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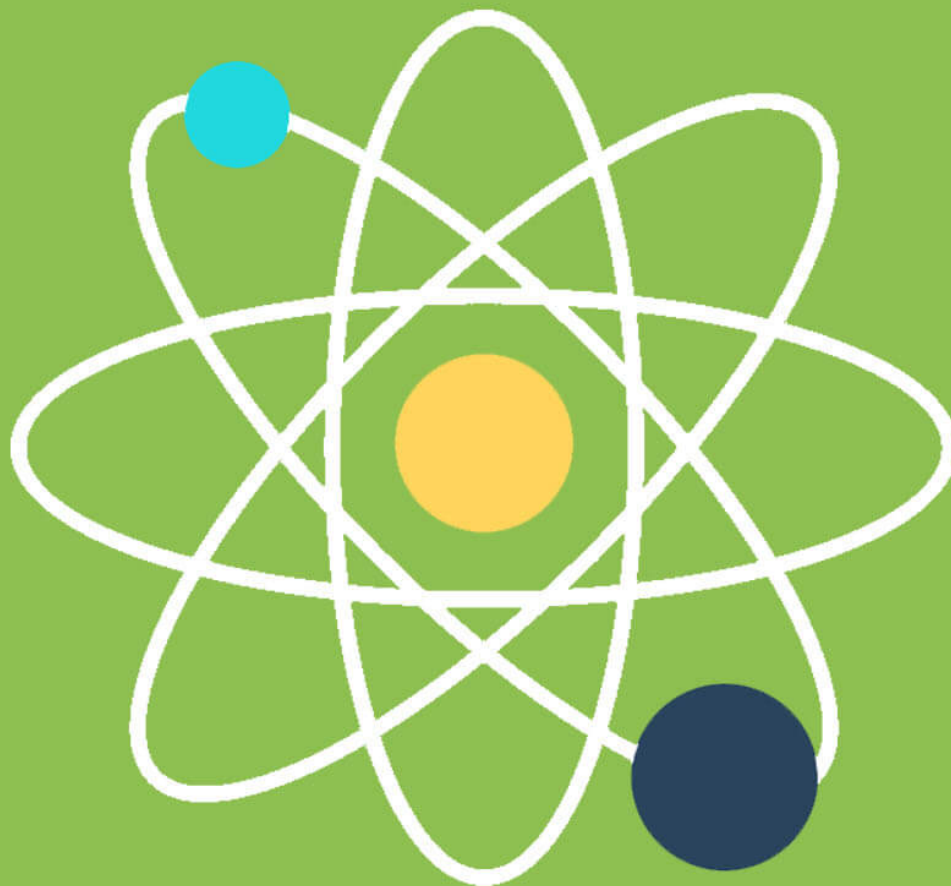
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4.2 Resonance, Shapes & Giant Structures



IB Chemistry - Revision Notes

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4.2.1 Resonance Structures

Resonance Structures

- The delocalization of electrons can explain the structures of some species that don't seem to fit with a Lewis structure
- Delocalized 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 nitrate (V) ion gives a molecule with a double and two single bonds
- There are three possible Lewis Structures
- These structures are called resonance structures
- However, studies of the electron density and bond length in the nitrate (V) 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 structures of the nitrate (V) ion

- To determine the Lewis structure of the nitrate (V) ion first count the number of valence electrons and then add one electron for the negative charge on the ion

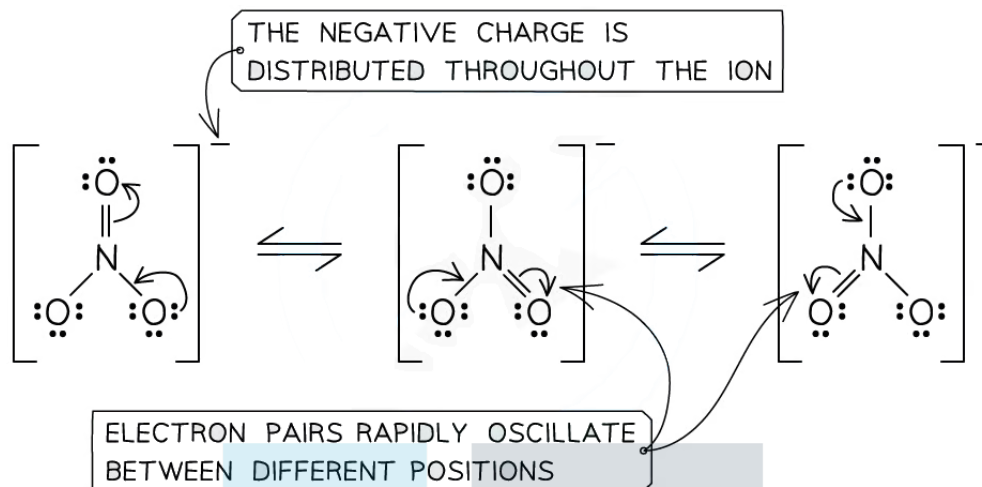
$$\text{Number of valence electrons} = \text{N} + 3\text{O} + 1$$

$$= 5 + (3 \times 6) + 1 = \mathbf{24 \text{ electrons}}$$

- Three structures are possible, consisting of a double bond and two singles:

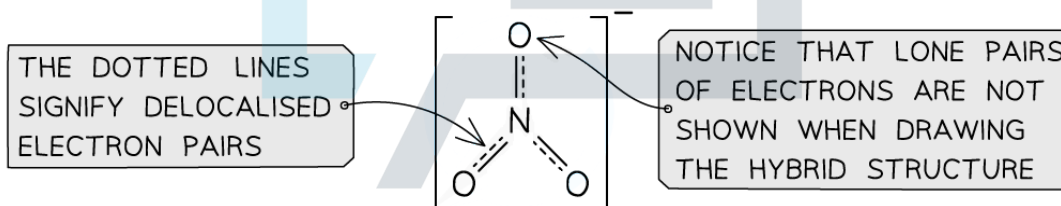
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Resonance structures in the nitrate ion

