

DP IB Chemistry: HL



Your notes

14.2 Further Aspects of Bonding

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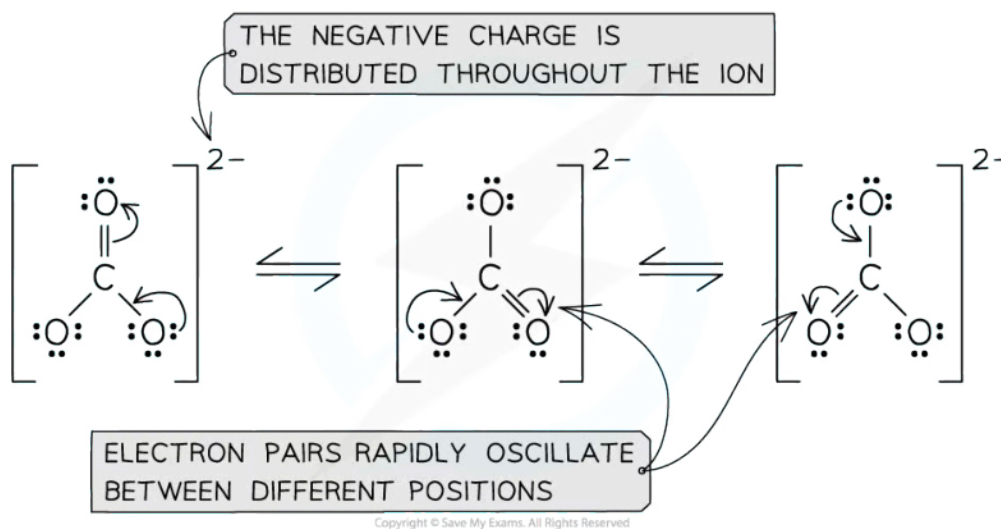


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14.2.1 Delocalisation & Resonance

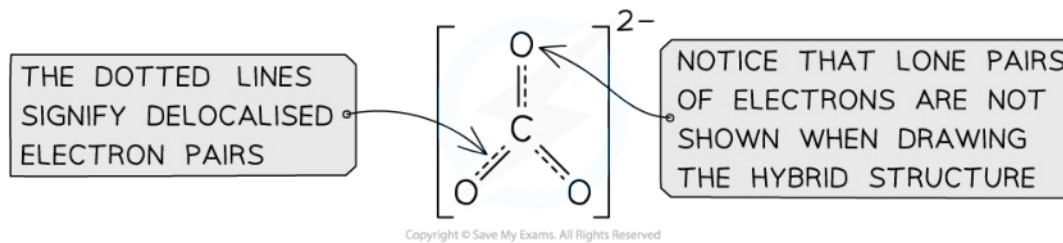
Delocalisation & Resonance

- The delocalisation of electrons can explain the structures of some species that don't seem to fit with a Lewis structure
- Delocalised electrons are electrons in a molecule, ion or solid metal that are not associated with a single atom or one covalent bond
- The Lewis diagram for the carbonate ion gives a molecule with a double and two single bonds
- There are three possible Lewis structures



The three resonance structures for the carbonate ion

- These structures are called **resonance structures**
- However, studies of the electron density and bond length in the carbonate ion indicate all the bonds are equal in length and the electron density is spread evenly between the three oxygen atoms
 - The bond length is intermediate between a single and a double bond
 - The actual structure is something in between the resonance structures and is known as a resonance hybrid



Resonance hybrid for the carbonate ion

- Dotted lines are used to show the position of the delocalised electrons
- The criteria for forming resonance hybrids structures is that molecules must have a double bond (π bond) that is capable of migrating from one part of a molecule to another
- This usually arises when there are adjacent atoms with equal electronegativity and lone pairs of electrons that can re-arrange themselves and allow the double bonds to be in different positions

Conjugation & Bond Order

- Structures which have alternative single and double bonds are known as **conjugated systems**
- Electrons migrate between p-orbitals via adjacent sigma bonds
- The result is a sort of fractional bond, neither a single nor a double, so to accommodate this situation chemists use the concept of **bond order**:

$$\text{bond order} = \frac{\text{total number of bonding pairs}}{\text{total number of positions}}$$

