NOBLE GAS by BARUN KUMAR MONDAL

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Introduction

The chemistry of noble gases began with a room temperature synthesis of the first xenon compound in the solid state, xenon hexafluoroplatinate ($XePtF_6$) by Neil Bartlett.[1] The true and indeed very complex nature of the "$XePtF_6$" compound was confirmed by experiments conducted nearly 40 years after the initial preparation.[2] The history of the breaking of the inertness of the noble gases is certainly complex and fascinating, full of many misleading reports, surprises, and ingenuity.[3]

For over 60 years the 6 gases helium, neon, argon, krypton, xenon, and radon were the confirmed bachelors among the known elements. All the other elements would enter into chemical combination with one or another of their kind, irrespective of whether they were solids, gases, or liquids in their normal state. Not so helium, neon, argon, krypton, xenon, and radon. They were chemically aloof and would have nothing to do with other elements, or even with one another.

This behavior earned them a unique position in the Periodic Table of the Elements and they were called names like the "inert gases" or the "noble gases".* They were also labeled the "rare gases", although helium and argon are not really "rare".†

Properties of the noble gases

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic number, Z	2	10	18	36	54	86
Ground state electronic configuration	$1s^2$	$[He]2s^22p^6$	$[Ne]3s^23p^6$	$[Ar]3d^{10}4s^24p^6$	$[Kr]4d^{10}5s^25p^6$	$[Xe]4f^{14}5d^{10}6s^26p^6$
Melting point, mp/K	–†	24.5	84	116	161	202
Boiling point, bp/K	4.2	27	87	120	165	211
Standard enthalpy of fusion, $\Delta_{fus}H^{\ominus}(mp)/kJ\ mol^{-1}$	–	0.34	1.12	1.37	1.81	–
Standard enthalpy of vaporization, $\Delta_{vap}H^{\ominus}(bp)/kJ\ mol^{-1}$	0.08	1.71	6.43	9.08	12.62	18.0
First ionization energy, $IE_1/kJ\ mol^{-1}$	2372	2081	1521	1351	1170	1037
Van der Waals radius, r_v/pm	99	160	191	197	214	–

Properties of the noble gases

Element	Principal Source	Uses
helium	natural gas wells	provide an inert atmosphere for welding, inflation of meteorological balloons and blimps, carrier gas for chromatography, high vacuum leak detection, cryogenics, coolant for superconducting magnets, nitrogen substitute for deep-sea diving, pressurize liquid rocket fuels, helium dating of rocks
neon	fractional distillation of liquid air	fluorescent tubes, lasers, vacuum tubes, high-voltage indicators, cryogenics
argon	fractional distillation of liquid air	provide an inert atmosphere for welding, fluorescent tubes, blanketing material for the production of titanium and other metals, lasers, deaeration of solutions
krypton	fractional distillation of liquid air	fluorescent tubes, high-speed photographic lamps, lasers
xenon	fractional distillation of liquid air	fluorescent tubes, lasers, stroboscopic lamps, high intensity headlights
radon	uranium ores	rarely used commercially

Compounds of Xenon

The principal compounds of xenon

Compound	Oxidation state	Physical state	Molecular shape
XeF_2	+2	colorless crystals	linear
XeF_4	+4	colorless crystals	square planar
$XeOF_4$	+6	colorless liquid	square pyramidal
XeO_2F_2	+6	colorless crystals	seesaw
XeO_3	+6	colorless crystals	trigonal pyramidal
XeO_4	+8	colorless gas	tetrahedral

Xe forms colorless fluorides, XeF_2, XeF_4, XeF_6

$$\left.\begin{array}{l} XeF_2 \\ XeF_4 \\ XeF_6 \end{array}\right\} \xrightarrow[\text{in liq } BrF_5]{\text{Excess } AsF_5} \left\{\begin{array}{l} [XeF_3]^+[AsF_6]^- \\ XeF_4 \\ [XeF_5]^+[AsF_6]^- \end{array}\right.$$

