**Point Groups**

**Point Group** = the set of symmetry operations for a molecule

**Group Theory** = mathematical treatment of the properties of the group which can be used to find properties of the molecule

**Assigning the Point Group of a Molecule**

1. Determine if the molecule is of high or low symmetry by inspection

**A. Low Symmetry Groups**

<table>
<thead>
<tr>
<th>Group</th>
<th>Symmetry</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>No symmetry other than the identity operation</td>
<td>CHFClBr</td>
</tr>
<tr>
<td>$C_s$</td>
<td>Only one mirror plane</td>
<td>H$_2$C≡CClBr</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Only an inversion center; few molecular examples</td>
<td>HClBrC—CHClBr (staggered conformation)</td>
</tr>
</tbody>
</table>
### B. High Symmetry Groups

<table>
<thead>
<tr>
<th>Group</th>
<th>Description</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_d$</td>
<td>Most (but not all!) molecules in this point group have the familiar tetrahedral geometry. They have four $C_3$ axes, three $C_2$ axes, three $S_4$ axes, and six $\sigma_d$ planes. They have no $C_4$ axes.</td>
<td><img src="https://via.placeholder.com/150" alt="Catalan" /></td>
</tr>
<tr>
<td>$O_h$</td>
<td>These molecules include those of octahedral structure, although some other geometrical forms, such as the cube, share the same set of symmetry operations. Among their 48 symmetry elements are four $C_3$ axes, three $C_4$ axes, and an inversion center.</td>
<td><img src="https://via.placeholder.com/150" alt="Octahedral" /></td>
</tr>
<tr>
<td>$C_{\infty v}$</td>
<td>These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They do not have a center of inversion.</td>
<td><img src="https://via.placeholder.com/150" alt="Linear" /></td>
</tr>
<tr>
<td>$D_{\infty h}$</td>
<td>These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They also have perpendicular $C_2$ axes and a perpendicular reflection plane.</td>
<td><img src="https://via.placeholder.com/150" alt="Perpendicular" /></td>
</tr>
<tr>
<td>$I_h$</td>
<td>Icosahedral structures are best recognized by their six $C_5$ axes (as well as many other symmetry operations—120 total!).</td>
<td><img src="https://via.placeholder.com/150" alt="Icosahedral" /></td>
</tr>
<tr>
<td></td>
<td>$B_{12}H_{12}^{2-}$, with BH at each vertex of an icosahedron</td>
<td></td>
</tr>
</tbody>
</table>
2. If not, find the principle axis
3. If there are $C_2$ axes perpendicular to $C_n$ the molecule is in D If not, the molecule will be in C or S
4. If $\sigma_h$ perpendicular to $C_n$ then $D_{nh}$ or $C_{nh}$ If not, go to the next step
5. If $\sigma$ contains $C_n$ then $C_{nv}$ or $D_{nd}$ If not, $D_n$ or $C_n$ or $S_{2n}$
6. If $S_{2n}$ along $C_n$ then $S_{2n}$
7. If not $C_n$
The determination of point groups of molecules

only one rotational axis = $C_2$

two $\sigma_v$, but no $\sigma_h$ mirror planes means point group is $C_{2v}$

The point group of the water molecule is $C_{2v}$
Naming point groups:

The name of the point group has information about the symmetry elements present. The letter is the rotational group and the subscript number after the letter indicates the order of the principal rotational axis (e.g. 3-fold or 4 fold etc.):

- A ‘C’ indicates only one rotational axis.

  - $C_3$: 3-fold rotational axis
  - $C_{3v}$: has $\sigma_v$ but no $\sigma_h$ mirror plane

- A ‘D’ indicates an $n$-fold principal rotation axis plus $n$ 2-fold axes at right angles to it.

  - $D_{4d}$: 4-fold principal axis, $d = \text{no} \sigma_h$ mirror plane
  - $D_{4h}$: 'h' indicates a $\sigma_h$ mirror plane
A subscript ‘$h$’ means that there is a $\sigma_h$ mirror plane at right angles to the $n$-fold principal axis:

![Diagram of $D_{4h}$ and $D_{3d}$ point groups](image)

A subscript ‘$d$’ (or $v$ for $C$ groups) means there is no $\sigma_h$ mirror plane, but only $n \sigma_v$ mirror planes containing the principal $C_n$ axis.
Naming platonic solids:

Platonic solids: Five special polyhedra: Tetrahedron, Cube, Octahedron, Dodecahedron, and Icosahedron

Their faces are all exactly the same. The same number of faces meet at each vertex.

\[ T = \text{tetrahedral} = 4 \text{ three-fold axes} \]
\[ O = \text{octahedral} = 3 \text{ four-fold axes} \]
\[ I = \text{icosahedral} = 6 \text{ five-fold axes} \]

\[ C_{60} \] ‘bucky-ball’ or ‘Fullerene’
Flow chart for determining point groups.

