THE NOBLE GASES

21-1 Occurrence, Isolation, and Applications

The noble gases (Table 21-1) are minor constituents of the atmosphere, from which Sir William Ramsay was first able to isolate the elements Ne, Ar, Kr, and Xe. William F. Hillebrand had isolated helium gas from uranium minerals, and Ramsay was able to demonstrate that the gas has the same spectrum as the element identified spectroscopically in the sun by Sir J. Norman Lockyer and Sir E. Frankland in 1868.

Helium occurs in radioactive minerals and, notably, in some natural gases in the United States. Its origin is entirely from the decay of uranium or thorium isotopes that emit α-particles. These α-particles are helium nuclei that acquire electrons from surrounding elements, and if the rock is sufficiently impermeable, the helium remains trapped. The gas radon, all of whose isotopes are radioactive with short half-lives, was characterized in the decay series from uranium and thorium.

The elements Ne, Ar, Kr, and Xe are obtained from fractionation of liquid air. The gases were originally termed inert, and thought to have no chemical reactivity at all. They provided the key to the problem of valency, the interpretation of the periodic table, and the concept of the closed-electron shell configuration. Although we now know that some of the noble gases can form compounds, they still provide a point of reference in these respects.

A main use of helium is as the liquid in cryoscopy. Argon may be used to provide an inert atmosphere in laboratory apparatus, in welding, and in gas-filled electric light bulbs. Neon is used for discharge lighting tubes, giving the familiar red glow of “neon” signs.

Radon, formed from other elements by radioactive decay sequences, is a health hazard in houses in certain granite areas. It is taken into the lungs, where by-products from its decay sequences cause cancer. Thorough ventilation of the houses is important in such areas.

21-2 The Chemistry of Xenon

During studies with the very reactive gas PtF₆, Bartlett found that a crystalline solid, \([O_2^+][PtF_6^-]\), was formed with oxygen. He noted that since the ionization enthalpy of Xe is almost identical with that of O₂, an analogous reaction might be expected and, indeed, in 1962 he reported the first compound containing a noble gas, a red crystalline solid first believed to be \([Xe^+][PtF_6^-]\), but now known to be more complex.
### Table 21-1  Some Properties of the Noble Gases

<table>
<thead>
<tr>
<th>Element</th>
<th>Outer Configuration</th>
<th>First Ionization Enthalpy (kJ mol⁻¹)</th>
<th>Normal bp(K)</th>
<th>Vol. % in atmosphere (× 10⁴)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1s²</td>
<td>2369</td>
<td>4.2</td>
<td>5.2</td>
</tr>
<tr>
<td>Ne</td>
<td>2s²2p⁶</td>
<td>2078</td>
<td>27.1</td>
<td>18.2</td>
</tr>
<tr>
<td>Ar</td>
<td>3s²3p⁶</td>
<td>1519</td>
<td>87.3</td>
<td>9340.0</td>
</tr>
<tr>
<td>Kr</td>
<td>4s²4p⁶</td>
<td>1349</td>
<td>120.3</td>
<td>11.4</td>
</tr>
<tr>
<td>Xe</td>
<td>5s²5p⁶</td>
<td>1169</td>
<td>166.1</td>
<td>0.08</td>
</tr>
<tr>
<td>Rn</td>
<td>6s²6p⁶</td>
<td>1036</td>
<td>208.2</td>
<td></td>
</tr>
</tbody>
</table>

There is now an extensive chemistry of xenon with bonds to F and O; one compound with a Xe—N bond is known, but compounds with bonds to other elements are highly unstable. A few krypton compounds exist, but while there should be an extensive chemistry of Rn, the short lifetimes of the isotopes make study impossible. Xenon only reacts directly with fluorine, but oxygen compounds can be obtained from the fluorides. Certain compounds are very stable and can be made in large quantities. Table 21-2 lists some of the more important compounds and their properties.

