radon fluoride is stable, distils at $230\text{–}250°/10^{-6}$ mm and appears to be an ionic compound. It is reduced by hydrogen to radon and hydrogen fluoride at 500°. Attempts to prepare radon chloride and radon oxide by thermal or photochemical means have so far been unsuccessful.

CHEMICAL REACTIONS OF XENON COMPOUNDS

The chemical reactions of the compounds of xenon have been extensively studied and some typical examples will now be discussed.

Non-aqueous Chemistry

The fluorides of xenon react quantitatively with hydrogen at about 400° and this has been used as a method of analysis.

$$\begin{aligned} XeF_2 + H_2 &= Xe + 2HF \\ XeF_4 + 2H_2 &= Xe + 4HF \\ XeF_6 + 3H_2 &= Xe + 6HF \end{aligned}$$

Xenon oxytetrafluoride reacts similarly with a large excess of hydrogen at 350°:

$$XeOF_4 + 3H_2 = Xe + H_2O + 4HF$$

Reaction with gaseous hydrogen chloride is much more rapid and can be carried out even at −78°:

$$XeF_4 + 4HCl = Xe + 4HF + 2Cl_2$$

It is noteworthy that no indication of a xenon chloride was detected in this reaction.

Xenon tetrafluoride is a good fluorinating agent; it attacks mercury at room temperarure and a solution of the tetrafluoride in anhydrous hydrogen fluoride reacts quantitatively with platinum:

$$\begin{aligned} XeF_4 + 2Hg &= Xe + 2HgF_2 \\ XeF_4 + Pt &= Xe + PtF_4 \end{aligned}$$

Likewise the tetrafluoride fluorinates boron trichloride to a mixture of boron chloride fluorides, BCl_xF_{3-x}, and carbon tetrachloride yields CCl_3F. Nitrogen dioxide is fluorinated to nitryl fluoride, whereas sulphur tetrafluoride and selenium tetrafluoride are slowly oxidized to the corresponding hexafluorides:

$$\begin{aligned} XeF_4 + 4NO_2 &= Xe + 4NO_2F \\ XeF_4 + 2SF_4 &= Xe + 2SF_6 \\ XeF_4 + 2SeF_4 &= Xe + 2SeF_6 \end{aligned}$$

Liquid ammonia ignites and reacts explosively on contact with xenon tetrafluoride; xenon, nitrogen and ammonium fluoride are among the products. The reaction can be represented formally as the initial formation of hydrogen fluoride, which then reacts with excess of ammonia to form ammonium fluoride:

$$\begin{aligned} 3XeF_4 + 4NH_3 &= 3Xe + 12HF + 2N_2 \\ 12HF + 12NH_3 &= 12NH_4F \end{aligned}$$

Xenon tetrafluoride is itself quantitatively oxidized by dioxygen difluoride at −78° according to the equation:

$$XeF_4 + O_2F_2 = XeF_6 + O_2$$

This reaction represents a 'chemical' synthesis of a xenon fluoride which involves fluorination with a compound of fluorine rather than by the element itself. Other chemical syntheses have also been achieved. Thus, when xenon is heated with 2·2 mole-equivalents of CF_3OF at 250 atm and 225°, xenon difluoride is formed. A similar reaction with FSO_2OF at 150 atm and 175° also produces xenon difluoride. The same compound is formed when xenon and carbon tetrafluoride are passed through an electric discharge.

It will be recalled that the first authentic example of a stoichiometric compound of a noble gas was xenon hexafluoroplatinate, $XePtF_6$. Similar compounds are formed by other reactive hexafluorides, *e.g.* $XeRhF_6$ (deep red), $XeRuF_6$ and $XePuF_6$. However, no compounds were formed with the stabler hexafluorides, IrF_6, UF_6 and NpF_6.

When xenon reacts with an excess of platinum hexafluoride other compounds are formed with compositions ranging up to $Xe(PtF_6)_2$, but their structure has not been definitely established and they have been formulated both as ionic and as fluorine-bridged covalent compounds: $Xe^{2+}(PtF_6^-)_2$ and $F_5Pt\text{–}F\text{–}Xe\text{–}F\text{–}PtF_5$. The ionic structure is suggested by the infra-red spectrum, which shows only two absorptions as expected for the PtF_6^- ion. This is also consistent with the fact that xenon hexafluoroplatinate(VI) reacts with rubidium fluoride in iodine pentafluoride as solvent to form the well-known orange-red salt, $RbPtF_6$. Likewise, caesium fluoride reacts with $Xe(PtF_6)_2$ in the same solvent to give $CsPtF_6$.

