NEP Semester-V

Inorganic Chemistry

Noble gases: Group 18 elements

Contents: Occurrence and uses, rationalisation of inertness of noble gases, clathrates; preparation and properties of XeF_2, XeF_4 and XeF_6; Nature of bonding in noble gas compounds (Valence bond treatment and MO treatment for XeF_2). Molecular shapes of noble gas compounds (VSEPR theory).

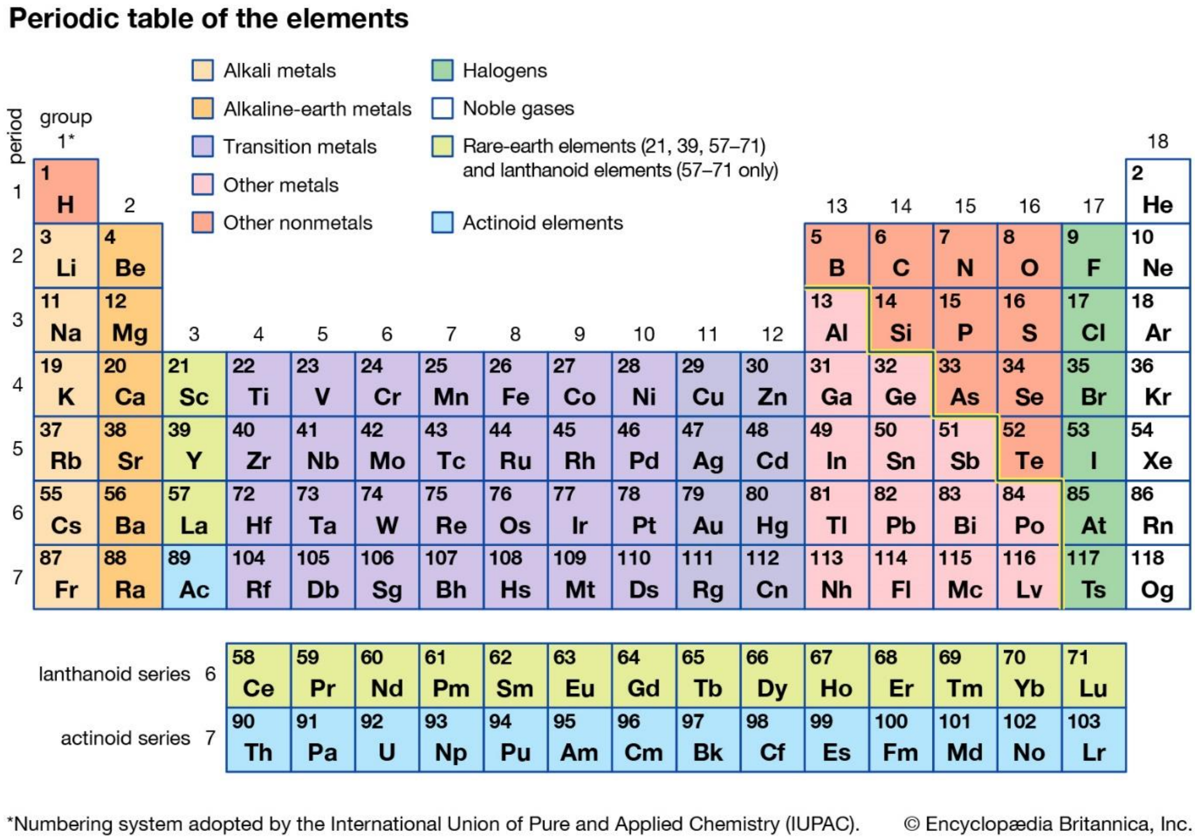
Introduction

@ The final group in the p block contains seven elements (He, Ne, Ar, Kr, Xe, Rn, Og)

@ Group 18 elements, placed on the extreme right, are known as Noble gases.

@ They are also known as inert gases (chemically inert, inappropriate as they, especially Xe has several compounds) and seldom as rare gases (low abundance, currently not used as Ar is more abundant than CO_2).

@ ^{118}Og is the newest member (synthesized in 2002, recognized in 2015) of this group, Oganesson



Occurrence of Noble Gases

@ Helium makes up 23% by mass of the Universe and the Sun, and is the second most abundant element after hydrogen; it is rare in the atmosphere because its atoms travel fast enough to escape from the Earth. All the other noble gases occur in the atmosphere.

@ The abundances of Ar (0.94% by volume) and Ne (1.5×10^{-3} %) make these two elements more plentiful than many familiar elements (such as As and Bi) in the Earths' crust.

@ Xe and Rn are the rarest elements of the group.

@ He, Ne, Ar, Kr and Xe are naturally available.

@ A mixture of Noble gases was first obtained by Cavendish in 1784.

@ Cavendish removed N_2 from air by adding excess O_2 and sparkling.

@ NO_2 formed was adsorbed in NaOH solution.

@ Excess O_2 was removed by burning with S absorbing the SO_2 in NaOH solution.

@ This produced a small volume of mixture of unreactive gases.

@ He is recovered from natural gas deposits where hydrocarbons are liquified, leaving He gas

@ Ar is recovered by fractional distillation of liquid air. It originates in air from β decay of K.

$$^{40}_{19}K + ^{0}_{-1}e \rightarrow ^{40}_{18}Ar$$

@ Rn is radioactive, produced by the decay of Ra and Th minerals.

$$^{226}_{88}Ra \rightarrow ^{40}_{18}Ar + ^{4}_{2}He$$

Use of Noble Gases

@ He has the lowest boiling point and hence is extensively used in cryoscopy as a cryogen.

@ He is also used in weather balloons and airships (less flammable than H_2). Mixture of He and O_2 (4:1) is used in for breathing (preferably over N_2) by deep sea divers. Since N_2 is soluble in blood, sudden change in pressure causes degassing and gives bubbles of N_2 in the blood. This causes the painful or fatal condition called 'bend'. He is slightly soluble so the risk of bends is reduced. The same mixture is used to treat acute asthma attacks as its density presents less resistance in the lungs compared to oxygen-air mixtures.

