Hydrides, Oxides, and Halides of the s- and p-block elements

Hydrogen

- Hydrogen forms more compounds than any other element
  -> Three electronic possible processes:
    (1) loss of a valence electron to give $H^+$ (proton acids)
    (2) acquisition of an electron to give $H^-$ (hydrides)
    (3) formation of a covalent bond as in $\text{CH}_4$

Note: There are many “in between cases”:
- Formation of metallic hydrides (not regarded as simple ionic hydrides)
- Formation of hydrogen bridge bonds in electron deficient compounds or transition metal complexes
- Hydrogen bonding in polar solvents
Hydrides

- All compounds of hydrogen could be termed “hydrides”, but not all display “hydridic” character
  --> Hydridic substances react either as hydride ion (H⁻) donors or clearly contain anionic hydrogen:

- “Neutral” hydrogen compounds (e.g. CH₄) have bonds with highly covalent character
- “Acidic” hydrogen compounds have highly polarized bonds which dissociate in polar solvents:

Classification of Binary Hydrides

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<thead>
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<tbody>
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<tr>
<td>Cs</td>
<td>Ba</td>
<td>Lu</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
<td>Tl</td>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
<td>At</td>
<td>Rn</td>
</tr>
</tbody>
</table>

- Salt-like
- Intermediate between salt-like and covalent
- Covalent
- Metallic
- Binary hydrides are unknown
Synthesis of Hydrogen Compounds

• Direct combination of elements:

• Protonation of a Brønsted base

• Metathesis (= double replacement) of a halide with a hydride

Reactions of Hydrogen Compounds

• Heterolytic cleavage by hydride transfer:

• Heterolytic cleavage by proton transfer:

• Homolytic cleavage:

• Oxidation (gives $E_nO_m$ and $H_2O$, except metallic and group 17)
Bond Energies

<table>
<thead>
<tr>
<th>Element-Hydrogen Bond Energies (average), kJ mol⁻¹</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>B-H 389</td>
<td>C-H 411</td>
</tr>
<tr>
<td>In-H 243</td>
<td>Sn-H &lt;314</td>
</tr>
</tbody>
</table>

Proton Affinity

- The proton affinity ($A_p$) is defined as the energy associated with the heterolytic cleavage of the E–H bond in the gas phase:

\[
H^+ + E^- \rightarrow E^- + H^+ \quad \text{with} \quad -A_p
\]
Proton Affinity Data

<table>
<thead>
<tr>
<th>Proton Affinities for $\text{EH}_n^{1-}$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3^-$</td>
</tr>
<tr>
<td>1745</td>
</tr>
<tr>
<td>$\text{SiH}_3^-$</td>
</tr>
<tr>
<td>1554</td>
</tr>
<tr>
<td>$\text{GeH}_3^-$</td>
</tr>
<tr>
<td>1509</td>
</tr>
</tbody>
</table>

*Proton affinity refers to the reaction $\text{E-H} = \text{H}^+ + \text{E}^-$; values in kJ/mol

Hydrides of Boron

- Diborane $\text{B}_2\text{H}_6$ is a gas (bp $-92.6^\circ\text{C}$) that is flammable in air and instantly hydrolyzed by $\text{H}_2\text{O}$:

- Borane $\text{BH}_3$ is unstable and is formed via thermal decomposition of diborane:

- The oxidation of diborane $\text{B}_2\text{H}_6$ is extremely exothermic:
Structure and Bonding in Boranes

- The structure and bonding in boranes is unlike those of other hydrides (e.g. CH₄).
- There are not sufficient electrons to allow formation of conventional two-electron bonds → electron deficient bonds.
- In the valence bond model the B–H–B bridge in diborane can be described as a three-center-two-electron bond (3c-2e bond):

Neutral Boranes

Beside diborane there is a large number of borane cluster compounds:
Structure and Bonding in Boranes

• To account for the structure and bonding in higher borane there are a total of five structurally different bonding elements present:

<table>
<thead>
<tr>
<th>Bonding element</th>
<th>Bonding type</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terminal boron-hydrogen bond</td>
<td>2c–2e</td>
<td>B—H</td>
</tr>
<tr>
<td>Hydrogen bridge bond</td>
<td>3c–2e</td>
<td></td>
</tr>
<tr>
<td>Boron-boron bond</td>
<td>2c–2e</td>
<td>B–B</td>
</tr>
<tr>
<td>Open B–B–B bond</td>
<td>3c–2e</td>
<td></td>
</tr>
<tr>
<td>Closed boron bond</td>
<td>3c–2e</td>
<td></td>
</tr>
</tbody>
</table>

Valence Description of Boranes
Hydrogen Storage

Holding hydrogen gas in your hands...

Various metal alloys are commercially available as a safe way to store hydrogen.

Nanocrystalline hydrides show a very fast kinetics for the absorption and desorption process:

<table>
<thead>
<tr>
<th>Storage capacities for different methods:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ gas at 100 bar</td>
<td>0.81 mole/cm³</td>
</tr>
<tr>
<td>Liquid H₂</td>
<td>7.0 mole/cm³</td>
</tr>
<tr>
<td>Hydride MgH₂</td>
<td>11.1 mole/cm³</td>
</tr>
</tbody>
</table>

Carbon Nanotubes

- Recently, carbon nanotubes have been showed to reversibly store hydrogen gas:

  | Graphite-like structure of carbon-nanotubes: | TEM image of a carbon-nanotube assembly: | Loading and unloading of nanotubes with hydrogen: |
Hydrogen + Fuel Cells = Electricity

+ Transportation =

Higher Fuel Efficiency

+ Zero Pollution

Classification of Binary Oxides

<table>
<thead>
<tr>
<th>1</th>
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<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂O</td>
<td>BeO</td>
<td>B₂O₃</td>
<td>CO</td>
<td>NO</td>
<td>O₂</td>
<td>F₂O</td>
<td>F₂O₂</td>
</tr>
<tr>
<td>Na₂O</td>
<td>MgO</td>
<td>Al₂O₃</td>
<td>SiO₂</td>
<td>P₄O₁₀</td>
<td>SO₂</td>
<td>Cl₂O</td>
<td>Cl₂O₇</td>
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<tr>
<td>K₂O</td>
<td>CaO</td>
<td>Ga₂O₃</td>
<td>GeO₂</td>
<td>As₄O₆</td>
<td>SeO₂</td>
<td>Br₂O</td>
<td>Br₂O₂</td>
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<tr>
<td>Rb₂O</td>
<td>SrO</td>
<td>In₂O₃</td>
<td>SnO₂</td>
<td>Sb₄O₆</td>
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<td>I₂O₄</td>
<td>I₂O₉</td>
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<tr>
<td>BaO</td>
<td>Tl₂O₃</td>
<td>Tl₂O</td>
<td>PbO₂</td>
<td>Bi₂O₅</td>
<td>PoO₂</td>
<td>XeO₃</td>
<td>XeO₄</td>
</tr>
</tbody>
</table>

Ionic | Polymeric | Molecular covalent
Properties of Oxides

- Ionic oxides always react with water to give basic solutions
- The more covalent oxides that react with water always generate acidic solutions
- Polymeric oxides: there are basically two different types
  - Truly extended structures:
  - Molecular species such as $\text{P}_4\text{O}_6$ or $\text{P}_4\text{O}_{10}$ (and other group 15 analogs)
    -> There is a great difference in reactivity depending on the nature of their “polymeric” structure

Silicate Minerals

- Silicon forms a very large number of compounds containing tetrahedral $\text{SiO}_4^{4-}$ anions
  -> contained in many minerals (more than 80% of the earth’s crust atoms are silicon and oxygen!)
- Quartz is the most common form of silica ($\text{SiO}_2$)

Crystal structure of β-Quartz
Why is Silica Polymeric?