Property	XeF_2	XeF_4	XeF_6
Melting point / K	413	390	322
$\Delta_f H^\ominus$(s, 298 K) / kJ mol^{-1}	−163	−267	−338
$\Delta_f H^\ominus$(g, 298 K) / kJ mol^{-1}	−107	−206	−279
Calculated $\Delta_f H^\ominus$(298 K) / kJ mol^{-1}†	−100.0±1.3	−182.1±4.2	−244.0±8.4
Mean Xe–F bond enthalpy term / kJ mol^{-1}	133	131	126
Xe–F bond distance / pm	200‡	195‡	189*
Molecular shape	Linear	Square planar	Octahedral

(a) Xenon-fluorine compounds

Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions.

$$\underset{\text{(xenon in excess)}}{Xe\,(g) + F_2\,(g)} \xrightarrow{673\,K,\ 1\,bar} XeF_2(s)$$

$$\underset{\text{(1:5 ratio)}}{Xe\,(g) + 2F_2\,(g)} \xrightarrow{873\,K,\ 7\,bar} XeF_4(s)$$

$$\underset{\text{(1:20 ratio)}}{Xe\,(g) + 3F_2\,(g)} \xrightarrow{573\,K,\ 60-70\,bar} XeF_6(s)$$

XeF_6 can also be prepared by the interaction of XeF_4 and O_2F_2 at 143K.

$$XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$$

XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K. They are powerful fluorinating agents. They are readily hydrolysed even by traces of water. For example, XeF_2 is hydrolysed to give Xe, HF and O_2.

$$2XeF_2\,(s) + 2H_2O(l) \rightarrow 2Xe\,(g) + 4\,HF(aq) + O_2(g)$$

The structures of the three xenon fluorides can be deduced from VSEPR and these are shown in Fig. 7.9. XeF_2 and XeF_4 have linear and square planar structures respectively. XeF_6 has seven electron pairs (6 bonding pairs and one lone pair) and would, thus, have a distorted octahedral structure as found experimentally in the gas phase.

Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.

$$XeF_2 + PF_5 \rightarrow [XeF]^+\,[PF_6]^-; \quad XeF_4 + SbF_5 \rightarrow [XeF_3]^+\,[SbF_6]^-$$

$$XeF_6 + MF \rightarrow M^+\,[XeF_7]^-\ (M = Na, K, Rb \text{ or } Cs)$$

(b) Xenon-oxygen compounds

Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

$$6XeF_4 + 12\ H_2O \rightarrow 4Xe + 2XeO_3 + 24\ HF + 3\ O_2$$

$$XeF_6 + 3\ H_2O \rightarrow XeO_3 + 6\ HF$$

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2\ HF$$

$$XeF_6 + 2\ H_2O \rightarrow XeO_2F_2 + 4HF$$

XeO_3 is a colourless explosive solid and has a pyramidal molecular structure (Fig. 7.9). $XeOF_4$ is a colourless volatile liquid and has a square pyramidal molecular structure (Fig.7.9).