- For example, in the case of the carbonate ion:

$$\text{bond order in CO}_3^{2-} = \frac{\text{total number of CO}_3^{2-} \text{ bonding pairs}}{\text{total number of positions}} = \frac{4}{3} = \mathbf{1.33}$$

- Evidence for bond orders comes from measurements of bond lengths
 - A single C-O bond is 143 pm and a double C=O is 122 pm
 - The C-O bonds in the carbonate ion are all identical and 129 pm in length which is part way between a single and double
- Other examples that you should know about are benzene, ozone and the carboxylate anion

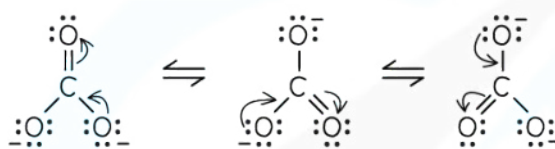
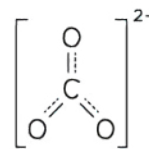



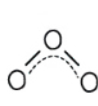
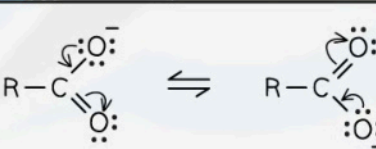
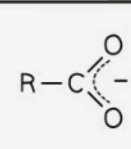
Resonance hybrids table



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Species	Lewis resonance structures	Resonance hybrid
Carbonate ion, CO_3^{2-}		
Benzene, C_6H_6		
Ozone, O_3		
Carboxylate ion, RCOO^-		

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14.2.2 Ozone Revisited

Ozone Revisited

- We have seen previously that ozone is a molecule with two resonance structures leading to a resonance hybrid



The two Lewis resonance structures for ozone

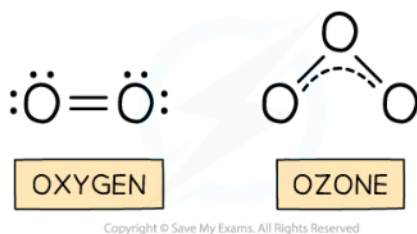
- The central oxygen atom has three electron **domains** and a lone pair, so the domain geometry is trigonal planar and the molecular geometry is bent linear
- The presence of the lone pair repels the bonding pairs more strongly so the bond angle is reduced to 117°



The molecular structure of ozone

- The bond order for each bond in ozone is

$$\text{bond order in O}_3 = \frac{\text{total number of O}_3 \text{ bonding pairs}}{\text{total number of positions}} = \frac{3}{2} = 1.5$$
- This gives a polar molecule with bonds that are weaker than the double bond in oxygen molecules



The structure of oxygen and ozone

- You would expect O-O bonds to be non-polar as the atoms have the same electronegativity; this is correct, but overall the molecule is polar due to the uneven distribution of electron cloud charge
- The formal charge on the Lewis structures show that the electrons are unevenly distributed

FC = (number of valence electrons) - $\frac{1}{2}$ (number of bonding electrons) - (number of non-bonding electrons)

$$\text{FC (oxygen A)} = (6) - \frac{1}{2}(2) - (6) = -1$$

$$\text{FC (oxygen B)} = (6) - \frac{1}{2}(6) - (2) = +1$$

$$\text{FC (oxygen C)} = (6) - \frac{1}{2}(4) - (4) = 0$$



Formal charges on the oxygens in ozone



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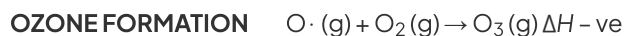
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Catalytic Depletion

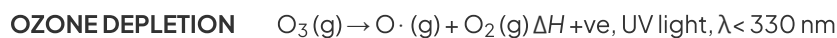
- The bonding and structure of ozone is key to understanding how the catalytic depletion of ozone occurs in the stratosphere
- High energy UV radiation in the stratosphere breaks the oxygen-oxygen double bond creating oxygen atoms



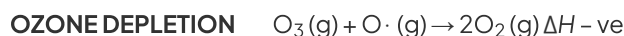
- These oxygen atoms have unpaired electrons - they are known as **free radicals**
- The free radicals are highly reactive and quickly attack oxygen molecules forming ozone in an exothermic reaction, which raises the temperature of the stratosphere



