7 Shapes of Molecules

The shapes of molecules are determined by the arrangement of its atoms and this is determined by the electrons in the outer valence shell of the central atom. We will start by looking at the shapes of two very common molecules, carbon dioxide and water.

The carbon dioxide molecule

The Lewis electron dot structure of carbon dioxide (Figure 7.1) shows two pairs of bonding electrons on each side of the carbon atom, forming a double bond with each oxygen atom. The pairs of electrons are negatively charged, so they repel each other and try to get as far apart as possible. The atoms end up arranged in a straight line making a **linear molecule**.

Figure 7.1 Carbon dioxide – Lewis electron dot structure and shape of the molecule.

The water molecule

With the formula H_2O, you might also expect the shape of a water molecule to be linear: H – O – H. But the water molecule is not straight, it is a **bent molecule**. The reason for this bent shape lies in the arrangement of the valence electrons orbiting the central oxygen atom, which we can see in the Lewis electron dot structure.

Figure 7.2 Lewis electron dot structure of water and bent molecule.

The outer shell of the oxygen atom contains 4 pairs of electrons: 2 bonding and 2 non-bonding pairs. A non-bonding pair of electrons is called a lone pair. These 4 pairs of electrons are all negatively charged, so they repel each other, arranging themselves as far apart as possible. The pairs of electrons end up arranged in the shape of a tetrahedron (Figure7.3). A **tetrahedron** is a type of pyramid with 4 identical triangular faces, 3 faces meeting at each corner or vertex.

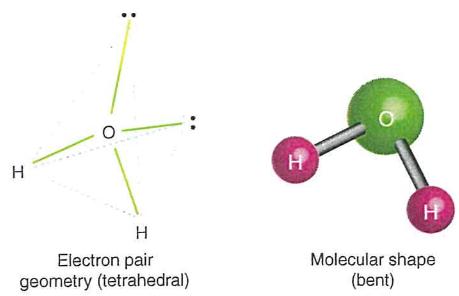


Figure 7.3 Electron pair arrangement and shape of the water molecule.

The shape of the molecule is determined by the positions of the two hydrogen atoms and the oxygen atom. The two hydrogen atoms are at two corners of the tetrahedron. The other two points of the tetrahedron are occupied by the two non-bonding electron pairs. Think of it this way – we cannot 'see' the electron pairs – all that is 'visible' is the bent shape formed by the hydrogen and oxygen atoms. The electron pairs are arranged like a tetrahedron, but the molecule itself is a bent shape.

QUESTIONS

1. (a) Write the Lewis electron dot structure for water.
   (b) Identify the most stable geometrical arrangement of the electron pairs in an atom's valence shell.
   (c) Identify the shape of the water molecule.
   (d) Explain why the shape is not described as tetrahedral.
2. (a) Write the Lewis electron diagram for carbon dioxide.
   (b) Illustrate the shape of a carbon dioxide molecule.
3. What is meant by each of the following?
   (a) Linear molecule.
   (b) Tetradedron.
   (c) Lone pair.
4. Is it correct to say that, 'The hydrogen atoms in a molecule of water repel each other forming a bent shape'? Justify your response.
5. Check your knowledge with this quick quiz.
   (a) In the water molecule, the 4 electron pairs around the central oxygen atom (attract/repel) each other.
   (b) The 4 electron pairs around the central oxygen atom in the water molecule are arranged in the shape of a ....
   (c) Identify the shape of the water molecule.
   (d) Identify the shape of the carbon dioxide molecule.

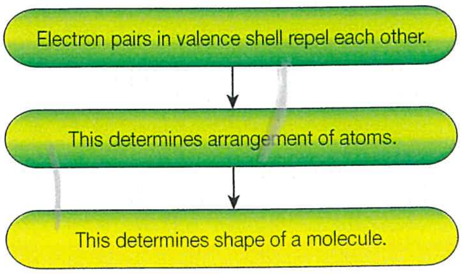
8 The VSEPR Theory

VSEPR stands for the **valence shell electron pair repulsion theory**.