- Why is carbon dioxide monomeric (a molecular species), whereas silicon dioxide (=silica) is polymeric? 
  -> the pi-bonds that involve p-orbitals other than 2p (3rd row and heavier elements) are weaker than two sigma bonds:

\[
\begin{align*}
C-O &: 335 \text{ kJmol}^{-1} \times 2 = 670 \text{ kJmol}^{-1} \\
C=O &: 715 \text{ kJmol}^{-1}
\end{align*}
\]

\[
\begin{align*}
Si-O &: 420 \text{ kJmol}^{-1} \times 2 = 840 \text{ kJmol}^{-1} \\
Si=O &: 590 \text{ kJmol}^{-1}
\end{align*}
\]

- Although \( \text{SiO}_2 \) does not react with water to generate an acidic solution, its acidic properties are revealed by the reaction with base:

\[
\text{SiO}_2 + 4 \text{OH}^- \rightarrow \text{SiO}_4^{4-} + 2 \text{H}_2\text{O}
\]

- \( \text{SiO}_4^{4-} \) reacts with protons to generate condensed species:

\[
\text{SiO}_4^{4-} + 2 \text{H}_3\text{O}^+ \rightarrow [\text{O}_3\text{Si-O-SiO}_3]^{6-} + 3 \text{H}_2\text{O}
\]

- Further condensations lead to more highly polymerized species 
  -> formation of silicate minerals
Aluminosilicates

- $\text{Al}^{3+}$ can replace $\text{Si}^{4+}$ as long as electroneutrality is maintained by compensating cations forming feldspars, zeolites and ultramarines.

$\Rightarrow$ both natural and synthetic zeolites find wide applications as cation exchangers (some cations will fit more snugly in the cavities), “molecular sieves” to absorb water or other uncharged small molecules ($\text{CO}_2$, $\text{NH}_3$, organic compounds)

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula (idealized composition)</th>
<th>Ring sizes</th>
</tr>
</thead>
<tbody>
<tr>
<td>faujasite$^a$</td>
<td>$\text{Na}<em>{10}\text{Al}</em>{24}\text{Si}<em>{12}\text{O}</em>{64}\cdot 24\text{H}_2\text{O}$</td>
<td>4.6.12</td>
</tr>
<tr>
<td>natrolite$^a$</td>
<td>$\text{Na}<em>{10}\text{Al}</em>{24}\text{Si}<em>{12}\text{O}</em>{64}\cdot 16\text{H}_2\text{O}$</td>
<td>4.8</td>
</tr>
<tr>
<td>stilbite$^a$</td>
<td>$\text{Na}<em>{10}\text{Ca}</em>{8}\text{Al}<em>{16}\text{Si}</em>{12}\text{O}_{64}\cdot 56\text{H}_2\text{O}$</td>
<td>4.5.6.8.10</td>
</tr>
<tr>
<td>Linde $\lambda$</td>
<td>$\text{Na}<em>{10}\text{Al}</em>{24}\text{Si}<em>{12}\text{O}</em>{64}\cdot 27\text{H}_2\text{O}$</td>
<td>4.6.8</td>
</tr>
<tr>
<td>ZSM-5$^a$</td>
<td>$\text{Na}<em>{10}\text{Al}</em>{24}\text{Si}<em>{12}\text{O}</em>{64}\cdot 16\text{H}_2\text{O}$</td>
<td>4.5.6.7.8.10</td>
</tr>
<tr>
<td>boggasite$^b$</td>
<td>$\text{Na}<em>{10}\text{Al}</em>{24}\text{Si}<em>{12}\text{O}</em>{64}\cdot 70\text{H}_2\text{O}$</td>
<td>4.5.6.10.12</td>
</tr>
<tr>
<td>sodalite$^b$</td>
<td>$\text{Na}<em>{10}\text{Al}</em>{24}\text{Si}<em>{12}\text{O}</em>{64}\cdot 2\text{H}_2\text{O}$</td>
<td>4.6</td>
</tr>
<tr>
<td>mordenite$^b$</td>
<td>$\text{Na}<em>{10}\text{Al}</em>{24}\text{Si}<em>{12}\text{O}</em>{64}\cdot 24\text{H}_2\text{O}$</td>
<td>4.5.6.8.12</td>
</tr>
<tr>
<td>rho$^b$</td>
<td>$\text{Na}<em>{10}\text{Al}</em>{24}\text{Si}<em>{12}\text{O}</em>{64}\cdot 44\text{H}_2\text{O}$</td>
<td>4.6.8</td>
</tr>
</tbody>
</table>


