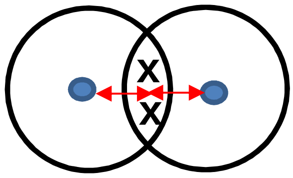
Covalent Bonding

Covalent substances are formed when two or more non-metal atoms link up and form a molecule.
The electronic configuration of each atom usually corresponds to that of a noble gas.
The shared pair of electrons (one e from each atom) is called a covalent bond. The atoms' nuclei are attracted towards the shared pair of electrons.

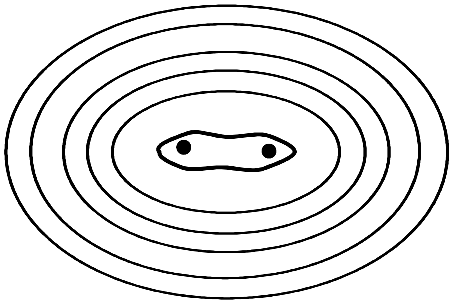
A covalent bond strong and is caused by the electrostatic attraction between the bonding pair of electrons and the two nuclei.



The strength of covalent bond can be demonstrated by the high melting points of giant atomic structures like diamond and graphite. They have high melting points because they contain many strong covalent bonds in a macromolecular structure. It takes a lot of energy to break the many strong bonds.

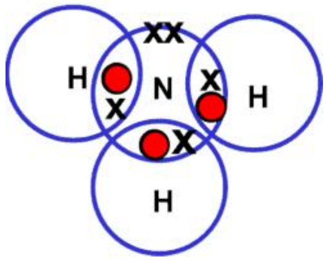
The X-ray diffractions for the hydrogen molecule show high concentration of negative charge between H nuclei. This negative charge is strongly attracted by both nuclei so attractive interactions exceed repulsive ones.

In a covalent compound there is significant electron density between the atoms.

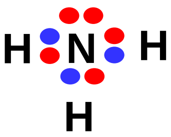


Ways of representing covalent molecules

Electron Configuration Diagrams
Dot and Cross diagrams

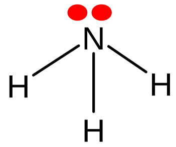


Lewis structures



Lewis structures are like dot and cross diagrams, but only identical dots are used. I have used different colours but it is not necessary. Using only dots shows that all electrons are identical. The dots and crosses can lead some people to think the electrons are different.

Line diagrams

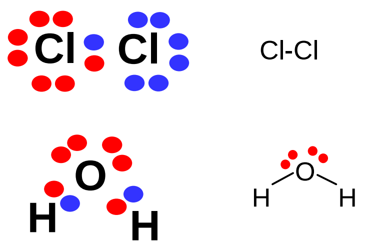


Each line represents a covalent bond. It is good practice to add the non bonding pairs of electrons on these diagrams too.

These electron configuration diagrams only show the outer shell electrons (called valence electrons) that are involved in bonding. The electrons are drawn in pairs to represent the pairs of electrons in electron orbitals. The electron pairs are called bonding pairs if they are shared between two atoms. If the electron pairs are not involved in bonding then they are called non- bonding pairs (or lone pairs). The non bonding pairs are important in determining the shape of molecules.

The Octet Rule

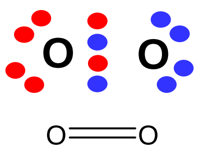
When most atoms combine to form covalent molecules they gain electronic structures with eight electrons in their outer valence shell. They gain a noble gas structure of eight electrons in their outer shell. This is called the octet rule.
Hydrogen is an exception as it only needs two electrons to fill its outer shell.



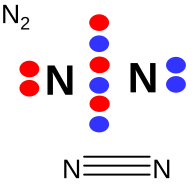
Multiple bonds

Multiple bonds occur when more than 2 electrons are shared between two atoms	
Single bond	1 pair of electrons shared
Double bond	2 pairs of electrons shared
Triple bond	3 pairs of electrons shared

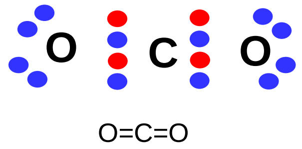
O_2



N_2

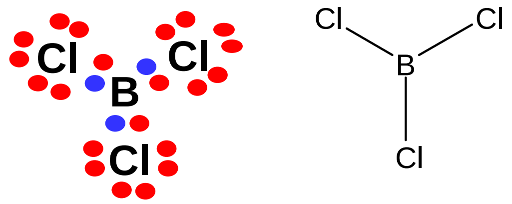


CO_2



Compounds that do not meet octet rule.