- Dotted lines are used to show the position of the delocalised electrons



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Resonance hybrid nitrate (V) ion

Copy The criteria for forming resonance hybrid structures is that molecules must have a double bond (pi 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
- Other examples that you should know about are the carbonate ion, benzene, ozone and the carboxylate anion

Resonance Hybrids Table

- Below are some other resonance structures and hybrids that you should know:



| 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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4.2.2 Shapes of Molecules

Shapes of Molecules

- When an atom forms a covalent bond with another atom, the electrons in the different bonds and the non-bonding electrons in the outer shell all behave as negatively charged clouds and repel each other
- In order to minimise this repulsion, all the outer shell electrons spread out as far apart in space as possible
- Molecular shapes and the angles between bonds can be predicted by the **valence shell electron pair repulsion theory** known by the abbreviation **VSEPR** theory
- VSEPR** theory consists of three basic rules:
 - All electron pairs and all lone pairs arrange themselves as far apart in space as is possible.
 - Lone pairs repel more strongly than bonding pairs.
 - Multiple bonds behave like single bonds
- These three rules can be used to predict the shape of any covalent molecule or ion, and the angles between the bonds
- The regions of negative cloud charge are known as **domains** and can have one, two or three pairs electrons

Two electron domains

- If there are two electron domains on the central atom, the angle between the bonds is 180°
- Molecules which adopt this shape are said to be **LINEAR**
- Examples of linear molecules include BeCl_2 , CO_2 , and $\text{HC}\equiv\text{CH}$

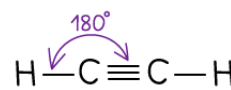
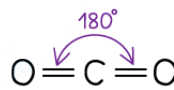
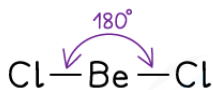
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LEWIS
STRUCTURES



MOLECULAR
SHAPES



Two electron domain molecules

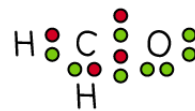
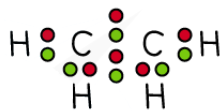
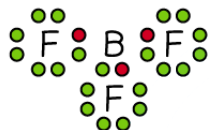
Three electron domains

- If there are three electron domains on the central atom, the angle between the bonds is 120°

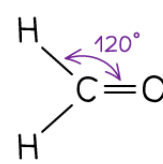
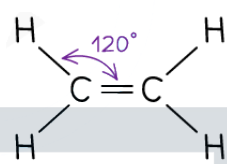
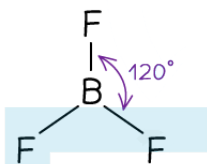


- Molecules which adopt this shape are said to be **TRIANGULAR PLANAR** or **TRIGONAL PLANAR**
- Examples of three electron domains which are all bonding pairs include BF_3 and CH_2CH_2 and CH_2O

LEWIS STRUCTURES



MOLECULAR SHAPES

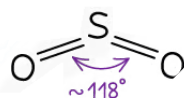


Molecules with three electron domains

- If one of these electron domains is a lone pair, the bond angle is slightly less than 120° due to the stronger repulsion from lone pairs, forcing the bonding pairs closer together. E.g. SO_2
- The bond angle is approximately $\sim 118^\circ$



LEWIS STRUCTURE



MOLECULAR SHAPE

The shape of sulfur dioxide

- Sulfur dioxide is an example of a molecule that '**expands the octet**' as you will see there are 10 electrons around the sulfur atom which is possible for 3rd period elements and above
- This shape is no longer called triangular planar as the shape names are only based on the atoms present, this molecule is **BENT LINEAR**

Four electron domains

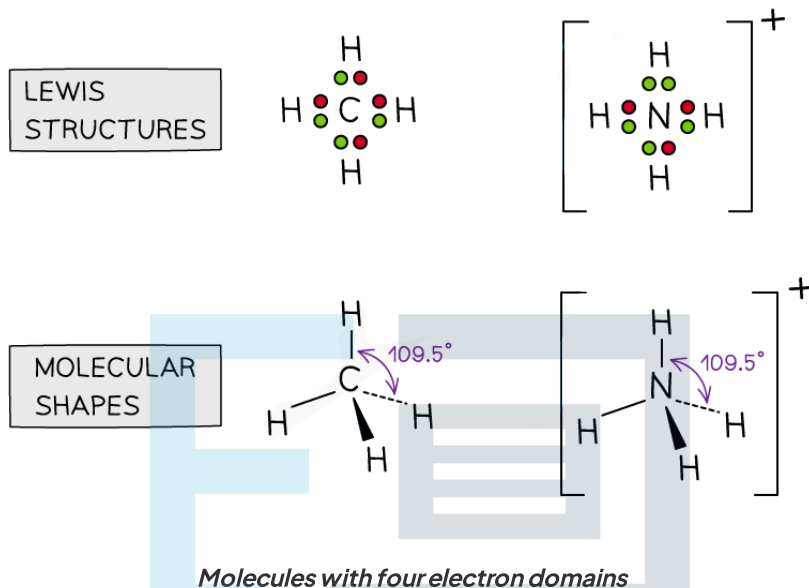
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- If there are four electron domains on the central atom, the angle between the bonds is approx 109° . E.g. CH_4 , NH_4^+
- Molecules which adopt this shape are said to be **TETRAHEDRAL**

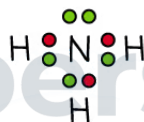


- If one of the electron domains is a lone pair, the bond angle is slightly less than 109° , due to the extra lone pair repulsion which pushes the bonds closer together (approx 107°). E.g. NH_3 ,