@ He is used to obtain low temperature required for superconductivity and lasers.

@ He is used as coolant in nuclear reactor.

@ Helium, being very light and non-inflammable is used to lift weather balloons and to inflate Superconductivity thereby increasing their payload.

@ He is also used as a flow gas in gas in liquid chromatography and in microanalysis.

@ Small amounts of Ne are used in neon discharge tubes and gives reddish orange glow.

@ Ne is used as safety device for protecting electrical equipment from high voltages

@ The largest use of Ar is to provide an inert atmosphere for metallurgical process (welding stainless steel, titanium, magnesium, aluminium and in production of titanium) and for production of air sensitive compounds.

@ Ar is also used for filling incandescent metal filament electric bulbs.

@ He and Ar are also used as cryogenic refrigerant

@ Kr and Xe are also used in filling incandescent metal filament electric bulbs (better than Ar)

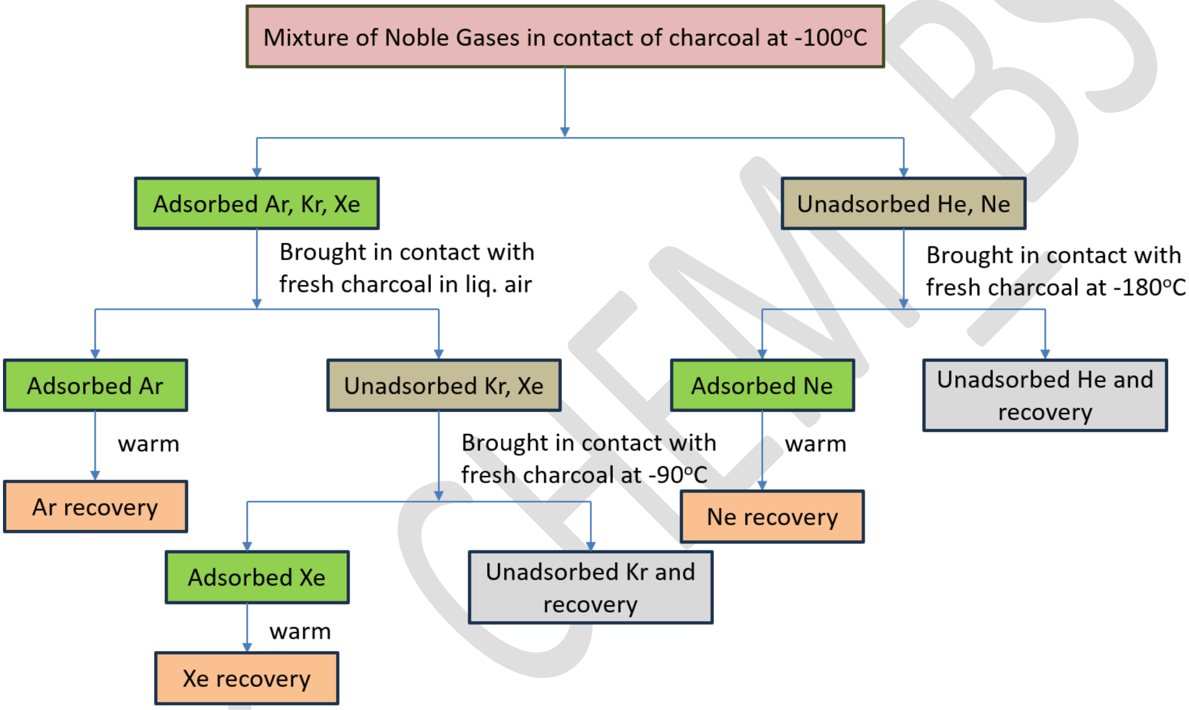
@ Xe is used as propellant for ion thrusters in space craft.

@ Xe is used general anaesthetic (but very expensive) and its isotope ^{129}Xe is used in medical imaging (Magnetic resonance imaging)

@ Rn is used in the treatment (limited) of cancer

Isolation of Noble gas

Chemico-physical method



Physical Properties Noble gases

@ Noble gases colorless and odorless mono-atomic gases, discovered by Ramsay.

@ Rn and Og are radioactive.

@ Ar is the most abundant noble gas.

@ All noble gases can be liquified.

@ Except He (second most abundant in universe), all the noble gases have 8 valence electrons.

@ General electronic (valence shell) configuration ns^2np^6.

@ Possess zero electron affinity and highest ionization energy.

@ They have very low melting and boiling points Enthalpy of vaporization is low (increases down the group due to increase in polarizability), held by weak van der Walls forces.

@ The van der Waals attraction between the molecules/atoms increases with the increase in the number of electrons per molecule or atom. Heavy molecules containing more electrons attract one another more and hance melting and boiling points increase with the increase in atomic number (down the group).

@ Boiling and melting points are low, decreases down the group. (He - lowest boiling liquid, -269 °C)

@ Helium has two isotopes, ^{3}He and ^{4}He (~ 100% of atmospheric He). ^{3}He behaves normally and ^{4}He has strange properties. When cooled below 2.2 K at 1-atm pressure, ordinary liquid ^{4}He, called He-I, changes to an abnormal form called He-II. The temperature at which the transition from He-I to He-II takes place is known as Lambda point. Below this temperature, its thermal conductivity increases a million-fold and the viscosity becomes effectively zero, hence it is described as a superfluid.

Element	**Electronic configuration**	**van der Walls radius (Å)**	**IE (kJ/mol)**
He	$1s^2$	1.20	2372
Ne	$2s^2\ 2p^6$	1.31	2080
Ar	$3s^2\ 3p^6$	1.74	1521
Kr	$3d^{10}\ 4s^2\ 4p^6$	1.89	1351
Xe	$4d^{10}\ 5s^2\ 5p^6$	2.10	1170
Rn	$4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$	2.15	1037

Chemical properties of Noble gases

@ Noble gases are chemically inert due to completely field electronic shells (highest IE and zero EA)

@ Under certain conditions, some of the noble gases form compounds.

