## COVALENT BONDING

[MH5; Chapter 7]

- Covalent bonds occur when electrons are equally shared between two atoms.
- The electrons are not always equally shared by both atoms; these bonds are said to be polar covalent.
- We assume that only electrons in the valence shell are involved in forming covalent bonds.
- These electrons are simultaneously attracted to both nuclei; a favourable, lower - energy, arrangement.
- The nuclei are "insulated" from each other by electrons; so the electrons feel attraction of 2 nuclei.
- Two bonded atoms are in a lower energy state than two separate atoms; resulting in the formation of a stable covalently bonded molecule:

$$
\mathrm{H}(\mathrm{~g})+\mathrm{H}(\mathrm{~g}) \rightarrow \mathrm{H}_{2}(\mathrm{~g})
$$

- Two electrons (indicated by dots, as shown below) are shared; a single bond is formed.
- Lewis dot structure:

- Since each H atom has electron configuration $1 s^{1}, \mathrm{H}$ atoms form only one bond (which consists of 2 shared electrons):


## EXAMPLES:

$$
H-H
$$

$$
\mathrm{H}-\mathrm{Cl}
$$



## Lewis Structures and The Octet Rule [MH5; 7.1]

- G.N. Lewis observed that the electron configuration of the inert gases seemed to result in an extremely stable atom.
- His idea was that non metal atoms may share electrons to form bonds; by doing so they acquire the same electron configuration as an inert gas.
- As only valence electrons are involved in forming bonds, first-row elements Li through F form a maximum of four bonds, (4 electron pairs), which fill the $2 s$ and 2 p orbitals.
- Lewis Structures are diagrams which show how many bonds there are in a covalently bonded molecule and the location of any non bonding electron pairs.
- We sometimes use a generic notation to show how many bonds (and possibly non bonding electron pairs) there are placed around a "central" atom.
- This is the AXE notation, where $A$ represents the central atom, $X$ represents the number of bonds (or bonding pairs of electrons) and $E$ represent the number of any non bonding (or "lone") pairs of electrons located on the central atom.

Methane: $\mathrm{CH}_{4}$
Carbon is $2 s^{2} 2 p^{2} ; 4$ valence electrons. Carbon will form 4 bonds.



AXt

Ammonia: $\mathrm{NH}_{3}$
Nitrogen is $2 s^{2} 2 p^{3} ; 5$ valence electrons.
The formula $\mathrm{NH}_{3}$ indicates only $3 \mathrm{~N}-\mathrm{H}$ bonds are formed, which requires only 3 electrons from nitrogen, so there must be one non bonding pair of electrons on the nitrogen.


Ammonium ion: $\mathrm{NH}_{4}^{+}$

- $\mathrm{NH}_{4}{ }^{+}$is formed by adding $\mathrm{H}^{+}$to $\mathrm{NH}_{3}$. Nitrogen donates the non bonding pair of electrons to the $\mathrm{H}^{+}$(which has no electrons) to form a coordinate covalent bond. The arrangement of the electron pairs has not changed.


Water: $\mathrm{H}_{2} \mathrm{O}$
Oxygen is the central atom with a configuration of $2 s^{2} 2 p^{4}$. As there are only two $\mathrm{O}-\mathrm{H}$ bonds in water, there must be two non bonding pairs of electrons on the oxygen.


- $\mathrm{H}^{+}$may be added to water to form Hydronium ion, $\mathrm{H}_{3} \mathrm{O}^{+}$in exactly the same manner as $\mathrm{H}^{+}$was added to $\mathrm{NH}_{3}$ to form $\mathrm{NH}_{4}^{+}$.


Hydrogen Fluoride: HF Fluorine is $2 s^{2} 2 p^{5}$


Notice the three pairs of non bonding electrons on the fluorine.

Neon atom: Ne Neon is $2 s^{2} 2 p^{6}$


Neon already has 8 electrons and no unpaired electrons. There is no tendency to form bonds.

- Notice that in all these examples, each atom thinks that it has 8 electrons (except for Hydrogen); either because it really does (in the case of Neon) or because it is sharing electrons with other atoms which results in the formation of bonds.
- This behaviour is summarized in the Octet Rule:
"In a first - row element, bond formation does not go beyond a total of four $e^{-}$pairs (bonding + non-bonding) in the valence shell."
- There are $103+$ elements. The octet rule applies to only 8 of them but they include some important elements !
- Second - Row elements are NOT limited by the octet rule because a

3d orbital is available.....they may form more than 4 bonds as the 3d orbital allows for the formation of more electron pairs.

- All these examples show single bonds - the sharing of one e pair.
- Many compounds contain double bonds, which involve the sharing of two pairs of electrons.


## EXAMPLE:

Carbon dioxide, $\mathrm{CO}_{2}$ :


What is wrong with $\mathrm{O}-\mathrm{C}-\mathrm{O}$ ?
$\cdot \ddot{0}-\ddot{C}-\ddot{0}$.