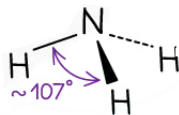
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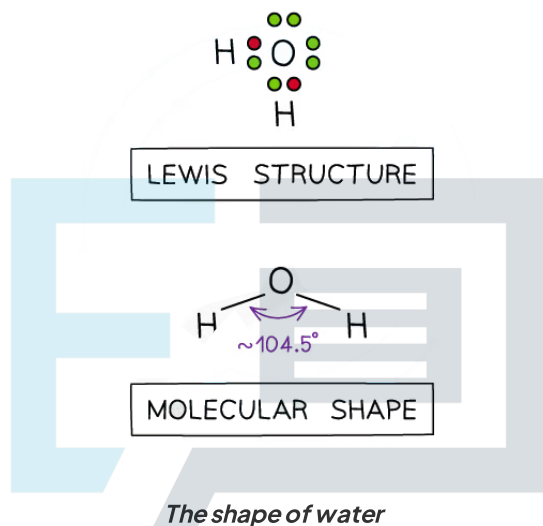
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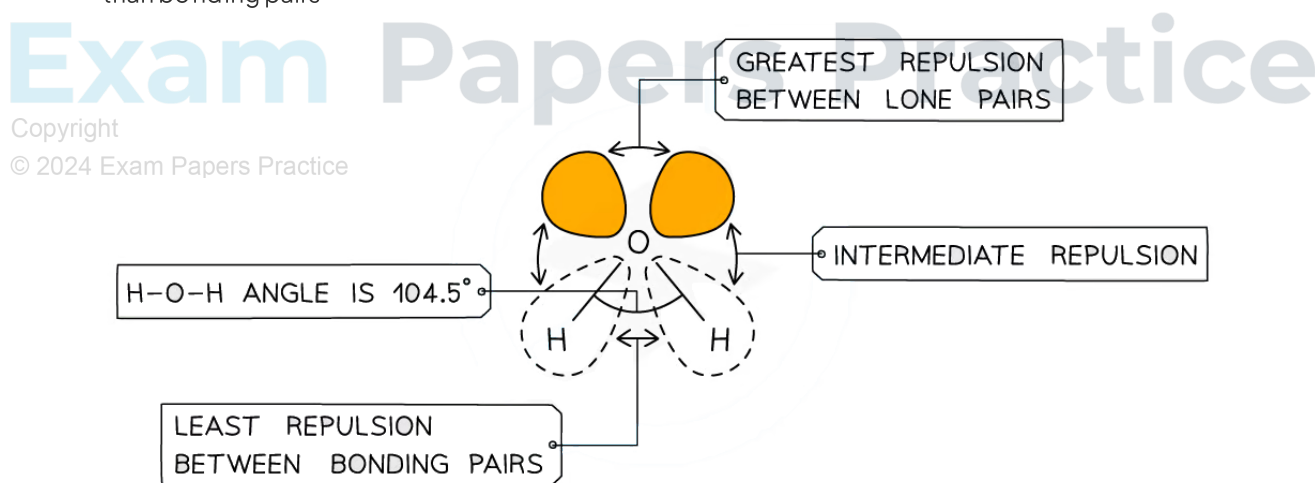
MOLECULAR SHAPE

The shape of ammonia

- Molecules which adopt this shape are said to be **TRIANGULAR PYRAMIDAL** or **TRIGONAL PYRAMIDAL**
- If two of the electron domains are lone pairs, the bond angle is also slightly less than 109° , due to the extra lone pair repulsion (approx 104°). E.g. H_2O
- Molecules which adopt this shape are said to be **BENT** or **ANGULAR** or **BENT LINEAR** or **V-shaped** (when viewed upside down)



- Lone pairs are pulled more closely to the central atoms so they exert a greater repulsive force than bonding pairs



Different types of electron pairs have different repulsive forces

Summary table of electron domains and molecular shapes

- These are the domains and molecular geometries you need to know for Standard Level:

Exam Tip

Be careful to distinguish between molecular shape and electron domain shape as it can be easy to confuse the two. Sometimes they are the same as is the case of methane, but other times they can be different like ammonia which has a tetrahedral domain shape, but triangular pyramid molecular shape. Always draw the Lewis structure before you attempt to deduce the shape and bond angle as you could easily miss some lone pairs



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4.2.3 Predicting Molecular Shapes

Predicting Shapes & Bond Angles

- Before you predict the shape of any molecule work out the Lewis structure to determine the number of bonding and lone pairs
- Apply the VSEPR rules and you should be successful in deducing the correct shape and bond angle

Worked example

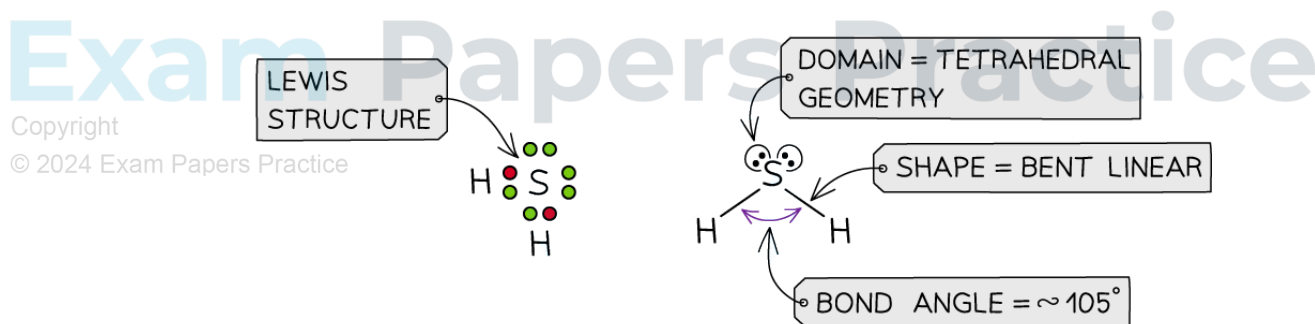
Predict the domain geometry, shape and bond angle in the following molecules or ions:

1. H_2S
2. NH_2Cl
3. NO_2^+
4. ClF_2^+

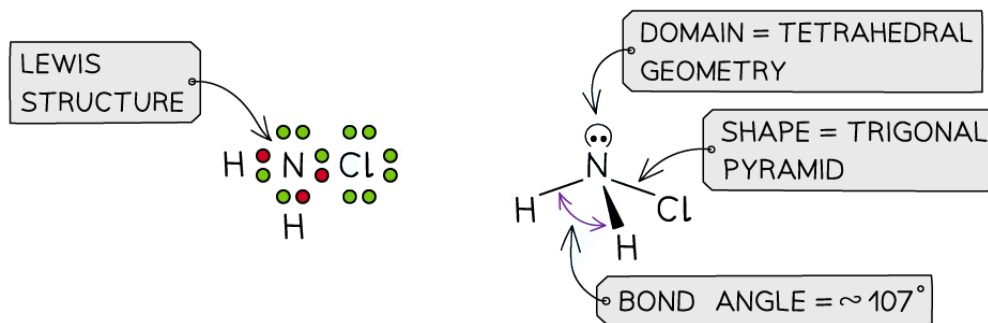
Answers:

Answer 1: The total number of valence electrons in H_2S is $= 1 + 1 + 6 = 8$, so there are four pairs of electrons around S

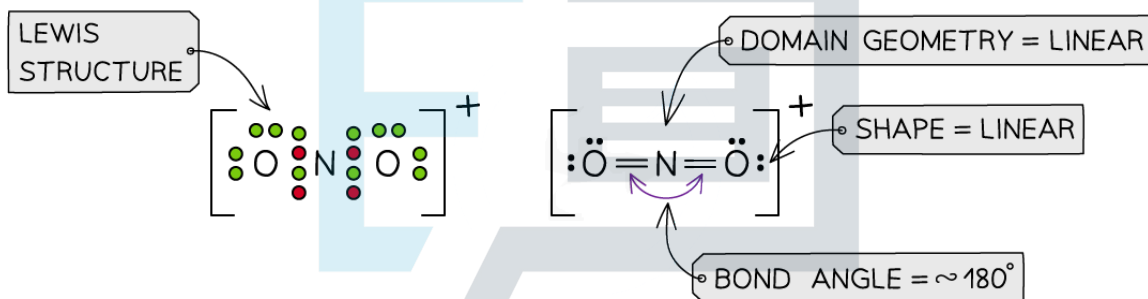
Hydrogen only forms one bond, so there are two bonding pairs and two lone pairs:



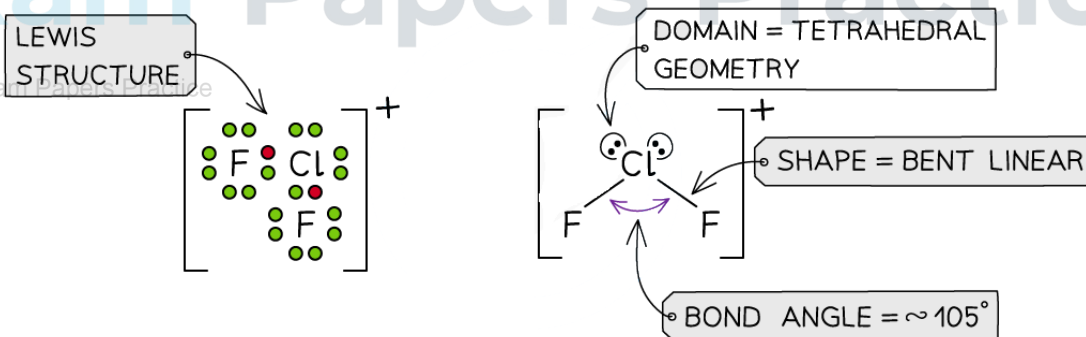
Answer 2: The total number of valence electrons in NH_2Cl is $= 5 + 1 + 1 + 7 = 14$



Answer 3: The total number of valence electrons in NO_2^+ = $5 + 6 + 6 - 1 = 16$ (subtracting one for the positive charge)



Answer 4: The total number of valence electrons in ClF_2^+ = $7 + 7 + 7 - 1 = 20$ (subtracting one for the positive charge)



