4 CHAPTER

NOBLE GASES

Objectives

- Isolation of Noble Gases
- Compounds of Noble Gases
- Chemistry of Noble Gases
- Uses of Helium Neon and Argon

ISOLATION OF NOBLE GASES

4.1.1 General

The zero group of the long form of the periodic table consists of six elements, collectively known as inert gases. The elements are: helium, neon, argon, krypton, xenon and radon.

The elements of zero group are the end members of each series of the long form of the periodic table. First series ends with helium, second with neon, third with argon and so on.

All the zero group elements are gases

The zero group is the only group in the long form of the periodic table, in which all members are gases. The elements of the zero group are chemically inactive under ordinary conditions and hence are called inert gases or inactive gases.

The general outermost electronic configuration of inert gases is $ns^2\ np^6$, except for helium. Helium has $1s^2$ configuration. The electronic configuration of the inert gases is shown in the Table 4.1.

Table 4.1 Electronic configuration of noble gases

Name of the element	Symbol	Atomic Number	Electronic Configuration
Helium	He	2	$1s^2$
Neon	Ne	10	$1s^2\ 2s^2 2p^6$
Argon	Ar	18	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6$
Krypton	Kr	36	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^{10}\ 4s^2 4p^6$
Xenon	Xe	54	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^{10}\ 4s^2 4p^6 4d^{10}\ 5s^2 5p^6$
Radon	Rn	86	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 3d^{10}\ 4s^2 4p^6 4d^{10}\ 4f^{14}\ 5s^2 5p^6 5d^{10}\ 6s^2 6p^6$

Besides similarity in the electronic configuration, the following points justify the inclusion of all six gases in the same group of the periodic table. A gradation in the properties is also observed with the increase of atomic numbers.

All the elements of the zero group are colourless, odourless and tasteless gases. These gases cannot be oxidized. They do not undergo combustion themselves in air and also do not help in burning. Some physical properties of these gasses are listed in Table 4.2.

All the inert gases possess low melting and boiling points, due to weak intermolecular attractive forces. The boiling points increase down the group.

Table 4.2 Physical properties of noble gases

Noble gas	Abundance in air (% by vol)	First ionization energy ($kJmol^{-1}$)	Enthalpy of vapourization ($kJmol^{-1}$)	Melting point (K)	Boiling point (K)	Atomic radii (nm)	Solubility at 1 atm and 298 K (ppm)
He	0.00052	2372	0.08	---	4.2	0.12	8.6
Ne	0.0018	2080	1.7	24.6	27.2	0.16	10.5
Ar	0.934	1520	6.5	83.8	87.1	0.191	36.6
Kr	0.00145	1351	9.1	15.8	120.3	0.201	59.4
Xe	0.00001	1170	12.7	160.2	165.0	0.220	108.0
Rn	-	1037	18.1	202.2	211.0	0.235	-----

The ionization potentials are high, suggesting that the elements are very stable and it is difficult to remove electrons. The electron affinities of the elements are taken as zero.

These gases are sparingly soluble in water and solubility slightly increases down the group. All, except helium are absorbed by coconut charcoal at suitable temperatures. All these gases are monoatomic and give characteristic line spectra. The atomic radius of these elements is large, as the practically measured radius is van der Waals radius.

4.1.2 Isolation

The inert gases are called noble gases as they show some chemical activity under certain specified conditions. The inert gases are also called rare gases as their natural availability is very less. They are also called aerogens, since most of them are available in air. Radon is a radioactive element and short lived. The other five gases of zero group always occur in free state.

Air is a potential source of noble gases

The main sources of noble gases are air, natural gas, spring water and radioactive minerals. Air is potential source of the first five noble gases. They all form about 1% by volume of air. Argon is the principal noble gas constituent of the air.

Helium was believed to be the decay product of radioactive metals like thorium, uranium and radium. Minerals like pitchblende and monazite contain considerable amounts of occluded helium.

$$^{226}_{88}Ra \longrightarrow {}^{4}_{2}He + {}^{222}_{86}Rn \; ; \; {}^{224}_{88}Ra \longrightarrow {}^{4}_{2}He + {}^{220}_{86}Rn \; ; \; {}^{224}_{88}Ra \longrightarrow {}^{4}_{2}He + {}^{219}_{86}Rn$$

P.4.1 The density of nitrogen obtained by the distillation of liquid air is more than that obtained by the decomposition of ammonium nitrate. Why?

Solution Ammonium nitrate gives pure nitrogen on decomposition. Nitrogen obtained from liquid air has a heavier impurity argon. Hence, nitrogen obtained from liquid air is denser.

P.4.2 Two noble gases are obtained by the decay of radium. What are they?

Solution Radioactive disintegration of radium is through alpha decay. Radon is obtained. Alpha particle gains 2 electrons and gives helium.