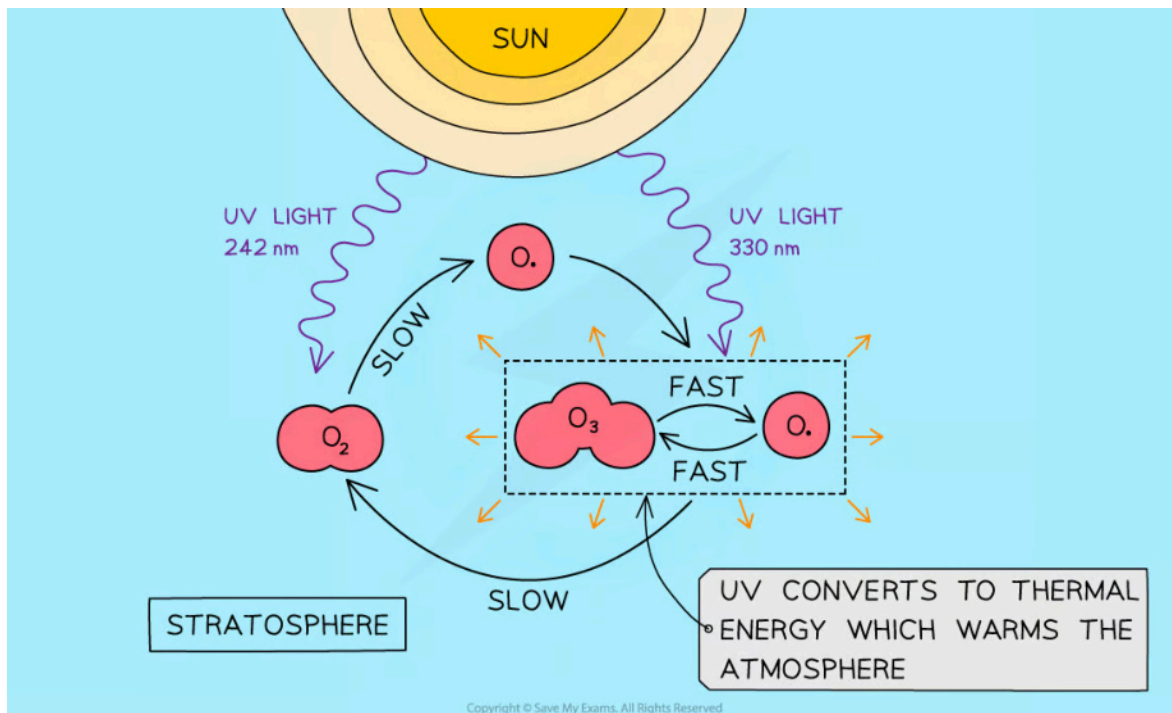
- Ozone requires less energy to break than oxygen
 - It produces an oxygen molecule and an oxygen free radical:



- The radical reacts with another ozone molecule making two molecules of oxygen in an exothermic reaction



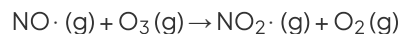
- The temperature in the stratosphere is maintained by the balance of ozone formation and ozone depletion in a process known as the Chapman Cycle
- It is not a closed system as matter and energy flow in and out, but it is what is called a steady state



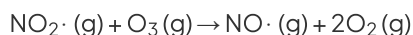
The Chapman cycle

Catalytic Depletion

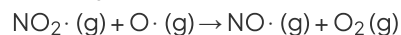
- The two main man made culprits that accelerate the depletion of ozone are **nitrogen oxides** and **CFCs**
- Nitrogen monoxide, NO, is produced from the high temperatures inside internal combustion engines
- If you count the valence electrons in nitrogen monoxide ($5 + 6 = 11$), the odd number tells you it is a **free radical** as it has an unpaired electron
- The nitrogen monoxide reacts with ozone forming oxygen and a nitrogen dioxide radical



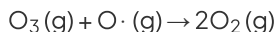
- The nitrogen dioxide produced is also a free radical (it has $5 + 6 + 6 = 17$ electrons) and you can show the second step where it reacts with another molecule of ozone, producing oxygen and regenerating the NO \cdot radical:



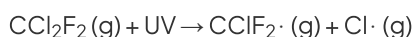
- An alternative to the second step shows the NO $_2\cdot$ reacting with an oxygen radical to produce the same products but in a different stoichiometry