Exam Tip

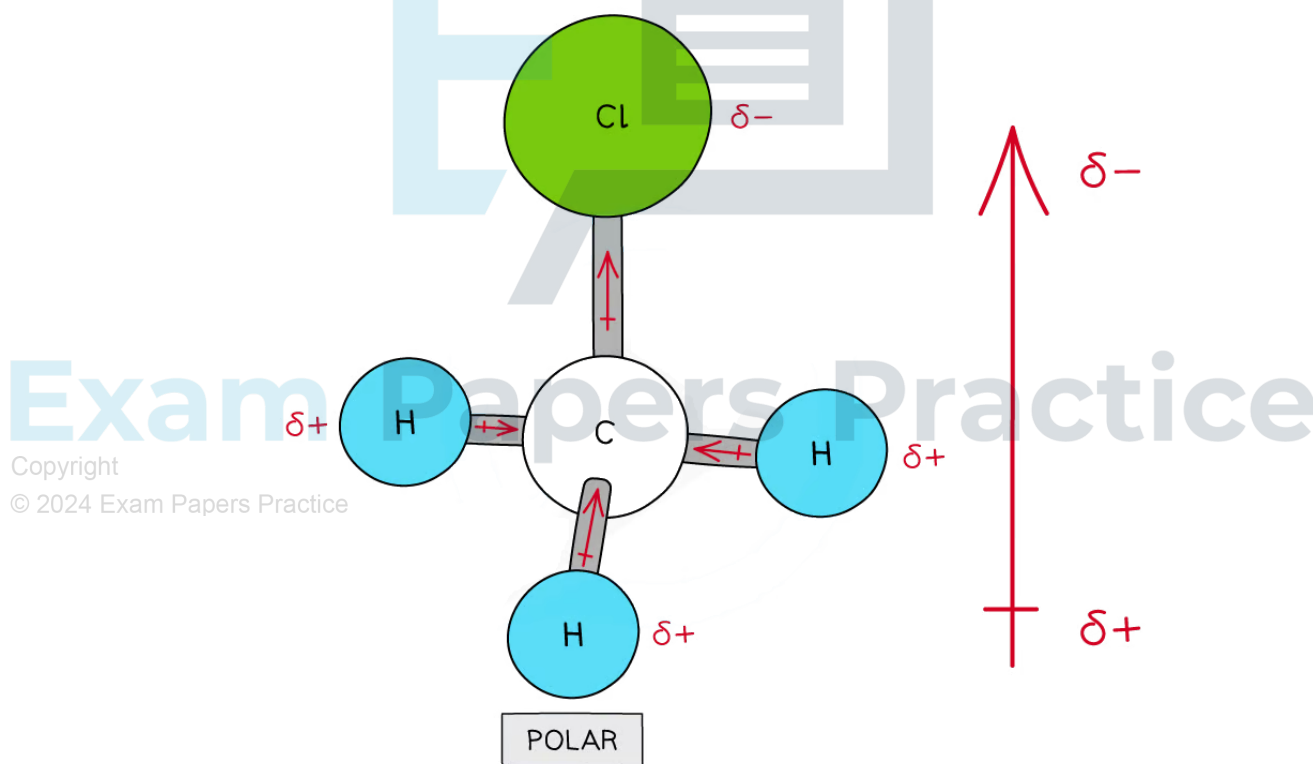
For Standard Level Chemistry you are only required to know the shape of molecules up to four electron domains.

4.2.4 Molecular Polarity

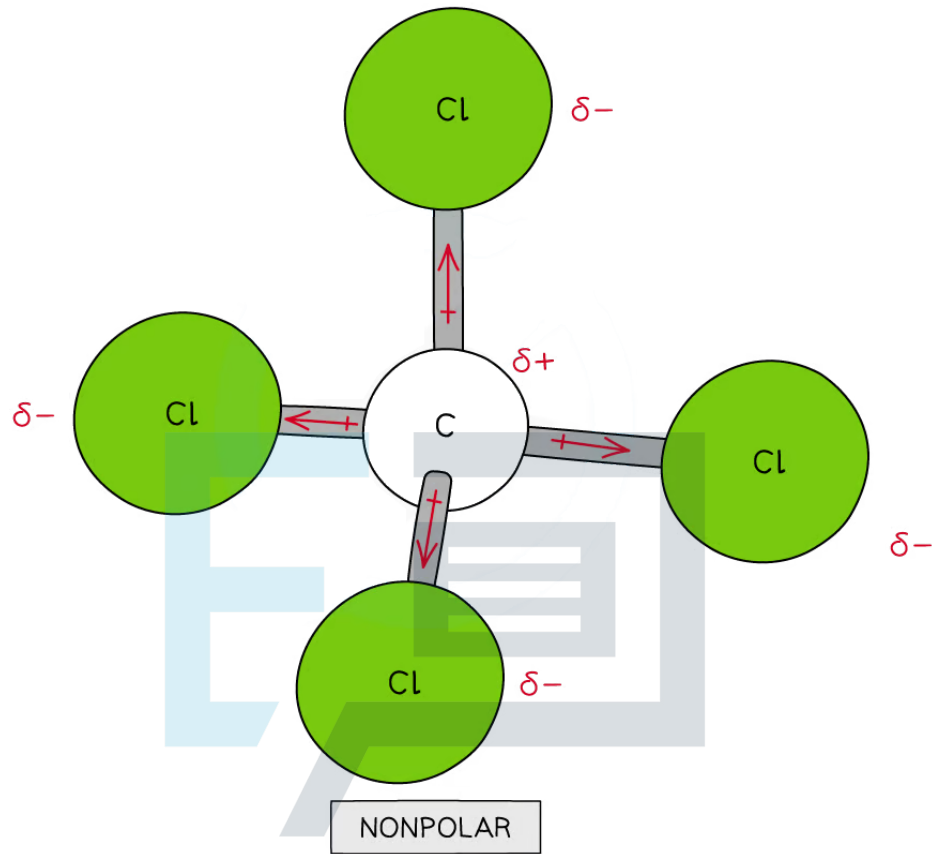
Molecular Polarity

Assigning polarity to molecules

- There is a difference between **bond polarity** and **molecular polarity**
- To determine whether a molecule is polar, the following things have to be taken into consideration:
 - The polarity of each bond
 - How the bonds are arranged in the molecule
- Some molecules have **polar bonds** but are overall not **polar** because the polar bonds in the molecule are arranged in such way that the individual dipole moments **cancel each other out**