- no atom has an octet
- each Oxygen has an unpaired electron
- In the correct structure $O=C=O$, all electrons are paired up through the formation of double bonds.
- A triple bond has 3 electron pairs shared.


## EXAMPLES:

$$
\begin{array}{ll}
: N \equiv N: & \text { Nitrogen gas, 4 pairs on each } N \\
H-C \equiv C-H & \text { Acetylene } \\
H-C \equiv N: & \text { Hydrogen cyanide }
\end{array}
$$

Note:

- Bond length ( = nucleus-to-nucleus distance) decreases in the order: Single Bond > Double Bond > Triple Bond (for same linked atoms);

EXAMPLES:

| $C-C$ | $C=C$ | $C \equiv C$ |
| :--- | :--- | :--- |
| 0.154 nn | 0.134 nm | 0.120 nm |
| $N-N$ | $N=N$ | $N \equiv N$ |
| 0.145 nm | 0.125 mm | 0.110 nm |

Handy to Remember....
H: 1 bond (always! !)
0: 2 bonds, 2 NB pairs
N: 3 bonds, INB pair
C: 4 bonds
$F$ : 1 bond, $3 N B$ pairs

Rules for writing Lewis Structures

1) Count the number of valence electrons of all atoms (and add or subtract electrons for an overall -ve and +ie charge, respectively)

$$
\begin{array}{lllr}
\mathrm{SiCl}_{4} & \mathrm{NO}_{2}^{+} & \mathrm{HCN} & \mathrm{BrO}_{4}^{-} \\
4+4(7) & 5+2(6)-1 & 1+4+5 & 7+ \\
=32 & =16 & =10 & =32
\end{array}
$$

2) Put the atoms in their correct relative positions.

To do this, you need to know which is the central atom.
This will usually be a unique atom and/or the heaviest atom or the least electronegative atom.
The order of symbols may give the skeleton.... (e.g. HCN). It cant be H!! Then put in a skeleton of single bonds ( - ).

EXAMPLES:

$$
\begin{array}{cc}
C l \\
C-S_{i}-C l & O-N-O \\
1 & 16 e^{-}-2\left(2 e^{-}\right) \\
l & =12 e^{-} \\
32 e^{-}-4(2) & 0 \\
=24 e^{-} & 1 \\
H-C-N & 0-B r-0 \\
10 e^{-}-2\left(2 e^{-}\right) & 1 \\
=6 e^{-} & 32 e^{-}-4\left(2 e^{-}\right) \\
& =24 e^{-}
\end{array}
$$

3) Count up the number of valence electrons used in the bonds; it's 2 electrons per bond.
Subtract the number of electrons in the bonds from the total number of electrons to find the number of non bonding electrons to be distributed.
4) Distribute the remaining electrons to first give octets to terminal (end of chain) atoms (except H), then put the rest on the central atom.

$: \ddot{C}:$

:Cl:

5) Assigning Formal Charges.

The Formal Charge on an atom is the difference between the number of electrons an isolated atom has and the number assigned to it in the Lewis Structure.
Assigned electrons include lone pairs on the atom, and the number of electrons that the atom donated to the covalent bond. (This is usually one electron.)


$$
H-C \equiv N:
$$

Note that the Sum of formal charges = overall charge on species
6) If the central atom does not have an octet of electrons (at least), convert lone pairs on terminal $C, N, O$ or $S$ atoms into pairs shared with the central atom.
Doing this forms a double bond. (Do it twice for a triple bond!) Usually, the central atom will have a +eve Formal Charge and the terminal atoms will have -ve Formal Charges.
So....if you have a +eve, a -ve, and a non bonding pair of electrons, you can form a double bond.

7) Does your structure make sense?

If there appear to be several possibilities for a structure, the most stable is that with:
Formal charges as close to zero as possible;
-ve formal charges on the most electronegative atoms:
+ve charges on the least electronegative atoms.

- These guidelines will also help you decide on the "best" Lewis
structure; sometimes you can write two structures which both obey the octet rule.


## Deciding between different Lewis structures

- It might not be obvious whether to write $A_{2} B$ as:

$$
A-A-B \text { or } \quad A-B-A
$$

- An actual example is whether we should write $\mathrm{CH}_{4} \mathrm{O}$, methanol as either:


- Both of these structures obey the octet rule.
- We could invoke the idea that $C$ always forms 4 bonds, but we can also use formal charges.
- In the first structure, all atoms have a formal charge of 0 .
- In the second structure, the carbon bears a formal charge of -1 , and the oxygen has a formal charge of +1 .
- As the negative charge should appear on the most electronegative atom, it becomes apparent that this is not the "best" Lewis structure.