P.4.3 Why do noble gases have comparatively large atomic sizes ?

Solution In case of noble gases vander waals radii are considered and for other elements covalent radii are considered.

EXERCISE - 4.1.1

1. Mention the abundance of noble gases in air.
2. Comment on the occurance of noble gases.
3. Why are the elements of zero group inert?

CHEMISTRY OF NOBLE GASES

4.2.1 Compounds

Noble gases have stable electronic configuration. Hence these gases are not expected to form chemical compounds with other elements.

The electron affinity values of these elements are zero. The atoms of these elements thus have no tendency to accept electrons. Hence these elements do not form anions. The ionization potentials of these elements are very high. The atoms of these elements, thus have little tendency of lose electrons. Hence these elements do not form cations.

The first and reasonably stable compound of any noble gas was prepared by Bartlett in 1962. It was based on the fact that first ionisation enthalpy of molecular oxygen (1175 kJ mol^{-1}) was almost equal with that of xenon (1170 kJ mol^{-1}). Bartlett made xenon to react with platinum hexafluoride and obtained red solid compound of composition Xenon hexafluoroplatinate (IV), $Xe[PtF_6]$. The excitement caused by this discovery led to active search for the other noble gas compounds.

$XePtF_6$ is the first known compound of a noble gases

Among noble gases, xenon is known to be reactive. It is known to form compounds with most electronegative elements fluorine, oxygen and more electronegative groups like $OSeF_6$, $OTeF_5$. The important compounds of xenon are: fluorides, oxides and oxyfluorides. Xenon cannot form compounds with nitrogen and chlorine because of their low electronegativity.

Xenon difluoride is obtained when a 2:1 mixture of xenon and fluorine are heated in a nickel tube at 673°C.

$$Xe + F_2 \longrightarrow XeF_2$$

The central atom xenon has two bond pairs and three lone pars in XeF_2. The molecule is linear and is non-polar. Xenon difluoride acts as a strong oxidant. XeF_2 on hydrolysis gives Xe, HF and O_2

Xexon forms three fluorides with fluonine

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

Xenon tetrafluoride is obtained when a 1 : 5 mixture of xenon and fluorine are heated in a nickel tube at 873°C, at a pressure of 6 atm.

$$Xe + 2F_2 \longrightarrow XeF_4$$

It undergoes sublimation. Xenon tetrafluoride molecule has four bond pairs and two lone pairs on the central atom. The shape of the molecule is square planar and is non-planar. Xenon tetrafluoride on treating with water forms xenon trioxide.

This reaction is a disproportional reaction. Xenon trioxide is a solid at room temperature, but explosive.

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

Xenon hexafluoride is obtained when a 1 : 20 mixture of xenon and fluorine are heated in a nickel tube at 573°C, at a pressure of 60 atm. It is also prepared by the reaction of XeF_4 with O_2F_2 at 143 K.

$$Xe + 3F_2 \longrightarrow XeF_6 \ ; \ XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

Xenon hexafluoride has six bond pairs and a lone pair on the central atom. The shape of the molecule is distorted octahedral and is expected to be polar molecule. Xenon hexafluoride upon hydrolysis gives xenon oxyfluorides and finally xenontrioxide.

Xenon fluorides are colourless crystalline solids at 298 K

$$6XeF_6 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime readity.

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

$$XeF_2 + PF_5 \longrightarrow XeF^+ PF_6^- \ ; \ XeF_6 + KF \longrightarrow K^+ XeF_7^-$$

Xenon fluorides are covalent

All the three types of xenon fluorides are covalent molecules. The hybridization of xenon in these molecules and the shapes of molecules are summarized in Table 4.3. The structures of the xenon fluoride molecules are shown in the Fig 4.1. Bonding in XeF_2, XeF_4 and XeF_6 are explained by using the first, second and third excited state electronic configuration of xenon respectively.

Table 4.3 Shapes of Fluorides of Xenon

Compound of xenon	Oxidation state of Xe	Melting point	Type of hybridisation	Number of lone pairs	Shape of molecule
Xenondifluoride	+2	402K	sp^3d	3	Linear
Xenontetrafluoride	+4	390K	sp^3d^2	2	Square planar
Xenonhexafluoride	+6	323K	sp^3d^3	1	Disoctahedral