$^b$ Natural: substitution of ions often occurs in natural zeolites.

$^c$ Synthetic.
Classification of Oxides

Circles: amphoteric behavior
Octagons: amphoteric in lower oxidation states, acidic in higher

Acid-base Properties of Oxides

- Basic oxides react with water to generate hydroxide:

- Similar reactivity is observed for group 1 and 2 salts of anions of other p-block elements:

- Amphoteric oxides display both acidic and basic reactivity:
Aluminum

- Aluminum is manufactured by electrolysis of alumina, which is obtained from Bauxite (1886, Hall-Heroult process)
  
  - The ore is mixed with hot solution of NaOH, which will dissolve the oxides of aluminum and silicon but not other impurities
  - The alumina is recovered by precipitation using CO$_2$, an acidic oxide:
    \[
    2[\text{Al(OH)}_4]^- + 2 \text{CO}_2 \rightarrow \text{Al}_2\text{O}_3 + 2 \text{HCO}_3^- + 3 \text{H}_2\text{O}
    \]
  - The purified alumina is mixed with cryolite (mixture of NaF and AlF$_3$) and heated to 980°C to melt the solids
  - The mixture is electrolyzed at 4-5 Volts and 50,000-150,000 Amps.
    - One pound of aluminum requires 6-8 kilowatts of energy!

A 300 W light bulb can run for one hour with the energy it takes to make a single pop can...

Electrolysis of Alumina

**Electrolysis of Aluminum**

Bauxite ore is purified to Al$_2$O$_3$, which is mixed with cryolite, a mixture of NaF and AlF$_3$, which melts at 1000°C.
Acidic Oxides

- Acidic oxides react with water to generate hydronium ions (H₃O⁺):
  \[ \text{SO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + 2 \text{HSO}_3^- \]

- \( \text{P}_4\text{O}_{10} \) is the acidic anhydride of phosphoric acid (\( \text{H}_3\text{PO}_4 \)) and can be used to generate acid anhydrides of other hydroxylic acids:
  \[ \text{P}_4\text{O}_{10} + 12 \text{HONO}_2 \rightarrow 6 \text{N}_2\text{O}_5 + 4 \text{H}_3\text{PO}_4 \]

\( \rightarrow \) \( \text{N}_2\text{O}_5 \) reacts with water to regenerate \( \text{HONO}_2 \)

(Note: NO and \( \text{N}_2\text{O} \) are not acidic nitrogen oxides)
Nitric Acid

• \( \text{NO}_2 \) undergoes a redox process upon reaction with water:

\[
\begin{align*}
\text{N}_2 + \text{O}_2 & \rightarrow 2 \text{NO}_3 \\
2 \text{NH}_3 + 5/2 \text{O}_2 & \rightarrow 2 \text{NO} + 3 \text{H}_2 \text{O}
\end{align*}
\]

Molecules Containing Nitrogen and Oxygen

• \( \text{NO}_2 \) is synthesized from \( \text{N}_2 \) and \( \text{H}_2 \) as follows:

\[
\begin{align*}
\text{N}_2 + \text{O}_2 & \rightarrow 2 \text{NO} \\
2 \text{NO} + \text{H}_2 & \rightarrow 2 \text{NO}_2 + \text{H}_2 \text{O}
\end{align*}
\]
Binary Halides

- As for the hydrides and oxides, halides form ionic, polymeric and molecular (covalent) binary compounds with other elements:

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<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td></td>
<td>BeF₂</td>
<td>BF₃</td>
<td>CF₄</td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>MgF₂</td>
<td></td>
<td>AlF₃</td>
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<td>GeF₄</td>
<td>AsF₅</td>
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<td>IF₇</td>
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<td>PbF₄</td>
<td>BiF₅</td>
<td></td>
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</tbody>
</table>

Synthesis of Binary Halides

- Direct interaction with the elements:
  - Most elements can be directly reacted with halogens to form halides:

    - For metals, HF, HCl, and HBr may also be used

- Treatment of oxides with other halogen compounds:
  - Oxides are often replaced by halogens-containing compounds:
    \[ Pr₂O₃ + 6 \text{NH}_₄\text{Cl} \rightarrow 3 \text{PrCl}_₃ + 3 \text{H}_₂\text{O} + 6 \text{NH}_₃ \]

- Halogen exchange:
  - Many halides react to exchange halogen with elemental halogens, acid halides or halide salts
    -> this is especially important for the synthesis of fluorides from chlorides
Molecular Halides

- Most of the electronegative elements, and metals in high oxidation states form molecular halides
  \(\rightarrow\) gases, liquids or solids with molecules held together only by dispersion (van der Waals) forces

- Molecular halides are often easily hydrolyzed:
  \[
  \text{BCl}_3 + 3 \text{H}_2\text{O} \rightarrow \text{B(OH)}_3 + 3 \text{H}^+ + 3 \text{Cl}^- \\
  \text{SiCl}_4 + 4 \text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4 \text{H}^+ + 4 \text{Cl}^-
  \]

Bridged Halides

- Polymeric halide compounds are formed with elements of intermediate electronegativity
  \(\rightarrow\) the partial positive charge on the bonding partner can further interact with the partial negative charge on the halide forming bridged structures
Bonding in Bridged Halides

- The bonding in bridged halides is similar as in boranes
- The A–X–A bridge in bridged halides can be described as a three-center-four-electron bond (3c-4e bond)
- There are not sufficient bonding orbitals to allow formation of conventional two-electron bonds → orbital deficient bond
  
  Note: the bond order is only 0.5 (per A–X bond), since 2 electrons are in nonbonding orbitals!

Polyatomic Halide Ions

- In addition to the common monoatomic halide ions, numerous polyatomic species (cationic and anionic) have been prepared:

\[ \text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^- \]

\[ K = 698 \text{ at } 25^\circ \text{C in aq. solution} \]

Some examples of polyiodide ions

*Distances in triiodide vary depending on the cation. In some cases both I–I distances are identical, but in the majority of cases they are different. Differences in I–I distances as great as 33 pm have been reported.*
Description of Bonding in $I_3^-$

- The linear structure of $I_3^-$ can be described via a sp$^3$d hybridized central atom and a total of five electron pairs (two BPs, 3 LPs)
- Alternatively, the central atom can be looked at as sp$^2$+p hybridized resulting a *three-center-four-electron bond*
  → the resulting bond order is 0.5, which readily accounts for the weaker axial bond found in molecules such as PX$_5$, BrF$_3$, etc.
  **Note:** I–I bond length in $I_3^-$ 290 pm, in I$_2$ 267 pm!

Interhalogens

- Halogens form many compounds containing two or more different halogens
  → these might be diatomic (ClF) or polyatomic (such as ClF$_3$, BrF$_5$ or IF$_7$)

<table>
<thead>
<tr>
<th>Formation oxidation state of central atom</th>
<th>Number of lone pairs on central atom</th>
<th>Compounds and ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>+7</td>
<td>0</td>
<td>IF$_7^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IF$_5^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IF$_3^-$</td>
</tr>
<tr>
<td>+5</td>
<td>1</td>
<td>CIF$_4$, BrF$_3$, IF$_3^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CIF$_3^-$ BrF$_2$, IF$_3^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CIF$_2^-$ BrF$_3$, IF$_3^-$</td>
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<tr>
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<td>CIF$_3^-$ BrF$_3$, IF$_3^-$</td>
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<tr>
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<td>CIF$_4^-$ BrF$_3$, I$_2$Cl$_4^-$</td>
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<td>CIF$_3^-$ BrF$_3$, I$_2$Cl$_4^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CIF$_3^-$ BrF$_3^-$ I$_2$Br$_2$</td>
</tr>
</tbody>
</table>