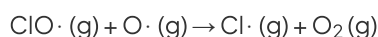
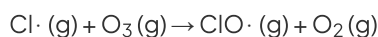
- The nitrogen monoxide is regenerated so it has a catalytic role in the process
- Combining the two equations and cancelling out the NO \cdot and NO $_2\cdot$ and you arrive at the overall depletion of ozone



- A similar process happens with CFCs
- The C-Cl bond in the CFCs is weaker than the C-F bond and breaks more easily in the presence of UV light creating chlorine radicals



- The chlorine radicals attack ozone and are regenerated at the end of the cycle



- Once again a molecule of ozone has been destroyed by a catalytic free radical
- The net effect of these reactions is that these pollutants have created an imbalance in the natural ozone cycle leading to an overall depletion in stratospheric ozone
- CFCs are greatly damaging to stratospheric ozone and have been largely replaced by safer alternatives following the 1985 Montreal Protocol
- The depletion of ozone has allowed greater amounts of harmful UV light to reach the surface of the Earth
- UV light has been linked to greater incidence of skin cancer and cataracts as well as the destruction of phytoplankton and reduced plant growth

Examiner Tip

There are different conventions about showing radicals. Sometimes the dot is shown above the symbol of the element, sometimes to the left of the species and sometimes to the right. In this course, radical dots are often ignored in exam mark schemes about ozone depletion, so you wouldn't be penalised if you omitted them or put them in different places. However, where the symbol for a radical is specified in the syllabus is in the halogenation of alkanes so you should include them there. The syllabus just states that radicals must be represented by a single dot.



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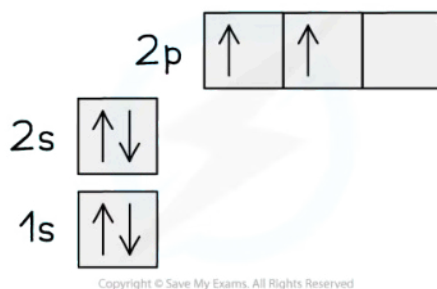
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14.2.3 Hybrid Orbitals

Hybrid Orbitals

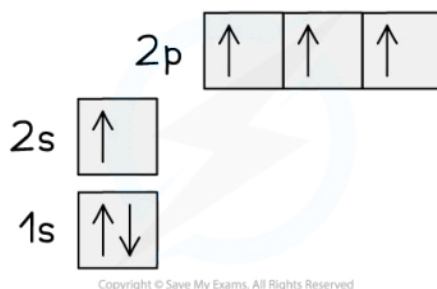
Hybridisation

- The ground state of the electrons in a carbon atom is $1s^2 2s^2 2p^2$
- This can be represented using a spin diagram as shown:



Orbital spin diagram for carbon in the ground state

- This electronic structure would imply that carbon forms two covalent bonds using the unpaired 2p electrons
- Since the 2s electrons are paired there would be no reason for them to be involved in bonding
- However studies of carbon compounds show that carbon typically forms four covalent bonds that are all equal in energy
- This puzzle has been explained using the theory of **bond hybridisation**
- A half full p-subshell has a slightly lower energy than a partially filled one. The difference in energy between the 2s and 2p subshells is small, so an electron can fairly easily be promoted from the 2s to the 2p giving the new arrangement:



Orbital spin diagram for carbon in the excited state

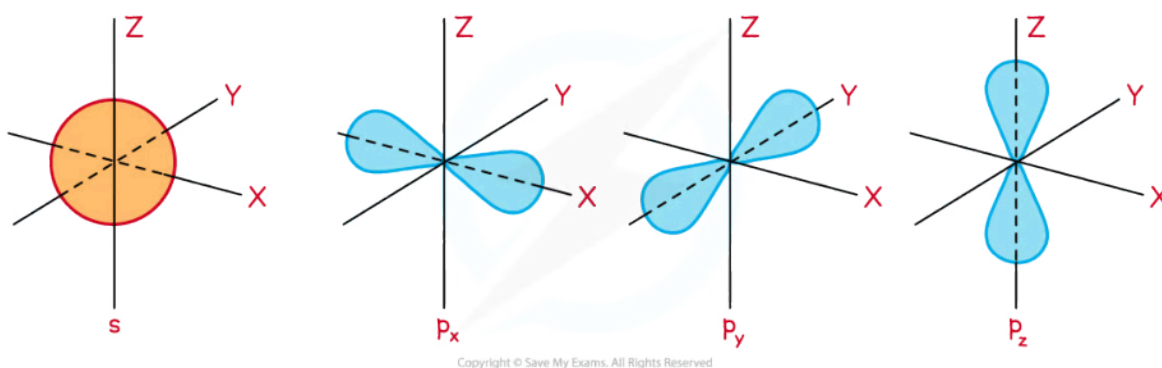
- The 2s and 2p subshells blend together and form four new hybrid orbitals (called sp^3 orbitals, after the merger of an s and 3 p orbitals)
- This would give four unpaired electrons of equal energy, capable of forming four covalent bonds.



