Unit VI - Chemistry of Noble Gases

The noble gases make up a group of chemical elements with similar properties; under standard conditions, they are all odorless, colorless, monatomic gases with very low chemical reactivity. The six naturally occurring noble gases are helium, neon, argon, krypton, xenon, and the radioactive radon.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Electronic Configuration</th>
<th>Group Number</th>
<th>Period Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>2</td>
<td>1s$^2$</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>Neon</td>
<td>10</td>
<td>1s$^2$2s$^2$2p$^6$</td>
<td>18</td>
<td>2</td>
</tr>
<tr>
<td>Argon</td>
<td>18</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$</td>
<td>18</td>
<td>3</td>
</tr>
<tr>
<td>Krypton</td>
<td>36</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$3d$^{10}$4s$^2$4p$^6$</td>
<td>18</td>
<td>4</td>
</tr>
<tr>
<td>Xenon</td>
<td>54</td>
<td>1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$3d$^{10}$4s$^2$4p$^6$</td>
<td>18</td>
<td>5</td>
</tr>
<tr>
<td>Radon</td>
<td>86</td>
<td>1s$^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$</td>
<td>18</td>
<td>6</td>
</tr>
</tbody>
</table>

Chemistry of Xenon (Xe)

Xenon (Xe), chemical element, a heavy and extremely rare gas of Group 18 (noble gases) of the periodic table. It was the first noble gas found to form true chemical compounds. More than 4.5 times heavier than air, xenon is colourless, odourless, and tasteless. Solid xenon belongs to the face-centred cubic crystal system, which implies that its molecules, which consist of single atoms, behave as spheres packed together as closely as possible. The name xenon is derived from the Greek word xenos, “strange” or “foreign.”
Compounds of Xenon

Not all the noble gases combine with oxygen and fluorine. Only the heavier noble gases like Xe (larger atomic radius) will react with oxygen and fluorine. Noble gas form compounds with oxygen and fluorine only because they are most electronegative elements. So they can ionise Xenon easily.

1. Xenon Fluorides.

Xenon forms three fluorides, XeF2, XeF4 and XeF6. These can be obtained by the direct interaction between xenon and fluorine under appropriate experimental conditions.
XeF₂, XeF₄ and XeF₆ 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, XeF₂ is hydrolysed to give Xe, HF and O₂.

**Reaction of XeF₂ with water.**

\[
2\text{XeF}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Xe}(\text{g}) + 4\text{HF(aq)} + \text{O}_2(\text{g})
\]

2. **Xenon oxides.**

The oxide and oxyfluorides of xenon are obtained from the fluorides. Xenon trioxide can be prepared by the hydrolysis of XeF₆ and XeF₄.

\[
\text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF}
\]

\[
2\text{XeF}_4 + 3\text{H}_2\text{O} \rightarrow \text{Xe} + \text{XeO}_3 + 6\text{HF} + \text{F}_2
\]

3. **Xenon Oxyfluorides**

The oxyfluorides of xenon namely xenon oxydifluoride, (XeOF₂) and xenon oxytetrafluoride, (XeOF₄) are also obtained by the partial hydrolysis of XeF₄ and XeF₆ respectively.

\[
\text{XeF}_4 + \text{H}_2\text{O} \rightarrow \text{XeOF}_2 + 2\text{HF}
\]

\[
\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}
\]
Structures of Xenon Compounds

The structure of xenon compounds can be explained on the basis of the VSEPR theory as well as the concept of hybridization. The structures of oxyfluorides and oxides of xenon can best be explained by the concept of hybridization. The types of hybridization in these molecules and their shapes are also listed in the below table.