Pyrolysis (1 hr at 165°) of a solid having the composition $Xe(PtF_6)_{1\cdot 8}$ gave xenon tetrafluoride and a new, brick-red, diamagnetic compound, $XePt_2F_{10}$.

Xenon tetrafluoride does not form complexes with sodium fluoride or potassium fluoride at temperatures up to 200° or with boron trifluoride at temperatures up to 100°. It therefore shows little tendency to act either as an electron-pair acceptor or an electron-pair donor (ligand). However, xenon tetrafluoride dissolves in antimony pentafluoride to give a gas and a yellow, diamagnetic complex, $XeF_2,2SbF_5$, m.p. 63°. The compound can be obtained directly from xenon difluoride and distils unchanged under reduced pressure at 120°. A similar straw-coloured complex, $XeF_2,2TaF_5$, m.p. 81°, is obtained from xenon tetrafluoride and tantalum pentafluoride. On the basis of their volatility and diamagnetism it seems probable that these adducts are bonded by bridging fluorine atoms, $F_5M\text{–}F\text{–}Xe\text{–}F\text{–}MF_5$.

Aqueous Solution Chemistry

The aqueous solution chemistry of xenon is fairly extensive and somewhat complicated. Species containing Xe^{VI} and Xe^{VIII} are well established and several salts have been isolated.

Xenon difluoride hydrolyses very slowly in water but more rapidly in alkaline solution:

$$XeF_2 + H_2O = Xe + \tfrac{1}{2}O_2 + 2HF$$

All the combined xenon is liberated as the element, indicating that 'hydrolysis' involves oxidation of water to oxygen and reduction of Xe^{II} to Xe^0.

Hydrolysis of the tetrafluoride gives varying products, depending on the conditons; hydrolysis is again accompanied by oxidation of water to oxygen and also by the disproportionation of xenon(IV) to higher and lower oxidation states. During the hydrolysis the surface of the tetrafluoride becomes bright canary-yellow, and this yellow solid dissolves with evolution of gas to give a colourless solution. The lifetime of the yellow solid is about 10 sec in alkaline solution, 8 min in water and 20 min in 3M sulphuric acid. About half of the tetrafluoride is used in oxidizing the water and about half disproportionates. The overall reaction can therefore be represented by the equation:

$$\begin{aligned}&3XeF_4 + (6 + x)H_2O\\ &\quad = 2Xe + \tfrac{3}{2}O_2 + XeO_3,xH_2O + 12HF\end{aligned}$$

Evaporation of the products of acid hydrolysis results in the isolation of xenon trioxide as noted in the previous section (p. 181). In the presence of barium carbonate, barium xenate (Ba_3XeO_6) is formed but this rapidly goes over to the perxenate, Ba_2XeO_6.

In contrast to the variable products isolated from simple hydrolysis experiments, the reaction with aqueous potassium iodide can be made quantitative under appropriate conditions, and this reaction has been used for analysis of the tetrafluoride:

$$XeF_4 + 4KI_{aq} = Xe + 2I_2 + 4KF$$

The liberated xenon was measured gas-volumetrically, the iodine determined by the usual thiosulphate titration, and the fluoride determined gravimetrically as calcium fluoride.

Hydrolysis of xenon hexafluoride with small amounts of water yields the oxytetrafluoride (*see* previous section, p. 180). Normally, however, the hexafluoride oxidizes water to oxygen and also disproportionates to Xe^{VIII} and lower oxidation states of xenon. Xe^{VIII} is fairly stable in alkaline solution but is unstable in acid, so that normally Xe^{VI} is the highest oxidation state in products of acid hydrolysis.

Perxenates can be prepared by titration of an aqueous solution of xenon trioxide with sodium hydroxide (0·5–18M); disproportionation occurs as indicated by the following overall equation:

$$2XeO_3 + 4NaOH + 6H_2O = Xe + O_2 + Na_4XeO_6,8H_2O$$

Potassium hydroxide gives the yellow, explosive complex, $K_4XeO_6,2XeO_3$.

