The *p*-block Elements (Group 18 elements) - Part 5

Objectives

After going through this lesson, the learners will be able to understand the following:

- Occurrence of noble gases
- General physical and chemical properties of noble gases
- Preparation and properties of compounds of xenon
- Shapes of compounds of Xenon
- Uses of noble gases

Contents Outline

- Introduction
- General Properties of Noble Gases
- Xenon Fluoride Compounds and Properties
- Uses of Noble Gases
- Summary

Occurrence

All the noble gases except radon occur in the atmosphere. They are the minor constituent of the air, the atmospheric abundance being ~ 1% by volume of which argon is the major constituent. Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite. The main commercial source of helium is natural gas to an extent of 2-7%. Xenon and radon are the rarest elements of the group. Radon (^{222}Rn) is a decay product of ^{226}Ra and is obtained by pumping off the gas from radium chloride solutions. Ne, Ar, Xe and Kr are obtained by fractional distillation of liquid air.

Helium is the second most abundant element in the Universe. It was first found extraterrestrially in 1868 before being found on earth. J.N. Lockeyer and E. Frankland detected its presence as a new element in the spectrum of the sun's chromophore. In 1869 they suggested the name helium for this element. (Greek word, *helios*, meaning sun). The terrestrial presence of helium was confirmed by W. Ramsay in 1881.

Argon was first detected in 1785 by H. Kavendish while he was working to determine the composition of air, but he could not identify it as an element. It was almost a century later that W. Ramsay in 1895, while measuring the densities of gases present in air, confirmed the presence of a new element which he named as Argon (Greek word, *argos*, meaning idle or lazy).

Introduction

There are six elements in Group 18- Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr) , Xenon (Xe) and Radon (Rn). Radon is a radioactive element. The elements of this group were earlier termed as inert gases or rare gases. Both of these terms are now no longer used as they are not so rare and not completely inactive. They do show some chemical reactivity in the form of some xenon and krypton compounds and hence are termed as noble gases.

General Properties of Noble Gases

Electronic Configuration

All noble gases have general electronic configuration ns^2np^6 except helium which has $1s^2$ configuration (Table 5.1). Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

Table 5.1 Atomic and physical properties of Noble Gases

Propery	He	Ne	Ar	Kr	Xe	Rn*
Atomic number	2	10	18	36	54	86
Atomic mass/ g mol^{-1}	4.00	20.18	39.95	83.80	131.30	222.00
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]$4f^{14}5d^{10}6s^26p^6$
Atomic radius/pm	120	160	190	200	220	–
Ionisation enthalpy /kJmol^{-1}	2372	2080	1520	1351	1170	1037
Electron gain enthalpy /kJmol^{-1}	48	116	96	96	77	68
Density (at STP)/gcm^{-3}	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}	9.7×10^{-3}
Melting point/K	–	24.6	83.8	115.9	161.3	202
Boiling point/K	4.2	27.1	87.2	119.7	165.0	211
Atmospheric content (% by volume)	5.24×10^{-4}	–	1.82×10^{-3}	0.934	1.14×10^{-4}	8.7×10^{-6}

* *radioactive*

Ionization Enthalpy

Due to the stability associated with closed shell electronic configuration, these gases exhibit very high ionisation enthalpy. The ionisation enthalpy however decreases down the group with increase in atomic size.

Atomic Radii

Atomic radii increase down the group with increase in atomic number due to increase in number of shell. The atomic radii of noble gases are by far the largest in their respective period due to the reason that they have van der waal radii.

Electron Gain Enthalpy

Since noble gases have completely filled valence shells, they have no tendency to accept the electrons and therefore, have large positive values of electron gain enthalpy. As we move down the group, size of the atom increases so electron gain enthalpy becomes less positive.

Physical Properties of Noble Gases

- All the noble gases are colourless, odourless and tasteless, monoatomic gases.
- They are sparingly soluble in water and the solubility increases down the group.
- They have very low melting and boiling points because the only type of interatomic interaction in these elements is the weak dispersion forces. Helium has the lowest boiling point (4.2 K) of any known substance. It is unique as it can't be solidified.
- Noble gases, especially He, have an unusual property of diffusing through most commonly used laboratory materials like glasses, rubber and plastic. The van der waals attraction increases with increase in atomic size therefore ease of liquefaction increases as we move down the group from He to Xe.
- Noble gases form clathrates or cage compounds i.e gases are entrapped within the cavities of crystal lattices of certain organic or inorganic compounds. He and Ne do not form clathrate since they are too small to be trapped in cavities.

Chemical Properties of noble gases

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

i. The noble gases completely filled the closed shell configuration.
ii. They have high ionisation enthalpy and no tendency to accept electrons.

