

14.1

Further aspects of covalent bonding and structure**Understandings:**

- Covalent bonds result from the overlap of atomic orbitals. A sigma bond (σ) is formed by the direct head-on/end-to-end overlap of atomic orbitals, resulting in electron density concentrated between the nuclei of the bonding atoms. A pi bond (π) is formed by the sideways overlap of atomic orbitals, resulting in electron density above and below the plane of the nuclei of the bonding atoms.

Guidance

The linear combination of atomic orbitals to form molecular orbitals should be covered in the context of the formation of sigma (σ) and pi (π) bonds.

- Formal charge (FC) can be used to decide which Lewis (electron dot) structure is preferred from several. The FC is the charge an atom would have if all atoms in the molecule had the same electronegativity. $FC = (\text{number of valence electrons}) - \frac{1}{2}(\text{number of bonding electrons}) - (\text{number of non-bonding electrons})$. The Lewis (electron dot) structure with the atoms having FC values closest to zero is preferred.
- Exceptions to the octet rule include some species having incomplete octets and expanded octets.

Guidance

Molecular polarities of geometries corresponding to five and six electron domains should also be covered.

- Delocalization involves electrons that are shared by/between all atoms in a molecule or ion as opposed to being localized between a pair of atoms.
- Resonance involves using two or more Lewis (electron dot) structures to represent a particular molecule or ion. A resonance structure is one of two or more alternative Lewis (electron dot) structures for a molecule or ion that cannot be described fully with one Lewis (electron dot) structure alone.

Some molecules contain a central atom with an expanded octet

Atoms in Period 3 and below can form expanded octets by utilising vacant d-orbital to hold a pair of electrons.

This is possible as they are relatively close in energy.

Species with five electron domains

Molecules with five electron domains will position them in a **triangular bipyramidal** shape, which has angles of 90° , 120° , and 180° . If all five electron domains are bonding electrons, the shape of the molecule is also triangular bipyramidal.



$$3s + 5 = 40 \text{ valence } e^-$$

As we have seen previously, lone pairs can alter these bond angles and also require us to name the geometry when considering only the position of atoms.

- One non-bonding pair gives an **unsymmetrical tetrahedron** or **see-saw** shape.



Around the middle $\rightarrow 2 \times 90^\circ$
 $2 \times 120^\circ$
 At the top $\rightarrow 3 \times 90^\circ$

There will be some distortion of the shape due to the greater repulsion of the non-bonding pair of electrons, so bond angles will be 90° , 117° , and 180° .

- Two non-bonding pairs gives a **T-shaped** structure.



equatorial

The bond angles are 90° and 180° .

- Three non-bonding pairs gives a **linear** shape.

For example I_3^-



Compounds containing two different halogen atoms bonded together are called interhalogen compounds. They are interesting because they contain halogen atoms in unusual oxidation states: the more electronegative halogen has its typical negative oxidation number whereas the less electronegative halogen has a positive oxidation number. For example in ClF_3 , described here, the oxidation number of each F is -1 and the oxidation number of Cl is +3. You can read more about oxidation numbers in Chapter 9.

Species with six electron domains

Molecules with six electron domains will position them in an **octahedral** shape with angles of 90° . So a molecule having all six of its electron domains as bonding pairs of electrons will have this symmetrical octahedral shape.



The bond angles are 90° .

The shape of a molecule in which there are one or more non-bonding pairs of electrons is based on considering where the non-bonding pairs will be placed for maximum repulsion.

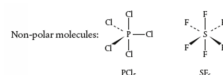
- One non-bonding pair gives a **square pyramidal** shape.



- Two non-bonding pairs will maximize their distance apart by arranging those pairs at 180° to each other. This gives a **square planar** shape.



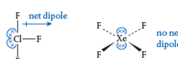
Polarity in these molecules?



If the atoms attached to the central atom are not all the same, there may or may not be a net dipole depending on the symmetry. For example, SbF_5 has a net dipole and is polar; PCl_5F_2 has no net dipole due to cancellation, so it is non-polar.



The presence of lone pairs often, but not always, results in a polar molecule. It again depends on symmetry and whether dipoles cancel. For example, ClF_3 is polar, whereas XeF_4 is not.



Exercises

34 Predict the shapes and bond angles of the following molecules and ions:

- (a) XeF_2 (b) ClO_2^- (c) OF_2 (d) XeO_4

- (e) PCl_5 (f) IF_5

35 How many electron domains are there around the central atom in molecules that have the following geometry?

- (a) square planar (b) octahedral (c) square pyramidal

- (d) trigonal bipyramidal (e) linear

36 What bond angles do you expect for each of the following?

- (a) the F-Cl-F angle in $KClF_2$

- (b) the Cl-F-Cl angle in PCl_5

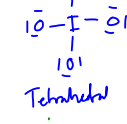
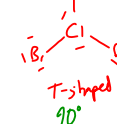
- (c) the F-S-F angle in SF_6

37 Determine whether the species in Q14 (a)-(f) (page 158) are polar or non-polar.

- 38 Which of the following molecules would be expected to be polar?