Perxenates are more conveniently prepared by alkaline hydrolysis of xenon hexafluoride. The white sodium and barium salts are the most stable and from these the less-stable yellow salts of Pb^{2+} and UO_2^{2+} have been prepared metathetically. The least stable perxenate yet studied is the black silver salt which decomposes violently at 150°.

In common with the oxyacid salts of many other heavy elements, various perxenates can be obtained, the general formula being $M_{2n}XeO_{4+n},yH_2O$. Thus, salts of formulae $Na_4XeO_6,2H_2O$, $Na_4XeO_6,8H_2O$, Na_5HXeO_7 (*i.e.* $n = 2\frac{1}{2}$, $y = \frac{1}{2}$) and Na_6XeO_7,H_2O have been isolated. The integrity of several of these salts has been established by X-ray powder photography:

Formula	*Structure*	*a*	*b*	*c*
$Na_4XeO_6,2H_2O$	orthorhombic	6·25	5·77	10·28
$Na_4XeO_6,8H_2O$	orthorhombic	10·36	10·45	11·87
Na_5HXeO_7	cubic	$a_0 = 9{\cdot}391$		

The infra-red spectra of solid perxenates indicate that the ν_3 (antisymmetric stretching) mode of the XeO_6 group absorbs at 650–680 cm^{-1}. This is close to the value of the same mode in antimonates, tellurates and paraperiodates and indicates that the Xe–O bond in the XeO_6 complex is similar to the Sb–O, Te–O and I–O bonds in the octahedral groupings SbO_6, TeO_6 and IO_6.

The solubility of the dry sodium salt, Na_4XeO_6, in water at 25° is 7 g/l and in 0·5M sodium hydroxide 0·2 g/l. It is, however, perhaps a little early to anticipate the general use of perxenate as a gravimetric reagent for sodium!

As already indicated, solutions containing Xe^{VI} are strongly oxidizing. Iodide, bromide and chloride are all rapidly oxidized to the element, and iodine and bromine are then slowly oxidized to iodate and bromate. Manganese(II) is slowly converted to manganate and then permanganate. Fe^{II} is rapidly oxidized to Fe^{III} and Hg^0 to Hg^{II}. As expected, perxenates, containing Xe^{VIII}, are even stronger oxidants. They oxidize more rapidly and take iodate to periodate; water is oxidized slowly in alkaline solution but rapidly in acid solution. These and similar observations enable the following approximate redox tables to be constructed:

$$\textit{Acid}\quad Xe \overset{1{\cdot}8V}{\rule[0.5ex]{5em}{0.4pt}} XeO_3 \overset{3{\cdot}0\ V}{\rule[0.5ex]{5em}{0.4pt}} H_4XeO_6$$

$$\textit{Base}\quad Xe \overset{0{\cdot}9V}{\rule[0.5ex]{5em}{0.4pt}} HXeO_4^- \overset{0{\cdot}9V}{\rule[0.5ex]{5em}{0.4pt}} HXeO_6^{3-}$$

STABILITY AND NATURE OF BONDING

Thermochemistry

The difluoride, tetrafluoride and hexafluoride of xenon are thermodynamically stable and are formed exothermically from their elements. The bonds in these compounds are chemical bonds with an energy content well within the normal range. It is known that the mean bond-energy E(Te–F) in TeF_6 is 78 kcal/mole and E(I–F) in IF_5 is 63 kcal/mole; extrapolation to the isoelectronic molecule XeF_4 might therefore lead one to expect E(Xe–F) in the range 20–40 kcal/mole, and this is observed.