## MORE EXAMPLES:

$\mathrm{NO}_{2}^{-}: \mathrm{He}^{-}=5+2(6)+1=18 e^{-}-2\left(2 e^{-}\right)=14 e^{-}$

$$
\begin{aligned}
& \Rightarrow: \ddot{0}-\ddot{N}=\ddot{0} \\
& A X_{2} E \\
& \mathrm{SO}_{3}: \# e^{-}=6+3(6)=24 e^{-}-3\left(2 e^{-}\right)=18 e^{-} \\
& \theta: \ddot{0}-\frac{+3}{+3}-\ddot{0}: \quad \Rightarrow \\
& : 0: \Theta \\
& \ddot{0}=\delta=\ddot{0} \\
& \mathrm{NO}_{3}^{-}: \quad 5+3(6)+1=24 e^{-}-3(2 e)=18 e- \\
& \theta: \ddot{0}-\frac{+2}{N-0}: \theta \\
& : 0: \Theta \\
& \Rightarrow \quad \begin{array}{c}
\theta: \ddot{O}-\stackrel{\oplus}{N}-\ddot{0}: \Theta \\
: O:
\end{array} \\
& \text { N-lst row } \\
& \mathrm{PO}_{4}{ }^{3-}: 5+4(6)+3 e^{-}=\frac{32 e^{-}}{}-4\left(2 e^{-}\right) \quad \therefore \text { max of } 4 \text { bonds } \\
& : \ddot{O}:- \\
& =24 e^{-} \quad: \ddot{O}:- \\
& \theta: \ddot{O}-P^{1}-\ddot{0}: \Theta \\
& 1 \\
& : 0: \Theta
\end{aligned}
$$

$$
\begin{aligned}
& : 0: \Theta
\end{aligned}
$$

## Contributing, or Resonance Structures

- Sometimes there is more than one possible structure which seems to be reasonable with respect to all the rules outlined so far.
- When this happens, we write contributing structures; to include all of these possible structures.
- In the case of ozone: $\mathrm{O}_{3}: 18 e^{-}-2\left(2 e^{-}\right)=14 e^{-}$
$\Theta: \ddot{0}-\ddot{0}-0$

- Often, two or more equivalent contributing structures are possible, differing only in the position of the electrons.
- This often takes the form of "moving double bonds around".

For the acetate ion, $\mathrm{CH}_{3} \mathrm{COO}^{-}$, we could write:


- It turns out though, that both C-O bonds are identical and neither Lewis dot structure is correct!
- In practice each may be considered to be 'contributing' to the actual structure (often called "resonance structures") and the $\leftrightarrow$ symbol is used to indicate this.
- The actual structure is an average of the two contributing structures:


MORE EXAMPLES:


Benzene, $\mathrm{C}_{6} \mathrm{H}_{6}$ :



- The examples so far have shown equivalent resonance structures, but non-equivalent resonance structures are also possible.

- Which one of these is more likely?
- In general, the existence of resonance structures implies that the species are more stable than might be expected.
- This is especially true in the delocalization of negative charge over several O atoms, such as in $\mathrm{ClO}_{4}^{-}: \quad 4$ possible structures

- Finally, note that resonance structures must have exactly the same nuclear positions/connectivity - you cannot move atoms around, whereas you can move electrons around.

Bond Order

- Normally, the bond order of an atom - atom linkage is an integer: 1 for $C-C, 2$ for $C=C$ etc.
- In resonance structures, all the linkages for the same atoms are identical, neither single or double bonds.
- We assign these linkages fractional bond orders; in $\mathrm{SO}_{4}{ }^{2-}$, instead of 2 linkages of bond order 1, and 2 linkages of bond order 2; we say each of the four linkages has bond order 1.5.

EXAMPLES:

$$
\begin{array}{ccc}
\mathrm{SO}_{4}^{2-}: & 0 & \\
\Theta_{0} & 11 & 0 \\
0 & -5 & 0 \\
& 11 & \\
& 0 & 0 \\
O_{3}: & 0 & 0 \\
& 0 & 0 \\
& 0 & 0
\end{array}
$$

$$
2 s=0 \Rightarrow 2 \times 2=4
$$

$$
2 \leq-0 \Rightarrow 2 \times 1=\frac{2}{6}
$$

$$
\text { Ar. Bond Ceder }=\frac{6}{4}=1.5
$$

$$
\left.\begin{array}{l}
10=0 \Rightarrow 2 \\
10-0 \Rightarrow 1
\end{array}\right\} 3
$$

Ar. Bond Order $=\frac{3}{2}=1.5$

$$
\left.\begin{array}{l}
1 N=0 \Rightarrow 2 \\
2 N-0 \Rightarrow 2
\end{array}\right\} 4
$$

$$
\text { Ar.B.O. }=\frac{5}{4}=11 / 4
$$

$$
\begin{aligned}
& \mathrm{NO}_{3}{ }^{-} \\
& \theta_{0} \stackrel{\substack{0 \\
11 \\
N_{0}} 0}{ } \\
& \mathrm{PO}_{4}{ }^{3-} \text { : } \\
& 0-\begin{array}{c}
0 \\
11 \\
-P-0 \\
1 \\
0
\end{array}
\end{aligned}
$$

## EXCEPTIONS TO THE OCTET RULE

Electron Deficient Molecules

- Some molecules contain odd numbers of electrons.


