**4.3 Covalent structures**

**Learning objectives**

* Understand what is meant by a coordinate covalent bond
* Work out Lewis structures for molecules and ions
* Work out the shapes of molecules and ions with up to four electron domains
* Predict bond angles in molecules and ions
* Predict whether a molecule will be polar or non-polar
* Describe the structures and bonding of giant covalent substances
* Explain the physical properties of giant covalent substances in terms of structure and bonding
* **The octet rule**

You met the concept that atoms in covalent bonds have a tendency to have a full valence shell with a total of eight electrons.

This is known as the **octet rule**. In most covalent molecules and polyatomic ions (for example, NH4+ or CO32−), each atom has an octet in its outer shell. There are exceptions to this rule.

**Some exceptions to the octet rule**

1. BF3

In BF3, boron has only six electrons in its outer shell. Boron has three valence electrons and can therefore share a maximum of three electrons.

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1. BeCl2

The beryllium atom only has a total of 4 electrons in its outer shell since beryllium has 2 electrons in its outer shell.

1. SF6

In sulfur hexafluoride, sulfur has expanded its octet.

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**Coordinate covalent bonds (dative covalent bonds)**

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| **A coordinate covalent bond is a type of covalent bond in which both electrons come from the same atom.** |

Example: Ammonia and H+ bond to form NH4+ ion.

NH3 + H+ → NH4+

H+ does not have any electrons with which to form a covalent bond, but NH3 has a lone pair of electrons that can be used to form a covalent bond.

Once a coordinate covalent bond has been formed, it is identical to an ‘ordinary’ covalent bond. A coordinate covalent bond is sometimes shown as an arrow.

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Other examples of coordinate bonding

Draw lewis diagrams to show bonding in:

1. H3O+ Hydronium ion
2. NH3 and BF3 and explain the meaning of the term adduct and Lewis acid base reaction.
3. Carbon monoxide CO

If they bond with 2 covalent bonds, the oxygen atom has a full outer shell (octet), the carbon atom has only six electrons in its outer shell.



***The structure of carbon monoxide if two ‘ordinary’ covalent bonds were formed.***

Both atoms can attain an octet if the oxygen atom donates a pair of electrons to carbon in the formation of a coordinate covalent bond.Both atoms have a lone pair of electrons.



***The structure of carbon monoxide if two ‘ordinary’ covalent bonds and one coordinate covalent bond were formed.***



***Other ways of showing the bonding in carbon monoxide.***

Electrons may be shown individually as dots or crosses, or a line may be used to represent a pair of electrons, in the Lewis structures.

**Practice questions**

Draw the Lewis structures for the following.

1. **NF3**
2. **CO**3 2− carbonate ion

Carbon is the central atom and the oxygens are the outer atoms. Because the carbon atom has only four electrons in its outer shell, it does not have enough electrons to form three double bonds with the oxygens, but it does have enough electrons to form one double bond and two single bonds.

The overall charge on the ion must be included and square brackets drawn around the ion.

**Resonance structures**

There is more than one way of drawing the structure of the **CO**3 2−ion depending on where we put the C=O (and lone pairs).



These individual structures differ only in the position of the double bond and are called **resonance structures**. In CO32−, the carbon– oxygen bonds are all equal in length. The actual structure is described as a hybrid of the individual resonance structures. This is shown by the double headed arrow.

Draw the resonance structures for the following and state the number of possible structures.

1. Benzene C6H6
2. Ozone O3

**Two possible Lewis structures for the same molecule SO2**

Two different Lewis structures are possible for SO2 depending on whether the octet on S is expanded or not.

**Approach 1:**

**Sulfur does not expand its octet**

Sulfur has six electrons in its outer shell and can, therefore, form a maximum of two normal covalent bonds. If these are both formed to the same oxygen atom, we get the structure shown.



The structure can be completed by a coordinate bond between the sulfur and the second oxygen.

**Approach 2:**

When sulfur forms two double bonds with oxygen it will have ten electrons in its outer shell and is said to have expanded its octet.

This is possible for elements in period 3 and beyond because they have d orbitals available for bonding.

Both approaches to working out Lewis structures are valid, although more detailed considerations which involve working out the formal charge on each atom suggest that the second structure is a better representation.

The bond lengths in SO2 also suggest the presence of two double bonds in the molecule.