The standard heat of formation of crystalline xenon tetrafluoride from gaseous xenon and fluorine has been determined by studying the reaction of xenon tetrafluoride with aqueous potassium iodide in a rocking bomb-calorimeter and analysing the contents after the reaction. The mean of four determinations gave:

$$-\Delta H^\circ_f(\text{XeF}_4\ \text{cryst}) = 60{\cdot}1\ \text{kcal/mole}$$

As the heat of sublimation of the tetrafluoride is 15·3 kcal/mole and the heat of dissociation of fluorine is 36·7 kcal/mole, then

$$-\Delta H^\circ_f(\text{XeF}_4\ \text{gas}) = 44{\cdot}8\ \text{kcal/mole}$$

and $E(\text{Xe–F})$ in $\text{XeF}_4 = 29{\cdot}6$ kcal/mole

The relevant thermochemical cycle is set out below (heat evolved is positive, heat absorbed is negative).

$$\begin{tikzcd}
\text{Xe(g)} \arrow[d, "0\ \text{kcal}"'] & +\ 2\text{F}_2\text{(g)} \arrow[d, "-73{\cdot}4\ \text{kcal}"] \arrow[r, "+60{\cdot}1\ \text{kcal}"] & \text{XeF}_4\text{(c)} \arrow[d, "-15{\cdot}3\ \text{kcal}"] \\
\text{Xe(g)} & +\ 4\text{F(g)} \arrow[r, "+118{\cdot}2\ \text{kcal}"'] & \text{XeF}_4\text{(g)}
\end{tikzcd}$$

A second method, involving the reduction of xenon tetrafluoride with hydrogen at 130° in an isothermal calorimeter, gave a preliminary value for the heat of reduction of 202 kcal. This corresponds to $-\Delta H^\circ_f(\text{XeF}_4\ \text{gas}) = 54{\cdot}8$ kcal/mole and a mean bond-energy $E(\text{Xe–F}) = 32{\cdot}0$ kcal/mole. This is in reasonable agreement with the independent value derived above.

The specific heat and heat capacity of xenon tetrafluoride have been measured between $-263°$ and $+27°$ and no anomalies were detected. At 25° the specific heat is 0·1367 cal/g, and the heat capacity, $C_p = 28{\cdot}334$ cal/mole. The measurements lead to the standard entropy, S_{298} (XeF_4 cryst) $= 35{\cdot}0 \pm 1$ cal deg^{-1} mole^{-1}, and hence to an entropy of formation, $\Delta S^\circ = 102{\cdot}5$ cal deg^{-1} mole^{-1}. The free energy of formation can then be obtained from the relation $-\Delta G^\circ_{298} = -\Delta H + T\Delta S = 29{\cdot}4$ kcal/mole, indicating the considerable thermodynamic stability of the tetrafluoride.

Reduction of xenon hexafluoride by hydrogen under similar conditions to those used for the tetrafluoride leads to the following results:

$$-\Delta H(\text{reduction}) = 306{\cdot}5\ \text{kcal/mole}$$
$$-\Delta H_f(\text{XeF}_6\ \text{gas}) = 78{\cdot}7\ \text{kcal/mole}$$
$$E(\text{Xe–F})\ \text{in}\ \text{XeF}_6 = 31{\cdot}5\ \text{kcal/mole}$$

The fact that xenon hexafluoride is a 'normal,' unexceptional compound is further emphasized by comparing its mean bond energy with that of its neighbours in the Periodic Table.[5] Thus, if the mean bond energies in SbF_3 (92 kcal), TeF_4 (86 kcal) and IF_5 (63 kcal) are plotted against atomic number and extrapolated by one unit to XeF_6, the 'predicted' bond energy is 31 kcal, close to the value observed.

The thermodynamic data for gaseous xenon difluoride at 1 atm and 250° have been calculated from the vibrational spectroscopic data given in Fig. 2. The free energy ($-\Delta G$) and entropy ($-\Delta S$) of formation are:

$$-\Delta G_{523}(\text{XeF}_2\ \text{gas at 1 atm}) = 5{\cdot}510\ \text{kcal/mole}$$
$$-\Delta S_{523}(\text{XeF}_2\ \text{gas at 1 atm}) = 26{\cdot}96\ \text{cal deg}^{-1}\ \text{mole}^{-1}$$

From the relation $-\Delta G = -\Delta H + T\Delta S$, the heat of formation at 250° is

$$-\Delta H_{523}(\text{XeF}_2\ \text{gas at 1 atm}) = 19{\cdot}6\ \text{kcal/mole}$$

The value at 25° will be similar, and from this and the heat of dissociation of fluorine one obtains

$$E(\text{Xe–F})\ \text{in}\ \text{XeF}_2 = 28{\cdot}2\ \text{kcal/mole}$$

The similarity of the Xe–F bond energy in XeF_2 (28·2 kcal), XeF_4 (29·6–32 kcal) and XeF_6 (31·5 kcal) is noteworthy, as also is the apparent slight increase in bond energy with co-ordination number. This latter trend may well be within the experimental error of these diverse determinations (probably about ± 2 kcal) but if substantiated is unusual, since increase in co-ordination number of an element almost invariably diminishes the mean bond energy.