- (a) $ClBr_3$ (b) IO_2^- (c) TeF_6 (d) BrF_2

- (e) PCl_5 (f) ClF_3



Formal charge is a useful tool for comparing Lewis (electron dot) structures

As we have seen, it is possible to draw different Lewis structures for different molecules (leading to resonance structures) and some atoms can also break the Octet Rule. To help us work out the actual structure between the possible options we must consider the **formal charge** on each atom.

For example SO_2 .

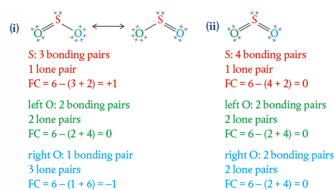
which in different sources is represented as: (i) $\text{O}=\text{S}=\text{O}$ \longleftrightarrow $\text{O}^+=\text{S}=\text{O}^-$ or

(ii) as a structure with an expanded octet on S $\text{O}=\text{S}=\text{O}$.

Formal charge requires us to assign electrons to each atom assuming every atom has an equal electronegativity.

$$\text{formal charge (FC)} = \text{number of valence electrons in unbonded atom (V)} - \text{number of electrons assigned to atom in Lewis (electron dot) structure}$$

- The number of valence electrons (V) is determined from the element's group in the Periodic Table.
- The number of electrons assigned to an atom in the Lewis (electron dot) structure is calculated by assuming that:
 - each atom has an equal share of a bonding electron pair (one electron per atom), even if it is a coordinate bond (dative);
 - an atom owns its lone pairs completely (L).



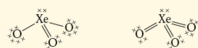
The formal charges in each resonance structure can be summarized as follows:



We can conclude that structure (ii) where all atoms have a formal charge of zero is the most stable structure for SO_2 .

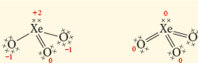
Worked example

Use the concept of formal charge to determine which of the following Lewis (electron dot) structures for XeO_3 is preferred?



Solution

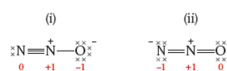
	$\text{O}=\text{Xe}=\text{O}$	$\text{O}=\text{Xe}=\text{O}$
Xe	$\text{FC} = 8 - (4 + 2) = +2$	$\text{FC} = 8 - (6 + 2) = 0$
left O	$\text{FC} = 6 - (1 + 6) = -1$	$\text{FC} = 6 - (2 + 4) = 0$
central O	$\text{FC} = 6 - (2 + 4) = 0$	$\text{FC} = 6 - (2 + 4) = 0$
right O	$\text{FC} = 6 - (1 + 6) = -1$	$\text{FC} = 6 - (2 + 4) = 0$



The structure on the right with the lowest formal charge is preferred.

What if we come across different Lewis structures that have the same formal charge?

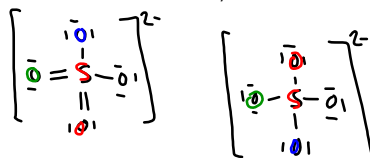
For example, two Lewis (electron dot) structures with formal charges are shown for N_2O .



Because in reality we will have more e^- density around the most electronegativity.

NOTE: The formal charges on a molecule will always add up to zero and on an ion they will add up to the charge.

Which of these structures is more likely for the sulfate ion?



Structure 1:
 $\text{S} = 6 - 6 = 0$
 $\text{O} = 6 - 6 = 0$
 $\text{O} = 6 - 7 = -1$
 $\text{O} = 6 - 7 = -1$
 $\text{O} = 6 - 6 = 0$

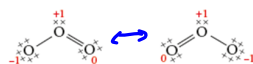
Structure 2:
 $\text{S} = 6 - 4 = +2$
 $\text{O} = 6 - 7 = -1$
 $\text{O} = 6 - 7 = -1$
 $\text{O} = 6 - 7 = -1$
 $\text{O} = 6 - 7 = -1$

Ozone: a case study in resonance, molecular polarity, and formal charge

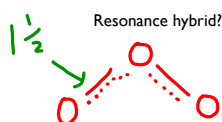
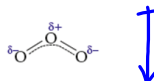


(Bond orders)

Ozone is polar - As all atoms in ozone are oxygen, we would expect this molecule to be non-polar. However, by calculating the formal charges we find that actually there is an unequal spread of electrons over the structure.