@ Hydrates of noble gases: The hydrates of these gases are formed by compressing the gases with water. For example, $Xe \cdot 6H_2O$.

@ Compounds formed by physical trapping (Clathrates): Ar, Kr and Xe form solid compounds with certain organic molecules such as phenol and hydroquinone under pressure.

@ Though the gases are trapped, they do not form bonds.

@ Down the group, the ionisation energy of the noble gases decreases. Thus, there is an increase in chemical reactivity of the noble gases as we go down the group from, He to Rn

@ He, Ne, and Ar do not form any other compound due to their extremely high IEs.

@ The IE of Kr is lower and Kr does form some fluorides (KrF_2).

@ Although IE of Rn is lower than Xe, it has no stable isotopes, (RnF_2).

@ Xe reacts directly only with F_2.

@ Oxygen compound of Xe can be obtained from fluorides.

Rationalization of inertness of Noble Gases

@ Complete pairing of all the electrons: The stable electronic configuration ns^2np^6 is responsible for inertness of these elements.

@ High ionization energy: Due to stable electronic configuration, a large amount of energy is required to remove an outermost electron and hence do not form ions under ordinary conditions.

@ Negligible or zero electron affinity: Due to stable electronic configuration, these elements have no tendency to form anion and hence chemically inert.

@ Absence of extra bonding orbitals: Due to absence of any extra bonding orbitals, the atoms of these elements do not form any bond with other atoms.

@ In spite of these factors, elements such as Kr and Xe are known to form compounds with oxygen and fluorine.

@ Reactivity trend: Rn > Xe > Kr > Ar > Ne > He

Clathrates of Noble Gases

@ The first chemical compounds of noble gases is known as clathrate.

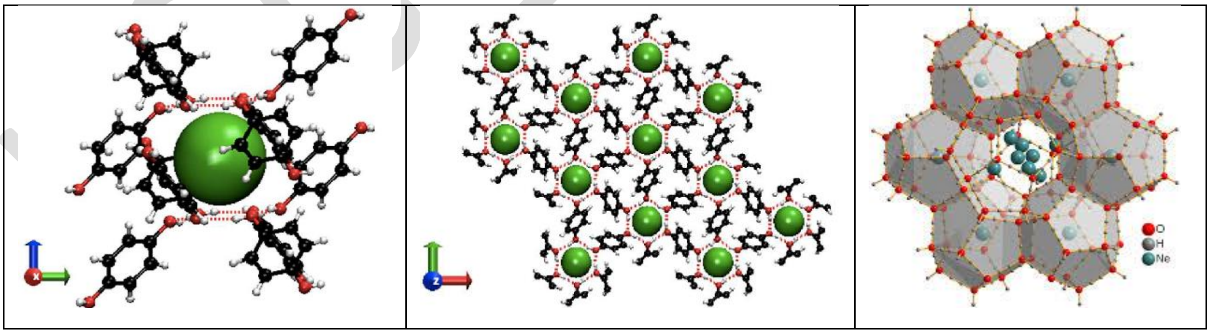
@ Clathrate is a cage compound in which noble gas atoms with suitable size are trapped in the crystal lattice of suitable organic/inorganic compounds such as such as quinol or water

@ The formation of clathrate seems to depend on relative molecular dimensions rather than on any chemical affinity.

@ Though the gases are trapped, they do not form bonds.

@ If an aqueous solution of β-quinol is crystallized under a pressure of 10-40 atmosphere of Ar, Kr or Xe, the gas gets trapped in the cavities of about 4 Å diameter in the β-quinol crystals. The composition of these clathrate compounds corresponds to 3 Quinol:1 noble gas.

@ The crystals are quite stable and can persist for several years.



@ When the clathrate is dissolved or heated, the hydrogen bonded arrangement of β-quinol breaks down and the noble gas escapes.

@ Ar, Kr and Xe can also be trapped in cavities when water is frozen under a high pressure of the gas. These are normally called 'the noble gas hydrate'. These are also clathrate with formulae approximating to $6H_2O$:1 noble gas.

@ Hydrates may not be stoichiometric since the degree to which the cavities are filled depends on the partial pressure of the guest material

@ The hydrates increase in thermal stability down the group as the noble gases become more polarisable. With xenon, at a partial pressure of 1atm, the hydrate is stable upto 275 K.

@ Because of their very low polarizability, small size and low boiling points, no hydrates/clathrates of He and Ne have been prepared.

@ Heavier noble gas (Ar) can also be trapped in cavities in synthetic zeolite containing 20% of Ar.

Use: He and Ne can be separated from Ar, Kr and Xe when quinol crystallizes from its solution in presence of their mixture. Clathrates of Ar, Kr and Xe provide convenient means of handling and transporting of their isotopes. Kr-85 clathrate provides a safe source for β-radiation while Xe-133 clathrate provides a useful source of γ-radiation.

Compounds of Xenon

@ The first Noble gas compound, $XePtF_6$ was reported by Neil Bartlett in 1962.

@ The preparation of this compound is based on the discovery of O_2PtF_6 from mixing of O_2 and PtF_6.

$$PtF_6 + O_2 \rightarrow [O_2]^+[PtF_6]^-$$

@ The compound O_2PtF_6 is ionic and represented as $[O_2]^+[PtF_6]^-$

@ PtF_6 is very strong oxidizing agent and can remove one electron from oxygen.

@ Bartlett predicted that Xe should also react with PtF_6.

@ The IE of oxygen gas (1180 kJ/mol) is almost identical with that of Xe (1170 kJ/mol), and hence lattice energies of the corresponding compounds should be similar.

@ Bartlett mixed Xe and PtF_6, yellow solid of xenon hexafluoroplatinate (V), $[Xe]^+[PtF_6]^-$ is thought to be formed at room temperature.