### Table 21-2  Some Xenon Compounds

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Compound</th>
<th>Form</th>
<th>mp(°C)</th>
<th>Structure</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>XeF₂</td>
<td>Colorless crystals</td>
<td>129</td>
<td>Linear</td>
<td>Hydrolyzed to Xe + O₂; very soluble in HF(ℓ)</td>
</tr>
<tr>
<td>IV</td>
<td>XeF₄</td>
<td>Colorless crystals</td>
<td>117</td>
<td>Square</td>
<td>Stable</td>
</tr>
<tr>
<td>VI</td>
<td>XeF₆</td>
<td>Colorless crystals</td>
<td>49.6</td>
<td>Complex, see text</td>
<td>Stable</td>
</tr>
<tr>
<td></td>
<td>Cs₂XeF₈</td>
<td>Yellow solid</td>
<td>-46</td>
<td>Square pyramid</td>
<td>Stable</td>
</tr>
<tr>
<td></td>
<td>XeOF₄</td>
<td>Colorless liquid</td>
<td>31</td>
<td>Seesaw F-axial</td>
<td>Stable</td>
</tr>
<tr>
<td></td>
<td>XeO₂F₂</td>
<td>Colorless crystals</td>
<td>31</td>
<td>Pyramidal</td>
<td>Explosive, hygroscopic; stable in solution</td>
</tr>
<tr>
<td></td>
<td>XeO₃</td>
<td>Colorless crystals</td>
<td>31</td>
<td>Pyramidal</td>
<td>Explosive</td>
</tr>
<tr>
<td>VIII</td>
<td>XeO₄</td>
<td>Colorless gas</td>
<td>-35.9</td>
<td>Tetrahedral</td>
<td>Explosive</td>
</tr>
<tr>
<td></td>
<td>XeO₆⁻</td>
<td>Colorless salts</td>
<td></td>
<td>Octahedral</td>
<td>Anions HXeO₆⁻, H₂XeO₆²⁻, H₃XeO₆ also exist</td>
</tr>
</tbody>
</table>
Fluorides

Thermodynamic studies of Reactions 21-2.1 to 21-2.3

\[ \text{Xe} + \text{F}_2 = \text{XeF}_2 \quad (21-2.1) \]
\[ \text{XeF}_2 + \text{F}_2 = \text{XeF}_4 \quad (21-2.2) \]
\[ \text{XeF}_4 + \text{F}_2 = \text{XeF}_6 \quad (21-2.3) \]

show that only these three fluorides exist. The three equilibria are established rapidly only above 250 °C, and the synthesis of one fluoride either from the others or instead of the others must be performed above this temperature. The three fluorides are volatile substances, subliming readily at 25 °C. They can be stored in nickel vessels, but XeF₄ and XeF₆ are exceptionally readily hydrolyzed, and even traces of water must be excluded.

\textit{Xenon difluoride} (XeF₂) is best made by interaction of Xe with a deficiency of F₂ at high pressures. The deficiency of F₂ insures exclusive formation of the difluoride. It dissolves in water to give solutions with a pungent odor of XeF₂. Hydrolysis is slow in acid solution, but rapid in the presence of bases, due to Reaction 21-2.4.

\[ \text{XeF}_2 + 2 \text{OH}^- = \text{Xe} + \frac{3}{2} \text{O}_2 + 2 \text{F}^- + \text{H}_2\text{O} \quad (21-2.4) \]

Such aqueous solutions are strong oxidizers, converting HCl to Cl₂ and Ce³⁺ to Ce⁴⁺. Xenon difluoride is also a mild fluorinating agent for organic compounds; for example, benzene forms C₆H₅F.

\textit{Xenon tetrafluoride} (XeF₄) is the easiest of the three fluorides to prepare. On heating a 1:5 mixture of Xe and F₂ at 400 °C and about 6-atm pressure for a few hours, XeF₄ is formed quantitatively. It resembles XeF₂ except for its behavior on hydrolysis, as discussed later. Xenon tetrafluoride will fluorinate aromatic rings in compounds such as toluene.