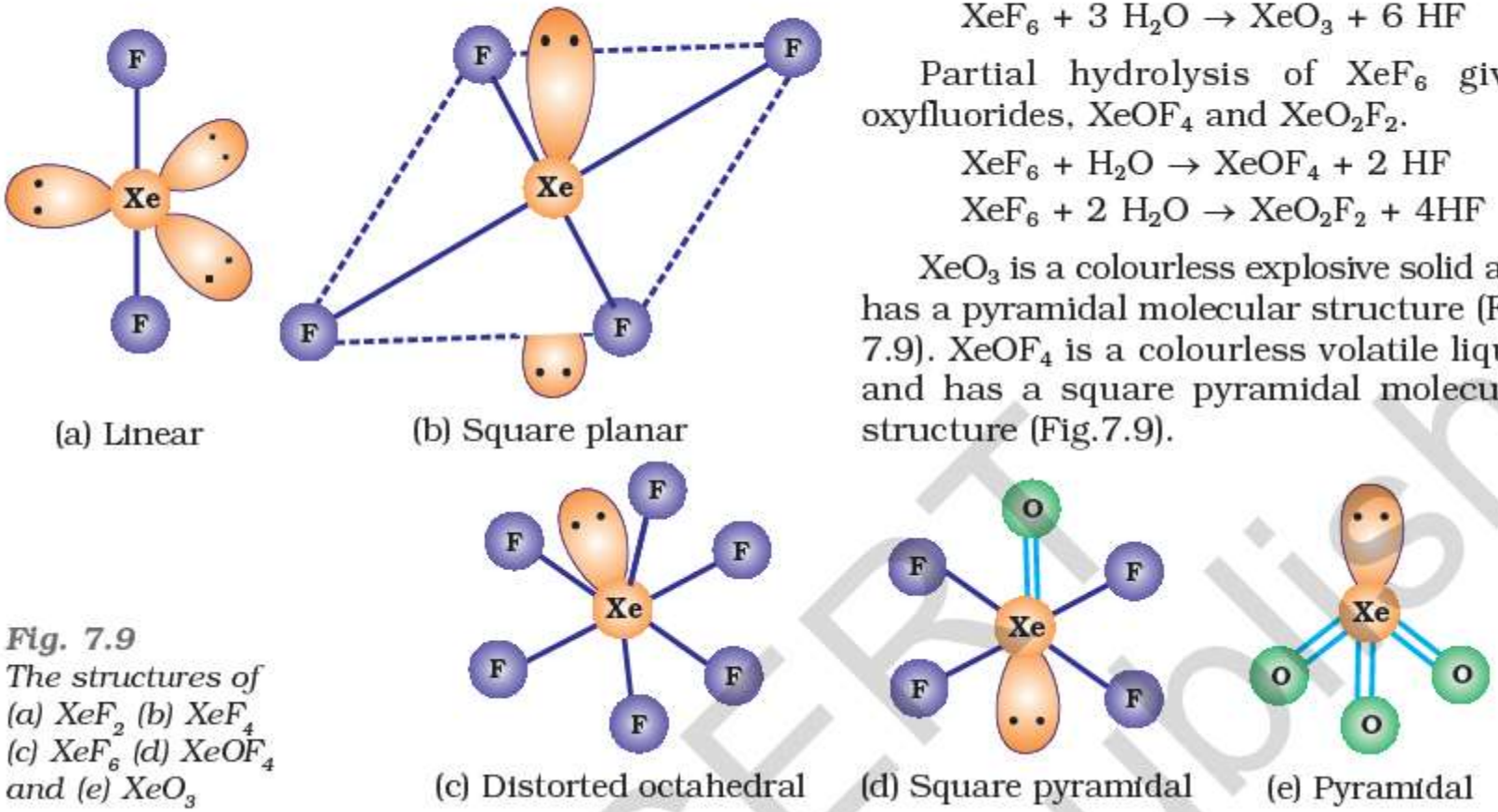


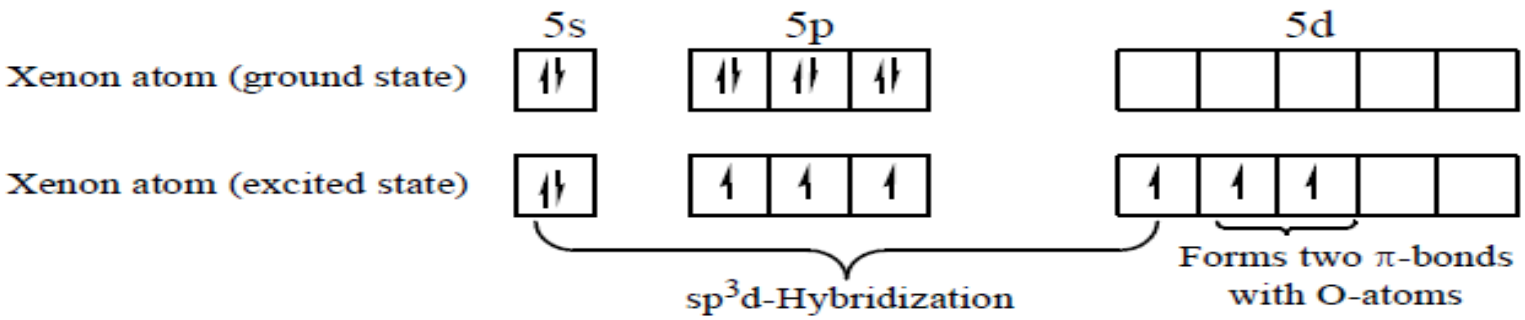
Fig. 7.9
The structures of (a) XeF_2 (b) XeF_4 (c) XeF_6 (d) $XeOF_4$ and (e) XeO_3

