Noble gases and their compounds

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Where are the noble gases?

The elements in group 0, on the right of the periodic table, are called the **noble gases**.
The group of noble gases is regarded as zero group of the periodic table. These are gases at ordinary temperature and do not have chemical reactivity. Due to chemical inertness, these were called inter gases. The elements Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), Xenon (Xe) and Radon (Rn) comprise noble gases.
Atomic World: Fast and Furious

Helium

3,000 miles per hour
1 mile/sec
Air (oxygen + nitrogen)
1,000 miles per hour
7,000,000,000 collisions per second
• Now-a-days, as number of compounds of these gases, particularly of xenon and krypton have been prepared, this shows that these gases are not completely inert.

• They are called noble gases instead of inert gases which signifies that these gases have some reactivity.

• Because of the low abundance of these gases on earth, they have also been called rare gases.
Mendeleef had not left any space for the noble gases in the periodic table.

Obviously, he could not imagine the existence of elements which have almost no chemical reactivity.
Ramsay, discoverer of these gases, proposed a new group for these elements on the basis of their atomic masses and lack of chemical reactivity.

This group is called zero group of the periodic table. The zero group also suggests chemical inertness or zero valency.
Before the discovery of noble gases, there was a sudden change from the most electronegative halogens (on right hand side) to most electropositive alkali metals (left hand side) in the periodic table.

The addition of zero group between VII A group and IA group has solved this anomaly.
• The position of noble gases in the periodic table was later on confirmed by Moseley who constructed the periodic table on the basis of atomic numbers.

• The values of atomic number of noble gases strongly suggest that they should be placed after halogens and before alkali metals.
## Physical Properties
### Noble gases

<table>
<thead>
<tr>
<th>Element</th>
<th>Outer electronic configuration</th>
<th>Vander Wall's radius (Å)</th>
<th>First IE (kj mol⁻¹)</th>
<th>m.pt. (K)</th>
<th>b.pt. (K)</th>
<th>ΔH_{fus} (kj mol⁻¹)</th>
<th>ΔH_{vap} (kj mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1s² 2p⁶</td>
<td>-</td>
<td>2372</td>
<td>-</td>
<td>4.2</td>
<td>0.02</td>
<td>0.08</td>
</tr>
<tr>
<td>Ne</td>
<td>2s² 2p⁶</td>
<td>1.31</td>
<td>2080</td>
<td>24.4</td>
<td>27.1</td>
<td>0.33</td>
<td>1.77</td>
</tr>
<tr>
<td>Ar</td>
<td>3s² 3p⁶</td>
<td>1.74</td>
<td>1519</td>
<td>83.6</td>
<td>87.3</td>
<td>1.18</td>
<td>6.5</td>
</tr>
<tr>
<td>Kr</td>
<td>4s² 4p⁶</td>
<td>1.89</td>
<td>1351</td>
<td>116</td>
<td>120</td>
<td>1.64</td>
<td>9.0</td>
</tr>
<tr>
<td>Xe</td>
<td>5s² 5p⁶</td>
<td>2.10</td>
<td>1170</td>
<td>161</td>
<td>166</td>
<td>2.3</td>
<td>12.6</td>
</tr>
<tr>
<td>Rn</td>
<td>6s² 6p⁶</td>
<td>2.15</td>
<td>1037</td>
<td>200</td>
<td>211</td>
<td>2.9</td>
<td>16.4</td>
</tr>
</tbody>
</table>
Chemical Inertness of these gases is supported by the reasons:

i) The atoms have stable completely field electronic shells

ii) They have high ionisation energies

iii) The noble have almost zero electron affinities. Therefore, they do not have any tendency to gain, lose or share electrons with other atoms.
Chemical properties of Nobel Gases

- The atoms of inert gases have saturated shells, therefore they are chemically inert.
- Recent studies have shown that under certain specific condition, they enter into chemical combinations and form some rare chemical compounds.
- The specific conditions and the types of compounds formed by these gases are disused below.
Under excited condition:- Sparking Helium at low pressure in presence of mercury, tungsten etc. forms compounds like HgHe$_2$, HgHe$_{10}$, WHe$_2$.

Helium compounds are also formed in discharge tubes like BiHe$_2$, FeHe, Pt$_3$He, PdHe. These compounds are not considered as true chemical compounds as He is absorbed on the surface.
• Compounds formed through co-ordination- Argon forms a number of unstable compound with varying no. of BF$_3$ molecules e.g. Ar.BF$_3$, Ar.6BF$_3$.

• In these compounds, argon atoms donates a pair of electrons to Boron atom of BF$_3$.

• In case of higher compounds fluorine atoms of BF$_3$ also donate pair of electrons.

• Hydrates of noble gases: The hydrates of these gases are formed by compressing the gases with water e.g., Xe.6 H$_2$O.

