**14.1 Further aspects of covalent bonding and structure HL**

**Learning objectives**

* Use the concept of formal charge to decide between alternative Lewis structures
* Understand that there are exceptions to the octet rule
* Use VSEPR to predict the shapes of molecules and ions with five or six electron domains
* Explain the formation of sigma and pi bonds in molecules
* Predict the number of sigma and pi bonds in molecules
* Use the concepts of resonance and delocalisation to explain the bonding in molecules and ions
* Explain the absorption of different frequencies of UV light by oxygen and ozone
* Describe the mechanism of CFC and NOx catalysed ozone depletion

**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.
* 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 = (Number of valence electrons)-½(Number of bonding electrons)-(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. 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.

**Formal charge and alternative Lewis structures**

It is possible to draw more than one Lewis structure for compounds such as SO2. The concept of formal charge is used to select the best Lewis structure when more than one is possible, that is, the one that provides the best representation of the structure of the actual molecule.

‘Formal charge’ is the charge that an atom in a molecule would have if we assume that the electrons in a covalent bond are equally shared between the atoms that are bonded. ( same electronegativity for all atoms).

Atoms in a molecule can gain a formal charge either if a coordinate covalent bond is formed or if the molecule has an overall charge (it is an ion).

If a coordinate covalent bond is formed, the donor atom has given away an electron, it now has a formal charge of 1+ and the receiver atom has a formal charge of 1−

**FC = (number of valence electrons in the uncombined atom) –** $\frac{1}{2}$ **(number of bonding electrons) − (number of non-bonding electrons)**

**In general, the preferred Lewis structure is the one in which the formal charges are closest to zero.**

Formal charges closest to zero will generally result in a more stable structure because the separation of charge in a structure requires energy.

**Example of SO2 two structures**

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It can be seen that structure B is the preferred one because there are no formal charges on the atoms.

**Formal charge closest to zero means that there will be the most even distribution of charge in the molecule or the ion. This is the most stable structure because separation of charge requires energy to keep them separated.**

***Question***

***Draw the two possible structures of sulfate (VI) ion and by use of formal charge determine the preferred structure.***

 **SO42-**

 



What about Phosphate ion PO43- ion?

**Exceptions to the octet rule**

Some molecules, such as BF3, BCl3 and BeCl2 (g), in which the central atom has fewer than 8 electrons in its outer shell are said to have an **incomplete octet**.

some molecules and ions, such as SO42-, PO43- and SO2, for which a structure could be drawn with the central atom having more than eight electrons in its outer shell, has **expanded its octet.**

For an atom to be able to expand its octet, it must be in period 3 or beyond.

***Question***

***Explain why PF5 can exist but NF5 cannot.***

**Shapes of molecules and ions with five or six electron domains around the central atom**

*The basic shapes for five and six electron domains*



The positions around the middle plane of a trigonal bipyramid are described as **equatorial** while the positions above and below the central triangle are described as **axial.**

**Question**

**Draw the Lewis structure and molecular shape of PF5 and SF6**

**In a trigonal bipyramid, the axial and equatorial positions are not equivalent. Lone pairs always go in an equatorial position. This applies only to trigonal bipyramidal structures.**

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**Question**

**Draw the Lewis structure and molecular shape of sulfur (IV) fluoride SF4 and describe the shape of the molecule.**

Bonding pair of electrons= 4, non-bonding pair of electrons = 1, electron domains=5

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 **Shape Seesaw arrow like**

**Draw and describe the shapes of the following molecules**

1. **ClF3 chlorine(III) fluoride**
2. **I3− triiodide ion 5 electron domains**
3. **XeF4 Xenon(IV) fluoride**
4. **BrF5 Bromine(V) fluoride**

The shapes of molecules and ions with more than four electron domains.

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**Sigma and pi bonds- Atomic orbitals overlap to form two types of covalent bond: sigma and pi**

A covalent bond is formed when two atomic orbitals, each containing one electron, overlap. When these orbitals overlap head-on, the bond formed is a normal single bond and is called a sigma (σ) bond.

**Atomic orbitals are found in atoms**, but **electrons occupy molecular orbitals in molecules**. Molecular orbitals, like atomic orbitals, **can hold a maximum of two electrons**.

Two s atomic orbitals combine to form a σ molecular orbital.

The shape of this molecular orbital can be predicted from the shapes of the two atomic orbitals.

**The sigma (σ) bond (Head-on overlap)**

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. It is always the bond that forms in a single covalent bond.

**Examples**

Formation of sigma bond by overlap of (a) s orbitals, e.g. H + H → H2, (b) p orbitals end-on, e.g. F + F → F2. and (c) s and p orbitals, e.g. H + F → HF. The symbol for the element denotes the position of the nucleus. In all cases, the electron density is greatest along the bond axis.



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

*Sigma bonds result from the axial (head-on) overlap of atomic orbitals. The electron distribution in a sigma bond lies mostly along the axis joining the two nuclei.*



**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. pi bonds only form within a double bond or a triple bond.

 **Example of bonding in ethene C2H4 double bond**

 

When carbon atoms and hydrogen atoms come together to form ethene, sigma bonds are formed. Only three orbitals are used in bonding to the other carbon atom and to two hydrogen atoms, so there is a p orbital (containing 1 electron) remaining on each C atom. These p orbitals can overlap side-on to form a pi (π) bond.