**Alternative method for working out Lewis structures**

This approach is useful for working out the Lewis structures of molecules/ions just containing period 2 atoms.

**1** Add up the total number of valence electrons of all the atoms in the molecule/ion.

**2** Divide by two to get the total number of valence electron pairs.

**3** Each pair of electrons is represented by a line.

**4** Arrange the lines (electron pairs) so that all the atoms are joined together by at least single bonds and the outer atoms have full outer shells, i.e. are connected to four lines.

**5** Rearrange the lines (electron pairs) so that every period 2 atom has four pairs of electrons. The outer atoms already have four pairs, so this should normally involve moving only lone pairs so that they become bonding pairs of electrons.

**Use these steps to draw the structure of:**

1. **NO**3 –
2. **NO**2 –

**O3**

Ozone is isoelectronic with NO2 − and has the same Lewis structure

 

**NO2 + and CO2**

NO2+ and CO2 are isoelectronic and have the same Lewis structure.





**Shapes of molecules: valence shell electron pair repulsion theory**

We can predict the shapes of molecules using the **valence shell electron pair repulsion (VSEPR) theory**.

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| **Pairs of electrons (electron domains) in the valence (outer) shell of an atom repel each other and will therefore take up positions in space to minimise these repulsions – to be as far apart in space as possible.** |

The pairs of electrons may be either non-bonding pairs (lone pairs) or bonding pairs (pairs of electrons involved in covalent bonds).

More precisely, it is a question of how points can be arranged on the surface of a sphere to be as far away from each other as possible.

A double bond is made up of two pairs of electrons, but these electron pairs are constrained to occupy the same region of space. A double bond (or a triple bond) therefore behaves, in terms of repulsion, as if it were just one electron pair and so it is better to talk about the number of **electron domains** – where an electron domain is either a lone pair, the electron pair that makes up a single bond or the electrons pairs that together make up a multiple bond.



***Basic molecule shapes and bond angles.***

**CH**4





***The Lewis structure for CH4.***   ***CH4 is tetrahedral.***

The number of electron pairs in the outer shell of the central atom (C) is four, i.e. there are four electron domains. These four electron domains repel each other and take up positions in space as far away from each other as possible. The shape that allows four things to be as far away from each other as possible is **tetrahedral**.

**Draw the structures to show the shapes of the following molecules**

1. Ammonia
2. **CO**2
3. **SO**2

**Lone pairs and bond angles**

The order of repulsion strength for pairs of electrons is:

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| **lone pair–lone pair > lone pair–bonding pair > bonding pair–bonding pair** |

This is because lone pairs are held closer to the central nucleus than are bonding pairs.



The lone pairs are thus closer to the bonding pairs of electrons than the bonding pairs are to each other and repel them more strongly.

This means that the repulsion due to lone pairs causes other bond angles to become smaller.

Consider CH4, NH3 and H2O, each of which has four electron pairs in the outer shell of the central atom.

**Exam tip**

A general rule of thumb, if you are asked to predict a bond angle in a particular molecule, just take two or three degrees off the basic angle (the bond angle in the basic shape) for each lone pair present on the central atom. For example, a bent molecule based on a trigonal planar structure (one lone pair on the central atom) could have a bond angle of 120 − 3 = 117°. There is no scientific basis for doing this, but it is useful for answering examination questions.



**Predicting the shapes of ions**

The approach to predicting the shapes of ions is exactly the same as for neutral molecules.

NH4 +

Bonding pairs of electrons: 4

Non-bonding pairs of electrons: 0

Electron domains: 4

Because these four electron domains repel each other and take up positions in space to be as far apart as possible the electron pairs are distributed in a tetrahedral arrangement.



What are the shapes for the following ions? Draw the structures to illustrate.

1. H3O+

Bonding angle 107

1. NO2 –

Bonding angle 117

**Molecules with more than one central atom**

The approach to predicting the shapes of molecules with more than one central atom is the same as for other molecules, except that each ‘central atom’ must be considered separately.

N2H4

In this molecule, the two N atoms are ‘central atoms’ and each one must be considered separately.

 

***The Lewis structure for N2H4. The structure of N2H4.***

It can be seen in the figure that the arrangement of electron pairs around each nitrogen is tetrahedral and, with one lone pair on each nitrogen, the shape about each N atom is trigonal pyramidal.