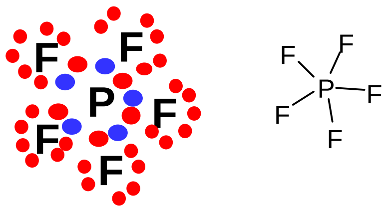
There are some covalent compounds of beryllium, boron and aluminium that do not have a full octet of electrons in their outer shell. These compounds can sometimes gain an octet through additional coordinate bonding. This is covered on the next page.



Boron only has six electrons in its outer valence shell in this compound

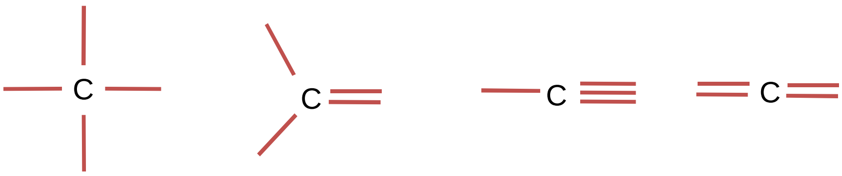
Expanding the octet.

The are many compounds where there are more than eight electrons in the outer shell. We call this expanding the octet.
This can happen with larger atoms in the 3rd or 4th period that have available d-sub shell orbitals.
It happens most commonly when the central atom has a high oxidation state.
Elements in period 2 cannot expand their octet as they do not have available d sub shell orbitals.



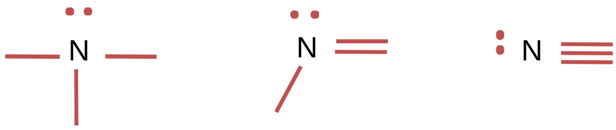
Normal bonding patterns

Carbon (4 bonds)



Nitrogen (3 bonds)

(Phosphorus)

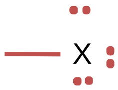


Oxygen (2 bonds)

(Sulphur)

Halogen (1 bond)

(F, Cl, Br, I)



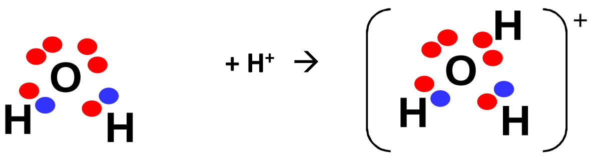
Hydrogen (1 bond)

Dative Covalent bonding

A Dative covalent bond forms when the shared pair of electrons in the covalent bond come from only one of the bonding atoms. A dative covalent bond is also called co-ordinate bonding.

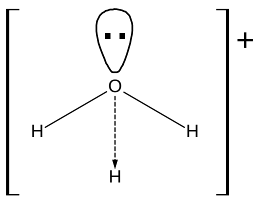
Oxonium ion H_3O^+

One of the lone pairs on the oxygen is used to share with the hydrogen ion which needs two electrons to fill its outer shell.

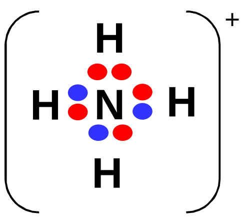


The positive charge is now distributed all over the ion and all the O-H bonds are equivalent.

The dative bond is shown as an arrow rather than a single line. The arrow points away from the atom which donates the pair of electrons.

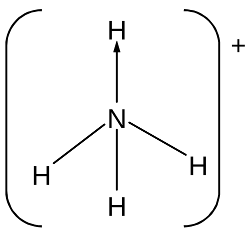


Ammonium ion NH_4^+



The lone pair of the N is shared with the hydrogen ion which needs two electrons to fill its outer shell.