@ The reaction is complicated and the actual product is $[XeF]^+[Pt_2F_{11}]^-$.

$$Xe[PtF_6] + PtF_6 \xrightarrow{26^oC} [XeF]^+[PtF_6]^- + PtF_5 \xrightarrow{\text{heat } 60^oC} [XeF]^+[Pt_2F_{11}]^-$$

Xenon difluoride, XeF_2

Preparation

@ XeF_2 is prepared by heating a mixture of Xe and F_2 in 2:1 ratio at 400^0C in a sealed nickel tube. On cooling quickly, a colorless solid XeF_2 is obtained.

$$Xe\ (g) + F_2\ (g) \xrightarrow[400^oC]{\text{Ni vessel, 1 atm}} XeF_2\ (s)$$

Properties

@ Xenon difluoride is a colorless, crystalline solid with melting point 129^oC.

@ It reacts with hydrogen to give hydrogen fluoride and xenon.

$$XeF_2 + H_2 \rightarrow Xe + 2HF$$

@ It reacts with strong Lewis's acid to form xenon fluoride cations (fluoride donor).

$$XeF_2 + SbF_5 \rightarrow [XeF]^+[SbF_6]^-$$

$$XeF_2 + AsF_5 \rightarrow [XeF]^+[AsF_6]^-$$

@ It is soluble in water, undergoes slow hydrolysis. Hydrolysis is more rapid with alkali.

$$2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$$

$$2XeF_2 + 4NaOH \rightarrow 2Xe + 4NaF + O_2 + 2H_2O$$

@ It oxidizes I_2 in presence of BF_3 to give IF

$$XeF_2 + I_2 \xrightarrow{BF_3} Xe + 2IF$$

@ It oxidizes Cl^- to Cl_2

$$2XeF_2 + 2HCl \rightarrow 2HF + Xe + Cl_2$$

@ It oxidizes and fluorinates hetero element in organohalide without attacking the alkyl/aryl groups

$$XeF_2 + CH_3I \rightarrow CH_3IF_2 + Xe$$

$$XeF_2 + C_6H_5I \rightarrow C_6H_5IF_2 + Xe$$

Structure and bonding in XeF_2

@ VBT can be used for explaining the bonding in XeF_2

@ The bonding may be explained by promoting an electron from the 5p level of Xe to the 5d level.

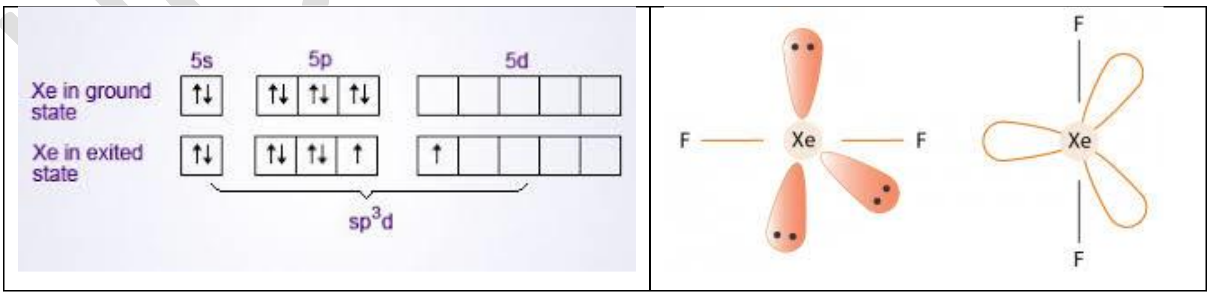
@ The two unpaired electrons of Xe form bonds with two F-atoms.

@ Undergoes sp^3d hybridization.

@ The five electron pairs point to the corners of a trigonal bipyramid.

@ Three LPs occupy the equatorial positions and two BPs occupy the apical/axial positions.

@ XeF_2 is a linear molecule with Xe-F distance of 2.00 Å



Objections

@ The 5d orbitals of Xe appear to be too large for effective overlap.

@ Bonding with F-atoms cause a large contraction in the size of d orbitals.

@ Mixing of orbitals is not much effective (large energy difference between 5p and 5d, 960 kJ/mol)

Molecular orbital theory

@ Molecular orbital explanation involving three centre (3c) bonds is more acceptable.

@ Outer electronic configuration of Xe and F-atoms are

Xe: $4d^{10}\,5s^2\,5p^6$ F: $2s^2\,2p^5$

@ It is assumed that bonding involves $5p_z$ orbital of Xe and $2p_z$ orbitals of two F-atoms.

@ For bonding, the orbitals with the same symmetry must overlap.

@ These three AOs combine to give three MOs, one bonding (ψ_1- right symmetry), one non-bonding (ψ_2) and one antibonding (ψ_3 - wrong symmetry).

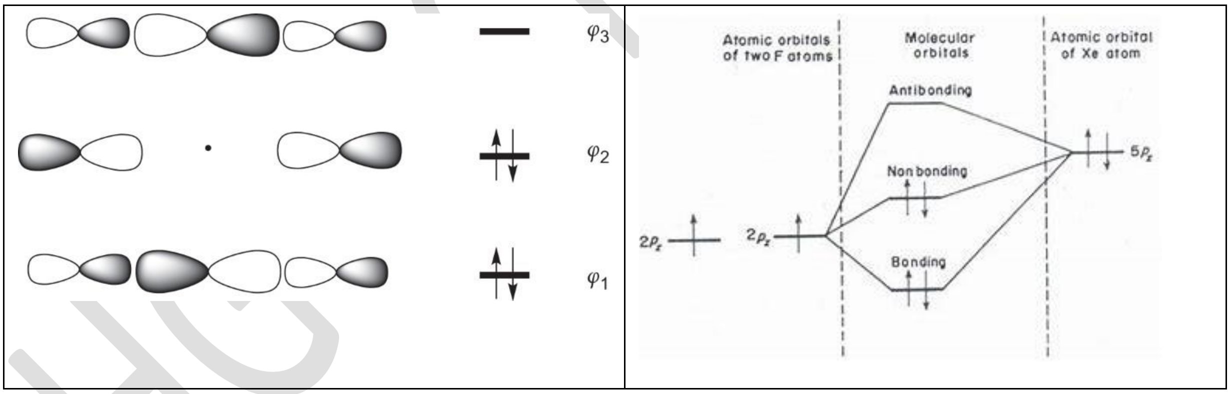
@ The original three AOs contained four electrons (two in $5p_z$ orbital of Xe and one each in $2p_z$ orbital of F-atom)

@ Out of these four, two electrons occupy the bonding MO, this pair of electrons is responsible for binding all three atoms.