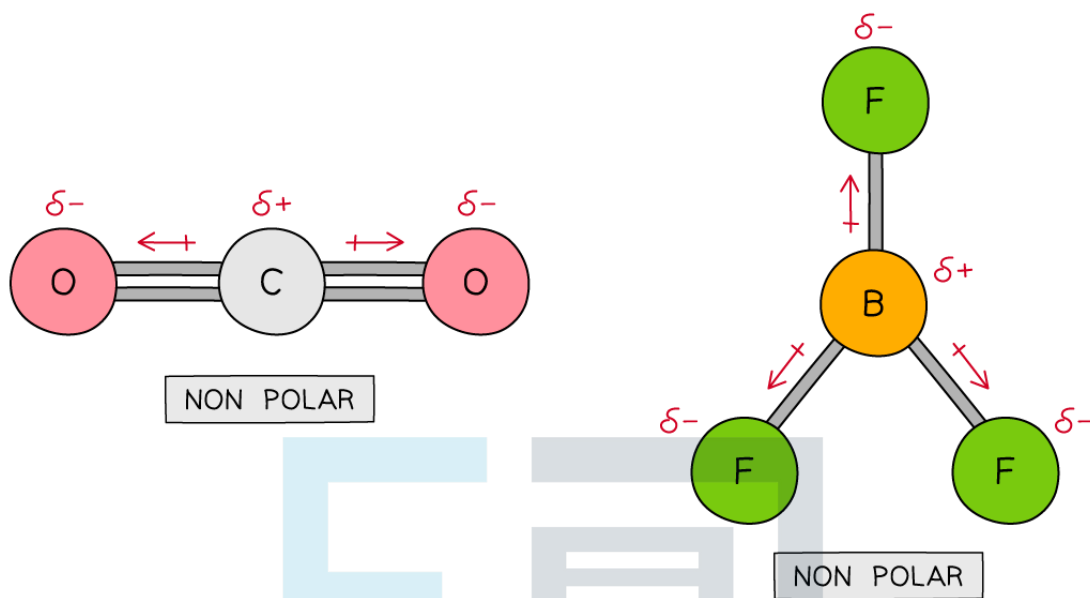
There are four polar covalent bonds in CH_3Cl which do not cancel each other out causing CH_3Cl to be a polar molecule; the overall dipole is towards the electronegative chlorine atom



Though CCl_4 has four polar covalent bonds, the individual dipole moments cancel each other out causing CCl_4 to be a nonpolar molecule

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© 2024 Further examples of molecules with no net dipole:



Carbon dioxide and boron trifluoride have polar bonds but no net dipole

- Try your hand at this polarity question:

Worked example

Which molecule is non-polar?

- A. NH₃
- B. CO
- C. SO₂
- D. AlBr₃

Answer:

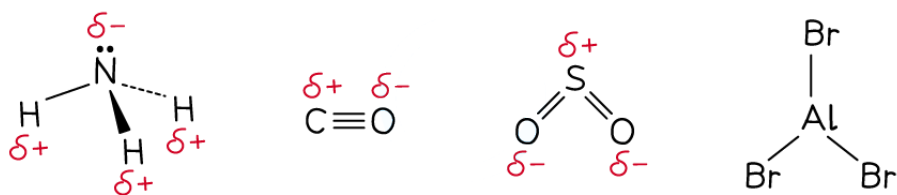
The correct option is **D**.

- The shapes and polarity of the molecules are as follows:

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Although the Al-Br bonds are polar, the trigonal planar molecule is symmetrical so the dipoles cancel out leaving a non-polar molecule

Exam Tip

One of the clues about molecular polarity is to look at the symmetry of the molecule

Molecules which are symmetrical are unlikely to be polar

4.2.5 Giant Covalent Structures

Giant Covalent Structures

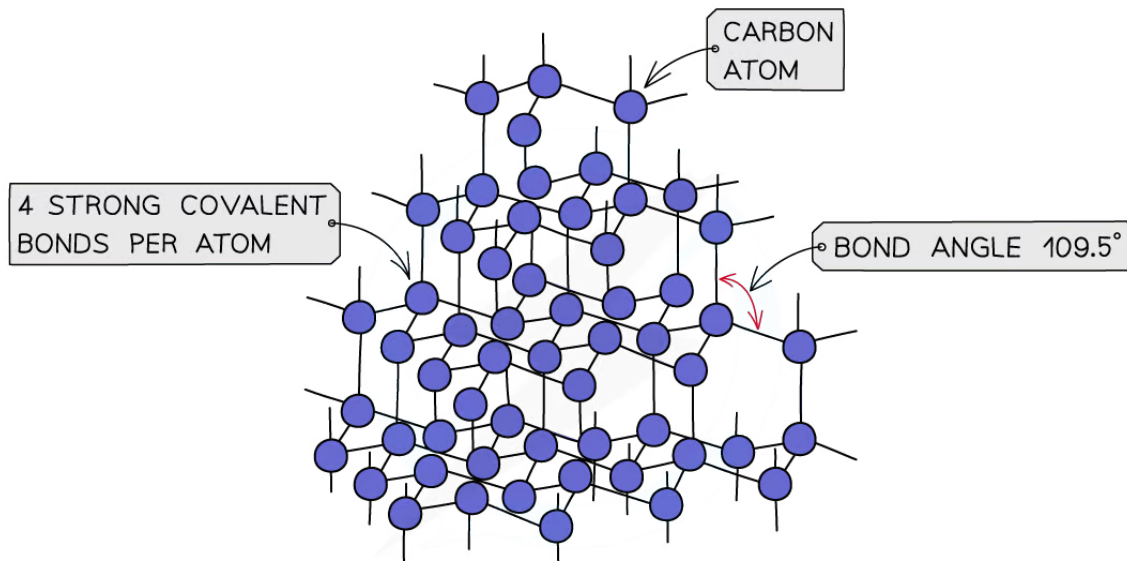
Covalent lattices

- **Covalent bonds** are bonds between nonmetals in which electrons are **shared** between the atoms
- In some cases, it is not possible to satisfy the bonding capacity of a substance in the form of a molecule; the bonds between atoms continue indefinitely, and a large lattice is formed. There are no individual molecules and covalent bonding exists between all adjacent atoms
- Such substances are called **giant covalent substances**, and the most important examples are C and SiO₂
- Graphite, diamond, buckminsterfullerene and graphene are allotropes of carbon

Giant Covalent Structures Examples

Diamond

- Diamond is a giant lattice of carbon atoms
- Each carbon is covalently bonded to four others in a tetrahedral arrangement with a bond angle of 109.5°
- The result is a giant lattice with strong bonds in all directions
- Diamond is the hardest substance known
 - For this reason it is used in drills and glass-cutting tools