• Compounds formed by physical trapping (Clathrates): The inert gases Argon, Krypton and Xenon form solid compounds with certain organic molecules such as phenol and hydroquinone under pressure. In such compounds the inert gas are enclosed in the crystal lattice of organic compounds known as clathrates or cage compounds.
Xenon forms a large no. of compounds with oxygen and fluorine in different oxidation states. These are xenon fluorides, xenon oxides and xenon oxifluorides.

1. XeF$_2$

**Preparation.**

1. Xenon di fluoride is best prepared by heating a mixture of xenon and fluorine in molecular ratio of 2:1 at 400$^\circ$C in a sealed nickel tube. On cooling quickly, a colourless solid XeF$_2$ is obtained.

\[
\text{Ni} \quad \text{Xe} + \text{F}_2 \xrightarrow{400^\circ \text{C}} \text{XeF}_2
\]
Properties

1. Xenon difluoride is a colourless, crystalline solid which melts at $129^0C$.

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

   \[ \text{XeF}_2 + \text{H}_2 \rightarrow \text{Xe} + 2\text{HF} \]
3. It gives substitution reactions with strong protonic acids.

\[ \text{XeF}_2 + \text{HX} \rightarrow \text{FXeX} + \text{HF} \]
\[ \text{FXeX} + \text{HX} \rightarrow \text{XeX}_2 + \text{HF} \]

Where \( X = \text{ClO}_4^-, \text{CF}_3\text{COO}^-, \text{SO}_3\text{F}^- \) etc.
4. It hydrolyses slowly but completely in acidic, neutral or alkaline solutions.

\[2 \text{XeF}_2 + 2\text{H}_2\text{O} \rightarrow 2 \text{Xe} + 4\text{HF} + \text{O}_2\]

\[2 \text{XeF}_2 + 4\text{NaOH} \rightarrow 2\text{Xe} + 4\text{NaF} + \text{O}_2 + 2\text{H}_2\text{O}\]

5. It oxidizes iodine in the presence of BF$_3$ to give IF.
2. \( \text{XeF}_4 \)

**Preparation.**

- It is prepared by heating a mixture of xenon and fluorine, in a nickel vassal, at 400\(^\circ\)C under pressure of 5-6 atm.
- It can also be synthesized by passing an electric discharge through a mixture of xenon and fluorine at -78\(^\circ\)C.

**Properties of \( \text{XeF}_4 \) are:**

- It is a colorless, crystalline solid, with m.pt. 117.1\(^\circ\)C, sublimes readily.
- Oxidized by hydrogen to HF at 30\(^\circ\)C.
- A stronger fluorinating agent than \( \text{XeF}_2 \).
3. **XeF₆**

**Preparation.**

1. It is prepared by heating xenon with excess of fluorine (in the molar ratio of 1:20) in a nickel vessel at 250-300°C under pressure of 50-60 atm.

   \[ \text{Xe} + 3\text{F}_2 \rightarrow \text{XeF}_6 \]

2. It can also be obtained by the oxidation of XeF₄ with O₂F₂ under pressure.

   \[ \text{XeF}_4 + \text{O}_2\text{F}_2 \rightarrow 130^\circ\text{C} \rightarrow \text{XeF}_6 + \text{O}_2 \]
Properties:- Crystalline substance, m.pt. 49.5°C, Mostly volatile, all the fluorides of xenon are greenish yellow colour vapour. It is extremely reactive. Therefore, it cannot be stored in glass or quartz vessels because of the following reactions which finally give the dangerously explosive xenon trioxide.

\[
\begin{align*}
2\text{XeF}_6 + \text{SiO}_2 & \rightarrow 2\text{XeOF}_4 + \text{SiF}_4 \\
2\text{XeOF}_4 + \text{SiO}_2 & \rightarrow 2\text{XeO}_2\text{F}_2 + \text{SiF}_4 \\
2\text{XeO}_2\text{F}_2 + \text{SiO}_2 & \rightarrow 2\text{XeO}_3 + \text{SiF}_4 \\
\text{(explosive)}
\end{align*}
\]
2 It reacts with fluoride ion acceptors to form adducts.

\[ \text{XeF}_6 + \text{PtF}_5 \rightarrow \text{XeOF}_4 + \text{PtF}_5 \rightarrow [\text{XeF}_5]^+ [\text{PtF}_6]^\text{-} \]

\[ \text{XeF}_6 + \text{SbF}_5 \rightarrow \text{XeF}_6 \cdot \text{SbF}_5 \rightarrow [\text{XeF}_5]^+ [\text{SbF}_6]^\text{-} \]

\[ \text{XeF}_6 + \text{AsF}_5 \rightarrow \text{XeF}_6 \cdot \text{AsF}_5 \rightarrow [\text{XeF}_5]^+ [\text{AsF}_6]^\text{-} \]
4. XeOF₄