@ The remaining two electrons occupy the non-bonding MO, situated primarily on F-atoms and gives some ionic character.

@ The bonding may be describes as three centre-four electron (3c-4e) σ-bonding.

@ A linear arrangement of the atoms gives the best overlap of orbitals.



Xenon tetrafluoride, XeF_4

Preparation

@ It is prepared by heating a mixture of Xe and F-atom in 1:5 ratio, in a nickel vessel, at 600°C under pressure of 5-6 atm.

$$Xe\,(g) + 2F_2\,(g) \xrightarrow[600^{o}C]{\text{Ni vessel, 6 atm}} XeF_4\,(s)$$

@ It can also be synthesized by reacting Xe with dioxygen difluoride at low temperature and pressure with high yield and purity**.**

$$Xe\,(g) + 2O_2F_2\,(g) \xrightarrow[\text{Low T and P}]{\text{Ni vessel}} XeF_4\,(s) + 2O_2$$

Properties

@ It is a colorless crystalline solid, with m.pt. 117.1°C, sublimes readily.

@ Disproportionation of XeF_4 in water (hydrolysis) produces XeO_3 (explosive).

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

@ Reaction with water at -80°C gives xenon oxofluoride

$$XeF_4 + H_2O \xrightarrow{-80^oC} XeOF_2 + 2HF$$

@ A stronger fluorinating agent than XeF_2

$$XeF_4 + Pt \rightarrow Xe + PtF_4$$

$$XeF_4 + 2SF_4 \rightarrow Xe + 2SF_6$$

@ It oxidizes iodide to iodine, chloride to chlorine

$$XeF_4 + 4KI \rightarrow 4KF + Xe + 2I_2$$

$$XeF_4 + 4HCl \rightarrow 4HF + Xe + 2Cl_2$$

@ It is also acts as a fluoride donor with Lewis's acids

$$XeF_4 + SbF_5 \rightarrow [XeF_3]^+[SbF_6]^-$$

$$XeF_4 + 2SbF_5 \rightarrow [XeF_3]^+[Sb_2F_{11}]^-$$

@ It is oxidized by hydrogen to HF at 30°C.

$$XeF_4 + 2H_2 \rightarrow Xe + 4HF$$

Structure and bonding in XeF_4

VSEPR model

@ The bonding may be explained by promoting two electrons from the 5p level of Xe to the 5d level.

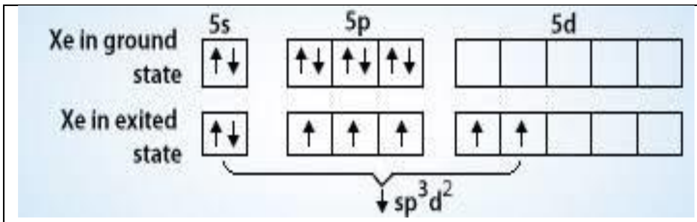
@ The four unpaired electrons form bonds with four F-atoms.

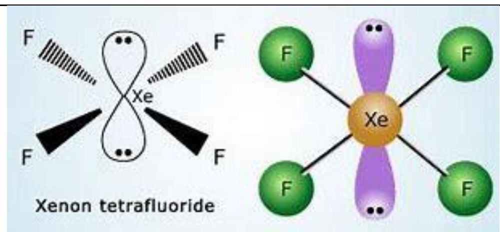
@ Undergoes sp^3d^2 hybridization.

@ The six electron pairs point to the corners of an octahedron.

@ Two LPs occupy the axial positions and four BPs occupy the molecular plane.

@ XeF_4 is a square planar molecule with Xe-F distance of 1.95 Å





Molecular orbital theory

@ A 5p_x orbital of Xe forms a 3c MO with 2p orbitals from two F-atoms.

@ The 5p_y orbital of Xe forms another 3c MO involving two more F-atoms

@ The two 3c orbitals are at right angles to each other, thus giving a square planar molecule.

Xenon hexafluoride, XeF_6

Preparation

@ It is prepared by heating Xe with excess of F_2 (in 1:20 ratio) in a nickel vessel at 300°C under pressure of about 60 atm.

$$Xe\,(g) + 3F_2\,(g) \xrightarrow[300^oC]{\text{Ni vessel, 60 atm}} XeF_6\,(g)$$

It can also be obtained by the oxidation of XeF_4 with O_2F_2 under pressure.

$$XeF_4\,(g) + O_2F_2\,(g) \xrightarrow[-130^oC]{\text{Ni vessel}} XeF_6\,(g) + O_2$$

Properties

@ Crystalline substance, MP 49.5°C.

@ It is extremely reactive and cannot be stored in glass or quartz vessels (gives explosive XeO_3).