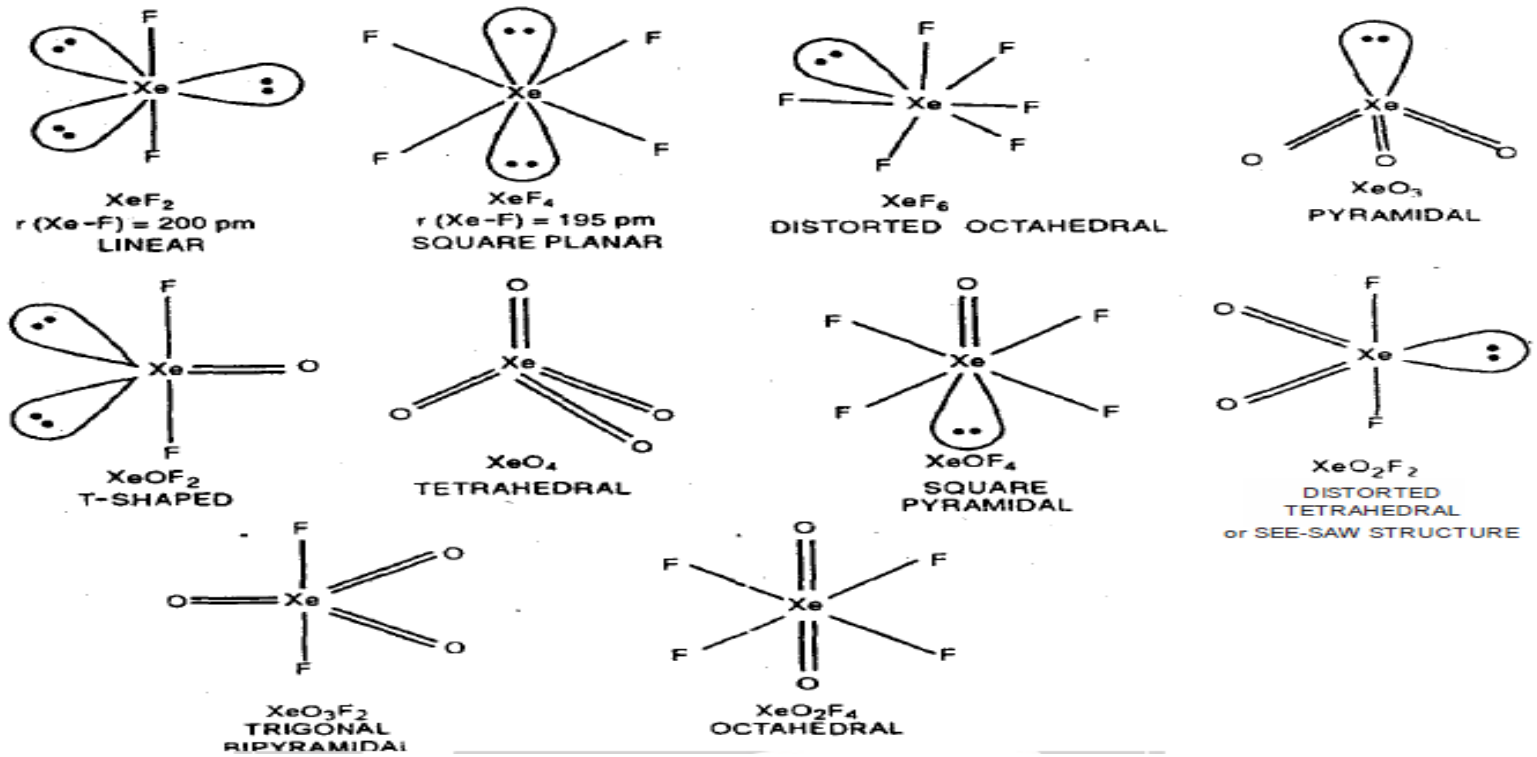
Structure of Xenon Compounds

Both VSEPR theory and concept of hybridization are applied to predict the molecular geometries of xenon compounds as discussed below.

There are two, four and six Xe–F covalent bonds in XeF_2, XeF_4 and XeF_6 respectively. Depending on the number of Xe–F covalent bonds to be formed in each case, the requisite number of electrons of the 5*p*-orbital of the valence shell of Xe get unpaired and promoted to the vacant 5*d*-orbitals followed by hybridization. According to VSEPR theory, the shape of the molecule is predicted by the total number of electron pairs (lone pairs + bond pairs) in the valence shell of the central Xe atom as shown in following Table. Their structures are given in following figure.