Preparation :

(i) Xenon Oxytetrafluoride is prepared by partial hydrolysis of Xenon hexa flouride

\[ \text{XeF}_6 + \text{H}_2\text{O} \quad \rightarrow \quad \text{XeOF}_4 + 2 \text{HF} \]

(ii) by the action of XeF₆ on silicon dioxide

\[ 2\text{XeF}_6 + \text{SiO}_2 \quad \rightarrow \quad \text{XeOF}_4 + \text{SiF}_4 \]
Soon as the yellow colour of XeF$_6$ disappears, the contents are immediately quenched with solid CO$_2$. It is done to avoid the formation of XeO$_3$ (explosive) as:

$$\text{XeOF}_4 + \text{SiO}_2 \rightarrow \text{XeO}_3 + \text{SiF}_4$$
Properties.

1. It is a colourless compound melting at -46°C.

2. It is reduced by hydrogen to xenon.
   \[ \text{XeOF}_4 + 3 \text{H}_2 \rightarrow \text{Xe} + \text{H}_2\text{O} + 4\text{HF} \]

3. It reacts with water or silica to form another oxyfluoride, \( \text{XeO}_2\text{F}_2 \), in which xenon remains in the same oxidation state. Further reaction gives explosive compound \( \text{XeO}_3 \).
4

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

\[
\text{XeO}_2\text{F}_2 + \text{H}_2\text{O} \rightarrow \text{XeO}_3 + 2\text{HF}
\]

\[
2\text{XeOF}_4 + \text{SiO}_2 \rightarrow 2\text{XeO}_2\text{F}_2 + \text{SiF}_4
\]

\[
2\text{XeO}_2\text{F}_2 + \text{SiO}_2 \rightarrow 2\text{XeO}_3 + \text{SiF}_4
\]
5. \( \text{XeO}_2\text{F}_2 \)

**Preparation:**

1. by mixing \( \text{XeO}_3 \) and \( \text{XeOF}_4 \) at temperature close to \(-78^\circ\text{C}\).

\[
\text{XeO}_3 + \text{XeOF}_4 \rightarrow 2\text{XeO}_2\text{F}_2
\]

The compound is purified by fractional distillation.

2. It is also formed when \( \text{XeOF}_4 \) is hydrolyzed or reacted with silica.

\[
2\text{XeOF}_4 + \text{SiO}_2 \rightarrow 2\text{XeO}_2\text{F}_2 + \text{SiF}_4
\]
\[
\text{XeOF}_4 + \text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 2\text{HF}
\]
1. It is a colourless solid.
2. Its melting point is 30.8°C.
3. It is easily hydrolyzed to give xenon trioxide.
   \[ \text{XeO}_2\text{F}_2 + \text{H}_2\text{O} \rightarrow \text{XeO}_3 + 2\text{HF}. \]
6. **XeO₃**

**Preparation.**

Xenon trioxide is prepared by the hydrolysis of XeF₆ or XeF₄

\[
6\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 2\text{XeO}_3 + 4\text{Xe} + 24\text{HF} + 3\text{O}_2
\]

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

It acts as a powerful oxidizing agent in acidic medium. For instance, it oxidizes Pu³⁺ to Pu⁴⁺ in the presence of H⁺ ions.

\[
6\text{Pu}^{3+} + \text{XeO}_3 + 6\text{H}^+ \rightarrow 6\text{Pu}^{4+} + \text{Xe} + 3\text{H}_2\text{O}
\]
7. XeO₄

Preparation :-

It is prepared by action of conc. H₂SO₄ on sodium or barium xenate (Na₄XeO₆ or Ba₂ Xe O₆) at room temp.

Na₄XeO₆ + 2H₂SO₄ ↝ XeO₄ + 2Na₂SO₄ + 2H₂O

Properties:

It is very unstable and decomposes to xenon and oxygen.
# Structure of Some Xenon Compounds

