Structures and bonding models for covalent compounds of p-block elements – Valence Bond

• Lewis structures (atom connectivities, all valence electrons, formal charges)
• Valence Shell Electron Pair Repulsion (VSEPR) (foolproof method of predicting molecular structure based upon the number of electron pairs around atom)
• Modified Lewis structures (depict molecular structure plus, valence electrons, and formal charges)
• Hybridization (equivalent orbitals for all valence shell electron pairs)
• Prediction of composition and structure of binary compounds (based on valence shell electron configurations of combining atoms and the notion that a chemical bond consists of a shared electron pair in a bonding orbital formed by overlap of orbitals on adjacent atoms)

Lewis Structures

• Lewis structures depict
  — Atom connectivities
  — All valence electrons of each atom in a molecule or ion
    ○ Bonding electron pairs represented by a line connecting atoms
    ○ Lone (non-bonding) pairs of electrons represented by pair of dots
  — Formal charges consistent with the number of electrons assigned to each atom
VESPR model/modified Lewis structures

- **VESPR model**
  - Foolproof method of predicting molecular structure based upon the number of σ bonding electron pairs and lone pairs; π bonding pairs **do not** influence the gross structure
- **Modified Lewis structures**
  - Depict molecular structure, location of all valence shell electrons, and formal charges when present

### Valence Shell Electron Repulsion Model

<table>
<thead>
<tr>
<th>No. e• pairs</th>
<th>Geometrical arrangement</th>
<th>Types of e• pairs</th>
<th>Molecular shapes</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear, 180°</td>
<td>2 bp</td>
<td>linear</td>
<td>BH₂</td>
</tr>
<tr>
<td>3</td>
<td>trigonal planar, 120°</td>
<td>3 bp, 2bp, 1lp</td>
<td>trigonal planar</td>
<td>BF₃, O₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>bent</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>tetrahedral 109° 28’</td>
<td>4 bp, 3 bp, 1 lp</td>
<td>tetrahedral</td>
<td>CH₄, NH₃, H₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 bp, 2 lp</td>
<td>trigonal pyramidal</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>bent</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>trigonal bipyramidal 120° e-e, 90° a-e</td>
<td>5 bp, 4 bp, 1 bp, 3 bp, 2 lp, 2 bp, 3 lp</td>
<td>trigonal bipyramidal see saw T-shape linear</td>
<td>PF₅, SF₄, ICl₃, I₃⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>octahedral, 90°</td>
<td>6 bp, 5 bp, 4 bp, 2 lp</td>
<td>Octahedral square pyramidal square planar</td>
<td>SF₆, IF₅, XeF₆</td>
</tr>
</tbody>
</table>
Hybridization

- All of the bonds in a molecule such as CH₄ are equivalent (identical) although carbon uses both s and p atomic orbitals for bonding.
- One model that accounts for this is **hybridization**, a concept in which orbitals having different ℓ values are combined to produce equivalent orbitals.
- There are five commonly invoked hybrid orbital sets, sp, sp², sp³, sp³d, and sp³d². For p-block elements these orbitals are in the same principle quantum level, i.e., same n value.
  - These involve combination of the orbitals specified by letter with the number of orbitals of each type specified by its superscript.
  - These hybrid sets consist of equivalent orbitals with defined angular orientations.

**sp hybrid orbitals**

two orbitals arranged in a linear fashion with two perpendicular atomic p orbitals
**sp² hybrid orbitals**

Three orbitals arranged in a trigonal planar fashion with a perpendicular atomic p orbital.

**sp³ hybrid orbitals**

Four orbitals arranged tetrahedrally.
Structure and bonding; Valence Bond, continued

- Prediction of composition and structure of binary compounds
  - Start with valence shell electron configurations of combining atoms and the notion that a chemical bond consists of a shared electron pair in a bonding orbital formed by overlap of orbitals on adjacent atoms. Overlapping orbitals may be atomic or hybrid orbitals as appropriate
- Formed by combination of two atoms each with a singly occupied orbital
- Or by combination of a filled orbital on one atom with an empty orbital on another
- Utilize valence orbitals as required up to maximum allowed for period