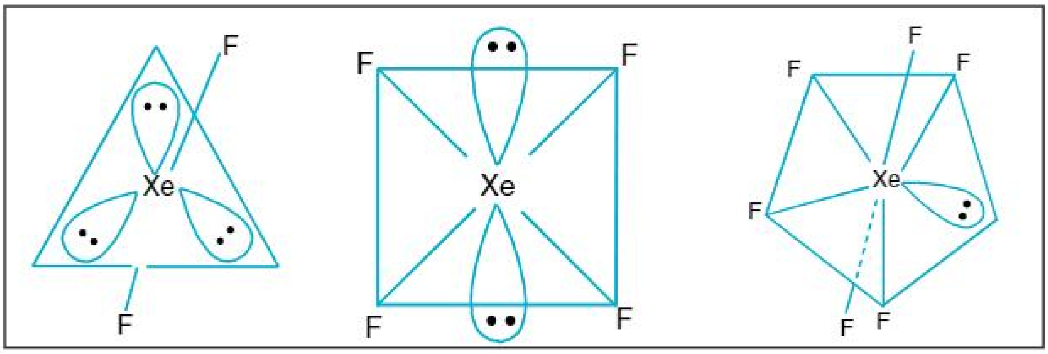

Fig 4.1 Structures of Xenon fluorides

Similar to xenon, binary compounds of krypton with fluorine are known. Radon difluoride is also reported. However, radon is almost not available in the atmosphere.

Xenontrioxide is a colourless explosive solid. It has pyramidal structure. Xenonmonoxy tetrafluoride is a colourless volatile liquid. It has square pyramidal structure.

P.4.4 Why does helium not form He_2 like Cl_2 molecule?

Solution Helium has no chemical affinity due to completely filled valency shell configuration. Therefore no diatomic molecule formed by helium. Chlorine shares one valence shell electron to form Cl_2.

P.4.5 Why has it been difficult to study the chemistry of radon?

Solution Radon is radioactive element with extremely low half-life period. During this period it is difficult to form compounds and thus makes its study difficult.

P.4.6 Why neon is totally inert?

Solution Ionisation potential is very high. Electron affinity is zero. Excitation is difficult due to lack of vacant d-orbitals in the valence shell.

P.4.7 Why xenon and krypton are chemically reactive?

Solution Down the group ionisation potential decreases. Thus Kr and Xe have low ionisation potential. Kr and Xe have empty d-orbitals in the valence shell to accomidate excited electrons. Hence Kr and Xe are chemically reactive.

4.2.2 Uses

Helium is a non- inflammable and light gas. Hence, it is used in filling balloons for meteorological observations. It is also used in gas- cooled nuclear reactors. Liquid helium (b.p. 4.2K) finds use as cryogenic agent for carrying out various experiments at low temperatures. It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis. It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

Neon is used for advertisement display

Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and in green houses.

Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs. It is also used in the laboratory for handling substances that are air-sensitive. There are no significant uses of Xenon and Krypton. They are used in light bulbs designed for special purposes.

P.4.8 Helium is preferred to nitrogen, by the deep sea divers. Why?

Solution Nitrogen has a tendency to dissolve in blood at high pressure, deep in the sea. Helium has no such tendency. Disolved nitrogen is released from blood when the divers come to the surface of the sea. It causes severe pain called 'Caisson sickness'.

P.4.9 Liquid helium is called super fluid. Why?

Solution At 4.2K, helium becomes liquid and is called He (I). On further cooling to 2.2K, He (II) is formed. Because of its low viscosity, it has fluid properties like a gas.

EXERCISE - 4.1.2

1. Discuss on the chemical reactivity of noble gases.
2. How are xenon difluoride, xenon tetrafluoride and xenon hexafluoride prepared? Write the structures of these molecules.
3. How are XeO_3 and $XeOF_4$ prepared?
4. Write important uses of helium.
5. Radon is expected to be more reactive, but its compounds are not known. Why?
6. A mixture of helium and oxygen is used to assist asthma patients. Why?
7. Why neon is used in advertisement lamps?

SYNOPSIS

1. Helium, neon, argon, krypton, xenon and radon are noble gas elements.
2. Noble gases constitute the elements of zero group in the long form of the periodic table.
3. Noble gases are called inert gases and are monoatomic. Noble gases are chemically inert because of 'octet' configuration.
4. Argon is the principal noble gas constituent in the air.
5. Helium is totally inert because of its small size, high ionisation potential and zero electron affinity.
6. The first and reasonable stable compound of any noble gas, xenonplatinum hexafluoride was prepared by Bartlett.
7. The compounds of xenon are usually three types: fluorides, oxides and oxyfluorides.
8. Helium is preferred to nitrogen by deep sea divers and asthma patients. The respiration mixture is 20% O_2 and 80% He by volume.
9. Neon is used in advertisement discharge lamps and in green houses
10. Argon is used to provide inert atomosphere in metallurgy and for filling electric bulbs.

EXERCISE - 4.2

1. Helium behaves unique during cooling. Explain.
2. Helium is chemically most inert. Justify.
3. Discuss on the shape of $XeOF_4$ molecule.
4. Helium is filled in gas thermometers. Why?
5. Discharge lamps containing neon gas is used in advertisement purpose. What is the reason?