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
<th>Oxidation state</th>
<th>m.pt. (°C)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>XeF₂</td>
<td>Xenon difluoride</td>
<td>+2</td>
<td>129</td>
<td>Linear</td>
</tr>
<tr>
<td>XeF₄</td>
<td>Xenon tetrafluoride</td>
<td>+4</td>
<td>117</td>
<td>Square Planner</td>
</tr>
<tr>
<td>XeF₆</td>
<td>Xenon hexafluoride</td>
<td>+6</td>
<td>49.6</td>
<td>Distorted octahedron</td>
</tr>
<tr>
<td>XeO₃</td>
<td>Xenon trioxide</td>
<td>+6</td>
<td>Explodes</td>
<td>Pyramidal tetrahedral with one corner unoccupied</td>
</tr>
<tr>
<td>formula</td>
<td>name</td>
<td>charge</td>
<td>ΔH (Kcal/mol)</td>
<td>geometry</td>
</tr>
<tr>
<td>------------</td>
<td>-------------------------------</td>
<td>--------</td>
<td>---------------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>XeO$_2$F$_2$</td>
<td>Xenon dioxy difluoride</td>
<td>+6</td>
<td>30.8</td>
<td>Trigonal lipyramid (with one position unoccupied)</td>
</tr>
<tr>
<td>XeOF$_4$</td>
<td>Xenon oxy tetrafluoride</td>
<td>+6</td>
<td>-46</td>
<td>Square pyramidal (octahedral with one position un occupied)</td>
</tr>
<tr>
<td>XeO$_4$</td>
<td>Xenon tetra oxide</td>
<td>+8</td>
<td>-35.9</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>XeO$_3$F$_2$</td>
<td>Xenon trioxy difluoride</td>
<td>+8</td>
<td>-54.1</td>
<td>Trigonal bipyramidal</td>
</tr>
<tr>
<td>Ba$_2$[XeO$_6$]-4</td>
<td>Barium perxenate</td>
<td>+8</td>
<td></td>
<td>octahedral</td>
</tr>
</tbody>
</table>
## Structure and Bonding in Xenon Compounds

<table>
<thead>
<tr>
<th>Formula</th>
<th>Structure</th>
<th>No. of e pairs</th>
<th>No. of lone pairs</th>
<th>VSEPR (Explanation of structure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XeF₂</td>
<td>Linear</td>
<td>5</td>
<td>3</td>
<td>Five electron pairs form trigonal bipyramidal with three lone pairs at equatorial positions</td>
</tr>
<tr>
<td>XeF₄</td>
<td>Square Planner</td>
<td>6</td>
<td>2</td>
<td>Six electron pairs form octahedron with two positions occupied by lone pairs</td>
</tr>
<tr>
<td>XeF₆</td>
<td>Distorted octahedron</td>
<td>7</td>
<td>1</td>
<td>Pentagonal bipyramidal or capped octahedron with one lone pair</td>
</tr>
<tr>
<td>XeO₃</td>
<td>Pyramidal</td>
<td>7</td>
<td>1</td>
<td>Three π bonds so that the remaining four electron pairs form a tetrahedron with one corner occupied by a lone pairs.</td>
</tr>
<tr>
<td>Formula</td>
<td>Structure</td>
<td>No. of e pairs</td>
<td>No. of lone pairs</td>
<td>VSEPR (Explanation of structure)</td>
</tr>
<tr>
<td>-------------</td>
<td>------------------</td>
<td>----------------</td>
<td>-------------------</td>
<td>-------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>XeO₂F₂</td>
<td>Trigonal lipyramid</td>
<td>7</td>
<td>1</td>
<td>Two π bonds so remaining five electron pair form trigonal bipyramid with one equatorial position occupied by a lone pair</td>
</tr>
<tr>
<td>XeOF₄</td>
<td>Square pyramidal</td>
<td>7</td>
<td>1</td>
<td>One π bond so remaining six electron pairs form an octahedron with one position occupied by a lone pair.</td>
</tr>
<tr>
<td>XeO₄</td>
<td>Tetrahedral</td>
<td>8</td>
<td>0</td>
<td>Four π bonds so remaining four electron pair form a tetrahedron</td>
</tr>
<tr>
<td>XeO₃F₂</td>
<td>Trigonal bipyramid</td>
<td>8</td>
<td>0</td>
<td>Three π bonds so remaining five electron pairs form trigonal bipyramid</td>
</tr>
<tr>
<td>Ba₂[XeO₆]</td>
<td>Octahedral</td>
<td>8</td>
<td>0</td>
<td>Two π bonds so remaining six electron pair form an octahedron.</td>
</tr>
</tbody>
</table>
Molecule | Type of Hybridization
---|---
XeF$_4$ | $sp^3d^2$

Geometrical Shape

Xe

F

F

F

F
Molecules & Type of hybridization

$\text{XeF}_6 \quad \text{sp}^3\text{d}^3$

$\text{XeO}_3 \quad \text{sp}^3$
$XeO_2F_2$ \[ sp^{3d} \]

$XeO_2F_4$ \[ Sp^{3d^2} \]
$\text{XeOF}_4 \quad \text{Sp}^3\text{d}^2$

$\text{XeO}_6 \quad \text{Sp}^3\text{d}^2$
Significance of Noble gases in development of theoretical chemistry.

1. *In Elucidation of distribution of electrons in atom*
2. *In periodic classification*
3. *In the development of electronic theory of valency*
4. *In radioactivity.*
REFERENCES


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