Composition and bonding

Group 2

\[ \text{sp} \]

\[ s \quad px \]
Composition and bonding

Group 13 ($\leq$ octet)

\[
\begin{array}{c}
\text{s} \quad \text{p}_x \quad \text{p}_y \quad \rightarrow \quad \text{sp}^2 \\
\end{array}
\]

120°

Composition and bonding

Group 14 ($\leq$ octet)

\[
\begin{array}{c}
\text{s} \quad \text{p}_x \quad \text{p}_y \quad \text{p}_z \quad \rightarrow \quad \text{sp}^3 \\
\end{array}
\]

109° 28′
Composition and bonding

Group 15 ($\leq$ octet)

Composition and bonding

Group 16 ($\leq$ octet)
Composition and bonding

Group 17 ($\leq$ octet)

\[ s + p_x + p_y + p_z \rightarrow sp^3 \]

Composition and bonding

Groups 13-17 (3rd row and beyond; 5 bp)

\[ s + p_x + p_y + p_z + d_z^2 \rightarrow sp^3d \]

(sp$^2$ + pd)
**Composition and bonding**

Groups 13-17 (3rd row and beyond; 4 bp, 1 lp)

\[ s + p_x + p_y + p_z + d_z^2 \rightarrow \]

\[ \text{sp}^3d \]

\[ (\text{sp}^2 + \text{pd}) \]

---

**Composition and bonding**

Groups 13-17 (3rd row and beyond; 3 bp, 2 lp)

\[ s + p_x + p_y + p_z + d_z^2 \rightarrow \]

\[ \text{sp}^3d \]

\[ (\text{sp}^2 + \text{pd}) \]
Electron density maps for (CH$_3$)$_2$TeCl$_2$

Density map in the CH$_3$-Te-CH$_3$ plane

Density map in Cl-Te-Cl plane (bisecting the C-Te-C angle)

Composition and bonding

Groups 13-17 (3rd row and beyond; 6 bp)

s + p$_x$ + p$_y$ + p$_z$ + d$_{2z^2}$ + d$_{x^2-y^2}$ → sp$^3$d$^2$
Composition and bonding

Groups 13-17 (3rd row and beyond; 5 bp, 1 lp)

\[ s + px + py + pz + dz^2 + dx^2 - y^2 \rightarrow sp^3d^2 \]

Composition and bonding

Groups 13-17 (3rd row and beyond; 4bp, 1 lp)

\[ s + px + py + pz + d_{z^2} + d_{x^2 - y^2} \rightarrow sp^3d^2 \]
Terminal atoms other than H and group 17

- Terminal atoms will always have filled valence shells in Lewis structures!

\[
\begin{align*}
\text{NO}_2^- & \quad \text{NO}_3^- \\
\text{NO}_2 & \quad \text{SO}_3^{2-} \\
\text{NO}_2^+ & 
\end{align*}
\]

Distances/angles in triatomic oxynitrogen species

\[
\begin{align*}
\text{NO}_2^- & \quad \text{bond angle} = 115^\circ \\
\text{NO}_2 & \quad \text{bond angle} = 134^\circ \\
\text{NO}_2^+ & \quad \text{bond angle} = 180^\circ 
\end{align*}
\]
Rules for assigning oxidation states

• The sum of the oxidation states for all atoms in a species must equal the charge on the species.
• The oxidation state of an atom in an elemental form is zero.
• The oxidation state of a monatomic ion is equal to its charge.
• Terminal atoms (or groups of atoms) are assigned an oxidation state consistent with the charge in their monatomic anionic form, i.e., filled valence shell.
• The most electronegative element is assigned a negative oxidation state in compounds of hydrogen.
• In compounds such as HO-OH, H₂N-NH₂, etc. the E-E bond does not contribute to the oxidation state of either atom. However, in compounds such as SSO₃²⁻ (S₂O₃²⁻, thiosulfate) assignment of a filled valence shell to the terminal sulfur gives it an oxidation state of -2.

Bonding in carbon compounds

• Four-coordinate carbon utilizes sp³ hybrid orbitals
• Three-coordinate carbon participating in multiple bonds is sp² hybridized
• Two-coordinate carbon participating in multiple bonds is sp hybridized