@ Careful hydrolysis of XeF_6 produces xenon oxytetrafluoride

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

@ Complete hydrolysis of XeF_6 produces xenon trioxide, an explosive

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

@ It reacts with fluoride ion acceptors to form adducts.

$$XeF_6 + SbF_5 \rightarrow [XeF_5]^+[SbF_6]^-$$

$$XeF_6 + PtF_5 \rightarrow [XeF_5]^+[PtF_6]^-$$

$$XeF_6 + AsF_5 \rightarrow [XeF_5]^+[AsF_6]^-$$

@ XeF_6 can act as a Lewis acid. It can also act as a fluoride acceptor with RbF and CsF. On heating, $[XeF_7]^-$ ion decomposes.

$$XeF_6 + RbF \rightarrow Rb^+[XeF_7]^-$$

$$Cs^+[XeF_7]^- \xrightarrow{50^oC} XeF_6 + Cs_2[XeF_8]$$

@ XeF_6 reacts with other oxygen sources such as $NaNO_3$, OPF_3 to form oxyfluoride.

$$XeF_6 + OPF_3 \rightarrow XeOF_4 + PF_5$$

$$XeF_6 + NaNO_3 \rightarrow XeOF_4 + NaF + FNO_2$$

@ It reacts with hydrogen to give HF

$$XeF_6 + 3H_2 \rightarrow Xe + 6HF$$

@ It reacts with silica to give Xenon oxytetrafluoride.

$$2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$$

Structure and bonding in XeF_6

VSEPR model

@ The bonding may be explained by promoting three electrons from the 5p level of Xe to the 5d level.

@ The six unpaired electrons form bonds with six F-atoms.

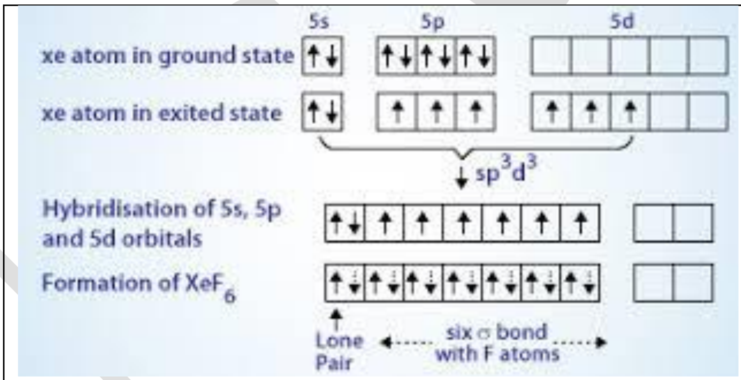
@ Undergoes sp^3d^3 hybridization.

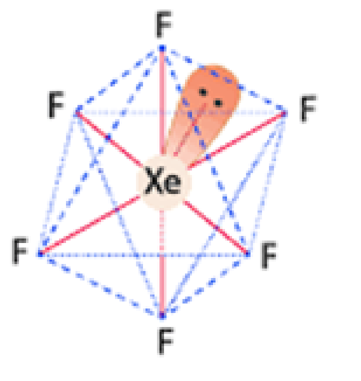
@ The seven electron pairs either gives a capped octahedron (LP pointing through one of the faces of the octahedron) or a pentagonal bipyramid.

@ Since there are six BPs and one LP, a capped octahedron would give a distorted octahedral molecule.

@ Xe-F distance of ……….Å

@ MOT fails in this case. According to MO theory, the structure of XeF_6 can be explained by considering three 3c-MO system mutually at right angles giving a regular octahedron.





Xenon Oxytetrafluoride, $XeOF_4$

Preparation

@ Xenon Oxytetrafluoride is prepared by partial hydrolysis of Xenon hexafluoride

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

@ By the action of XeF_6 on silicon dioxide

$$2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$$

Properties

@ It is a colorless compound melting at -46°C.

@ It is reduced by hydrogen to xenon.

$$2XeOF_4 + 3H_2 \rightarrow Xe + H_2O + 4HF$$

@ It reacts with silica to form xenon dioxydifluoride, XeO_2F_2, in which Xe remains in the same oxidation state, further reaction gives XeO_3 (explosive)

$$2XeOF_4 + SiO_2 \rightarrow 2XeO_2F_2 + SiF_4$$

$$2XeO_2F_2 + SiO_2 \rightarrow 2XeO_3 + SiF_4$$

@ It reacts with water give Xenon dioxydifluoride, which further reacts with water to give XeO_3.

$$XeOF_4 + H_2O \rightarrow XeO_2F_2 + 2HF$$

$$XeO_2F_2 + H_2O \rightarrow XeO_3 + 2HF$$

Structure

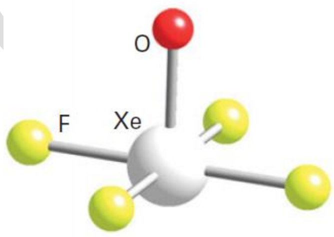
@ The bonding may be explained by promoting three electrons from the 5p level of Xe to the 5d level.

@ Out of six unpaired electrons, 4 σ bonds with four F-atoms.

@ Two unpaired electrons are used in forming one σ and one π bonds with O-atoms.

@ Undergoes sp^3d^2 hybridization.

@ The molecule adopts a regular square pyramidal arrangement with one lone pair in the axial plane.



8 $XeOF_4$

Xenon dioxydifluoride, XeO_2F_2

Preparation

@ By mixing XeO_3 and $XeOF_4$ at temperature close to -78°C. The compound is purified by fractional distillation.

$$XeOF_4 + XeO_3 \rightarrow 2XeO_2F_2$$

@ It is also formed when $XeOF_4$ is hydrolyzed or reacted with silica.

$$XeOF_4 + H_2O \rightarrow XeO_2F_2 + 2HF$$

$$2XeOF_4 + SiO_2 \rightarrow 2XeO_2F_2 + SiF_4$$

Properties

@ It is a colorless solid with melting point is 30.8°C.

@ It is easily hydrolyzed to give xenon trioxide.

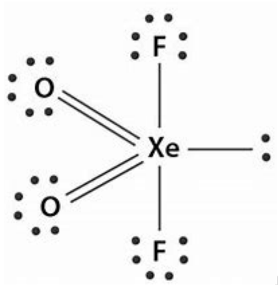
$$XeO_2F_2 + H_2O \rightarrow XeO_3 + 2HF$$

Structure

@ The bonding may be explained by promoting three electrons from the 5p level of Xe to the 5d level

@ Undergoes sp^3d hybridization

@ See saw structure with one lone pair in equatorial plane.