1. **is the molecule linear?**
   - yes ➔ *D*_∞h
   - no ➔ *C*_∞v

2. **is it T_d, O_h or I_h?**
   - yes ➔ *T*_d, *O*_h or *I*_h
   - no ➔

3. **is there a principal *C*_n axis?**
   - yes ➔
   - no ➔

4. **are there *n* *C*_2 axes perpendicular to the *C*_n axis?**
   - yes ➔
   - no ➔

5. **is there a *σ*_h plane perpendicular to the *C*_n axis?**
   - yes ➔
   - no ➔

6. **is there a *σ*_v plane containing the *C*_n axis?**
   - yes ➔
   - no ➔

7. **are there *σ*_v planes containing the *C*_n axis?**
   - yes ➔
   - no ➔
The point group of the carbon dioxide molecule

We start at the top of the flow-chart, and can see that the CO$_2$ molecule is linear, and has a center of inversion (i) so it is $D_{\infty h}$. Note the $C_\infty$ principal rotation axis.
Other linear molecules:

The top row of linear molecules all have a center of inversion ($i$) and so are $D_{\infty h}$.

The bottom row have no $i$ and so are $C_{\infty v}$.

All have a $C_{\infty}$ axis.
The Platonic solids:
tetrahedron  octahedron  icosahedron

Diagram showing the Platonic solids with the corresponding symmetry groups:
- Tetrahedron ($T_d$)
- Octahedron ($O_h$)
- Icosahedron ($I_h$)

Decision tree:
1. Is the molecule linear? Yes → Proceed to next question.
   No → Proceed to the next step.
2. Is there a center of inversion? Yes → $D_{\infty h}$.
   No → $C_{\infty v}$.
3. Is it $T_d$, $O_h$, or $I_h$? Yes → $T_d$, $O_h$, or $I_h$.
   No → Start over.
The $C_s$ point group:

$C_s$

Chloro-difluoro-iodo-methane

Is there a principal $C_n$ axis? 
- Yes
  - Are there $n$ $C_2$ axes perpendicular to the $C_n$ axis? 
    - Yes
      - Yes
    - No
      - No
  - No
      - Yes

Is there a mirror plane? 
- Yes
  - $C_s$
  - No
  - No

Is there a center of inversion? 
- Yes
  - $C_i$
  - No

Is there a $\sigma_h$ plane perpendicular to the $C_n$ axis? 
- Yes
  - $D_{nh}$
  - No

Most land animals have bilateral symmetry, and belong to the $C_s$ point group:
The $C_1$ point group:

Molecules that have no symmetry elements at all except the trivial one where they are rotated through $360^\circ$ and remain unchanged, belong to the $C_1$ point group. In other words, they have an axis of $360^\circ/360^\circ = 1$-fold, so have a $C_1$ axis. Examples are:

Bromo-chloro-fluoro-iodo-methane

chloro-iodo-amine
The division into $C_n$ and $D_n$ point groups:

After we have decided that there is a principal rotation axis, we come to the red box. If there are $n \ C_2$ axes at right angles to the principal axis, we have a $D_n$ point group. If not, it is a $C_n$ point group.
The $C_n$ point groups:

The $C_n$ point groups all have only a single rotational axis, which can theoretically be very high e.g. $C_5$ in the complex $[\text{IF}_6\text{O}]^-$ below. They are further divided into $C_n$, $C_{nv}$, and $C_{nh}$ point groups. The $C_n$ point groups have no other elements, the $C_{nv}$ point groups also have a $\sigma_v$ mirror plane containing the $C_n$ rotational axis, while the $C_{nh}$ point groups also have a $\sigma_h$ mirror plane at right angles to the principal rotational axis.
The point group of the water molecule

We start at the top of the flow-chart, and can see that the water molecule is not linear, and is not tetrahedral ($T_d$), octahedral ($O_h$), or icosahedral, ($I_h$) so we proceed down the chart.
Yes, there is a principal $C_n$ axis, so we proceed down the chart, but in answer to the next question, there are no further $C_2$ axes at right angles to the principal axis, which is the only axis, so we proceed down the chart
The point group of the water molecule is $C_{2v}$.

There is no $\sigma_h$ plane at right angles to the $C_2$ axis, but there are two $\sigma_v$ planes containing the $C_2$ axis.