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Orbital spin diagram for carbon showing sp^3 hybrid orbitals

- The theory of Quantum mechanics shows that the shape of a 1s orbital is spherical and a p orbital is dumbbell or figure-of-eight shaped
- There are three p orbitals all at right angles to each other, known as p_x , p_y and p_z

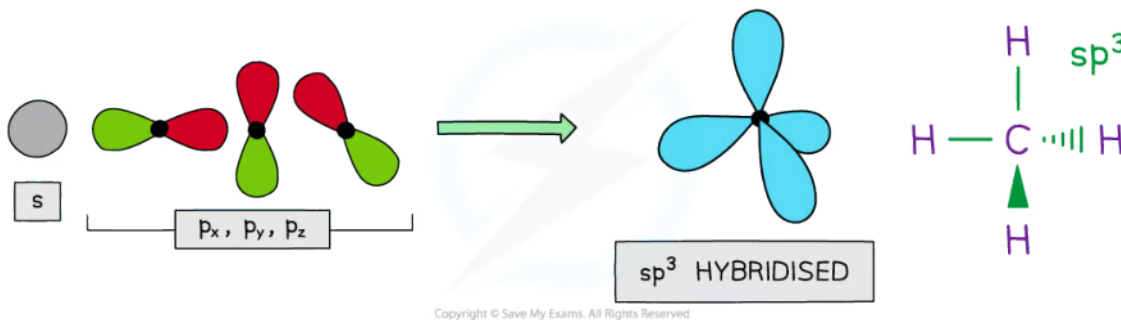


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The shape of s and p orbitals

sp^3 hybridisation

- Four hybrid orbitals are produced when the 2s and three 2p orbitals blend together
- These hybrids have $\frac{1}{4}$ s character and $\frac{3}{4}$ p character so they have a club shape reminiscent of an enlarged p orbital
- The four sp^3 hybrid orbitals space themselves out at 109.5° forming a tetrahedron
- This is the resolution of the structure seen when carbon forms single bonds, such as would be found in methane



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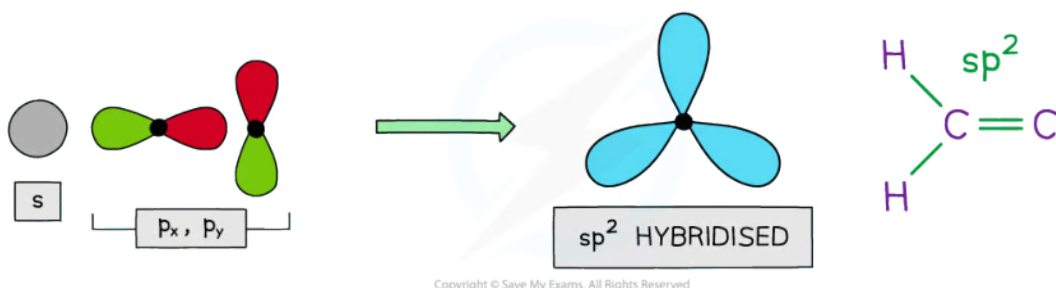
$4 \times sp^3$ hybrid orbitals

- The sp^3 orbitals merge with the s orbitals in hydrogen forming four equal sigma bonds

- It is not just bonding pairs of electrons that are accommodated in hybrid orbitals - lone pairs can also be present
- The domain geometry of ammonia is tetrahedral due to sp^3 hybrid orbitals where three bonding pairs and one lone pair are found

sp^2 hybridisation

- Three hybrid orbitals are produced when the 2s and two 2p orbitals blend together
- These hybrids have $\frac{1}{3}$ s character and $\frac{2}{3}$ p character
- The three sp^2 hybrid orbitals space themselves out at 120° forming a trigonal planar geometry
- This is the resolution of the structure seen when carbon forms two single bonds and a double bond with itself in alkenes