This theory states that the shapes of molecules are determined by the arrangement of its atoms and the arrangement of the atoms in a molecule is influenced by the arrangement of its outer shell electrons.

The electron clouds formed by electron pairs orbiting around each atom repel each other, moving as far away from each other as possible while still being attracted to the positive nucleus. These forces of repulsion determine where electrons will be at any moment and thus the arrangement of atoms and the shape of the molecule.

We could summarise this as follows.



To determine the shape of a molecule:

- The Lewis structure is drawn for the molecule.
- This shows the number of electron pairs in the valence shell of the central atom.
- Bonding electron pairs are distinguished from non-bonding electron pairs as the repulsion of non-bonding pairs is greater than the repulsion of bonding pairs.
- Geometric positions for the pairs of electrons are worked out.
- The geometric positions of attached atoms are worked out.
- The shape of the molecule is determined.

You will be working through examples of this in the next two chapters.

History of the VSEPR theory

The VSEPR theory was developed as an extension of the ideas of **GN Lewis** (1875-1946) who developed the idea of the Lewis electron dot formulas. Lewis proposed that chemical bonds were formed when two atoms shared a pair of electrons so as to form a noble gas structure.

Figure 8.1 Gilbert Newton Lewis.

In 1940, two English chemists, Nevil Sidgwick (1873-1952) and Herbert Powell (1906-1991) suggested that there is a correlation between the geometric shapes of molecules and the number and arrangement of valence electrons in atoms within molecules.

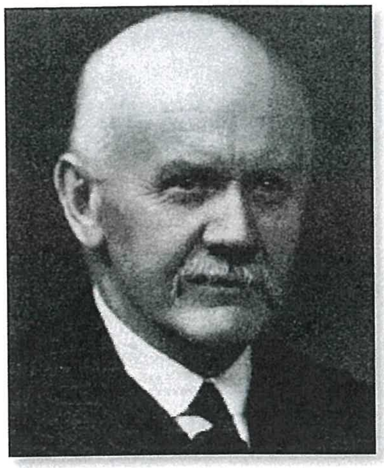


Figure 8.2 Nevil Vincent Sidgwick.

In 1957, this idea was extended by an Australian chemist, **Sydney Nyholm** (1917-1971) and a Canadian, Ronald Gillespie (1924-).

Figure 8.3 Sir Ronald Sydney Nyholm.

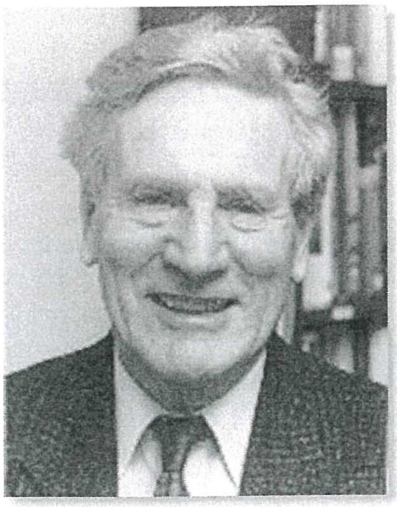


Figure 8.4 Ronald J Gillespie.

Nyholm and Gillespie described how electrostatic repulsion of electron pairs could determine the structure of molecules and they demonstrated how the structure could be predicted from this knowledge about electron pair repulsion. They used known information about chemical bonding to predict the internal electronic structure of molecules and they verified the shapes of molecules using X-ray crystallography.

The VSEPR theory acts as a model in chemistry to predict the shape of individual molecules. Two- and three-dimensional graphical models are used.