Oxy-compounds of xenon are less stable with respect to formation from the elements than are the fluorides but this reflects the greater stability of the doubly-bonded oxygen molecule compared with fluorine rather than the weakness of the Xe–O bond. (The bond dissociation energy of oxygen is 118·5 and of fluorine 36·7 kcal/mole.)

From the heat of explosion of xenon trioxide as measured in a bomb calorimeter, the heat of formation was found to be:

$$-\Delta H^\circ_f(\text{XeO}_3\ \text{cryst}) = -96 \pm 2\ \text{kcal/mole}$$

Exact calculation of the mean bond energy $E(\text{Xe–O})$ would require a knowledge of the heat of sublimation, as shown by the following thermochemical cycle:

$$\begin{tikzcd}
\mathrm{Xe(g)} \arrow[d, "0\ \mathrm{kcal}"'] & + \tfrac{3}{2}\mathrm{O_2(g)} \arrow[d, "-177{\cdot}8\ \mathrm{kcal}"] \arrow[r, "-96\ \mathrm{kcal}"] & \mathrm{XeO_3(c)} \arrow[d, "\Delta H_{\mathrm{subl}}"] \\
\mathrm{Xe(g)} & + 3\mathrm{O(g)} \arrow[r, "(81{\cdot}8 - \Delta H_{\mathrm{subl}})"'] & \mathrm{XeO_3(g)}
\end{tikzcd}$$

Hence $E(\text{Xe–O})$ in $\mathrm{XeO_3} = 27{\cdot}3 - \tfrac{1}{3}\Delta H_{\mathrm{subl}}$

The heat of sublimation is not measurable but if a plausible value of about 22 kcal is taken for this quantity then

$$E(\text{Xe–O}) \text{ in } \mathrm{XeO_3} \simeq 20 \text{ kcal}$$

This is somewhat smaller than the Xe–F bond energy but would not, by itself, confer explosive instability; the large endothermic heat of formation is due to the fact that the Xe–O bond energy is very much less than the O=O bond energy in molecular oxygen.

Extrapolations similar to those already mentioned suggest that the heats of formation of xenon chlorides, like that of xenon trioxide, would be negative. Likewise the heat of formation of krypton tetrafluoride from its elements should be approximately zero, but the difluoride is probably slightly exothermic.

Theories of Bonding

A satisfactory theory of bonding must explain convincingly not only the stoichiometry and shape of the noble-gas compounds but also deal adequately with the observed physical properties and bond energies. As the theory becomes more precise, confident predictions of the stable groupings of atoms should be forthcoming.

It is clear that van der Waals interactions are far too weak to explain the bonding in noble-gas compounds. Such interactions are normally only 1–5 kcal/mole whereas the observed bond energies are 20–30 kcal/mole. Nor does the assumption of ionic bonding adequately explain the energies involved. Even for xenon difluoride a simple calculation shows that the second-stage ionization potential is too large to confer stability on the structure $\mathrm{Xe^{2+}(F^-)_2}$ and the similarity in mean bond energies and bond distances for $\mathrm{XeF_2}$, $\mathrm{XeF_4}$ and $\mathrm{XeF_6}$ rules out the possibility of structures such as $\mathrm{Xe^{4+}(F^-)_4}$ and $\mathrm{Xe^{6+}(F^-)_6}$. Other lines of evidence against ionic bonding in these compounds are the observed crystal structures of $\mathrm{XeF_2}$ and $\mathrm{XeF_4}$, the volatility of the compounds and the absolute values of the bond distances, which are at least 0·3 Å shorter than would be predicted on the basis of the packing of ions.