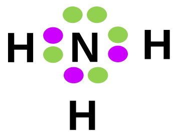
The ion has a +1 charge which is distributed all over the ion. All the N-H bonds are equivalent.

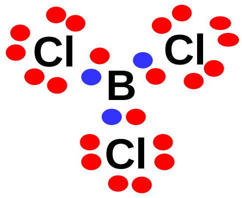


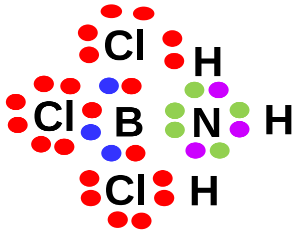
The dative covalent bond acts like an ordinary covalent bond when thinking about shape so in NH_4^+ the shape is tetrahedral.

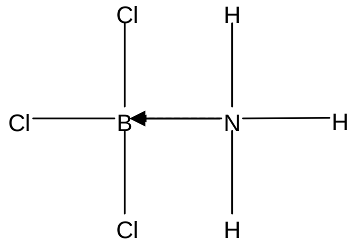
A Classic Example of Dative Covalent Bonding

The lone pair of electrons in the ammonia molecule can form a coordinate bond with the BCl_3 molecule where the boron atom has not got a full octet. By forming the coordinate bond the boron gains a full octet of electrons

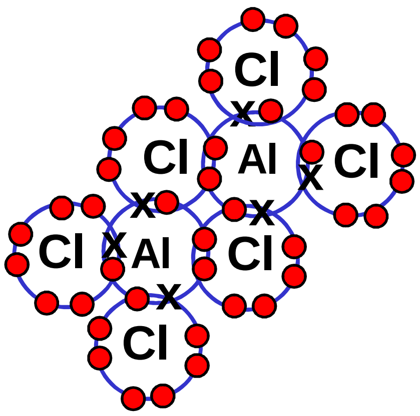




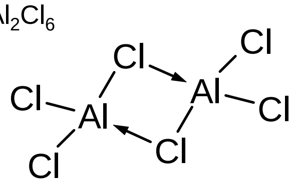




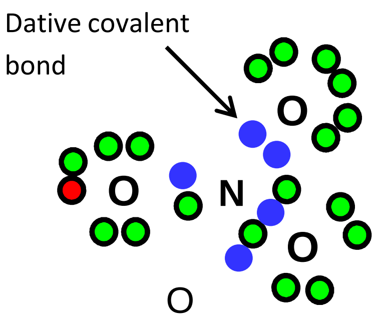
The direction of the arrow goes from the atom that is providing the lone pair to the atom that is deficient

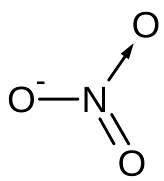


Two aluminium chloride ($AlCl_3$) molecules join together through two dative bonds to form the dimer Al_2Cl_6

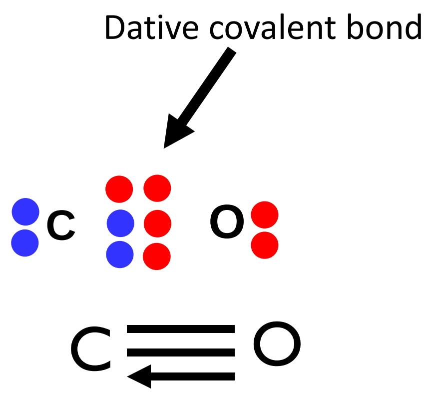


Nitrate ion NO_3^-



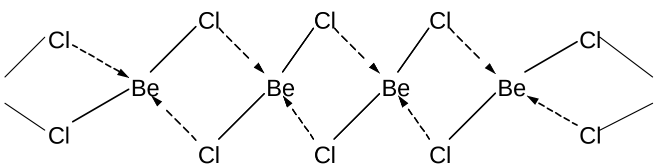


Carbon monoxide CO



Beryllium chloride $BeCl_2$

$BeCl_2$, on its own, is a linear molecule. Be does not have a full outer shell of electrons.



To achieve a full outer shell dative covalent bonds are formed. A lone pair of electrons from Cl is shared with a Be atom from another molecule. A chained polymer is formed.

