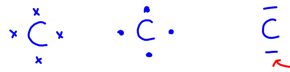
4.3 Covalent structures

Lewis diagrams are used to show the arrangement of electrons in covalent molecules

A carbon atom has 4 valence (outer shell) electrons. There are three ways we can reperesent its Lewis structure:



a pair of e^-

We can apply this theory to draw Lewis diagrams for covalent molecules:

1 Calculate the total number of valence electrons in the molecule by multiplying the number of valence electrons of each element by the number of atoms of the element in the formula and totalling these.

2 Draw the skeletal structure of the molecule to show how the atoms are linked to each other.

3 Use a pair of crosses, a pair of dots, or a single line to show one electron pair and put a pair in each bond between atoms.

4 Add more electron pairs to complete the octets (8 electrons) around the atoms (other than hydrogen which must have 2 electrons and the exceptions noted below).

5 If there are not enough electrons to complete the octets, form double bonds and if necessary triple bonds.

6 Check that the total number of electrons in your finished structure is equal to your calculation in the first step.

Example: CCl_4

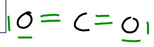
$C \rightarrow 4e^-$ CO_2

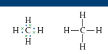
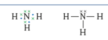
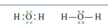
$O \rightarrow 6e^- \times 2 = 12e^-$

$16e^- \rightarrow \cancel{8} \text{ pairs } e^-$

$\cancel{6}$

$\cancel{2}$



Molecule	Total number of valence electrons	Lewis structure
CH_4	4 + (1 × 4) = 8	
NH_3	5 + (1 × 3) = 8	
H_2O	(1 × 2) + 6 = 8	
CO_2	4 + (6 × 2) = 16	
HCN	1 + 4 +5 = 10	

If there are charges on the species you need to draw then when counting valence electrons:

- Add 1 for a negative charge
- Remove 1 for a positive charge

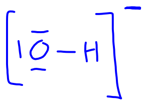
Draw a Lewis diagram for an OH^- ion and the SO_4^{2-} ion:

$O \rightarrow 6e^-$

$H \rightarrow 1e^-$

$+1e^-$

$8 \rightarrow 4 \text{ pair}$



In coordinate bonds both shared electrons come from one atom

We can represent coordinate (dative covalent) bonds using an arrow as we saw in Topic 13:

H_3O^+

We will see the relevance of these coordinate bonds in Topic 8 and 18.

NH_4^+

$H_2\ddot{O}: + H^+ \rightarrow H_3O^+$

CO

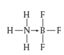
The octet rule is not always followed

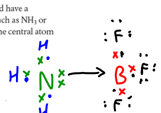
There are a few molecules that are exceptions to the octet rule. Small atoms such as beryllium (Be) and boron (B) form stable molecules in which the central atom has fewer than eight electrons in its valence shell. This is known as an **incomplete octet**. For example, the structures of $BeCl_2$ and BF_3 are shown below.

$BeCl_2$ valence electrons = 2 + (7 × 2) = 16

BF_3 valence electrons = 3 + (7 × 3) = 24

Molecules with incomplete octets are said to be **electron deficient**, and have a tendency to accept an electron pair from a molecule with a lone pair, such as NH_3 or H_2O. This leads to the formation of a coordinate compound in which the central atom has now gained an octet.





Exercises

14 Draw the Lewis structures of:
(a) HF **(b)** CF_3Cl **(c)** C_2H_6 **(d)** PCl_3
(e) C_2H_4 **(f)** C_2H_2

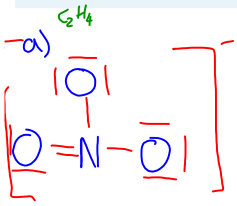
15 How many valence electrons are in the following molecules?
(a) $BeCl_2$ **(b)** BCl_3 **(c)** CCl_4 **(d)** PH_3
(e) SCl_2 **(f)** NCl_3

16 Use Lewis structures to show the formation of a coordinate bond between H_2O and H^+.

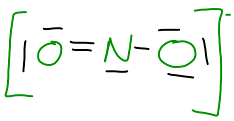
17 Draw the Lewis structures of:
(a) NO_3^- **(b)** NO^+ **(c)** NO_2^- **(d)** O_3
(e) N_2H_4

C_2H_4

a)



c)