Xenon trioxide, XeO_3

Preparation

@ Xenon trioxide is prepared by the hydrolysis of XeF_4 or XeF_6

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

$$XeF_4 + 3H_2O \rightarrow XeO_3 + 6HF$$

Properties

@ It acts as a powerful oxidizing agent in acidic medium. For instance, it oxidizes Pu^{3+} to Pu^{4+} in the presence of H^+ ions.

$$6Pu^{3+} + XeO_3 + 6H^+ \longrightarrow 6Pu^{4+} + Xe + 3H_2O$$

@ It is an explosive white hygroscopic solid. It reacts with XeF_6 and $XeOF_4$

$$XeO_3 + 2XeF_4 \rightarrow 3XeOF_4$$

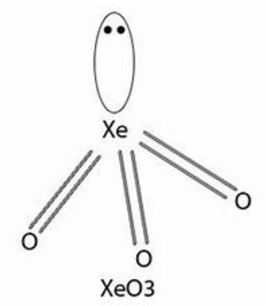
$$XeO_3 + XeOF_4 \rightarrow 2XeO_2F_4$$

Structure

@ The bonding may be explained by promoting three electrons from the 5p level of Xe to the 5d level

@ Three σ and three π bonds with three O-atoms. Undergoes sp^3 hybridization

@ Pyramidal structure with one lone pair.



Xenon tetroxide, XeO_4

Preparation

@ It is prepared by action of conc. H_2SO_4 on sodium or barium xenate (Na_4XeO_6 or Ba_2XeO_6) at room temperature.

$$Na_4XeO_6 + 2H_2SO_4 \rightarrow XeO_4 + 2Na_2SO_4 + 2H_2O$$

$$Ba_2XeO_6 + 2H_2SO_4 \rightarrow XeO_4 + BaSO_4 + 2H_2O$$

Properties

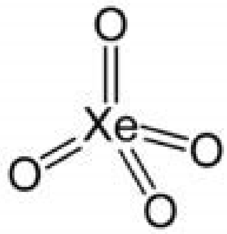
@ It is very unstable and decomposes to xenon and oxygen.

Structure

@ The bonding may be explained by promoting four electrons from the 5p level of Xe to the 5d level

@ Four σ and four π bonds with four O-atoms. Undergoes sp^3 hybridization

@ Tetrahedral structure.



Xenon oxoanions

@ Xenon trioxide soluble in water, but does not ionize. In alkaline solution, above pH 10.5 it forms xenate ion

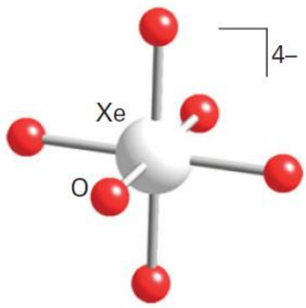
$$XeO_3 + NaOH \rightarrow Na^+[HXeO_4]^-$$

@ Xenate ion slowly disproportionate in solution to perxenate and Xe in alkaline medium.

$$2HXeO_4^- + 2OH^- \rightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O$$

@ Perxenate ion under acidic condition reverts to give xenate ion

$$XeO_6^{4-} + 3H^+ \rightarrow HXeO_4^- + ½ O_2 + H_2O$$



12 XeO_6^{4-}

Structures of some Xe-compounds

Formula	**Name**	**Oxidation state**	**Structure**
XeF_2	Xenon difluoride	+2	Linear
XeF_4	Xenon tetrafluoride	+4	Square Planner
XeF_6	Xenon hexafluoride	+6	Distorted octahedron
XeO_3	Xenon trioxide	+6	Pyramidal tetrahedral with one corner unoccupied
XeO_2F_2	Xenon dioxydifluoride	+6	Trigonal bipyramid (with one position unoccupied)
$XeOF_4$	Xenon oxytetrafluoride	+6	Square pyramidal (octahedral with one position unoccupied)
XeO_4	Xenon tetroxide	+8	Tetrahedral
XeO_3F_2	Xenon trioxydifluoride	+8	Trigonal bipyramidal
$Ba_2[XeO_6]^{4-}$	Barium perxenate	+8	Octahedral

Molecular Shapes of Noble Gas Compounds and VSEPR Theory:

@ Neither VBT nor MOT can explain the bonding in all the noble gas compounds.

@ VSEPR theory of Gillispie and Nyholm provides more rational explanation about the stereochemistry/structure of noble gas compounds.

@ VSEPR theory assumes the stereochemistry by considering the repulsions between valence shell electron pairs (bonding and nonbonding).

@ In XeF_2, the valence shell of Xe atom has ten electrons (eight from Xe-atom and one each from two F-atoms). These are distributed in five airs, two bonding and three nonbonding, which are directed to the comers of a trigonal bipyramid. Because of their greater mutual repulsion, the three nonbonding pairs are situated in the equatorial plane at 120º to each other, leaving the two bonding pairs perpendicular to the plane and so producing a linear F-Xe-F molecule.

@ Similarly, XeF_4 with six electron pairs is considered as pseudo-octahedral with its two nonbonding pair opposite to each other leaving the four F-bonds in a plane around Xe.

@ The seven electron pairs around Xe in XeF_6 suggest the possibility of a non-regular octahedral geometry and imply a distorted structure based on either mono-capped octahedral or a pentagonal pyramidal arrangement of electron pairs, with the Xe-F bonds bending away from the protruding nonbonding pair.

@ Three electron pairs of the Xe-atom can be used to complete the octet of three oxygen atoms, leaving one lone pair on xenon. This gives a trigonal pyramidal shape to XeO_3 molecule.
@ Similarly, in XeO_4, four electron pairs from Xe can coordinate with each of the four oxygens forming a tetrahedral molecule.
@ The tetrahedral SiO_4^{4-}, PO_4^{3-}, SO_4^{2-} ions (isoelectronic with XeO_4), are stabilised by pπ-dπ back bonding in which lone-pair electrons on oxygen spend some time in d orbitals on the central atom. But 5d-orbitals of Xe are ill-matched with 2p-orbitals of O, thus weak Xe-O bond is consistent with little pπ-dπ bonding and considerable polar character.