## EXAMPLES:

|  | NO | $\mathrm{NO}_{2}$ | $\mathrm{ClO}_{2}$, | $\mathrm{O}_{2}{ }^{-}$ |
| :--- | :--- | :--- | :--- | :--- |
| Valence $e^{-}$ | 11 | 17 | 19 | 13 |

- Obviously, all of these molecules will have an unpaired electron somewhere......
- These molecules are often called free radicals and are very reactive!

NO

$\mathrm{NO}_{2}$


- There are a few compounds in which the central atom does not obey the Octet Rule.....it is surrounded by 2 or 3 pairs of electrons instead of 4 pairs of electrons.
- The fluorides of beryllium and boron are $\mathrm{BeF}_{2}$ and $\mathrm{BF}_{3}$.
- Experimental evidence shows their structures as follows:

$$
F-B e-F
$$

$$
\alpha e^{-} \text {prs "around" }
$$

Be


$$
\begin{aligned}
& 30-\text { prs } \\
& \text { around B }
\end{aligned}
$$

Expanded Octets

- As was mentioned earlier, second row elements do not have to obey the octet rule; they can form more than four bonds.
- We say that the central atoms in these molecules have expanded octets.
- These atoms have d orbitals available for bonding; this is where the extra electron pairs are located.

EXAMPLES:
$P_{5}$ :

$$
\frac{1 L}{33} 1 \frac{1}{3 p} 1
$$

$$
\frac{1}{3 s}-\frac{1}{3 p} \frac{1}{1}-\frac{1}{3 d}-\cdots
$$

$\mathrm{SCl}_{6}:$

$$
\begin{aligned}
& \frac{1 L}{3 s} \text { nL } \frac{1}{3 p} 1 \\
& \frac{1}{3 s}-\frac{1}{3 p} \quad-\frac{1}{3 d}-
\end{aligned}
$$

Molecular Geometry: (VSEPR Theory) [MH5; 7.2]

- Lewis structures tell us the number and type of bonds around a central atom; also the location of any non bonding electron pairs.
- They do not tell us the 3-D arrangement of either the bonding or non bonding electron pairs around the central atom.
- The Valence Shell Electron Pair Repulsion Theory (commonly known as "VSEPR") was developed to predict molecular stereo-chemistry, or 3 - D shape.
- VSEPR Theory is based on four main assumptions:

1) Electrons, in pairs, are placed in the valence shell of the "central" atom.
2) Both bonding and non-bonding (NB) pairs are included.
3) Electron pairs repel each other and try to obtain the maximum possible separation.
4) NB electron pairs repel more strongly than bonding pairs.

- Molecular or ionic shapes are therefore determined by the total number of electron pairs in the valence shell of the central atom.
- To find the number of electron pairs:

1) Add up the \# of valence electrons on the free central atom.
2) Add 1 for each singly bonded atom.
3)Add 1 for each -ve charge; subtract 1 for each +ve charge.
3) Divide by 2 (to get number of electron pairs!)
4) NOTE: This does not work if there are terminal Oxygen (or

Nitrogen) atoms in the molecule....you must use Lewis structure rules

EXAMPLES:
$\mathrm{BCl}_{3}$
$S F_{5}+\quad S: 6$ valence $e^{-}, 5 s-F$ bonds

$$
\text { Jotal }=6+5-1=10 e-=5 p r s
$$

$\mathrm{PF}_{5} \quad P: 5$ valence $e^{-}$, $5 P-F$ bonds

$$
\text { Total }=10 e^{-}=5 \text { prs }
$$

$\mathrm{SCl}_{5}-\mathrm{s}$ : b valence $e^{-}, 5 \mathrm{~s}$ - $c l$ bonds

$$
\text { Jotal }=6+5+1=12 e^{-}=6 p r
$$

- We will use the $A X_{n}$ notation to describe the basic shape of the
- molecule or ion; $\boldsymbol{A}$ represents the central atom and $X$ represents the electron pairs, which result in the formation of single bonds to the central atom. " $n$ " indicates the number of electron pairs.
- To see how this works, we will work through molecules where $n=1$ to 6 .
- As we go, we will modify $A X_{n}$ to allow for non bonding pairs of electrons....so $A X_{n}$ becomes $A X_{n-z} E_{z}$, where $z$ represents the number of non bonding electron pairs.
- 1 pair; $A X$ : a trivial case, the molecule is linear: $\mathrm{H}-\mathrm{H}$
- 2 pairs; $A X_{2}$; the maximum separation of electron pairs is at $180^{\circ}$
EXAMPLE: $\mathrm{BeCl}_{2} \quad \mathrm{Be}: 2$ vale $e^{-}+2$ bonds

$$
C l-\underbrace{\mathrm{Be}}_{180^{\circ}}-\mathrm{Cl} \quad \therefore \quad A X_{2}
$$

$$
=4 e^{-}=2 p r
$$

- Only the electrons on the central atom Be determine the electron pair geometry; other electron pairs on Cl are ignored and are not usually shown.
- The geometry (or shape) for this molecule is linear.
- The other possibility for 2 electron pairs is AXE; this molecule has one bonding pair and one non bonding pair.
- This molecule must be linear, as in BF .