The bonding in xenon difluoride can formally be considered in terms of the promotion of a *5p* electron on xenon to a *5d* level. However, the energies involved suggest that this is unlikely to occur to any appreciable extent, and calculations indicate that the *5d* orbitals are rather too diffuse for good bonding anyway. It follows that further promotion to account for the tetra- and hexafluoride is even less favourable energetically. The valence-bond method then suggests the mixing in of other structures with these hybrids to improve the bond energy, *e.g.* $\mathrm{F{-}Xe^+F^-}$ and $\mathrm{F^-Xe^+{-}F}$, but this is not particularly satisfactory and in any event merely describes the ground state of the molecule and says nothing about its electronically excited states and hence its ultraviolet spectrum.[9] It should be noted, however, that this theory correctly predicts a linear molecule for the difluoride and a square-planar molecule for the tetrafluoride. It predicts a tetragonally distorted octahedron for the hexafluoride, and careful measurements are at present being undertaken to determine whether the structure of this compound is in fact a regular or an elongated octahedron.

The most satisfactory treatment of the bonding in xenon compounds is the molecular-orbital method. In this theory molecular orbitals are constructed from atomic orbitals on the xenon and fluorine atoms. The three criteria which determine whether a given set of atomic orbitals can combine to give molecular orbitals are:

(*a*) the atomic orbitals should have similar energies;

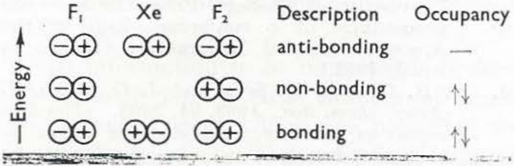
(*b*) they should have appreciable spatial overlap;

(*c*) they should have appropriate symmetry.

Molecular orbitals which have energies below the mean energy of the atomic orbitals from which they are constructed are called bonding molecular orbitals. Molecular orbitals which have energies close to those of the constituent atomic orbitals are called non-bonding molecular orbitals and those having energies above those of the constituent atomic orbitals are called anti-bonding molecular orbitals.

The theory can be illustrated by reference to xenon difluoride. The outer electronic configurations of xenon and fluorine are:

Let the molecular axis be the z axis. Then three atomic orbitals must be considered: the $5p_z$ orbital on the xenon atom and the $2p_z$ orbital on each of the fluorine atoms. These three atomic orbitals can combine to give three molecular orbitals, one of which is bonding, one non-bonding and one anti-bonding. The three atomic orbitals originally contained four electrons in all, *i.e.* two in the xenon $5p_z$ and one each in the two fluorine $2p_z$ orbitals. These four electrons are now placed so that two occupy the bonding molecular orbital and two occupy the non-bonding molecular orbital. The situation is illustrated in the following diagram:



It is clear that for best overlap the three atoms should lie in a straight line, as observed. Notice that the non-bonding orbital has no contribution from the xenon $2p_z$ orbital, since this has the wrong symmetry for combination, as indicated by the + and − signs. The approximate wave-mechanical description of these orbitals is:

$$\Psi_{ab} = \tfrac{1}{2}\psi(\mathrm{F}_1) + \frac{1}{\sqrt{2}}\psi(\mathrm{Xe}) + \tfrac{1}{2}\psi(\mathrm{F}_2)$$

$$\Psi_{nb} = \frac{1}{\sqrt{2}}\psi(\mathrm{F}_1) + 0\psi(\mathrm{Xe}) - \frac{1}{\sqrt{2}}\psi(\mathrm{F}_2)$$

$$\Psi_{b} = \tfrac{1}{2}\psi(\mathrm{F}_1) - \frac{1}{\sqrt{2}}\psi(\mathrm{Xe}) + \tfrac{1}{2}\psi(\mathrm{F}_2)$$

In these equations, b, nb and ab refer to bonding, non-bonding and antibonding molecular orbitals, Ψ, and the atomic orbitals, ψ, are labelled with an obvious notation. By squaring and adding the coefficients in each vertical and horizontal column it is simple to check that each atomic orbital has been used in all just once and that each molecular orbital is normalized to unity.