A π bond is formed by the sideways overlap of parallel p orbitals. The electron density in the π bond lies above and below the internuclear axis.

A triple bond consists of one σ bond and two π bonds. Ethyne

 

To summarise:

* a single bond consists of a σ bond
* a double bond consists of a σ bond and a π bond
* a triple bond consists of a σ bond and two π bonds.

 **Resonance and delocalization**

The Lewis structure for O3 with expected bond lengths.





1. *The Lewis structure for O3 with expected bond lengths*. b. *Resonance structures for O3*

It would be expected from this structure that there would be one short (O=O) and one long (O–O) bond. However, both bond lengths are equal at 0.128 nm. Neither of these structures in (b) alone can explain the equal O–O bond lengths, and so the idea of **a resonance hybrid is used**- a form that is neither one structure nor the other, but somewhere in between.

 

Two equivalent representations of the delocalisation in ozone. The dashed lines represent the delocalisation of electrons.

A more satisfying explanation of the equal bond lengths in O3 comes from the idea of **delocalisation of electrons.** Delocalisation is the sharing of a pair of electrons between three or more atoms. The delocalised system can be shown using dashed lines between atoms.

**Bond order**

A single bond is said to have a bond order of 1, a double bond has bond order 2 and a triple bond has bond order 3.

Because the π bond in ozone is shared between two O–O bonds rather than just one, we consider that each bond has a half share of it, and we talk about ozone having a bond order of 1.5.

Other examples of resonance structures.

**Question**

1. **NO2− is isoelectronic with O3 and the bonding can be described in the same way. Draw the Lewis and resonance structure for NO2−.**
2. **Draw and describe the resonance structure for the carbonate ion (CO32-) and benzene (C6H6).**

 **Absorption of ultraviolet light in the atmosphere**

Ozone (O3) and oxygen (O2) are important in protecting the surface of the Earth from the damaging effects of ultraviolet radiation. The ‘ozone layer’ is a region in the stratosphere where there is a higher concentration of ozone. Even in the ozone layer, the concentration of ozone is very low.

**Ultraviolet (UV) light from the Sun reaching the Earth can be divided into three components:**

* UV-C λ < 280 nm (highest energy)
* UV-B λ = 280–320 nm
* UV-A λ = 320–400 nm

The highest energy UV-C radiation (shorter than 242 nm) is absorbed by O2 molecules in the atmosphere, which causes them to undergo dissociation into oxygen free radicals:

 O2 → 2O•

The bond between the atoms in an O2 molecule is a double bond (bond order 2), but O3 has a delocalised structure where the bond order is 1.5. This means that the O-O bond in O3 is weaker than the O=O in O2 and so lower energy (longer wavelength) radiation (up to 330 nm) is absorbed by O3 molecules to break the bond:

 O3 → O• + O2

So, ozone molecules are particularly effective at absorbing lower energy UV-B radiation (and some UV-C). In the process the molecule is split apart into an oxygen molecule and an oxygen atom.

All the UV-C and most of the UV-B reaching the Earth from the Sun is absorbed by **oxygen (O2) in the upper parts** of the atmosphere and by ozone (O3) **in the stratosphere** before it reaches the Earth’s surface and only the less harmful UV- A reaches the earth.

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*Absorption of UV radiation in the atmosphere.*

**Catalysis of ozone depletion by CFCs and NOx**

These compounds produce highly reactive free radicals that catalyse the decomposition of ozone to oxygen.

Nitrogen monoxide, NO, is produced in vehicle engines by direct combination of nitrogen and oxygen from the air at high temperatures. It is a free radical as it has an odd number of electrons. Nitrogen dioxide, NO2, forms from the oxidation of nitrogen oxide and is also **a free radical (an atom/ unpaired electron on an atom).**

**Equations:**

NO· (g) + O3 (g) → NO2· (g) + O2 (g) (Depletion)

NO2· (g) + O· (g) → NO· (g) + O2 (g) ( regenerated)

NO· (g) has acted as a catalyst because it is regenerated during the reaction and the net change is the breakdown of ozone: O3 (g) + O· (g) → 2O2 (g)

Chlorofluorocarbons were widely used in aerosols, refrigerants, solvents, and plastics due to their low reactivity and low toxicity in the troposphere. But when they get into the stratosphere, the higher energy UV radiation breaks them down, releasing free chlorine atoms, which are also reactive free radicals.

Freon a CFC, undergoes photochemical decomposition as follows:

 CCl2F2 (g) → CClF2**·** (g) + Cl**·** (g)

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

 Cl·(g) + O3(g) → O2(g) + ClO·(g)

 ClO·(g) + O·(g) → O2(g) + Cl·(g)

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

 O3(g) + O·(g) → 2O2(g)

These reactions, and others like them, have upset the balance of the ozone cycle. The increased UV radiation reaching the Earth has been most pronounced in the Polar Regions, and has been a source of global concern since 1970S.