$$
: B-F
$$

- 3 pairs; $\mathbf{A X}_{3}$ : the maximum separation of electron pairs is at $120^{\circ}$.
- The shape of this molecule is triangular (or trigonal) planar.
EXAMPLE: $\quad \mathrm{BF}_{3}$
B: 3 val $e^{-}+3$ bonds
$=6 e^{-}=3 p r$
$\Rightarrow A X_{3}$
- This molecule is flat; any distortion out of the plane would decrease the $\mathrm{F}-\mathrm{B}-\mathrm{F}$ angles.
- When there are 3 electron pairs; $\mathrm{AX}_{2} \mathrm{E}$ is also a possibility.
- The basic arrangement of the electron pairs is still the triangular planar arrangement, such as in $\mathrm{SiF}_{2}$, which is drawn as:

- The shape of the $A X_{2} E$ molecule is called bent.
- While $A X E_{2}$ is also a possibility, and the arrangement of the electron pairs is the triangular planar arrangement, the only possible shape for the molecule (which is determined by the number of bonding pairs) must be linear.
- 4 pairs; $\mathbf{A X}_{4}$; this is a three dimensional molecule with bond angles of $109.5^{\circ}$.
- The shape of this molecule is called tetrahedral.

- It is worth a mention here that any carbon atom with four single bonds will always take this tetrahedral geometry!
- With four electron pairs, there are other combinations of bonding and non bonding pairs; these are $A X_{3} E, A X_{2} E_{2}$ and $A X E_{3}$.
- An example of $A X_{3} E$ is ammonia, $\mathrm{NH}_{3}$ :

- This molecule is often drawn as:

- Remember that the arrangement of the electron pairs (both bonding and non bonding) is tetrahedral, but the arrangement of the atoms is called trigonal (or triangular) pyramidal.
- It is always the arrangement of the atoms (due to the bonding pairs) that give the molecule its actual shape!
- The $A X_{2} E_{2}$ molecule has two bonding pairs and two non bonding pairs.
- The common example used for this geometry is water, $\mathrm{H}_{2} \mathrm{O}$.

- Notice once again that the arrangement of the electron pairs is tetrahedral, but the arrangement of atoms is bent.
- Yes, there are two different versions of "bent"; one is $\mathrm{AX}_{2} \mathrm{E}$ and the other is $A X_{2} E_{2}$.
- When drawing this molecule, the bonding pairs are usually shown in the same plane, with the non bonding pairs out of the plane.

- The combination of 1 bonding and 3 NB pairs, $\mathrm{AXE}_{3}$, is trivial; it must be linear as there are only 2 atoms.
- An example of this arrangement is H-F.
- When considering molecules where the central atom has five or six
electron pairs, recall that these are the atoms with so-called "expanded octets" which make use of empty d orbitals.
- 5 electron pairs is $A X_{5}$; the trigonal bipyramidal shape


## EXAMPLE: $\mathrm{PF}_{5}$



- There are two pyramids stuck base to base.
There are three equatorial $X$ atoms in a planar triangle and two axial $X$ atoms above and below the central atom.
- There are several possibilities for different combinations of bonding and non bonding pairs: $A X_{4} E, A X_{3} E_{2}$ and $A X_{2} E_{3}$
- When deciding on the location of the non bonding pairs, recall that the non bonding electron pairs require more space, so the molecule will take the shape that accommodates this requirement.
- An $^{\text {AX }}$ E molecule is $\mathrm{SF}_{4}$ :


$$
F-\ddot{S}_{F}^{\dot{S}^{1 / 1 / 1}}=F
$$

- This molecular shape is called a see-saw.
- $A n \mathrm{AX}_{3} \mathrm{E}_{2}$ molecule is $\mathrm{XeF}_{3}{ }^{+}$:


I
F

- Notice that the position of the non bonding pairs gives them the maximum amount of space in the $\mathbf{T}$ - Shaped molecule.
- The non bonding pairs of electrons have $120^{\circ}$ between them, compared to the bonding pairs which are at $90^{\circ}$ angles.
- The final molecule in this series is $\mathrm{AX}_{2} \mathrm{E}_{3}$; an example is $\mathrm{I}_{2} \mathrm{Cl}^{-}$:

- The non bonding electron pairs are at $120^{\circ}$ angles from each other: while the bonding pairs are at $180^{\circ}$ angles.
- This geometry is called linear (same as $A X_{2}$, which has no non bonding electron pairs).
- Molecules with 6 electron pairs are $\mathrm{AX}_{6}$; the octahedral geometry

EXAMPLE: $S_{6}$



- The octahedron consists of two square based pyramids; base to base.
- It has 8 faces, 12 edges and 6 corners.
- All bond angles in this molecule are $90^{\circ}$.
- There are two modifications of $A X_{6}$; these are $A X_{5} E$ and $A X_{4} E_{2}$.
- Once again, consider where the non bonding electron pair will have the most space when determining the shape of the molecule.
- An example of an $A X_{5} E$ molecule is $\mathrm{XeF}_{5}{ }^{*}$ :

- This is the square pyramid molecular shape.
- An example of an $\mathrm{AX}_{4} \mathrm{E}_{2}$ molecule is $\mathrm{ICl}_{4}{ }^{-}$:

- Notice that the non bonding pairs are situated at opposite ends of this square planar molecule.


## Molecules with Double or Triple Bonds

- In determining molecular shape, treat a double or triple bond like a single bond.
- An atom joined by a double bond occupies one "coordination site" around the central atom.
- Consider $\mathrm{CO}_{2}$, carbon dioxide; the Lewis dot structure will be:

- VSEPR predicts two bonds, $180^{\circ}$ apart, and linear.
- This would be an $A X_{2}$ molecule.
- When there are both double bonds and single bonds in a molecule, be aware that double bonds take up a little more space.
- For example, carbonyl fluoride $\mathrm{COF}_{2}$ :

$A X_{3}$
- $\mathrm{COF}_{2}$ is a planar triangular structure but the angles are not $120^{\circ}$.
- The carbonate ion, $\mathrm{CO}_{3}{ }^{2-}$, ( which is isoelectronic with $\mathrm{COF}_{2}$ ) is also planar triangular:

but here the bond angles are exactly $120^{\circ}$ because of the three resonance structures.
- Recall that the actual structure is an average of all resonance structures, so each bond is equivalent.
- We deal with triple bonds in the same manner.

$$
H-C \equiv \frac{C}{A x^{2}}-H
$$

- $\mathrm{C}_{2} \mathrm{H}_{2}$ is a linear molecule (take each carbon as the "central" atom!)
- A molecule or ion may have both double bonds and NB pairs.


## EXAMPLE:

Nitrite ion $\mathrm{NO}_{2}{ }^{-}$:

$\mathrm{AX}_{2} E$
Bent

- $\mathrm{NO}_{2}^{-}$is isoelectronic with ozone, $\mathrm{O}_{3} \ldots .$.

$A X_{2} E$
Bent
- In both molecules the bond angles are less than $120^{\circ}$ due to repulsion from the lone pair.
- If two different atoms are covalently bonded, the bonding electron pair is not equally shared between them.
- The atom with the greater attraction for the electron pair is said to be more electronegative.
- The result of an unsymmetrical charge distribution leads to a polar molecule.
- If the molecule contains a positive and a negative pole it is called dipolar.
- A non-polar molecule contains a symmetrical charge distribution.
- Electronegativity is a property of an element in a bonding situation, not of an isolated atom.
- It cannot be defined exactly; various scales have been described. [MH5; Table 6.5]
H
2.2
2.0
$C$
2.5
N
3.0
0
F
4.0

| Si | P | S | Cl |
| :--- | :--- | :--- | :--- |
| 1.9 | 2.2 | 2.6 | 3.2 |
|  |  |  |  |
|  |  | Se | Br |
|  |  | 2.5 | 3.0 |

I
2.7

- This is only important for reactive, non-metallic elements.
- Covalent bonds are said to be polarized with the more electronegative atom bearing a partial negative charge.
- In HF:

$$
\begin{gathered}
\delta+\quad \delta- \\
H-F \\
\Rightarrow
\end{gathered}
$$

- Such molecules are affected by an electric field and will try to line up.


-2004 Thomson - Brooks Coles
- The Ter 'unaligned' molecule will try to rotate in the electric field.
- It has a "dipole moment" which can be measured experimentally.
- A molecule of this type is a polar molecule.
- For a molecule to be polar, at least one polar bond must be present:

$$
\mathrm{H}-\mathrm{H}
$$

$$
\mathrm{Cl}-\mathrm{Cl}
$$

are non-polar molecules, not affected by an electric field.

- However, a molecule may be non-polar because the effects of the polar bonds cancel out.
- This depends on the shape or molecular geometry.
- Linear molecules are non-polar (the polar bonds are equal and opposite). $\delta^{-} \mathrm{Cl}_{l}-\mathrm{Be}^{+}-\mathrm{Cl}_{l} \delta-$
- But bent molecules, such as water, will be polar.

- Here the bond polarities do not cancel out (vector sum is not zero), and the molecule is polar.