Molecule	No. of bond pairs of electrons	No. of lone pairs of electrons	Total electrons pairs	Hybridisation	Shape
XeF_2	2	3	5	sp^3d	Linear
XeF_4	4	2	6	sp^3d^2	Square planar
XeF_6	6	1	7	sp^3d^3	Distorted octahedral


5s
5p
5d
Xenon atom (ground state)
Xenon atom (excited state)
sp3d-Hybridization
Forms two π-bonds
with O-atoms


XeF2
r (Xe-F) = 200 pm
LINEAR
XeF4
r (Xe-F) = 195 pm
SQUARE PLANAR
XeF6
DISTORTED OCTAHEDRAL
XeO3
PYRAMIDAL
XeOF2
T-SHAPED
XeO4
TETRAHEDRAL
XeOF4
SQUARE
PYRAMIDAL
XeO2F2
DISTORTED
TETRAHEDRAL
or SEE-SAW STRUCTURE
XeO3F2
TRIGONAL
BIPYRAMIDAL
XeO2F4
OCTAHEDRAL

Xenon (Xe)

Xenon has quite a rich chemistry, forming a variety of compounds with the most reactive elements, such as fluorine and oxygen. these compounds are unstable, often explosive and producing hazardous products such as HF. It reacts by expanding its octet. The fluorides are stable colourless/white solids at room temperature. Even with fluroine, reactions are reluctant and require harsh conditions and a catalyst:

Xenon difluoride (xenon(II) fluoride), a white solid:

$$Xe(g) + F_2(g) \rightarrow XeF_2(s)$$

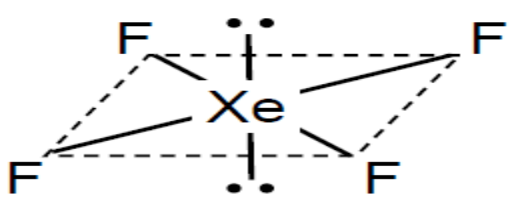
(1:4 ratio of $Xe:F_2$, passed through a Ni tube at 400°C)

$$F - Xe - F$$

Xenon tetrafluoride (xenon(IV) fluoride), a white solid:

$$Xe(g) + 2F_2(g) \rightarrow XeF_4(s)$$

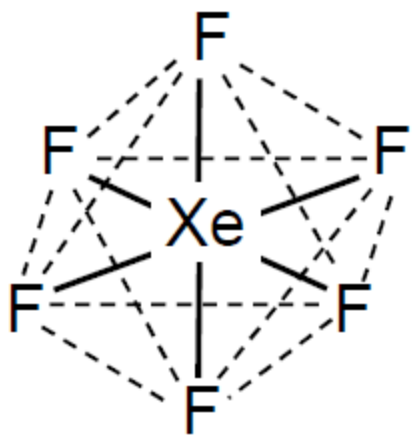
(1:5 ratio of $Xe:F_2$, heated for 1h at 13 atm in a Ni can at 400°C)



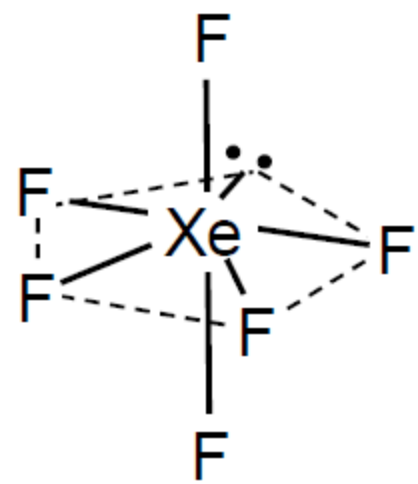
Xenon hexafluoride (xenon(VI) fluoride), a white solid (polymeric), readily sublimes to a yellow vapour (m.p. = 49.25, b.p. = 75.6°C) and forms $(XeF_6)_4$ molecules in solution:

$$Xe(g) + 3F_2(g) \rightarrow XeF_6(s)$$

(Heat Xe in excess F_2 at 200 atm)



The basic shape of XeF_6 is octahedral (left) but the octahedron is distorted, due to the presence of a 7th electron-pair (a lone pair) which is close to the Xe nucleus and so does not affect the designated shape, but distorts it – right (8 electrons from Xe + 6 from 6F = 14 electrons = 7 pairs).