\textit{Xenon hexafluoride} (XeF₆) is obtained by the interaction of XeF₄ and F₂ under pressure or directly from Xe and F₂ at temperatures above 250 °C and pressures greater than 50 atm. Xenon hexafluoride is extremely reactive, attacking even quartz as in Reaction 21-2.5.

\[ \text{SiO}_2 + 2 \text{XeF}_6 \longrightarrow 2 \text{XeOF}_4 + \text{SiF}_4 \quad (21-2.5) \]

Xenon hexafluoride is a strong acid according to the Lux–Flood definition that was discussed in Chapter 7. It accepts oxide ion from other compounds and inserts fluoride ion in its place. The order of decreasing Lux–Flood acidity is

\[ \text{XeF}_6 > \text{XeO}_2\text{F}_4 > \text{XeO}_4 > \text{XeOF}_4 > \text{XeF}_4 > \text{XeO}_2\text{F}_2 > \text{XeO}_3 > \text{XeF}_2 \]

Any acid reacts by accepting oxide from any base beneath it in this series, and replacing it with fluoride. This can be useful in synthesis, and Reaction 21-2.6 is an example.

\[ \text{XeOF}_4 + \text{XeO}_3 \longrightarrow 2 \text{XeO}_2\text{F}_2 \quad (21-2.6) \]

The colorless crystals of XeF₆ contain both tetramers and hexamers, each
made up of $\text{XeF}_5^+$ units linked by unsymmetrical and bent $\text{F}^-$ bridges, as shown in Fig. 21-1. Monomeric $\text{XeF}_6$ in the liquid or the vapor has a distorted octahedral structure because of a lone pair of electrons at Xe.

**Xenon Fluoride Complexes**

The xenon fluorides will react with strong Lewis acids such as $\text{SbF}_5$ or $\text{IrF}_5$ to give adducts. The three types of adducts formed by $\text{XeF}_2$ are $\text{XeF}_2 \cdot \text{MF}_5$, $2\text{XeF}_2 \cdot \text{MF}_5$, and $\text{XeF}_2 \cdot 2\text{MF}_5$, where $M = \text{Ru, Ir, Pt}$, and so on. Although $\text{XeF}_2 \cdot \text{IF}_5$ has a molecular rather than ionic structure, in most cases adduct formation involves fluoride ion transfer to give structures that contain ions, such as $\text{XeF}^+$ (formed by loss of $\text{F}^-$ from $\text{XeF}_2$), $\text{Xe}_2\text{F}_3^+$ (which has a planar Structure 21-1),

![Figure 21-1](image)

and $\text{XeF}_6^+$ (formed by transfer of $\text{F}^-$ from $\text{XeF}_6$). Examples include $[\text{XeF}_5^+][\text{PtF}_6^-]$ and Reaction 21-2.7.

\[
2 \text{XeF}_2 + \text{AsF}_5 \longrightarrow [\text{Xe}_2\text{F}_3^+] [\text{AsF}_6^-] \tag{21-2.7}
\]

Xenon hexafluoride can act as a Lewis acid toward $\text{F}^-$ and can be converted to heptafluoro or octafluoro xenates as in Reactions 21-2.8 and 21-2.9.

**Figure 21-1** The tetrameric (a) and the hexameric (b) units that make up the crystal structure of $\text{XeF}_6$. Each is built up of $\text{XeF}_5^+$ units bridged by $\text{F}^-$ ions. There are at least four crystalline forms of the substance, three of which are built up of tetramers and one which includes both tetramers and hexamers.
\[
\begin{align*}
\text{XeF}_6 + \text{RbF} & \rightarrow \text{RbXeF}_7 \quad (21-2.8) \\
2 \text{RbXeF}_7 & \rightarrow \text{XeF}_6 + \text{Rb}_2\text{XeF}_8 \quad (21-2.9)
\end{align*}
\]

These rubidium octafluoroxenates are among the most stable xenon compounds known and decompose only above 400 °C.