The term **bond energy** *is used* as a measurement of covalent bond strength. It is the energy needed to break one mole of bonds of (gaseous covalent) bonds into gaseous atoms

The larger the value of the average bond enthalpy, the stronger the covalent bond

Bond length measures the distance between the two nuclei in a covalent bond.

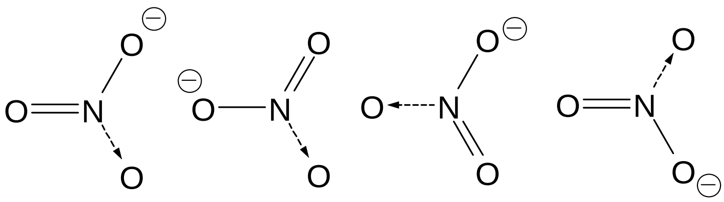
A shorter bond will have a higher bond energy as the there will be a stronger force of attraction between the nuclei and the shared pair of electrons as they are closer together.

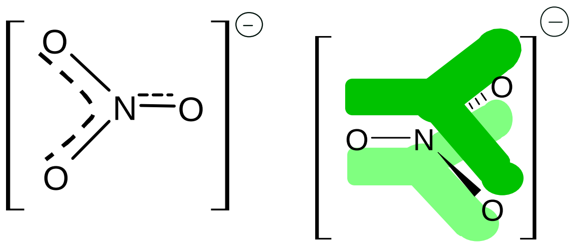
Effect of multiple bonds on bond strength and length.
Nuclei joined by multiple (i.e. double and triple) bonds have a **greater electron density** between them.
This causes an **greater force of attraction** between the nuclei and the electrons between them, resulting in a **shorter bond length** and **greater bond strength**.

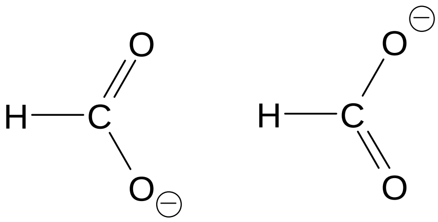
Resonance Structures

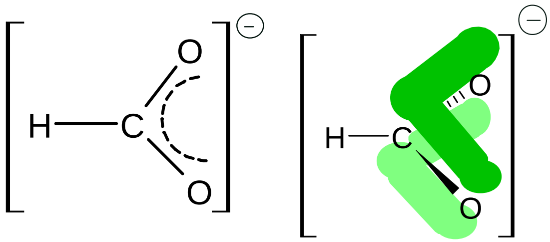
Resonance structures occur when there is more than one possible position for a double bond in a molecule.
These are formed when two or more alternative bonding systems can be drawn for the same molecule .

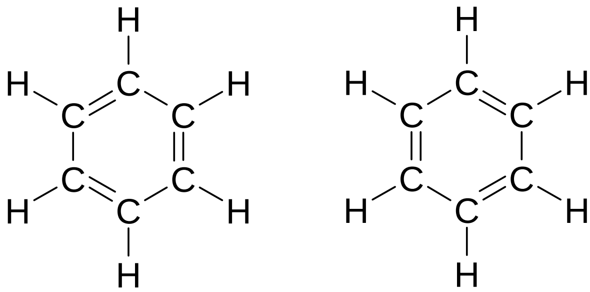
Alternative ways of representing the bonding **Delocalized structure**

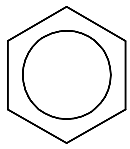












In reality the bonding in these systems is somewhere between the alternative structures. The delocalized structure tries to illustrate this.

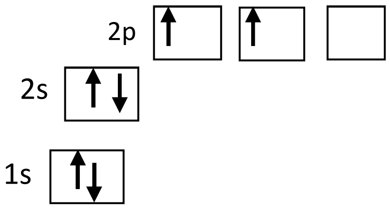
Covalent bonding in terms of orbital overlap

When atomic orbitals overlap they form molecular orbitals. The model can be used to show how single and double bonds form and can be used to show how why molecules have the shape they do.