If the squares of the coefficients are taken to indicate the extent of electron occupancy, and if it is remembered that Ψ_b and Ψ_{nb} each contain two electrons, then it becomes apparent that the xenon atom has $2\left(\frac{1}{\sqrt{2}}\right)^2 = 1$ p_z-electron in its neighbourhood whereas the free atom had two; hence it has a resultant net change of +1. Likewise, each fluorine atom is associated with $\left[2(\frac{1}{2})^2 + 2\left(\frac{1}{\sqrt{2}}\right)^2\right] = 1\frac{1}{2}$ p_z-electrons, so that it has a resultant charge of $-1/2$. The theory thus enables us to calculate approximately the charge distribution within the molecule. A more precise calculation leads to a charge of +1·4 on the xenon and −0·7 on each fluorine. As a result of this partial separation of charges within the molecule, the heat of sublimation of xenon difluoride contains a substantial coulombic component in addition to the ubiquitous van der Waals attraction, and is therefore considerably greater than the heat of sublimation of xenon itself, as indicated in Tables I and II. Indeed, an estimate of the heat of sublimation based on an array of atoms in the positions indicated in Fig. 1 and carrying the partial charges calculated above gives excellent agreement with the experimental value.

An important consequence of the molecular-orbital bond theory is that it predicts enhanced stability the lower the ionization potential of the central atom and the more electronegative the outer atoms. Compounds of xenon and radon with fluorine and oxygen are therefore expected to be the most stable, whereas krypton fluorides or radon chloride should have only marginal stability. Compounds of argon and neon are not expected.

The molecular-orbital theory outlined above is in no way unique to inert-gas compounds or unusual in any of its features. It had previously been used to discuss bonding in the polyhalide ions, such as I_3^-, ICl_2^-, ICl_4^-, etc., and in many other situations. It can be extended to deal with compounds such as xenon tetrafluoride and xenon hexafluoride simply by forming three-centre molecular orbitals in the x and y directions as well as in the z direction. The theory therefore predicts a square-planar shape for XeF_4 and a regular octahedral shape for XeF_6. The similarities in bond lengths and bond energies for these compounds can also be understood. Partial charges on xenon and fluorine are approximately $+2$ and $-\frac{1}{2}$ in XeF_4; and $+2$ and $-\frac{1}{3}$ in XeF_6.

A final feature of the theory should be mentioned—its ability to help interpret ultra-violet and visible absorption spectra. Thus when an electron is excited from Ψ_{nb} to Ψ_{ab} it will absorb energy at a frequency defined by $\nu = \Delta E/\boldsymbol{h}$ where $\boldsymbol{h}$ is Planck's constant and ΔE is the difference in energy between the two levels. More extensive calculations also consider the molecular orbitals of π-symmetry,[9] and a detailed analysis of the various energy levels is at present being carried out for the complicated case of xenon hexafluoride which, as mentioned earlier, is thermochroic.

CONCLUSION

Speculations on potential applications of noble-gas compounds have been numerous. Are these compounds a means of storing fluorine in a readily available form; can they be used as oxidants in rocket-propellant systems or as specific fluorinating reagents in chemical reactions? The use of perxenates as powerful aqueous oxidants has already been mentioned. Specialized uses for shock-sensitive oxides such as xenon trioxide might be found. One of the most objectionable atomic-fission products is the volatile xenon isotope, ^{133}Xe; conversion to an involatile compound could make this available in megacurie amounts. Involatile radon needles for tumour therapy is another possibility.

Whatever the future applications of these compounds one thing is certain: the discovery that xenon readily forms a wide range of stable compounds has proved to be one of the most stimulating and significant observations in chemistry for many years. It has forced us to think more deeply about the fundamentals of chemical bonding and has demonstrated in the most direct way possible how inadequate any 'stable octet' theory of valency must be. The stable octet, which was the first electronic theory of valency, was a great advance when it was originally expounded 50 years ago. It is disturbing to reflect that much elementary teaching of bond theory still relies on this concept despite the large areas of chemistry where it does not apply (*e.g.* ferrous and ferric compounds) and the many advances which have been made in our thinking during the last 40 years. An important lesson can also be learned from the fact that if, in 1962, a student had been asked 'What would happen if xenon were heated in the presence of fluorine?' and he had answered 'a volatile white crystalline solid of composition XeF_4 is formed quantitatively,' he would have been awarded no marks.

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