**Xenon–Oxygen Compounds**

Xenon trioxide is formed in the hydrolysis of XeF₄ and XeF₆ according to Reactions 21-2.10 and 21-2.11.

\[
\begin{align*}
3 \text{XeF}_4 + 6 \text{H}_2\text{O} & \rightarrow \text{XeO}_3 + 2 \text{Xe} + \frac{3}{2} \text{O}_2 + 12 \text{HF} \quad (21-2.10) \\
\text{XeF}_6 + 3 \text{H}_2\text{O} & \rightarrow \text{XeO}_3 + 6 \text{HF} \quad (21-2.11)
\end{align*}
\]

The colorless, odorless, and stable aqueous solutions of XeO₃ appear to contain XeO₃ molecules. On evaporation of water, XeO₃ is obtained as a white deliquescent solid that is dangerously explosive. In basic solution, a xenate(VI) ion (HXeO₄⁻) is formed, as in Reaction 21-2.12.

\[
\text{XeO}_3 + \text{OH}^- \rightarrow \text{HXeO}_4^- \quad (21-2.12)
\]

The ion HXeO₄⁻ slowly disproportionates to give a xenate(VIII) (or perxenate ion, XeO₆³⁻), as in Reaction 21-2.13.

\[
2 \text{HXeO}_4^- + 2 \text{OH}^- \rightarrow \text{XeO}_6^{1+} + \text{Xe} + \text{O}_2 + 2 \text{H}_2\text{O} \quad (21-2.13)
\]

Perxenates are also formed by oxidation of HXeO₄⁻ with ozone. The perxenate ions are yellow and are both powerful and rapid oxidizing agents. Salts such as Na₄XeO₆·8H₂O are stable and sparingly soluble in water.

In alkaline solution, the main form is the ion HXeO₆³⁻, and perxenates are only slowly reduced by water. However, in acid solution, reduction by water according to Reaction 21-2.14 is almost instantaneous, and the hydroxyl radical is involved as an intermediate.

\[
\text{H}_2\text{XeO}_6^0 + \text{H}^+ \rightarrow \text{HXeO}_4^- + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \quad (21-2.14)
\]

When barium perxenate is heated with concentrated sulfuric acid, xenon tetroxide (XeO₄) is formed as an explosive and unstable gas.

The aqueous chemistry of xenon is summarized by the potentials:

**Acid solution**

\[
\begin{align*}
\text{H}_4\text{XeO}_6 & \xrightarrow{2.36 \text{V}} \text{XeO}_3 \xrightarrow{2.12 \text{V}} \text{Xe} \\
\text{XeF}_3 & \xrightarrow{2.64 \text{V}} \text{Xe}
\end{align*}
\]

**Alkaline solution**

\[
\begin{align*}
\text{HXeO}_6^{3-} & \xrightarrow{0.94 \text{V}} \text{HXeO}_4^- \xrightarrow{1.26 \text{V}} \text{Xe}
\end{align*}
\]
21-3 Other Noble Gas Chemistry

Radon might be expected to display even more chemistry than xenon, but because of the radioactivity of all radon isotopes, rather little has been learned about it. Apparently, at least one radon fluoride of uncertain composition does exist.

The other noble gas atoms have higher ionization energies than the xenon atom, and they therefore are much less reactive. In a consistent manner those compounds formed by the lighter noble gases are less stable than those of xenon.