The reactivity of noble gases has been investigated occasionally, as all attempts to force them to react to form the compounds, were unsuccessful for quite a few years. In March 1962, Neil Bartlett, then at the University of British Columbia, while exploring the chemical nature of

PtF_6, noticed that when this compound was accidentally exposed to air, it produced a red compound which he identified as $O_2^+[PtF_6]^-$. From here he confirmed that PtF_6 is acting as an oxidising agent. He then realized that this compound should be able to oxidise Xe also as the first ionisation enthalpy of molecular oxygen (1175 kJ mol^{-1}) was almost identical with that of xenon (1170 kJ mol^{-1}). He made efforts to prepare the same type of compound with Xe and was successful in preparing another red colour compound $Xe^+[PtF_6]^-$ by mixing PtF_6 and xenon. After this discovery, a number of xenon compounds, mainly with most electronegative elements like fluorine and oxygen, have been synthesised. The compounds of krypton are fewer. Compounds of radon have not been isolated but have only been identified (e.g., RnF_2) by radiotracer technique. No true compounds of Ar,Ne or He have yet been prepared due to high ionization enthalpy.

Xenon- Fluorine Compounds and Their Properties

Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6.

Preparation

All three fluorides of xenon can be prepared by direct reaction between the elements under very carefully controlled conditions to get them in high purity.

$$\mathrm{Xe\,(g)} + F_2\,(g) \xrightarrow[1bar, Ni\ vessel]{673K} XeF_2\ \mathrm{(s)}$$

(xenon in excess)

$$\mathrm{Xe\,(g)} + 2F_2\,(g) \xrightarrow[7\ bar]{873K} XeF_4\ \mathrm{(s)}$$

(1:5 ratio)

$$\mathrm{Xe\,(g)} + 3F_2\,(g) \xrightarrow[60-70\ bar]{573K} XeF_6\ \mathrm{(s)}$$

(1:20 ratio)

XeF_6 can also be prepared by the oxidative fluorination of XeF_4 by O_2F_2 at 143K.

$$XeF_4\ \mathrm{(g)} + 2\ O_2F_2\ \mathrm{(g)} \xrightarrow{143K} XeF_6\ \mathrm{(s)} + O_2(g)$$

Properties of Xenon-Fluorine compounds

- XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K.
- They are powerful fluorinating agents.

$$XeF_4 + Pt \rightarrow Xe + [Pt F_4]^{2-}$$

- They are readily hydrolysed even by traces of water. The hydrolysis of difluoride is primarily a redox reaction. Xenon difluoride oxidise water to oxygen reducing themselves to elemental xenon.

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

XeF_4 reacts violently with water and undergoes disproportionation giving xenon and xenon trioxide which is a highly explosive solid.

$$6XeF_4\,(s) + 12\,H_2O\,(l) \rightarrow 4Xe\,(s) + 2XeO_3\,(s) + 24\,HF\,(aq) + 3\,O_2\,(g)$$

XeF_6 also reacts violently with water, to give highly explosive colourless solid XeO_3

$$XeF_6\,(s) + 3\,H_2O\,(l) \rightarrow XeO_3(s) + 6\,HF$$

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2 which are colourless volatile liquid and solid respectively

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

$$XeF_6\,(s) + 2\,H_2O\,(l) \rightarrow XeO_2F_2\,(s) + 4HF\,(aq)$$

- Xenon fluorides act as fluoride ion donors and react with fluoride ion acceptors to form fluoro complexes.

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

$$XeF_2 + PF_5 \rightarrow [XeF]^+\,[PF_6]^-\,;$$

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

Structures of Xenon Fluorides

The structures of the three xenon fluorides can be deduced from VSEPR and these are shown in Fig. 5.1. XeF_2 (2 bond pairs and three lone pairs) and XeF_4 (4 bond pairs and 2 lone pairs) 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. XeO_3 has a pyramidal molecular structure (Fig. 5.1). $XeOF_4$ has a square pyramidal molecular structure.