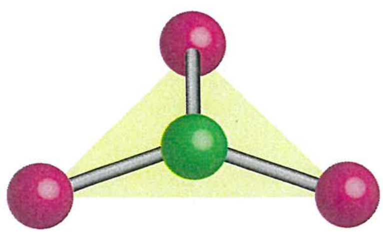
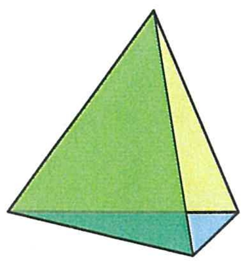
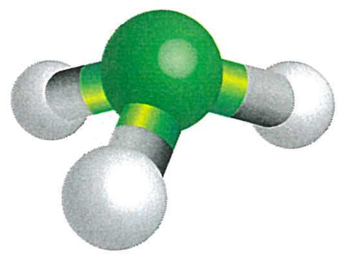
Before we look at how to predict the shapes of molecules it will help if you revise the three basic geometrical shapes shown in Table 8.1 below.

QUESTIONS

1. (a) Outline the VSEPR theory.
   (b) What is the use of the VSEPR theory to a chemist?
2. Compare and contrast two shapes – a tetrahedron and a trigonal pyramid.
3. Research the development of the VSEPR theory and use this to discuss one of the following statements – either (a) or (b).
   (a) The development of complex models and theories needs a wide range of evidence from many individuals and across disciplines.
   (b) Science is a global enterprise that relies on clear communication, internal conventions, peer review and reproducibility.

   Before you begin any research question such as this you should discuss with your teacher how you should present your findings and the length expected for your report.
4. Describe the stable valence shell arrangement of electrons in most atoms forming single bonds.
5. Identify scientists who made the following contributions to the VSEPR theory.
   (a) Developed the idea of electron dot formulas.
   (b) Showed a correlation between the geometric shapes of molecules and the number and arrangement of valence electrons in atoms within molecules.
   (c) Used information about chemical bonding to predict the internal electronic structure of molecules and verified the shapes of molecules using X-ray crystallography.
6. Test your knowledge with the following quick quiz.
   (a) What does the acronym VSEPR stand for?
   (b) What does repulsion mean?
   (c) Which show greater repulsion, bonding pairs or non-bonding pairs?
   (d) Name a technique used to verify shapes of molecules.

Table 8.1 Three shapes.

Trigonal planar	Tetrahedron	Trigonal pyramid
A flat or two dimensional triangular shape – all in one plane – formed by 1 atom at the centre and 3 at the corners of a triangle.	A type of pyramid which has 4 identical triangular faces, 3 faces meeting at each corner or vertex.	Like a flattened tetrahedron. Note that Egyptian pyramids have a square base but this shape has a triangle shaped base hence the name trigonal pyramid.
		

9 Shapes of Molecules and the VSEPR Theory

We can draw molecules as flat, linear structures, and some are actually flat and linear, e.g. a diatomic molecule such as H_2, N_2 or Cl_2 will be linear because the centres of the two atoms will always be in a straight line.

But most molecules are really **three dimensional**. To show their three-dimensional shape we need to either make models or do perspective drawings.

In perspective drawings we use a straight line to represent a bond which is lying approximately in the plane of the paper, a wedge shaped bond shows a bond which would project forwards out of the paper and a hatched bond is one which would project back into the paper (away from the person looking at it).

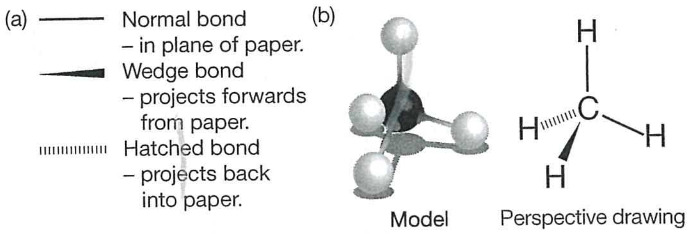


Figure 9.1 (a) Orientation of bonds. (b) An example – methane – three-dimensional model and perspective drawing.