Krypton difluoride (KrF₂) is obtained when an electric discharge is passed through a mixture of Kr and F₂ at −180 °C. It resembles XeF₂, being a volatile white solid constructed of linear FKrF molecules, but differs in that it is thermodynamically unstable, as indicated by Reactions 21-3.1 and 21-3.2.

\[
\begin{align*}
\text{KrF}_2(g) &= \text{Kr}(g) + \text{F}_2(g) \quad \Delta H^\circ = -63 \text{ kJ mol}^{-1} \quad (21-3.1) \\
\text{XeF}_2(g) &= \text{Xe}(g) + \text{F}_2(g) \quad \Delta H^\circ = 105 \text{ kJ mol}^{-1} \quad (21-3.2)
\end{align*}
\]

Some compounds with Xe—C bonds are known. An example is C₆F₅Xe⁺, which is made by Reaction 21-3.3.

\[
\text{XeF}_2 + \text{B(C}_6\text{F}_5)_3 \rightarrow [\text{C}_6\text{F}_5\text{Xe}^+]\text{[F}_3\text{BC}_6\text{F}_5^-] \quad (21-3.3)
\]

STUDY GUIDE

Study Questions

A. Review

1. What is the origin of terrestrial helium?
2. Why do the boiling points of the noble gases vary systematically with atomic number? What interatomic forces account for this variation?
3. How are XeF₂, XeF₄, and XeF₆ prepared?
4. Write balanced equations for the hydrolyses of XeF₂, XeF₄, and XeF₆.
5. How are xenates and perxenates made?

B. Additional Exercises

1. Write balanced equations for
   (a) The oxidation of HXeO₄⁻ by ozone.
   (b) The reduction of XeO₃ by I⁻ in acid solution to give Xe.
   (c) Oxidation of HCl by XeF₂.
   (d) Oxidation of Ce³⁺ by XeF₂.
   (e) Synthesis of [XeF]⁺[SbF₆].
2. Show the electron-pair geometry around each atom in Xe₂F₅⁺ and classify each atom using the AB₅E₁ system.
3. Draw the Lewis diagrams and show the electron-pair geometries around each atom in
4. Prepare a MO description of the bonding in XeF₂ using only a colinear set of \( p \) orbitals.

5. Discuss the following reactions in terms of the Lux–Flood definition of acids and bases:

(a) \( \text{XeF}_6 + \text{XeO}_2\text{F}_2 \rightarrow 2 \text{XeOF}_4 \)

(b) \( \text{XeO}_2\text{F}_2 + \text{XeO}_2\text{F}_2 \rightarrow \text{XeOF}_4 + \text{XeO}_4 \)

(c) \( \text{XeF}_2 + \text{Na}_2\text{XeO}_6 \rightarrow \text{no reaction} \)

C. Questions from the Literature of Inorganic Chemistry


(a) Write a plausible sequence of reactions for the hydrolysis of \( \text{XeF}_4 \) in excess water.

(b) Explain Reactions 1, 2, 4, 11, 12, 16, and 17 in terms of the Lux–Flood definition of acids and bases. Identify the acid and base in each reaction.

(c) Prepare an order of base strength for each of the bases featured in the reactions of (b).


(a) Explain how each of the following adducts may be considered to arise from fluoride ion transfer to give ionic compounds with weak F⁻ bridges in the solid state: (i) \( \text{XeF}_4\cdot2\text{SbF}_5 \); (ii) \( \text{XeF}_4\cdot\text{RuF}_5 \) and \( \text{XeF}_4\cdot\text{RuF}_5 \); (iii) \( \text{XeF}_4\cdot\text{SbF}_5 \) and \( \text{XeF}_4\cdot2\text{SbF}_5 \); and (iv) \( \text{XeOF}_3\cdot\text{SbF}_5 \) and \( \text{XeOF}_3\cdot2\text{SbF}_5 \)

(b) Describe the geometries (ignoring the weak F⁻ bridges) of the cations in the compounds of (a). Use the \( AB_{x}E_{y} \) classification, and pay close attention to the positions of the lone electron pairs.

(c) Do the oxygen atoms in \( \text{XeOF}_3^+ \) and \( \text{XeO}_2\text{F}_2 \) prefer equatorial or axial positions?

**SUPPLEMENTARY READING**