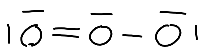


O_3

$O \rightarrow 6e^- \times 3 = 18e^- \rightarrow \cancel{9} \text{ pairs } e^-$

$\cancel{7}$

4

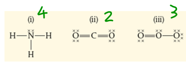


VSEPR theory: The shape of a molecule is determined by repulsion between electron domains

Predictions of molecular shape are based on the **Valence Shell Electron Pair Repulsion (VSEPR) theory**. As its name suggests, this theory is based on the simple notion that *because electron pairs in the same valence shell carry the same charge, they repel each other and so spread themselves as far apart as possible.*

As the electron pairs behave as a single unit, we often describe them as electron domains . Every lone pair, single bond, double bond and triple bond count as 1 electron domain.

How many are there in each example below?



As these domains repel each other, they are directly responsible for the position of bonds and therefore the shape of a covalent molecule.

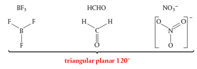
Species with two electron domains

Molecules with two electron domains will position them at **180°** to each other, giving a **linear** shape to the molecule.

$BeCl_2$ Cl—Be—Cl
CO_2 O=C=O
C_2H_2 H—C≡C—H
linear 180°

Species with three electron domains

Molecules with three electron domains will position them at **120°** to each other, giving a **triangular planar** shape to the electron domain geometry. If all three electron domains are bonding, the shape of the molecule will also be triangular planar.



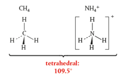
3 e⁻ domains

WARNING - Although lone pairs affect the shape of a molecule, when describing the geometry we only take into account where the bonded atoms are positioned.

Draw the Lewis diagram for ozone, O_3. Why do we call its geometry v-shaped or bent and NOT trigonal planar ?

Species with four electron domains

Molecules with four electron domains will position them at **109.5°** to each other, giving a **tetrahedral** shape to the electron domains. If all four electron domains are bonding, the shape of the molecule will also be tetrahedral.



Note: Lone pairs of electrons repel other domains more than bonding pairs of electrons.

	CH_4	NH_3	H_2O
Lewis structure	H–C–H (H above and below)	H–N–H (H below)	H–O–H
Number of electron domains	4	4	4
Electron domain geometry	tetrahedral	tetrahedral	tetrahedral
Number of lone pairs	0	1	2
Number of bonded electron domains	4	3	2
Molecular geometry	tetrahedral	trigonal pyramidal	bent or V-shaped
Bond angles	109.5°	approximately 107°	approximately 105°

Why are the bond angles progressively smaller?

As lone pairs repel other electron domains more strongly. More lone pairs → smaller bond angles.

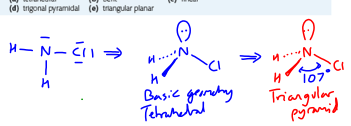
Exercises

18 Predict the shape and bond angles of the following molecules:
(a) H_2S (b) CF_4 (c) HCN (d) NF_3
(e) BCl_3 (f) NH_2Cl (g) OF_2

19 Predict the shape and bond angles of the following ions:
(a) CO_3^{2-} (b) NO_3^- (c) NO_2^+ (d) NO_2^-
(e) ClF_2^+ (f) $SnCl_3^-$

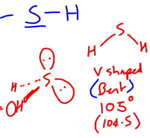
20 How many electron domains are there around the central atom in molecules that have the following shapes?
(a) tetrahedral (b) bent (c) linear
(d) trigonal pyramidal (e) triangular planar