The point group of the water molecule is $C_{2v}$. 
Other $C_{nv}$ molecules:

- Water ($C_{2v}$)
  - $C_2$ axis lies in mirror planes
- Ammonia ($C_{3v}$)
  - $C_3$ axis lies in mirror planes
- Square pyramidal complex ($C_{4v}$)
  - $C_4$ axis lies in four mirror planes
- Vanadyl tetrafluoride ($\text{VOF}_4$)
Some more $C_{2v}$ molecules:

- Phosphorus iodo-tetrafluoride ($PF_4I$)
- Sulfur tetrafluoride ($SF_4$)
- Carbonyl chloride ($COCl_2$)
The $C_n$ point groups:

These have a $C_n$ axis as their only symmetry element. Important examples are (hydrogens omitted for clarity):

- **Cyanobinaphthalene**
  - Viewed down $C_3$ axis
  - $C_3$

- **Cobalt(III) tris-glycinate**
  - Viewed down $C_3$ axis
  - $C_3$

- **Triphenylphosphine**
  - Viewed from the side
  - $C_3$

- **Cobalt(III) tris-glycinate**
  - Viewed from the side
  - $C_3$
The $D$ (Dihedral) Groups.

If there are in addition to the $C_n$ axis, one or more $C_2$ axes of symmetry, we have a molecule belonging to the $D$ point groups.

If the only extra symmetry elements besides the $C_n$ axis, are one or more $C_2$ axes perpendicular to the $C_n$ axis, then the molecule belongs to the $D_n$ point group. There must then be $n$ $C_2$ axes in the molecule.

Adding a vertical mirror plane to a $D_n$ group that then contains the principal axis gives a $D_{nd}$ group.

If there is in addition a mirror plane that bisects the principal axis, we have the $D_{nh}$ group.
The $D_{nh}$ point groups:

- Are there $n$ $C_2$ axes perpendicular to the $C_n$ axis? 
  - Yes $\rightarrow D_{nh}$
  - No 

- Are there $\sigma_v$ planes containing the $C_n$ axis? 
  - Yes $\rightarrow D_{nd}$
  - No $\rightarrow D_n$

$C_4$ principal axis

Four $C_2$ axes at right angles to $C_4$ axis

Mirror plane at right angles to $C_4$ axis
Examples of molecules belonging to $D_{nh}$ point groups:
Benzene, an example of the $D_{6h}$ point group:
The $D_n$ point groups:

- **are there $n$ $C_2$ axes perpendicular to the $C_n$ axis?**
  - yes
    - is there a $\sigma_h$ plane perpendicular to the $C_n$ axis?
      - yes $\rightarrow D_{nh}$
      - no $\rightarrow D_{nm}$
  - no $\rightarrow D_n$

- **are there $\sigma_v$ planes containing the $C_n$ axis?**
  - yes $\rightarrow D_{nd}$
  - no $\rightarrow D_n$

These have a principal $n$-fold axis, and $n$ 2-fold axes at right angles to it, but **no mirror planes**.

[Cu(en)$_2$]$^{2+}$ complex with H-atoms omitted for clarity. (en = ethylene diamine)
Some further views of the symmetry elements of $[\text{Cu(en)}_2]^{2+}$, point group $D_2$:

$[\text{Cu(en)}_2]^{2+}$ complex with H-atoms omitted for clarity. (en = ethylene diamine)
Some views of the symmetry elements of $[\text{Co(en)}_3]^{3+}$, point group $D_3$.

- View down the $C_3$ axis of $[\text{Co(en)}_3]^{3+}$ showing the three $C_2$ axes.
- View down one of the three $C_2$ axes of $[\text{Co(en)}_3]^{3+}$ at right angles to $C_3$. 

Diagram showing the $C_2$ and $C_3$ axes with the $D_3$ point group symbol.
Other examples of the $D_3$ point group

$[\text{Co(oxalate)}_3]^{3-}$

$[\text{Co(bipyridyl)}_3]^{3+}$
Molecules belonging to the $D_{nd}$ point groups

These have mirror planes parallel to the principal axis, but not at right angles to it.

$C_3$ axis

$\sigma_v$ planes contain the principal axis

$D_3d$

$C_5$ axis

Staggered form of ethane

Staggered form of ferrocene

$D_5d$
As predicted by VSEPR, the $[\text{ZrF}_8]^{4-}$ anion has a square anti-prismatic structure. At left is seen the $C_4$ principal axis. It has four $C_2$ axes at right angles to it, so it has $D_4$ symmetry. One $C_2$ axis is shown side-on (center). There are four $\sigma_v$ mirror planes (right), but no mirror plane at right angles to $C_4$, so the point group does not rate an $h$, and is $D_{4d}$.
[K(18-crown-6)]^+, an example of a \( D_{3d} \) point group:

The complex cation \([K(18\text{-crown-6})]^+\) above is an important structure that has \( D_{3d} \) symmetry. It has a \( C_3 \) principal axis with 3 \( C_2 \) axes at right angles to it, as well as three \( \sigma_v \) mirror planes that contain the \( C_3 \) axis, but no \( \sigma_h \) mirror plane (because it’s not flat, as seen at center), so is \( D_{3d} \).
Some Point groups