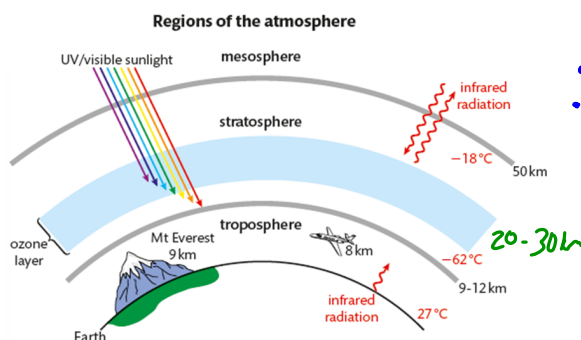


This gives a net dipole across the molecule, making it polar. This can be shown as follows.



FC = Number of e⁻ on un-bonded atom - Number assigned in Lewis diagram

Ozone is an essential component of the stratosphere



Why is the atmosphere essential for life on Earth?

- Protection UV-rays
- Moderation temperature

Ozone layer :

- Contains 90 % atmospheric ozone
- Levels maintained by a cycle of reactions.

N₂ = 79.1%

O₂ = 20.1%

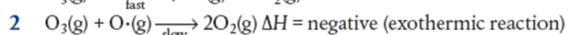
Ar = 1%

What is O₃ ?

Oxygen dissociation



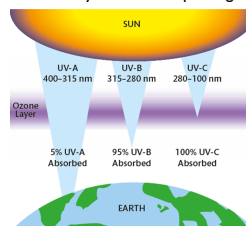
Ozone dissociation



Free radicals
They are extremely reactive

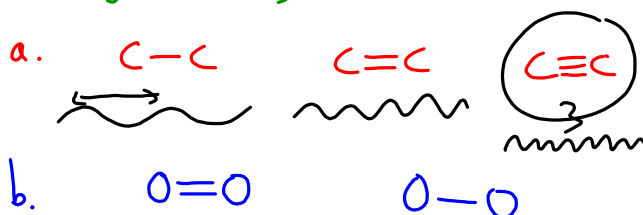
The wavelength show the energy of light that is absorbed to facilitate the 2 reactions. Why does O₂ require light of a shorter wavelength?

	Oxygen O ₂	Ozone O ₃
bond order	2	1.5
bond enthalpy	498 kJ mol ⁻¹	364 kJ mol ⁻¹
dissociated by UV light	<242 nm	<330 nm



The fact that ozone absorbs radiation of wavelengths in the range 200 nm to 315 nm is very significant. This corresponds to the higher range of ultraviolet light, known as UV-B and UV-C, which can cause damage to living tissue. So the ozone layer plays a vital role in protecting life on Earth from this radiation. This is a direct consequence of the specific nature of the bonding in ozone molecules.

Which bond would absorb radiation of a higher energy?

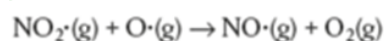
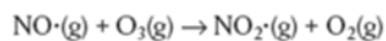


Catalytic destruction of ozone

As ozone is easily broken up by UV radiation, it is unstable and reacts with other compounds in the atmosphere.

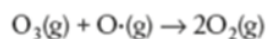
Nitrogen oxides (NO_x) and chlorofluorocarbons (CFC's) are 2 types of compound that form extremely reactive free radical that catalyse the decomposition of ozone even further.

NO· (and NO₂·) is produced in car engines and are both free radicals (as they both possess an unpaired electron).



This process accelerates the loss of ozone.

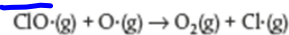
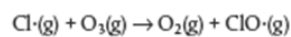
NO(g) has acted as a catalyst because it is regenerated during the reaction and the net change is the breakdown of ozone:



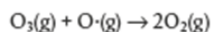
CFC's were widely used until they became linked with the destruction of ozone.



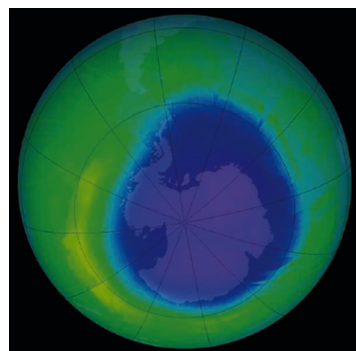
The weaker C-Cl bond breaks in preference to the C-F bond, and the chlorine radicals catalyse the decomposition of ozone.



Here Cl·(g) has acted as a catalyst and the net reaction is again:



The Montreal Protocol in 1987 banned the use of many ODC's (ozone depleting chemicals) and has been hailed as one of the most successful responses to an environmental issue.