Note that in these structures, xenon has expanded its octet to accommodate more electrons (vacant d-orbitals contribute to the formation of the molecular orbitals).

The fluorides all react with water, splitting the water molecules (hydrolysis):

$$XeF_6(s) + H_2O(l) \rightarrow XeOF_4 + 2HF(aq/g)$$

$$XeF_6(s) + 3H_2O(l) \rightarrow XeO_3 + 6HF(aq/g)$$

$$2XeF_4(s) + 4H_2O(l) \rightarrow Xe(g) + \tfrac{1}{2}O_2(g) + XeO_3 + 8HF(aq/g)$$

$$XeF_2(s) + H_2O(l) \rightarrow Xe(g) + \tfrac{1}{2}O_2(g) + 2HF(aq/g)$$

The fluorides are all strong oxidising and flourinating reagents (the HF produced on reaction with water is a highly reactive flourinating agent) e.g.

$$XeF_4(s) + 4KI \rightarrow Xe(g) + 2I_2(g) + 4KF(s)$$

$$XeF_4(s) + Pt(s) \rightarrow Xe(g) + PtF_4$$

$$XeF_4(s) + 2SF_4 \rightarrow Xe + 2SF_6$$

Xenon oxides,

Molecule	Hybridisation	Geometry	Shape
XeO_3	sp^3	Tetrahedral	Pyramidal
XeO_4	sp^3	Tetrahedral	tetrahedral
$XeOF_2$	sp^3d	Triogonal bipyramidal	T-shaped
$XeOF_4$	sp^3d^2	Square pyramidal	Square pyramidal
XeO_2F_2	sp^3d	Trigonal bipyramid	Distorted tetrahedral
XeO_3F_2	sp^3d	Trigonal bipyramid	Trigonal bipyramid
XeO_2F_4	sp^3d^3	Octahedral	Octahedral

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Xenon oxides

Xenon trioxide (a colourless/white crystalline solid) is produced by hydrolysis of XeF_4 or XeF_6:

$$XeF_6(s) + 3H_2O(l) \rightarrow XeO_3 + 6HF(aq/g)$$

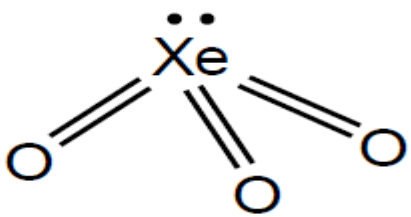
$$2XeF_4(s) + 4H_2O(l) \rightarrow Xe(g) + \tfrac{1}{2}O_2(g) + XeO_3 + 8HF(aq/g)$$

XeO_3 reacts with water to form xenon hydroxide:

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

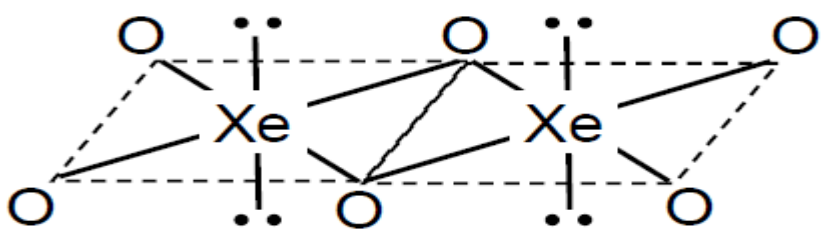
XeO_3 reacts with the oxyfluoride, $XeOF_4$ to form xenon dioxide (a yellow solid):

$$XeO_3 + XeOF_4 \rightarrow XeO_2$$



Xenon trioxide

Xenon dioxide forms a chain with square planar units:

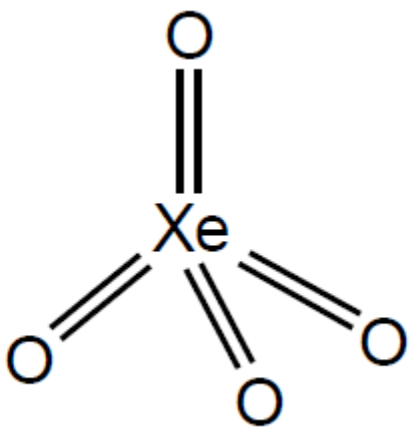


Xenon trioxide is unstable above 25°C and in contact with organic materials, tending to decompose explosively into Xe and O^2.