## MORE EXAMPLES:

$\mathrm{BF}_{3}$
A non-polar molecule.
The effect of three B-F bonds cancels out.
The molecule is planar.
$\mathrm{NH}_{3}$
A polar molecule because it is non-planar, and the bond dipoles do not cancel!

$\mathrm{CCl}_{4}$

$\mathrm{CHCl}_{3}$
Polar, because C-H
has a different polarity
from $C-C l$.

$\mathrm{SF}_{4}$
Polar, because shape is irregular.

* $\mathrm{XeF}_{4}$

Non-polar: bond dipoles cancel in square planar shape.


Also note the following examples: $\mathrm{PF}_{5}$ : non-polar $A X_{5}$



SF 6 $^{\text {; }}$ non-polar
$A X_{6}$



- Overall polarity is 'averaged out' in a set of resonance structures: $\mathrm{CO}_{3}{ }^{2-}$ $\mathrm{SO}_{4}{ }^{2-}$


Planar, non - polar
Tetrahedral, non - polar

- How is molecular shape related to the orbitals in the valence shell?
- Consider methane, $\mathrm{CH}_{4}$ :


Carbon uses the $2 s$ and $2 p_{x} 2 p_{y}$ and $2 p_{z}$ orbitals; 4 orbitals $P_{n}$ total.


Zs

$2 p_{x}$

$2 p_{y}$

$2 p_{z}$

- These pictures result from plotting out the $\psi^{2}$ equation representing each orbital.
- But are the bonding electrons in $\mathrm{CH}_{4}$ still in these orbitals?
- Applying the "logic" used earlier, we suppose an electron configuration $2 s^{1} 2 p_{x}{ }^{1} 2 p_{y}{ }^{1} 2 p_{z}{ }^{1}$.
- That would give us the imaginary structure:

- This is NOT the correct structure, which we know to be tetrahedral!
- What has happened is that the $2 s$ and three $2 p$ atomic orbitals are hybridized, or mixed and averaged to give a set of four equivalent $\mathbf{s p}^{3}$ hybrid orbitals arranged at the tetrahedral angles of $109.5^{\circ}$.
- This is the hybridization that gives us the $A X_{4}$ geometry.

- Each $s p^{3}$ hybrid orbital contains 2 electrons:
they may be bonding (as in methane, $\mathrm{CH}_{4}$ ) or......
both bonding and non bonding (as in $\mathrm{NH}_{3}$ and $\mathrm{H}_{2} \mathrm{O}$ ).
- How does this process actually occur? Stay tuned....


## Possible orbital combinations

There are only five hybrid orbital types:

1) $\%$ one $s$ plus one $p \rightarrow$ two sp hybrid orbitals $\rightarrow A X_{2}$ geometry

The two sp hybrid orbitals are directed $180^{\circ}$ apart.
Each can hold an electron pair, bonding or non-bonding.
The resulting geometry is linear, as in:

$$
\mathrm{Cl}-\mathrm{Be}-\mathrm{Cl} \quad \mathrm{H}-\mathrm{C} \equiv \mathrm{C}-\mathrm{H} \quad \mathrm{O}=\mathrm{C}=\mathrm{O}
$$

- Note that only 1 p orbital is used to form the sp hybrid, which means that there are still 2 "pure" p orbitals present, but not used in the formation of a single bond.

2) $\%$ one $s$ plus two $p \rightarrow$ three $s p^{2}$ hybrid orbitals $\rightarrow A X_{3}$ geometry These three hybrid orbitals are placed $120^{\circ}$ apart.
Three electron pairs can be accommodated, giving the trigonal, or triangular planar geometry.
As only 2 p orbitals are used, there is one unused pure p orbital.


EXAMPLES:
$\mathrm{BF}_{3}$

$\mathrm{CO}_{3}{ }^{2-}$
$\bigcirc$

3) $\div$ one $s$ plus three $p \rightarrow$ four $s p^{3}$ hybrid orbitals $\rightarrow A X_{4}$ geometry This is the hybridization already described for methane, $\mathrm{CH}_{4}$.
Four electron pairs can be accommodated in these hybrid orbitals. With this hybrid type, all three p orbitals are used in making the hybrid orbitals, so there are none left over, as in sp and $\mathrm{sp}^{2}$.


With $s p^{3}$ hybrids, the electron pair arrangement is always tetrahedral, but the shape will differ if NB pairs are present.

(a)
muro 1011

(b)

(c)
$\mathrm{CH}_{4}$
$\mathrm{AX}_{4}$
$\mathrm{NH}_{3}$
$A X_{3} E$
Triangular Pyramidal
$\mathrm{H}_{2} \mathrm{O}$
$A X_{2} E_{2}$

Tetrahedral
Bent
4) $\%$ one $s$ plus three $p$ plus one $d \rightarrow$ five $s p^{3} d$ hybrid orbitals $\rightarrow A X_{5}$ geometry
The electron arrangement is always trigonal bipyramidal which can accommodate 5 electron pairs.