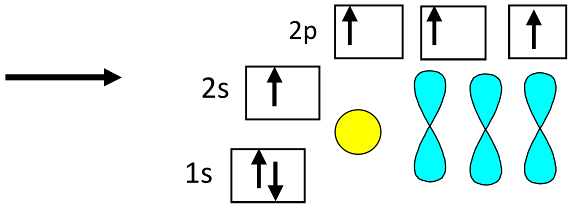
A single covalent bond is known as a sigma bond (σ). It is an area of electron density which is symmetrical about the axis joining the two atoms.

sp^3

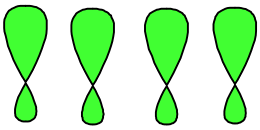
The ground state electronic configuration of a carbon atom is $\mathbf{1s^22s^22p^2}$

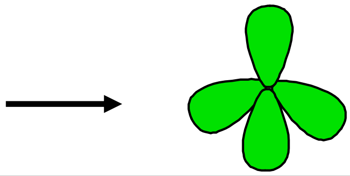


A more excited arrangement can be made if a little energy is used to promote one of the 2s electrons into the empty p orbital. The configuration is now $\mathbf{1s^22s^12p^3}$



Four orbitals (a 2s and three 2p's) hybridise to give four new hybrid orbitals – called sp^3 .

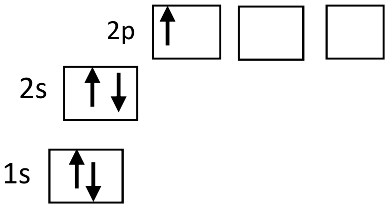




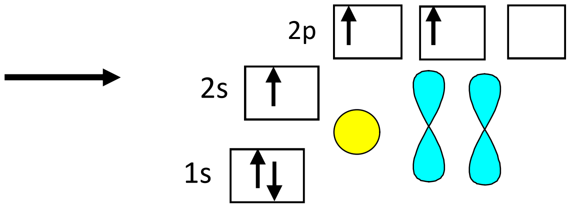
Four sp^3 hybrid orbitals will lead to a tetrahedral shape in molecules

Sp^2 as in Boron trichloride

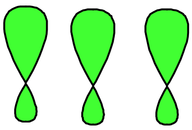
The ground state electronic configuration of a boron atom is $\mathbf{1s^22s^22p^1}$

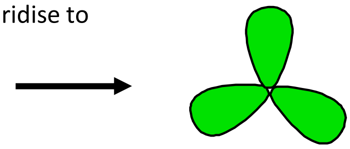


A more excited arrangement can be made if a little energy is used to promote one of the 2s electrons into the empty p orbital. The configuration is now $\mathbf{1s^22s^12p^2}$



Three orbitals (a 2s and two 2p's) can hybridise to give thee new hybrid orbitals – called sp^2 .

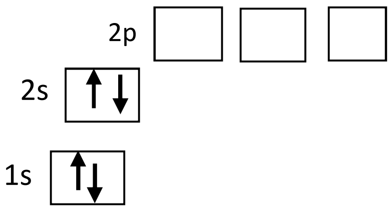




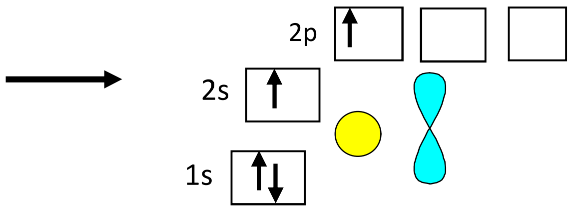
Three sp^2 hybrid orbitals will lead to a trigonal planar shape in molecules

Sp as in $BeCl_2$

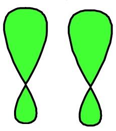
The ground state electronic configuration of a berylium atom is $\mathbf{1s^22s^2}$

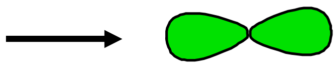


A more excited arrangement can be made if a little energy is used to promote one of the 2s electrons into the empty p orbital. The configuration is now $\mathbf{1s^22s^12p^1}$



sp two orbitals (a 2s and one 2p) can hybridise to give two new hybrid orbitals – called sp .