Xenon tetroxide, XeO_4, is highly unstable, decomposing explosively into xenon and fluorine at room temperature (or above – 35.9°C):

$$XeO_4(s) \rightarrow Xe(g) + 2O_2(g)$$

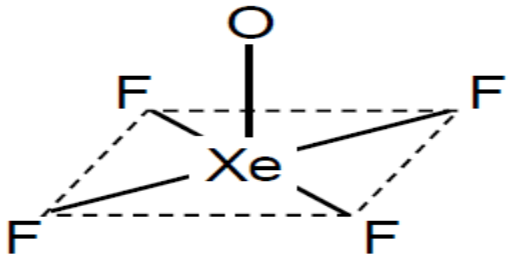
It is a yellow solid below -36°C.



Oxyfluorides

$XeOF_4$ (xenon(VI) oxyfluoride or xenon oxytetrafluoride) is a colourless liquid and is produced by hydrolysis of XeF_6:

$$XeF_6(s) + H_2O(l) \rightarrow XeOF_4 + 2HF(aq/g)$$

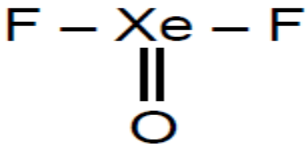


At low temperature Xe reacts with OF_2:

$$Xe(g) + OF_2 \rightarrow XeOF_2$$

$XeOF_2$ (xenon(IV) oxyfluoride or xenon oxydifluoride) is also formed by hydrolysis of XeF4 at low temperatures:

$$XeF_4(s) + H_2O(l) \rightarrow XeOF_2 + 2HF(aq/g)$$



At –20°C:

$$XeOF_2 \rightarrow XeO_2F_2 + XeF_2$$

XeO_2F_2 decomposes at room temperature: $XeO_2F_2 \rightarrow XeF_2 + O_2$

NOTE :

1. Helium has the unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.
2. **Clathrates of Noble gases.** Noble gases form a number of compounds in which the gases are entrapped within cavities of crystal lattices of certain organic and inorganic compounds. Such compounds are called clathrates or cage compounds. These are also sometimes referred to as host-guest compounds. The organic or inorganic compound with cavities is called the host while the gas atoms entrapped in it are called the guest. Only Ar, Kr and Xe form clathrates since their sizes match the size of cavities present in most of the organic and inorganic compounds. As such He and Ne do not form clathrates since they are too small to be entrapped within the cavities of organic and inorganic compounds.
3. **Interstitial compounds.** These compounds are formed when small atoms occupy positions in the interstices of the metal lattice. Only He forms such compounds since the atomic size of He is the smallest amongst the noble gases and matches the size of the interstices available in the lattice of most of the heavy metals.

Do you expect that the minimum energy necessary to eject a 3s electron from phosphorus in a photoelectron spectroscopy experiment for the process.

$$[Ne]3s^2 3p^3 \longrightarrow [Ne]\ 3s^1 3p^3 + e^-,$$

be larger than, smaller than, or the same as the 4th ionization energy (IE_4) of phosphorus?

(a) Smaller (b) Larger

(b) The same (d) cannot be answered from the given information

Photoelectron spectroscopy refers to energy measurement of electrons emitted from solids, gases or liquids by the photoelectric effect, in order to determine the binding energies of electrons in a substance. The minimum energy necessary to eject a 3s electron from phosphorus in a photoelectron spectroscopy experiment is found to be smaller than 4th ionization energy (IE_4) of phosphorus.

Correct option is (a)

Which of the following fluorides is not formed by xenon?

(a) XeF_2 (b) XeF_3 (c) XeF_4 (d) XeF_6

XeF_3 is a odd electron species, hence it is unstable so Xe does not formed XeF_3 type fluorides.

Correct option is (b)

The first noble gas compound reported is:

(a) XeO_3 (b) KrF_2 (c) XeF_6 (d) $Xe^+(PtF)_6^-$

The first compound of a noble gas $XePtF_6(s)$ was synthesized using a very strong oxidizing agent ($PtF_6(g)$)

Correct option is (d)

Which ones of the following compounds do not exist?