18
19
20



H_2S
H = 1 v.e⁻ → ×2
S = 6 v.e⁻ +6
8e⁻ → 4 pairs e⁻

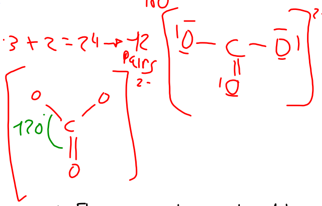
H – S – H



SiO_2
Si = 4e⁻
O_2 = 12e⁻
16e⁻ → 8 pairs

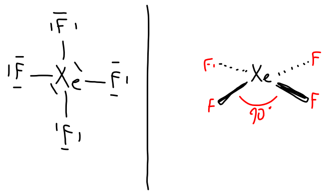
O = Si = O
O = Si = O
Linear 180°

CO_3^{2-}
4 + 6·3 + 2 = 24 → 12 pairs



1. Flourines can only form 1 covalent bond with a central atom.
2. Xe can break the octet rule.

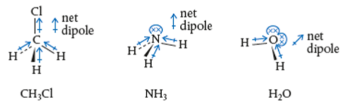
XeF_4



Molecules with polar bonds are not always polar

$\delta+$ H—Cl $\delta-$

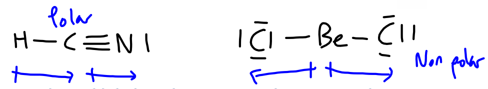
The molecules below are all polar because the dipoles do not cancel out.



Exercises

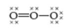
21 Predict whether the following will be polar or non-polar molecules:

(a) PH_3 (b) CF_4 (c) HCN (d) $BeCl_2$
(e) C_2H_4 (f) ClF (g) F_2 (h) BF_3

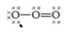


Electrons in multiple bonds can sometimes spread themselves between more than one bonding position

Delocalization is a characteristic of electrons in multiple bonds when there is more than one possible position for a double bond within a molecule. For example, let us look again at the Lewis structure of ozone, O_3, from page 159.



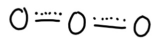
We can see that a different Lewis structure would be equally valid:



What does this data suggest?

	O–O single bond	O=O double bond	Oxygen–oxygen bonds in O_3 (Actual)
Bond length / pm	148	121	127
Bond enthalpy / kJ mol⁻¹ (Strength)	144	498	364

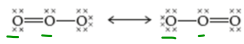
How could we represent this hybrid structure? Is it a valid Lewis diagram?



Bond order → $1\frac{1}{2}$

To represent it correctly we must show the individual reasonance structures. The actual structure is a mixture of these structures and we call it a a reasonance hybrid.

$\frac{2+1}{2} = \frac{3}{2}$



Worked example

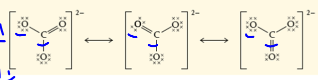
Draw the resonance structures for the carbonate ion CO_3^{2-}.

Solution

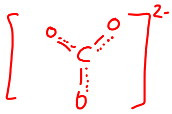
Count the number of valence electrons: 4 + (6 × 3) + 2 = 24

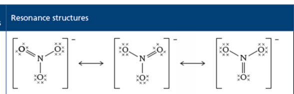
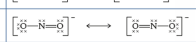
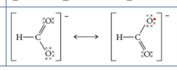
Draw the Lewis structure, noting that there are three possible positions for the double bond. This means there will be three resonance structures, as follows:

$\frac{1+2+1}{3} = \frac{4}{3} = 1\frac{1}{3}$

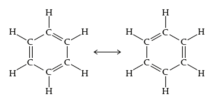


What is the bond order of each carbon-oxygen bond?



Species name and formula	Number of valence electrons	Resonance structures	Bond order
nitrate(V), NO_3^-	NO_3^- 24		$1\frac{1}{3}$
nitrate(III), NO_2^-	NO_2^- 18		$1\frac{1}{2}$
methanoate, $HCOO^-$	$HCOO^-$ 18		C–H = 1 C–O = $1\frac{1}{2}$

Benzene is another interesting example:



	C–C single bond	C=C double bond	Carbon–carbon bonds in benzene
Bond length / pm	154	134	140
Bond enthalpy / kJ mol⁻¹	346	614	507

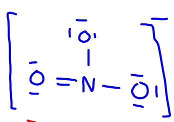
Exercises

23 Put the following species in order of increasing carbon–oxygen bond length:

CO CO_2 CO_3^{2-} CH_3OH

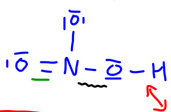
24 By reference to their resonance structures, compare the nitrogen–oxygen bond lengths in nitrate(V) (NO_3^-) and nitric(V) acid (HNO_3).