Formula	**Structure**	**EPs**	**LPs**	**VSEPR Explanation**
XeF_2 (+2)	Linear	5	3	Three LPs occupy at equatorial positions of TBP
XeF_4 (+4)	Square Planner	6	2	Six electron pairs form octahedron with two axial positions occupied by LPs
XeF_6 (+6)	Distorted octahedron	7	1	LP either at the center of a face or at the midpoint of an edge
XeO_3 (+6)	Pyramidal	7	1	Three π bonds so that the remaining four electron pairs form a tetrahedron with one corner occupied by a LP.
XeO_4 (+8)	Tetrahedral	8	0	Four π bonds so remaining four electron pair form a tetrahedron
$XeOF_2$ (+4)	T-shaped	6	2	Two BPs in Xe=O bond, two BPs in two Xe-F bond, LPs occupying two equatorial sites of TBP
XeO_2F_2 (+6)	Trigonal bipyramid	7	1	Four BPs in two Xe=O bond, two BPs in two Xe-F bond, LPs occupying two equatorial sites of TBP
$XeOF_4$ (+6)	Square pyramidal	7	1	Two bond pairs in Xe=O bond, four bond pairs in four Xe-F bonds, LP protruding from the base.
XeO_3F_2	Trigonal bipyramidal	8	0	Three π bonds so remaining five electron pairs form trigonal bipyramid
$Ba_2[XeO_6]^{4-}$	Octahedral	8	0	Two π bonds so remaining six electron pair form an octahedron.

Other compounds of noble gases

@ Kr and Rn-fluorides are known but their chemical properties are much less extensive.

@ Radon has a lower ionization energy than Xe, so it can be expected to form compounds even more readily. Evidence exists for the formation of RnF_2 and cationic compounds, such as $[RnF]^+[SbF_6]^-$, but detailed characterization is frustrated by their radioactivity.

@ Krypton has a much higher ionization energy than Xe and its ability to form compounds is more limited. Krypton difluoride, KrF_2, is prepared by passing an electric discharge or ionizing radiation through a fluorine-krypton mixture at low temperatures (−196°C). The krypton compound is a colourless volatile solid and the molecule is linear. It has a highly endergonic energy of formation and is a highly reactive compound that must be stored at low temperatures.

@ When monomeric HF is photolyzed in solid argon and annealed to 18K, HArF is formed. This compound is stable up to 27 K and contains the HAr^+ and F^- ions. The related molecular ions HHe^+, HNe^+, HKr^+ and HXe^+ have been observed by spectroscopy.

@ Titan, Saturn's moon, has a dense atmosphere in which levels of Kr and Xe are depleted in comparison to Ar. It is believed that the Kr and Xe are trapped in clathrates, whereas the smaller Ar atoms are trapped less effectively.

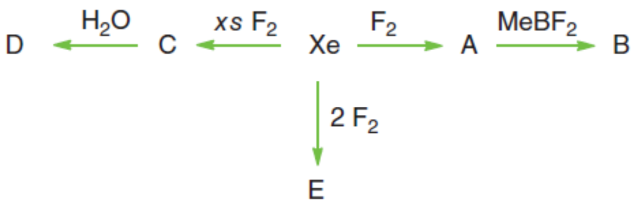
Exercises

1. Why there is a steady increase in boiling points from He to Rn?
2. Why no compounds of He and Ne are known?
3. Why noble gas, compounds are formed only with O_2, and F_2?
4. Why does the tendency to form clathrates increase down the group?
5. Given below in Column I are the few expected compounds of noble gases. Write down in Column II the shapes of these compounds on the basis of VSEPR theory.

XeF_4	
$XeOF_4$	
XeO_4	
XeF_6	
XeO_2F_2	

6. What are the factors which led Bartlett to think that Xe can be oxidised by PtF_6?
7. Would you expect nitrogen to form a compound of the type $N_2^+[PtF_6]^-$? Give reason for answer. (Ionisation energy of N_2 is 1403 kJ mol^{-1})
8. By means of balanced chemical equations and a statement of conditions, describe a suitable synthesis of (a) xenon difluoride, (b) xenon hexafluoride, (c) xenon trioxide.

9. Give a Lewis structure for XeF_7^- (b) Speculate on its possible structures by using the VSEPR model and analogy with other xenon fluoride anions.
10. Use VSEPR to predict the structures of (a) XeF_3^+, (b) XeF_3^-, (c) XeF_5^+, and (d) XeF_5^-.
11. Identify the xenon compounds A, B, C, D, and E



12. Based on VSEPR, predict the structures of $XeOF_2$, $XeOF_4$, XeO_2F_2, and XeO_3F_2.
13. Confirm that the observed gas-phase structures of XeF_2, XeF_4 and XeF_6 are consistent with VSEPR theory
14. Suggest products for the following reactions (which are not necessarily balanced on the left-hand sides):
    (a) $CsF + XeF_4 \rightarrow$
    (b) $SiO_2 + XeOF_4 \rightarrow$
    (c) $XeF_2 + SbF_5 \rightarrow$
    (d) $XeF_6 + OH^- \rightarrow$
15. Write a brief account of the chemistry of the xenon fluorides.

Books consulted and acknowledged

1. Concise Inorganic Chemistry, J. D. Lee
2. Advanced Inorganic Chemistry, Cotton and Wilkinson
3. Inorganic Chemistry, Atkins and Shriver
4. IGNOU BSc Material
5. Inorganic Chemistry, Sharp and Housecroft
6. Inorganic Chemistry, Misslar and Tarr
7. Principles of Inorganic Chemistry, Huheey, Keiter, Huheey, Medhi