$[AuXe_4]$, $[KrF_2]$, $[ArF_2]$ [He–F]

Choose the correct choice out of the following

(a) $[AuXe_4]$ and [He–F]

(b) $[KrF_2]$ and $[ArF_2]$

(c) $[Ar–F_2]$, and [He–F]

(d) $[ArF_2]$ [He–F], $[AuXe_4]$

$[Ar – F_2]$ and [He – F] does not exist

Correct option is (c)

Given the following reaction conditions for the formations of the fluorides of Xe

$$Xe(g) + F_2(g) \xrightarrow[\text{one atm pressure}]{400^\circ C} A\ldots \text{ (Xe in excess)}$$

$$Xe(g) + F_2(g) \xrightarrow[\text{six atmosphere}]{600^\circ C} B\ldots \text{ (Xe : } F_2 = 1:1.6)$$

$$Xe(g) + F_2(g) \xrightarrow[\text{60 atmosphere}]{300^\circ C} C\ldots \text{ (Xe : } F_2 = 1:20)$$

A, B and C in these reactions respectively are

(a) XeF_4, XeF_2, XeF_6

(b) XeF_2, XeF_4, XeF_6

(c) XeF_6, XeF_4, XeF_2

(d) XeF_2, XeF_6, XeF_4

XeF_2, XeF_4 and XeF_6 are obtained by a direct reaction between Xe and F_2. The condition under which the reaction is carried out

$$\underset{\text{(Excess)}}{Xe(g)} + F_2(g) \xrightarrow[\text{One atm pressure}]{400^\circ C} XeF_2(g)$$

$$\underset{\text{(1:1.6 ratio)}}{Xe(g) + F_2(g)} \xrightarrow[\text{six atm}]{600^\circ C} XeF_4(g)$$

$$\underset{\text{(1:20 ratio)}}{Xe(g) + F_2(g)} \xrightarrow[\text{60 atm}]{300^\circ C} XeF_6(g)$$

Correct option is (b)

Why are the elements of Group 18 known as noble gases ?

The elements present in Group 18 have their valence shell orbitals completely filled and, therefore, react with a few elements only under certain conditions. Therefore, they are now known as noble gases.

Noble gases have very low boiling points. Why?

Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling points.

Does the hydrolysis of XeF_6 lead to a redox reaction?

No, the products of hydrolysis are $XeOF_4$ and XeO_2F_2 where the oxidation states of all the elements remain the same as it was in the reacting state.

Uses of noble gases:

Helium:

- As helium is a light and non combustible gas it is used in filling the meteorological balloons.
- A mixture of 20% oxygen and 80% helium is used for artificial respiration by deep sea divers. This mixture is used by asthma patients for respiration.
- Liquid He is used as a cryogenic liquid for producing low temperatures.
- He gas is used in gas thermometers.
- It is used as heat transfer agent in nuclear reactors.
- It is used in electric transformers.
- It is used in welding of Mg, Al and stainless steel.
- It is used to provide inert atmosphere in the preparation of Mg, Al etc.

Neon:

- It gives orange red glow in a discharge tube at 2 mm of pressure.
- It is extensively used in glow lamps known as neon tubes for advertising purposes.
- When Ne is mixed with Hg vapor or Ar it produces various colors.
- The glow of neon lamps is visible even in fog and mist hence it is used in signal lights.
- It is used in safety devices, relays and rectifiers as it has a capacity for carrying high voltage currents.

Argon:

- A mixture of Ar and mercury vapour is used in fluorescent tubes.
- It is used in filling electric bulbs.
- It is used in filling electric counter tubes, thermoionic tubes and other discharge tubes.

Krypton:

- It is used in miners cap - lamps.
- The isotope Kr-85 is used in measuring the thickness of plastic sheets, metal sheets, joints and in electronic tubes for voltage regulations.

Xeon:

- It is used in photographic flash bulbs.
- Liquid xenon is used in detecting neutral mesons and gamma photons in the bubble chamber.

Radon:

- Radon is used in the treatment of cancer.

Radon is used in detecting the defects in steel castings.

COMPILED AND CIRCULATED BY BARUN KUMAR MONDAL,
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Hazard of inert gases sign

THANK YOU