NO_3^-

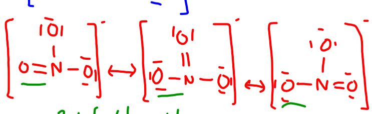


HNO_3

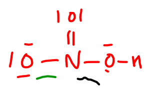
24 e⁻
12 pairs



$\frac{2+1}{2} = 1\frac{1}{2}$

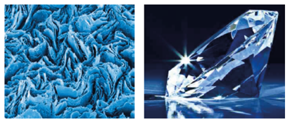


$\frac{2+1+1}{3} = 1\frac{1}{3}$



$\frac{1+1}{2} = 1$

Some covalent substances form giant molecular crystalline solids

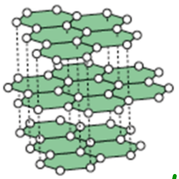
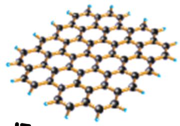


Some covalent substances exist as structures in which all atoms are bonded covalently to others forming a giant covalent structure instead of individual covalent molecules.

This has a large affect on their properties.

Allotropes are different forms of an element in the same physical state, such as oxygen (O_2) and ozone (O_3) which both exist as gases. Different bonding within these structures gives rise to distinct forms with different properties.

For carbon these are 4 allotropes :

	Graphite	Diamond	Fullerene C_{60}	Graphene
Structure				

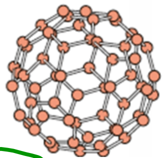
Hexagonal layers

Delocalised electrons can move freely in between the layers.

Tetrahedral

Smirnoff diamond

Very strong!



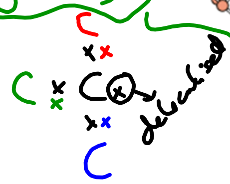
Even stronger than diamonds.

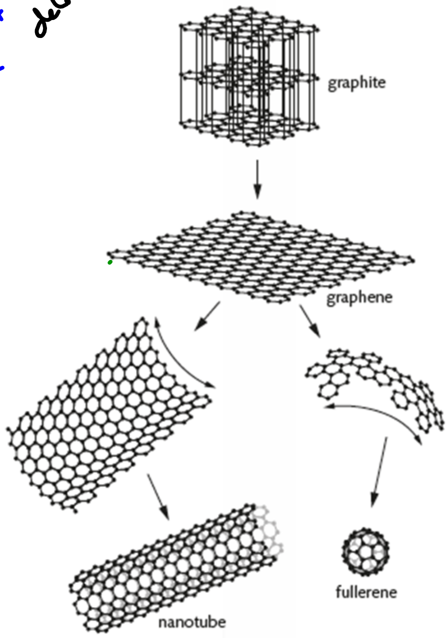
Flexible

Graphene

Conducts electricity

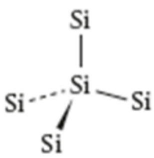
Very light





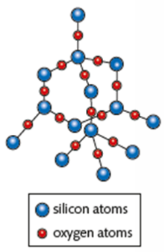
The development of tiny (<100 nm) structures involving graphite, graphene and nanotubes is called nanotechnology .

Stephen Fry - What is nano?



Silicon (also in Group 14) exists as a similar structure to diamond.

Silicon dioxide also exists as a giant covalent structure.



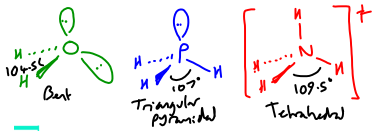
- strong;
- insoluble in water;
- high melting point;
- non-conductor of electricity.

Selectividad questions

Para las moléculas: agua, catión amonio y fosfina (trihidruro de fósforo):

a) Escribe las estructuras de Lewis. PH_3 NH_4^+

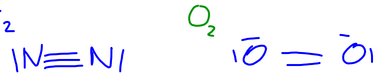
b) Razona cuál de estas moléculas tiene un mayor ángulo H—X—H (X se refiere al heteroátomo).



6. A la luz de las teorías de enlace de valencia y Lewis, razone por qué dos átomos de cloro tienden a juntarse para formar una molécula. Indique además dos ejemplos de moléculas que no cumplen la regla del octeto. Datos: número atómico cloro = 17.
(C. F. Navarra, 2008)

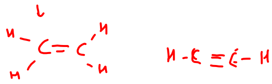
7. Dibuje las estructuras de Lewis de las moléculas de nitrógeno y de oxígeno e indique cuál de estas dos moléculas será más reactiva. Razone su respuesta.
(La Rioja, 2007)

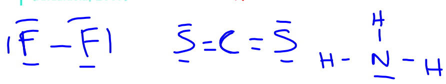
N_2 O_2



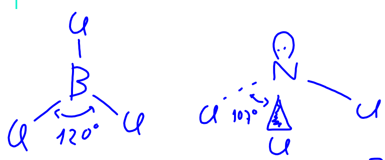
8. Dadas las siguientes moléculas: F_2, CS_2, C_2H_4, C_2H_2, H_2O y NH_3.
Indique en cuál o cuáles:
- Todos los enlaces son simples.
- Existe algún doble enlace.
- Existe algún triple enlace.