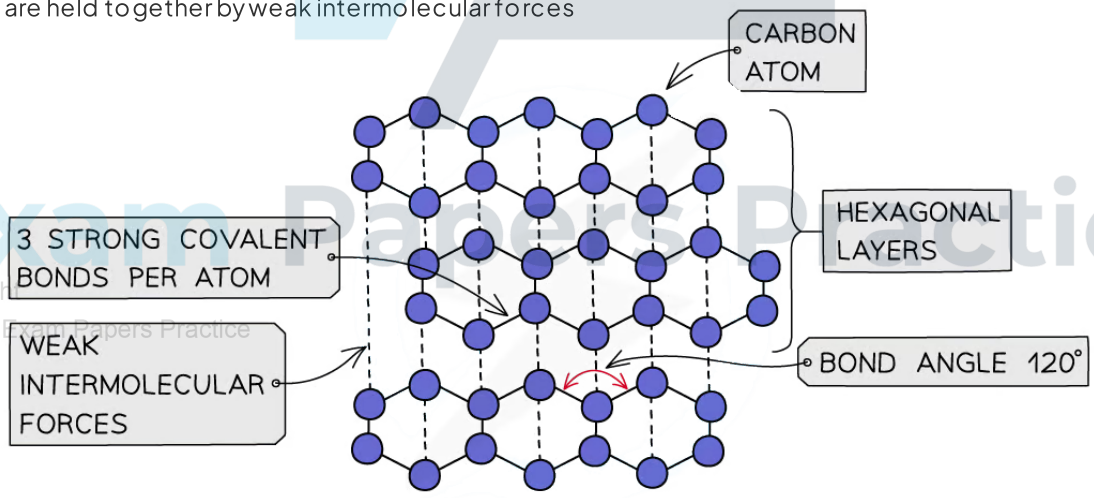


DIAMOND (CARBON)

Graphite

The structure of diamond

- In graphite, each carbon atom is bonded to three others in a layered structure
- The layers are made of hexagons with a bond angle of 120°
- The spare electron is delocalised and occupies the space in between the layers
- All atoms in the same layer are held together by strong covalent bonds, and the different layers are held together by weak intermolecular forces

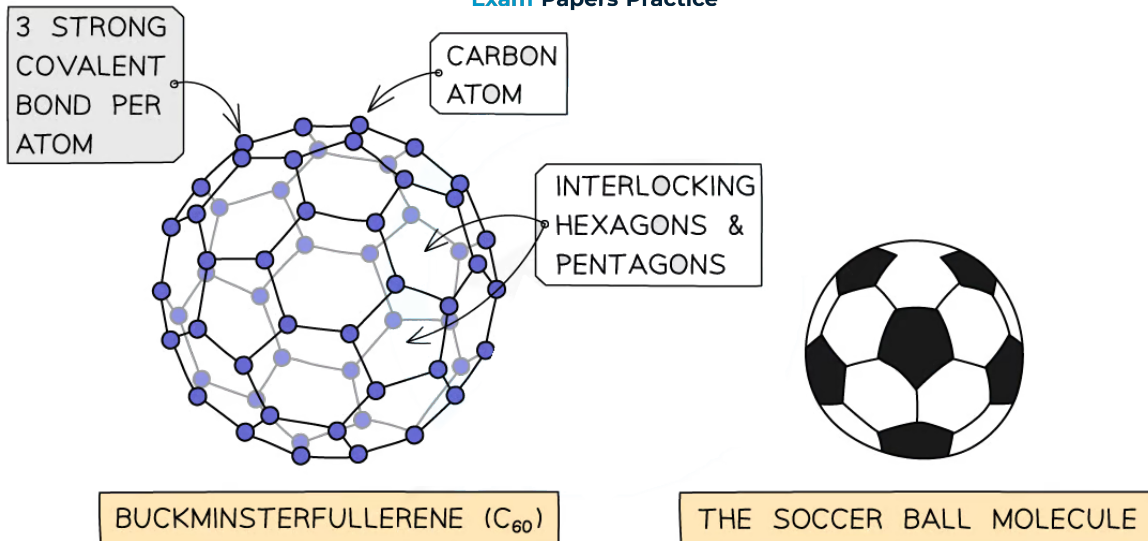


GRAPHITE (CARBON)

Buckminsterfullerene

The structure of graphite

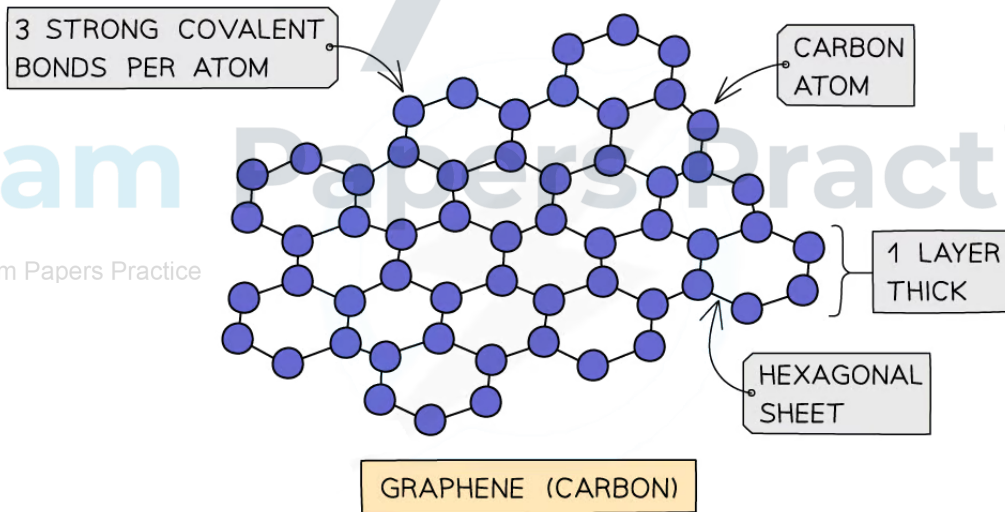
- **Buckminsterfullerene** is one type of fullerene, named after Buckminster Fuller, the American architect who designed domes like the Epcot Centre in Florida
- It contains 60 carbon atoms, each of which is bonded to three others by single covalent bonds
- The fourth electron is delocalised so the electrons can migrate throughout the structure making the buckyball a semi-conductor
- It has exactly the same shape as a soccer ball, hence the nickname the football molecule