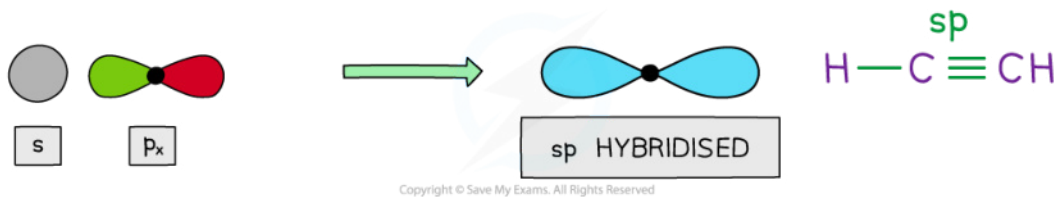


3 x sp^2 hybrid orbitals

- In the case of carbon, the sp^2 orbitals merge with the s orbitals in hydrogen and the sp^2 of an adjacent carbon, forming three equal sigma bonds
- The double bond is created by the side-to-side overlap of the unhybridised p-orbitals
- This bonding arrangement can also occur between a double bonded carbon and oxygen so is typically seen in the carbonyl group

sp hybridisation

- Two hybrid orbitals are produced when the 2s and one 2p orbital blend together
- These hybrids have $\frac{1}{2}$ s character and $\frac{1}{2}$ p character
- The two sp hybrid orbitals space themselves out at 180° forming linear geometry
- This is the resolution of the structure seen when carbon forms one single bonds and a triple bond with itself in alkynes



2 x sp hybrid orbitals

- In the case of carbon, the sp orbital merges with the s orbital in hydrogen and the sp of an adjacent carbon, forming two equal sigma bonds
- The triple bond is created by the side-to-side overlap of two pairs of the unhybridised p-orbitals, set at right angles to each other



Your notes



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Identifying Hybridisation

- You can predict the hybridisation present in molecules based on Lewis structures, electron domains, molecular geometries by applying the principles outlines in the previous section

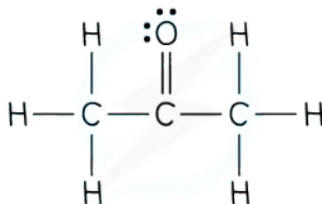
Worked example

Identify the domain geometry, molecular geometry and hybridisation in the underlined atom in a)

CH₃COCH₃ b) PH₃ c) NO₂

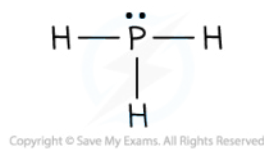
Answer

a) CH₃COCH₃



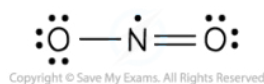
The Lewis structure shows that there are three electron domains around the central carbon, so the domain geometry is trigonal planar. There are two single bonds and one double bond, so the molecular geometry is also trigonal planar, and the carbon must have sp² hybridisation.

b) PH₃



The Lewis structure shows that there are four electron domains around the phosphorus, so the domain geometry is tetrahedral. There are three single single bonds and a lone pair, so the molecular geometry is trigonal pyramid. Four domains means the phosphorus must have sp³ hybridisation.

c) NO₂



The Lewis structure shows that there are three electron domains around the nitrogen, so the domain geometry is trigonal planar. There is one single bonds and one double bond, so the molecular geometry is bent linear, and the nitrogen must have sp^2 hybridisation



Your notes

Examiner Tip

You may be wondering why the unpaired electron lies on the nitrogen rather than on a oxygen in the Lewis structure for NO_2 . This is easily demonstrated by considering the formal charges and electronegativity. The preferred Lewis structure has negative charges located on the most electronegative atoms.

$$\text{FC (N)} = V - \frac{1}{2}B - N = (5) - \frac{1}{2}(6) - 1 = +1$$

$$\text{FC (single bonded O)} = (6) - \frac{1}{2}(2) - 6 = -1$$

$$\text{FC (double bonded O)} = (6) - \frac{1}{2}(4) - 4 = 0$$

Oxygen and nitrogen have electronegativity of 3.4 and 3.0, respectively (Table 8 in the Data booklet), so placing the electron on the nitrogen means it has a positive FC instead of the oxygen.