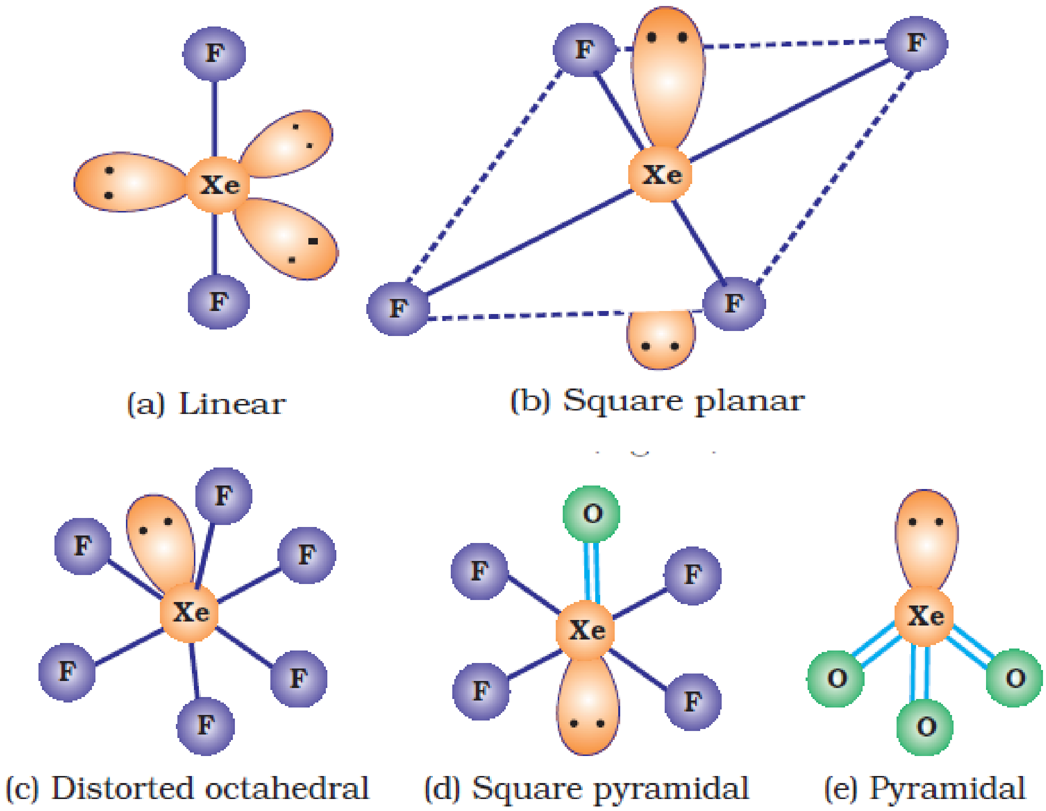


Fig 5.1 Shapes of Compounds of Xenon

Uses of Noble Gases

Helium

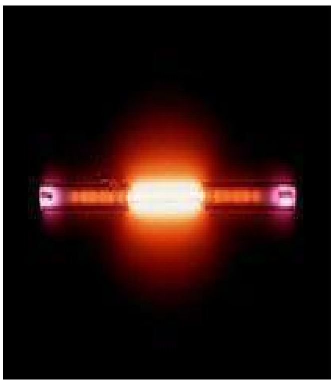


Fig. 5.2. Helium Discharge tube

(Image source: https://en.wikipedia.org/wiki/Gas-discharge_lamp#/)

- Helium is a non flammable 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. 4.2 K) 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.
- It is used in discharge tubes to produce orange glow

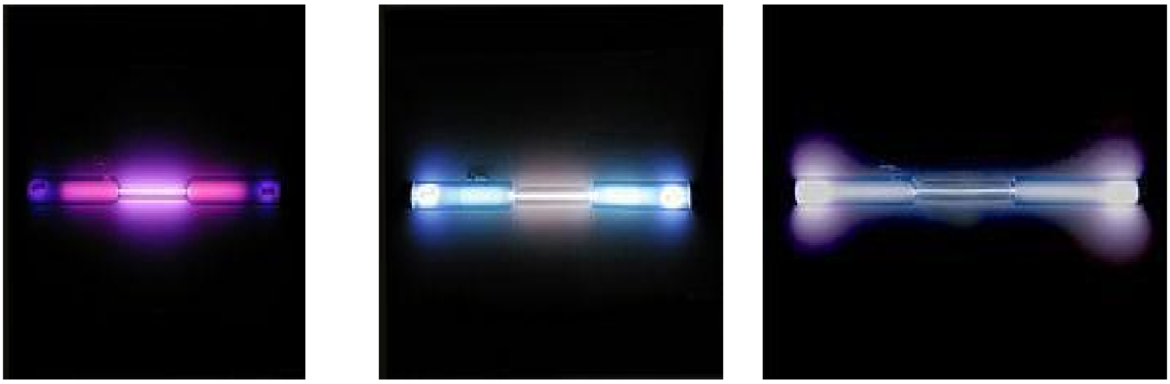
Neon

Fig. 5.3. Neon Discharge tube

(Image source: https://en.wikipedia.org/wiki/Gas-discharge_lamp#/)

- Neon is used in the discharge tubes and fluorescent bulbs for advertisement display purposes. Neon when used in the discharge tube produces an orange red glow which can be seen at long distances even in mists and fogs. However when mixed with other gases a different colour glow is produced. Neon bulbs are used in botanical gardens and in green houses.
- It is used in beacon light as a safety signal for air navigators since its light has fog penetration power.

Argon and Other Gases



(a) **(b)** **(c)**

Fig. 5.4. (a) Argon discharge tube (b) Krypton discharge tube (c) Xenon discharge tube

(Image source: https://en.wikipedia.org/wiki/Gas-discharge_lamp#/)

- 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.
- It is also used in neon signs for obtaining different colours.

There are no significant uses of Xenon and Krypton. They are more efficient than argon in gas filled lamps because of their lower thermal conductivites but due to their scarcity and high cost their use is limited.

Summary

Group 18 of the periodic table consists of elements collectively known as noble gases. All the gases except Rn occur in the atmosphere. Rn is obtained as the decay product of ^{226}Ra. They have closed valence shell electronic configuration due to which they have least tendency to react. The best characterised compounds are those of xenon with fluorine and oxygen only under certain conditions and only with highly electronegative fluorine and oxygen. These gases have several uses. Argon is used to provide an inert atmosphere, helium is used in filling balloons for meteorological observations, neon is used in discharge tubes and fluorescent bulbs.