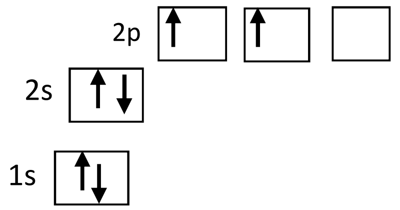




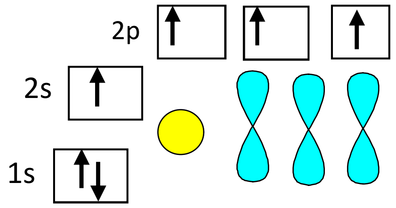
Two sp hybrid orbitals will lead to a linear shape in molecules

Forming multiple bonds. E.g the C=C bond

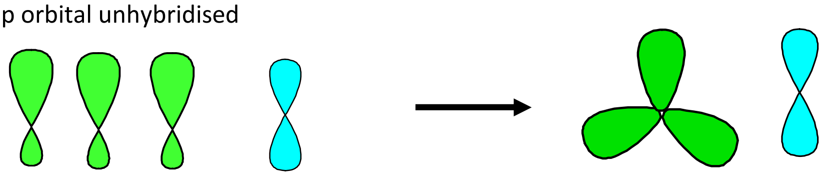
The ground state electronic configuration of a carbon atom is **$1s^2 2s^2 2p^2$**



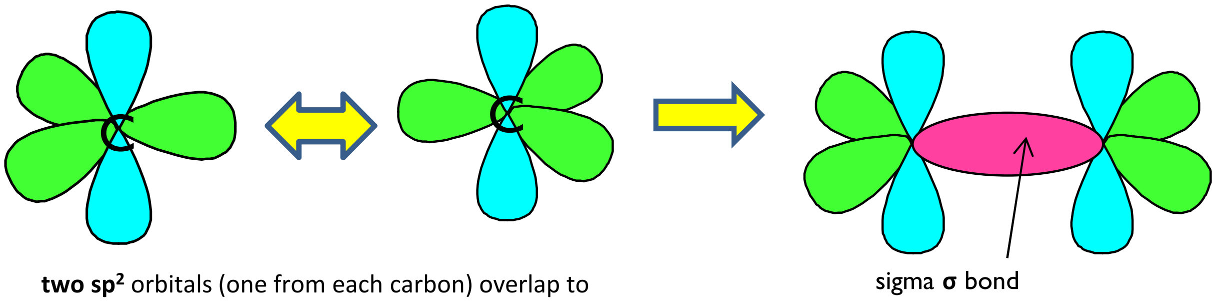
A more excited arrangement can be made if a little energy is used to promote one of the 2s electrons into the empty p orbital. The configuration is now **$1s^2 2s^1 2p^3$**



Three orbitals (a 2s and two 2p's) can hybridise to give thee new hybrid orbitals – called sp^2 . Leaving one p orbital unhybridised



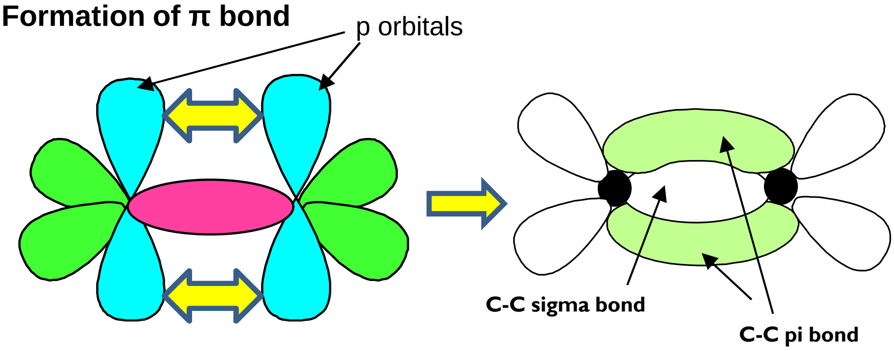
Formation of σ bond



two sp^2 orbitals (one from each carbon) overlap to form a single C-C bond called a sigma **σ** bond

Rotation can occur around a sigma bond

Formation of π bond



The π **bond** is formed by sideways overlap of **two p orbitals** on each carbon atom forming a π-bond above and below the plane of molecule.