EXAMPLES:

5) $\%$ one $s$ plus three $p$ plus two $d \rightarrow s i x ~ s p^{3} d^{2}$ hybrid orbitals $\rightarrow A X_{6}$ geometry.
Here the electron arrangement is octahedral, with 6 electron pairs.
EXAMPLES:

$$
\begin{aligned}
& S F_{6} \quad A X_{6} \\
& C F_{5} \quad A X_{5} E \\
& \mathrm{XeF}_{4} A X_{4} \mathrm{~F}_{2}
\end{aligned}
$$

$$
\begin{aligned}
& \text { BP } \\
& \text { 5BP,1NB } \\
& \text { 4BP,2NB }
\end{aligned}
$$

- The following diagram shows the makeup and positioning of the $s p^{3} d$ and $s p^{3} d^{2}$ hybrid orbitals.
- Notice that the hybrid orbitals are arranged to as to form the $A X_{5}$ and $A X_{6}$ geometries, respectively.

- The VSEPR approach obviously uses hybrid orbitals!!
- To decide upon the hybridization at the central atom, look at the total number of electron pairs on the central atom, counting one pair for each bond (single, double or triple), and one pair for each NB pair of electrons.
- You need as many hybrid orbitals as you have pairs of electrons.

SUMMARY:

| Number of <br> electron pairs | Geometry | Hybridization | Shape |
| :---: | :---: | :---: | :---: |
| 2 | $A X_{2}$ | $s p$ | Linear |
| 3 | $A X_{3}$ | $s p^{2}$ | Triangular Planer |
| 3 | $A X_{2} E$ | $s p^{2}$ | Bent |
| 4 | $A X_{4}$ | $s p^{3}$ | Tetrahedral |
| 4 | $A X_{3} E$ | $s p^{3}$ | Triangular Pyramid |
| 4 | $A X_{2} E_{2}$ | $s p^{3}$ | Bent |
| 5 | $A X_{5}$ | $s p^{3} d$ | Trigonal/ Bipyramidal |
| 5 | $A X_{1} E$ | $s p^{3} d$ | See Saw |
| 5 | $A X_{3} E_{2}$ | $s p^{3} d$ | T - Shaped |
| 5 | $A X_{2} E_{3}$ | $s p^{3} d$ | Linear |
| 6 | $A X_{6}$ | $s p^{3} d^{2}$ | Octahedral |
| 6 | $A X_{5} E$ | $s p^{3} d^{2}$ | Square Pyramid |
| 6 | $A X_{4} E_{2}$ | $s p^{3} d^{2}$ | Square Planar |

- Remember that the actual shape (and the accompanying name!) of the molecule changes when non-bonding electron pairs are introduced.


## Hybridization and Multiple Bonds

- Recall that when the geometry of a molecule is being determined, we count a multiple (be it double or triple) as one bond.
- We do this because the extra electron pairs in the double or triple bond have no effect on the geometry of the molecule.
- These extra electron pairs are not located in the hybrid orbitals; and it is the hybrid orbitals that determine the geometry of the molecule.
- So where are those extra electrons, and how do they make a multiple bond?
- Weill look at alkenes first; for example, $\mathrm{C}_{2} \mathrm{H}_{4}$.

- If we look at each carbon atom as a "central" atom, we see that there are 3 bonds (counting the double bond as one bond).
- What geometry (AXE) does this imply? $A X_{3}$
- What type of hybrid orbitals are used for this geometry?

- These three hybrid orbitals form three single, or sigma bonds (o-bonds). - used 3 prs of electrons
- What happens to the p-orbital which was not used in making the hybrid orbitals?
- "houses" an extra electron pair
- this "pure" p orbital did not take part in hybridization
- These un-used p-orbitals are called pi ( $\pi$ ) bonding orbitals and are located above and below the sigma bond axis.
- The overlap of these orbitals creates another bond, the $\pi$ bond.
- It is the sum of the $\sigma$ and $\pi$ bonds that creates what we call a "double bond".

- $s p^{2}$ hybrid orbit ab
- 3 б bonds
- pure $p$ orbital
( 1 on each $C$ )
$\Rightarrow 1$ II bond.
- A similar approach can be used with alkynes (a triple bond); eg, $\mathrm{C}_{2} \mathrm{H}_{2}$ Linear molecule

$$
H-C \equiv C-H
$$

$\therefore 2 e^{-}$-pairs

- What is the AXE type for this molecule?

$$
A X_{2}
$$

- What hybrid orbitals are being used to form $\sigma$ bonds?
- 2 sp hybrids $\rightarrow$ fam $2 \sigma$ bonds (on each C)
- How may pi bonding orbitals are there?
$\therefore 2 \pi$ bonding orbitals using 2 pure pobittals (on each)

$\sigma$ bonds
$\pi$ bond
$\pi$ bond
- A triple bond consists of one $\sigma$ and two $\pi$ bonds.