Note the size effect of central atom: only iodine forms compounds with 7 and 8 substituents
Pseudohalogens

- Parallels have been observed between the chemistry of the halogens and a number of other dimeric species (= pseudohalogens):
  - Neutral diatomic species: $\text{Cl}_2$
  - Ion of 1– charge: $\text{Cl}^–$
  - Formation of hydrohalic acids: $\text{HCl}$
  - Formation of interhalogen compounds: $\text{ICl, BrCl, CIF}$
  - Insolubility in water of salts with heavy metals such as $\text{Ag}^+$ and $\text{Pb}^{2+}$: $\text{AgCl, PbCl}_2$
  - Addition of halogens across multiple bonds

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral dimeric species</td>
<td>$\text{Cl}_2$</td>
</tr>
<tr>
<td>Ion of 1– charge</td>
<td>$\text{Cl}^–$</td>
</tr>
<tr>
<td>Formation of hydrohalic acids</td>
<td>$\text{HCl}$ (strong)</td>
</tr>
<tr>
<td>Formation of interhalogen compounds</td>
<td>$\text{Br}_2 + \text{Cl}_2 \rightarrow 2 \text{BrCl}$</td>
</tr>
<tr>
<td>Formation of heavy metal salts of low solubility</td>
<td>$\text{AgCl}$</td>
</tr>
<tr>
<td>Addition to unsaturated species</td>
<td>$\text{Cl}_2 + \text{C}=\text{C} \rightarrow \text{Cl} \text{C}=\text{C} \rightarrow \text{[Co(CO)]}_2$</td>
</tr>
</tbody>
</table>

Noble Gas Compounds

- Before 1962 no compounds containing covalently bonded noble gases were known
  -> since then a large number of fluorides and oxides have been prepared
- $\text{XeF}_2$ (linear) and $\text{XeF}_4$ (planar) have structures in accord with the VSEPR predictions, $\text{XeF}_6$ and $\text{XeF}_8^{2–}$ are difficult to interpret

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electron pairs</th>
<th>Hybridization</th>
<th>Predicted structure</th>
<th>Experimental structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{XeF}_2$</td>
<td>5</td>
<td>$sp^3d$</td>
<td>Linear (TBP)</td>
<td>Linear</td>
</tr>
<tr>
<td>$\text{XeF}_4$</td>
<td>6</td>
<td>$sp^3d^2$</td>
<td>Square (octahedral)</td>
<td>Square planar</td>
</tr>
<tr>
<td>$\text{XeF}_6$</td>
<td>7</td>
<td>$sp^3d^3$</td>
<td>Nonoctahedral (capped octahedron?)</td>
<td>Unknown exactly, but not octahedral</td>
</tr>
</tbody>
</table>
Noble gas fluorides are formed by mixing xenon and fluorine and activating the mixture by thermal or photochemical energy:

\[
\begin{align*}
\text{Xe} + \ F_2 & \rightarrow \text{XeF}_2 \\
\text{Xe} + 2 \ F_2 & \rightarrow \text{XeF}_4 \\
\text{Xe} + 3 \ F_2 & \rightarrow \text{XeF}_6
\end{align*}
\]

The challenge in these reactions is the isolation of pure compounds, since all three products tend to form.

Fig. 17.2 Equilibrium pressures of xenon fluorides as a function of temperature. Initial conditions: 125 mmol Xe, 1225 mmol F₂ per liter. At higher Xe to F₂ ratios the XeF₂ diminishes considerably and the remaining two curves shift to the left. [From Selig, H. Halogen Chem. 1967, 1, 403. Reproduced with permission.]