Some stable compounds of xenon and their structures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Oxidation of Xe</th>
<th>State of Hybridisation</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenon difluoride</td>
<td>XeF₂</td>
<td>+2</td>
<td>sp³d</td>
<td>Linear</td>
</tr>
<tr>
<td>Xenon tetrafluoride</td>
<td>XeF₄</td>
<td>+4</td>
<td>sp³d²</td>
<td>Square planar</td>
</tr>
<tr>
<td>Xenon hexafluoride</td>
<td>XeF₆</td>
<td>+6</td>
<td>sp³d³</td>
<td>Distorted octahedral*</td>
</tr>
<tr>
<td>Xenon oxydifluoride</td>
<td>XeOF₂</td>
<td>+4</td>
<td>sp³d</td>
<td>T shaped</td>
</tr>
<tr>
<td>Xenon oxytetrafluoride</td>
<td>XeOF₄</td>
<td>+6</td>
<td>sp³d²</td>
<td>Square pyramidal</td>
</tr>
<tr>
<td>Xenon trioxide</td>
<td>XeOF₃</td>
<td>+6</td>
<td>sp³</td>
<td>Pyramidal</td>
</tr>
</tbody>
</table>

*On the basis of hybridisation, the molecule should have pentagonal bipyramidal structure. However, this structure has not yet been confirmed. Thus, it is preferably believed to have distorted octahedral structure.

Note: The last compound in the table, Xenon trioxide has formula XeO₃ (make the correction)
Introduction: Xenon Difluoride is a chemical compound with the formula XeF₂. It was discovered in the year 1962. It is a powerful fluorinating agent. XeF₂ was considered to be a possible convenient replacement for elemental fluorine especially in addition reactions to a double bond. The oxidation state of xenon in Xenon Difluoride is +2. Xenon tetrafluoride has a negligible vapor pressure at -78°C and about 3 mm-Hg at room temperature. Xenon difluoride is a hazardous chemical, reacting with water moisture to form hydrofluoric acid.

**Synthesis.** 1. When a mixture of xenon and fluorine in the ratio of 2:1 is heated at 400°C in a sealed nickel vessel, XeF₂ is formed.

\[ \text{Xe} + F_2 \rightarrow \text{XeF}_2 \]

2. Dioxygen difluoride reacts with xenon at about 118°C to give XeF₂.

\[ \text{Xe} + \text{O}_2\text{F}_2 \rightarrow \text{XeF}_2 + \text{O}_2 \]

**Shape Hybridization and Structure of XeF₂**

In XeF₂, there is one molecule of Xenon and two molecules of Fluorine. A single molecule of Xenon has eight electrons, and a Fluorine molecule has seven valence electrons.

Total number of valence electrons = No. of valence electrons for Xenon + No. of valence electrons for Fluorine

\[-8 + 7 \times 2 = 8 + 14 = 22\]

**Hybridization** of a given molecule is vital to understand the geometry of the molecule. During bond formation, two or more orbitals with different energy levels combine and make hybrid orbitals. In XeF₂, the outer shell of Xenon has eight electrons out of which two electrons participate in bond formation.
The ground state of the Xenon has 8 electrons arranged in $s^2 p^6$ orbitals, whereas in XeF$_2$, the Xe molecule has an excited state. The arrangement of the electrons of Xenon changes to $s^2 p^5 d^1$ with two unpaired electrons. Hence the hybridization of the central atom Xe is sp$^3$d. Thus the hybridization of XeF$_2$ molecule is sp$^3$d.

The molecular geometry of Xenon Difluoride can be understood by knowing the VSEPR theory. This theory is based on the steric number of the central atom and the valence electrons of the compound. VSEPR is an abbreviation for Valence Shell Electron Pair repulsion theory.

Here the steric number for the central Xenon atom is 5. This means that a single molecule of Xenon can form bonds with five molecules. But here in XeF$_2$, it is forming bonds with two Fluorine atoms only. For Xenon, two electrons out of eight form bonds with the fluorine atoms. These six electrons are now the non-bonding electrons. These three lone pairs of electrons spread out in an arrangement that is on the equatorial position to the bonded pairs of electrons. It is clear from the geometry that bond angle of the compound is 180°.

Hence, XeF$_2$ structure features two covalent bonds between one xenon atom and two fluorine atoms. The xenon atom also holds 3 lone pairs of electrons.

**Dipole moment.** There is no net dipole moment in the compound due to the arrangement of the valence electrons in symmetry. Hence Xenon Difluoride is nonpolar as there is no polarity observed in the molecule.