Exercises

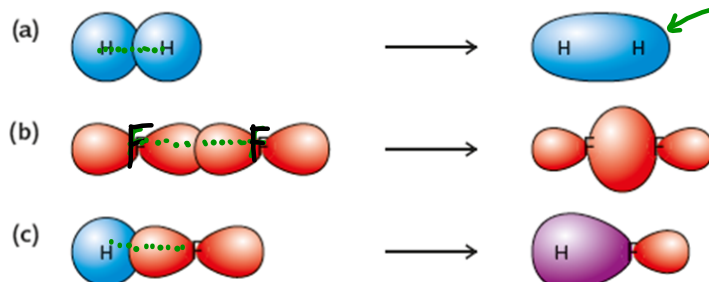
- 39 Use the concept of formal charge to explain why BF₃ is an exception to the octet rule.
- 40 Draw two different Lewis (electron dot) structures for SO₄²⁻, one of which obeys the octet rule for all its atoms, the other which has an octet for S expanded to 12 electrons. Use formal charges to determine which is the preferred structure.
- 41 Explain why ozone can be dissociated by light with a longer wavelength than that required to decompose oxygen.
- 42 Outline ways in which ozone levels are decreased by human activities, using equations to support your answer.

Atomic orbitals overlap to form two types of covalent bond: sigma and pi

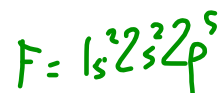
The sigma (σ) bond

(inter-nuclear axis)

When two atomic orbitals overlap along the bond axis – an imaginary line between the two nuclei – the bond is described as a **sigma bond**, denoted using the Greek letter σ . This type of bond forms by the overlap of s orbitals, p orbitals, and hybrid orbitals (to be described in the next section) in different combinations. It is always the bond that forms in a single covalent bond.



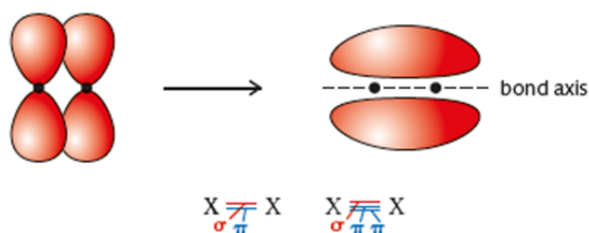
molecular orbital



In a sigma bond the electron density is concentrated between the nuclei of the bonded atoms.

The pi (π) bond

When two p orbitals overlap sideways, the electron density of the molecular orbital is concentrated in two regions, above and below the plane of the bond axis. This is known as a **pi bond**, denoted using the Greek letter π . This type of bond only forms by the overlap of p orbitals alongside the formation of a sigma bond. In other words, pi bonds only form within a double bond or a triple bond.



Why are pi bonds weaker than sigma bonds? (Think of the position of electrons)

The electrons in a sigma bond are predominantly between the nuclei so there are stronger forces of attraction holding them together.

Atomic orbitals which overlap	Type of bond	Example of bond and molecule
s and s	sigma	H–H in H_2
s and p	sigma	H–Cl in HCl
p and p end-on	sigma	Cl–Cl in Cl_2
hybrid orbitals and s	sigma	C–H in CH_4
hybrid orbitals with hybrid orbitals	sigma	C–C in CH_4 one of the C=C in C_2H_4 one of the C≡C in C_2H_2
p and p sideways	pi	one of the C=C in C_2H_4 two of the C≡C in C_2H_2

4. (Selecvidad style) The label on a bottle of hydrochloric acid (HCl) solution indicates that it has a percentage by mass of 20% and a density of 1.1 g/mL.

Use the following data to answer part a and b. Data: Atomic masses Cl = 35.5, H = 1

a

a. Calculate the volume of this acid required to prepare 500 mL of 0.1 mol dm⁻³ HCl.

(C3)

b. If you take 10 mL of this diluted acid (0.1 mol dm⁻³) and add 20 mL of the original concentrated acid what will be the resulting molarity of the solution?

$$\text{Molarity} = \frac{\text{no. moles}}{\text{L solution}} = \frac{0.001 \text{ mol} + 0.120 \text{ mol}}{0.01 \text{ L} + 0.02 \text{ L}} = 4.03 \text{ mol dm}^{-3}$$

$$* \text{ Moles} = C \times V = 0.1 \times 0.01 = 0.001 \text{ mol}$$

$$* \text{ Moles} = C \times V = 6.03 \times 0.02 = 0.120 \text{ mol}$$

$$V = \frac{\text{mol}}{C} \quad \begin{array}{l} \nearrow = 0.00603 \text{ mol/mL} \\ \searrow \rightarrow \frac{0.05 \text{ mol}}{0.00603 \text{ mol/mL}} = 8.29 \text{ mL} \end{array}$$

$$\boxed{1 \text{ g}} / \text{mL}$$

g \rightarrow moles

$$\text{moles} = \frac{\text{mass}}{M}$$