(Andalucía, 2007)

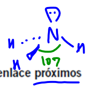




9. Indica razonadamente la geometría del tricloruro de boro y del tricloruro de nitrógeno. Justifica las diferencias entre ambos compuestos.
(Islas Baleares, 2005)



10. La molécula de amoniaco N ($Z = 7$); H ($Z = 1$): (V o F)



a) Tiene una geometría plana triangular. F
b) Tiene una geometría piramidal con unos ángulos de enlace próximos a 109°. ✓
c) Tiene una geometría tetraédrica en la que los átomos ocupan los vértices del tetraedro. F
d) Presenta tres formas resonantes. F

(Cataluña, 2008)

13. Si la molécula de agua es polar, ¿podría tener una estructura lineal en vez de angular como la tiene realmente? ¿Por qué?
(Cantabria, 2006)

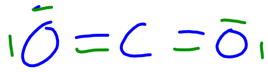
15. Dadas las moléculas HCl, KF y CH_2Cl_2:
a) Razone el tipo de enlace presente en cada una de ellas utilizando los datos de electronegatividad.
b) Escriba la estructura de Lewis y justifique la geometría de las moléculas que tienen enlaces covalentes.
Valores de *EN*: K = 0,81; H = 2,1; C = 2,5; Cl = 3,0; F = 4,0.
(C. Madrid, 2004)

1. Lewis diagram, geometry, bond angles

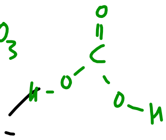
Exceptions to Octet Rule
Xe
Be → 2 pairs
B → 3 pairs

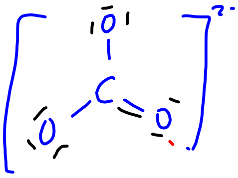
2. $CO_2 \rightarrow 6e^- \times 2 \rightarrow 12\ e^-$

↳ $4e^-$ → $16e$ (8 pairs)



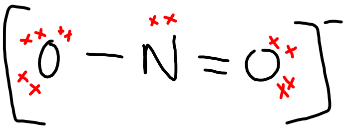
3. $[CO_3]^{2-}$ H_2CO_3





4. NO_2^-

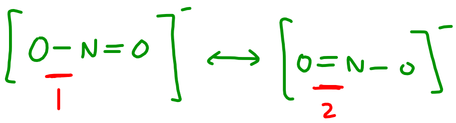
$5 + 6 \times 2 + 1 = 18e^-/2$
$= 9e^-$ pairs



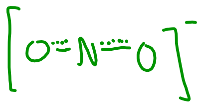
5. O_3

1. Draw PCl_3 → bond angles + geometry

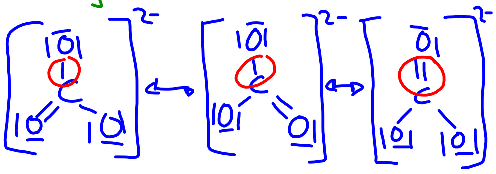
2. Draw resonance structures for CO_3^{2-}, draw a resonance hybrid; what is bond order?

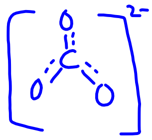


$\frac{1+2}{2} = 1\frac{1}{2}$



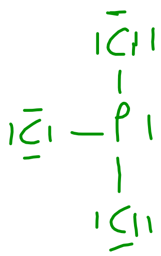
CO_3^{2-}
$4e^-$ $(3 \times 6e^-) + 2e^-$
$24e^-$
$12p$

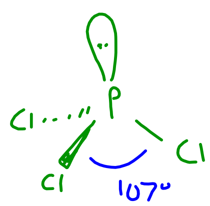




$\frac{1+1+2}{3} = \frac{4}{3}$

PCl_3





Trigonal pyramidal