**Draw the Lewis diagram for ethyne C2H2 and predict the shape.**

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***The basic and actual shapes of some specific molecules – see Subtopic 4.6 for information about atoms with more than four electron domains.***

**Polar molecules**

Whether an overall molecule is polar depends on the difference in electronegativity and shape of the molecule.

For a molecule to be polar it must have a positive end to the molecule and a negative end.

For instance HCl, NH3 and H2O are all polar. These molecules all have an overall **dipole moment**, and the arrow indicates the direction of the moment.



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| **Although individual bonds may be polar, a molecule may be non-polar overall if, because of the symmetry of the molecule, the dipole moments of the individual bonds cancel out.** |

Dipole moment is the product of the charge and the distance between the charges. The unit is the debye(D).

**Draw the shapes of CO2 BF3 and CCl4 and explain why overall the molecules are non-polar.**

**Exam tip**

**The examination answer as to why CCl4 is non-polar is ‘although each individual bond is polar due to the difference in electronegativity of the atoms, because of the symmetry of the molecule, the dipoles cancel’.**

Some polar and non-polar molecules are shown in Table below.

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**Giant covalent structures**

**Allotropes of carbon**

**Allotropes** are different forms of the same element. For instance, diamond, graphite, graphene and fullerenes are all allotropes of carbon. They all contain only carbon atoms, but these atoms are joined together differently in each structure.

**Diamond**

Diamond has a giant covalent (macromolecular) structure. There are no individual molecules – the whole structure, continuing in three dimensions, represents one giant molecule. Each carbon atom is joined to four others, in a **tetrahedral** array, by covalent bonds.

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**Properties:**

1. Diamond is hard and has a very high melting point and boiling point (about 4000 °C) because a lot of energy must be supplied to break covalent bonds (very strong) when diamond is melted/boiled.
2. Diamond does not conduct electricity, because all the electrons are held strongly in covalent bonds and are therefore not free to move around in the structure.
3. Diamond is not soluble in water or organic solvents because the forces between the atoms are too strong. The energy to break these covalent bonds would not be paid back when the C atoms were solvated.

**Graphite**

Like diamond, graphite has a giant covalent structure. Unlike diamond, however, it has a layer structure. Each C is covalently bonded to three others in a trigonal planar array.

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***Part of the structure of graphite, which is based on planar hexagonal rings. One hexagon is highlighted in red.***

**Properties:**

1. **Lubricant.** The presence of weak forces between the layers is usually given as the explanation that graphite is a good lubricant.
2. **Very high melting/boiling poin**t because covalent bonds within the layers must be broken when it is melted/boiled.
3. **Solubility.** Because of the strong covalent bonds between atoms, graphite is not soluble in water or non-polar solvents.
4. **Electrical conductivity.** Graphite conducts electricity because each C atom forms only three covalent bonds – the extra electrons not used in these bonds (carbon has four outer shell electrons) are able to move within the layers. p orbitals can overlap side-on to give a π **delocalised system.** Movement of electrons within this system allows the conduction of electricity within layers. Graphite is, however, an electrical insulator perpendicular to the plane of the layers.

**Graphene**

Graphene is a relatively new form of carbon that consists of a single layer of graphite.

Graphene has a very high tensile strength and would be expected to have a very high melting point because covalent bonds need to be broken to break the sheet. It is also a very good electrical (C forms only three bonds) and thermal conductor.

**C60 fullerene (buckminsterfullerene)**

The fourth allotrope of carbon is a molecular rather than a giant structure. It consists of individual C60 molecules, with covalent bonds within the molecule and London forces between the molecules.

C60 is insoluble in water but soluble in some organic solvents such as benzene. The energy to overcome the London forces between the C60 molecules is paid back by the energy released when London forces are formed between the C60 molecules and the solvent.

C60 does not conduct electricity.



**Silicon dioxide**

SiO2 (quartz) has a giant covalent structure. Each silicon atom is bonded to four oxygen atoms in a tetrahedral array. Each oxygen is bonded to two silicon atoms. Due to two lone pairs on each oxygen atom, the basic shape about each Si–O–Si unit is bent (based on a tetrahedron).

The oxide has high melting and boiling points, because covalent bonds between atoms must be broken in order to melt/boil it and this requires a lot of energy.