The π bond is weaker than the σ bond.

Covalent Bonding Questions

1. Define what a covalent bond is.

In all the following questions just draw the outer shell electrons

2. Draw Lewis structures to show the covalent bonding in:
a chlorine molecule, Cl_2
b Water H_2O
c hydrogen chloride, HCl

3 Draw Lewis structures and bond diagrams to show the covalent bonding in the following compounds with double and triple bonds
a oxygen molecule, O_2
b carbon dioxide CO_2
c Nitrogen N_2
d hydrogen cyanide, HCN (there is a triple bond between the carbon and the nitrogen atoms)

4 Draw Lewis structures and bond diagrams to show the covalent bonding in the following compounds which will have an atom with more than eight electrons in its outer shell.
a PF_5
b SF_6
c BrF_3
d XeF_4
e SF_4

5 Draw Lewis structures and bond diagrams to show the covalent bonding in the following compounds with a charge. In these assume the central atom has lost or gained the electron
a PF_4^+
b NH_2^-
c ClF_2^+
d BrF_4^-
e AlF_2^+
f carbide ion C_2^{2-} (Which two well-known diatomic gases are iso-electronic (same number of electrons) with the carbide ion?)

6 Draw Lewis structures and bond diagrams to show the covalent bonding in the following compounds. These will have some double bonds. In the negative ions, the extra electron will be on the outer oxygen and not the central atom
a carbonate ion CO_3^{2-}
b sulfate (VI) ion SO_4^{2-}
c sulfur dioxide SO_2
d sulfur trioxide SO_3
e phosphate ion PO_4^{3-}
f XeO_3

Dative Covalent Bonding Questions

1. Co-ordinate bonding can be described as dative covalency. In this context, what is the meaning of each of the terms *covalency* and *dative?*

2. Draw the dot and cross diagrams for the compounds of $AlCl_3$ and NH_3. Explain how the two substances join to form the compound $AlCl_3.NH_3$. Draw a bond diagram to show the bonding in this compound using an arrow to show the direction of the coordinate bond.

3. The following compounds contain a dative covalent bond. Through drawing dot and cross diagram show which bond is dative. Then draw a bond diagram to show the bonding in these compounds using an arrow to show the direction of the coordinate bond.
a) H_3O^+
b) NH_4^+
c) BrF_4^-
d) PH_4^+
e) CO

4. A molecule of NHF_2 reacts with a molecule of BF_3 as shown in the following equation.
$NHF_2 + BF_3 \rightarrow F_2HNBF_3$
Draw the Lewis structures for the compounds of BF_3 and NHF_2. Explain how the two substances join to form the compound F_2HNBF_3. Draw a diagram to show the bonding in this compound using an arrow to show the direction of the coordinate bond.

5. The azide N_3^- ion contains three Nitrogen atoms joined together in a line. It contains one dative covalent bond and all the Nitrogen atoms will end up with 8 electrons in their outer shell. Draw the Lewis structure to work out the bonding present in the azide ion. Then draw a bond diagram to show the bonding in this compound using an arrow to show the direction of the coordinate bond.

6. Lithium aluminium hydride, $LiAlH_4$, contains the AlH_4^- ion.
Draw a '*dot-and-cross*' diagram to show the bonding in an AlH_4^- ion.
Show outer electrons only.

7. *Two Aluminium chloride molecules ($AlCl_3$) join together by two coordinate bonds to form the dimer Al_2Cl_6. Draw a diagram to show the bonding in this compound using arrows to show the direction of the coordinate bonds.

8.* Draw a Lewis structure to show the bonding in nitrate ion (NO_3^-) . Then draw a bond diagram to show the bonding in this ion using an arrow to show the direction of the coordinate bond

9.* Beryllium Chloride $BeCl_2$ can form a polymer type structure by forming two coordinate bonds per molecule. Draw a bond diagram to show the bonding in a portion of this polymer using arrows to show the direction of the coordinate bonds.
10.* In the diagram of Borazine below , deduce which of the bonds present would be coordinate. Draw on the diagram arrows to show the direction of the coordinate bonds