The structure of buckminsterfullerene

Graphene

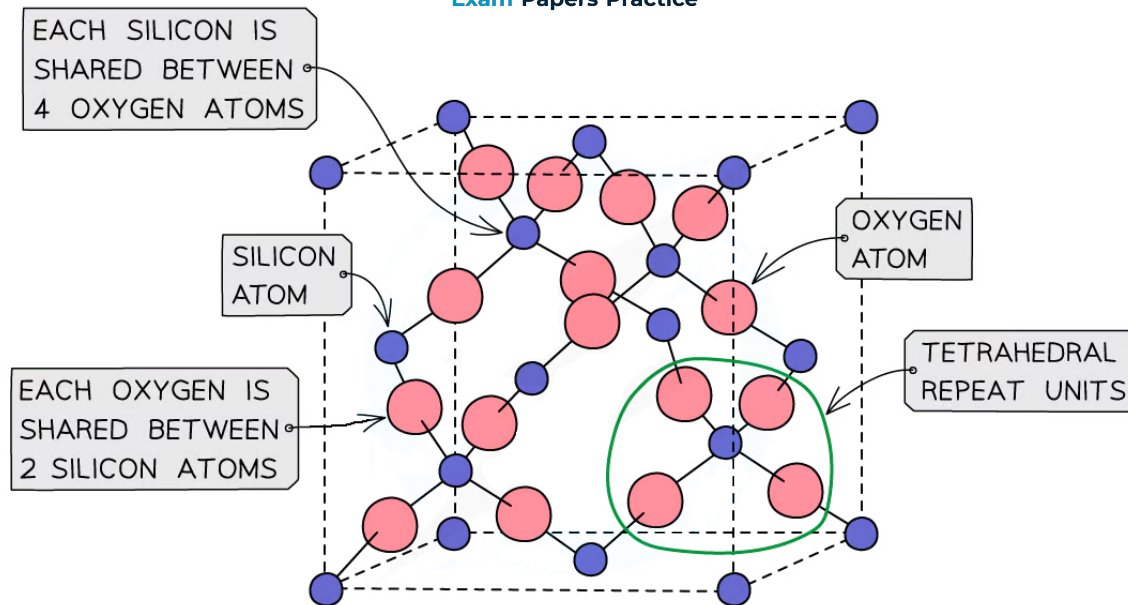
- Some substances contain an infinite lattice of covalently bonded atoms in two dimensions only to form layers. Graphene is an example
- Graphene is made of a single layer of carbon atoms that are bonded together in a repeating pattern of hexagons
- Graphene is one million times thinner than paper; so thin that it is actually considered two dimensional



The structure of graphene

Silicon(IV)oxide

- Silicon(IV)oxide is also known as silicon dioxide, but you will be more familiar with it as the white stuff on beaches!
- Silicon(IV)oxide adopts the same structure as diamond - a giant structure made of tetrahedral units all bonded by strong covalent bonds
- Each silicon is shared by four oxygens and each oxygen is shared by two silicons
- This gives an empirical formula of SiO₂



SILICON (IV) OXIDE (SiO_2)

The structure of silicon dioxide

Properties of Giant Covalent Structures

- Different types of **structure** and **bonding** have different effects on the **physical properties** of substances such as their **melting** and **boiling points**, **electrical conductivity** and **solubility**

Covalent bonding & giant covalent lattice structures

- **Giant covalent lattices** have very high **melting** and **boiling points**
 - These compounds have a large number of **covalent bonds** linking the whole structure
 - A lot of energy is required to break the lattice
- The compounds can be **hard** or **soft**
 - Graphite is **soft** as the forces between the carbon layers are weak
 - Diamond and silicon(IV) oxide are **hard** as it is difficult to break their 3D network of strong covalent bonds
 - Graphene is strong, flexible and transparent which makes it potentially a very useful material
- Most compounds are insoluble with water
- Most compounds do not **conduct electricity** however some do
 - Graphite has **delocalised** electrons between the carbon layers which can move along the layers when a voltage is applied
 - Graphene is an excellent conductor of electricity due to the **delocalised** electrons
 - Buckminsterfullerene is a semi-conductor
 - Diamond and silicon(IV) oxide do not conduct electricity as all four outer electrons on every carbon atom is involved in a **covalent bond** so there are no free electrons available

Characteristics of Giant Covalent Structures Table



| | Diamond | Graphite | Buckminsterfullerene | Graphene | Silicon dioxide |
|----------------------------------|---|-------------------|-----------------------|---|---|
| Melting and boiling point | Very high | Very high | Low | Very high | Very high |
| Electrical Conductivity | Non-conductor | Good | Semi-conductor | Very good conductor | Non-conductor |
| Appearance | Transparent crystals | Grey-black solid | Yellow solid | Transparent sheets | Transparent crystals |
| Special Characteristics | Hardest known naturally occurring substance | Soft and slippery | Very light and strong | Very strong and flexible; 100 times stronger than steel | Piezoelectric – produces electric charge from mechanical stress |

 **Exam Tip**

Although buckminsterfullerene is included in this section it is not classified as a giant structure as it has a fixed formula, C_{60}

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