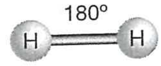
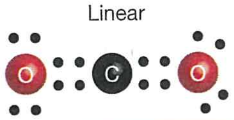
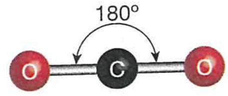
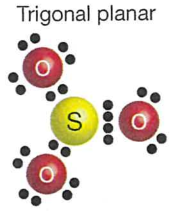
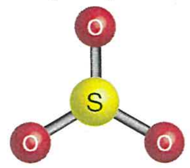
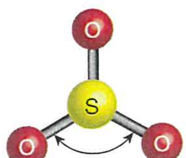
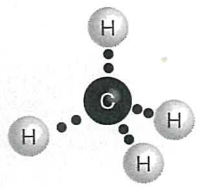
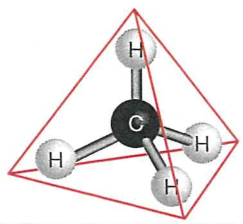
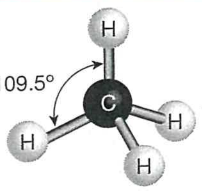
The shapes of molecules can be explained and predicted using three-dimensional representations of electrons as charge clouds and using valence shell electron pair repulsion (VSEPR) theory.

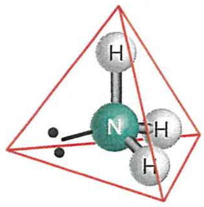
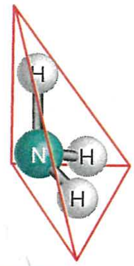
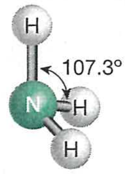
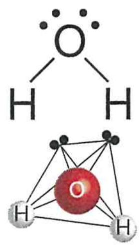
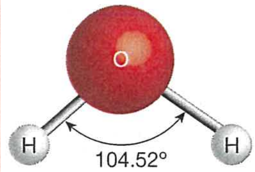
The shapes of molecules are determined by the arrangement of its atoms, and the arrangement of the atoms is influenced by its outer shell electrons. You will remember that the **electron cloud model** shows the most likely positions of electrons in an atom. An 'electron cloud' can be a **single**, **double** or **triple bond**. It can also be a **lone pair** of electrons, a pair of electrons which are both from the same atom and not involved in bonding. These electron clouds are all negatively charged (electrons are negative) so they tend to **repel each other**, moving as far away as possible while still being attracted to the positive nucleus. A lone pair can repel more strongly than a bonding pair. All of these forces acting on electrons determine where electrons will be at any moment and thus they determine the shape of the molecule – the shape of the space it occupies.

One more thing to remember – when **double** or **triple bonds** are formed between two atoms, the electron pairs are distorted from their tetrahedral arrangement and they form one electron cloud between the atoms. So remember to treat double and triple bonds as if they consist of one pair of electrons instead of two or three pairs. For example, in O=C=O each double bond is one electron cloud. The same applies to triple bonds such as in H–C≡N.

Table 9.1 shows some examples of shapes of molecules and how they are determined by the arrangement of electron pairs.

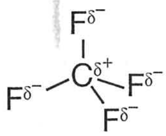
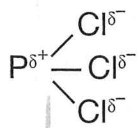
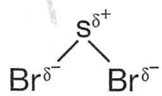
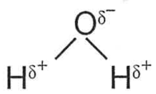
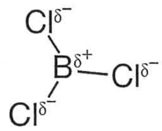
Table 9.1 Electron pairs and shapes of molecules.

Pairs of electrons	Arrangement of electron pairs around central atom of molecule	Shape of molecule	Bond angle	Examples
One electron cloud containing a bonding pair.	Linear 	Linear 	180° 	All diatomic molecules, e.g. H_2, N_2, Cl_2, HCl
Two electron clouds – each consisting of two bonding pairs – around central atom.	Linear 	Linear 	180° 	CO_2
Three electron clouds – one containing a double bond (two pairs of electrons). All bonding pairs, there are no lone pairs.	Trigonal planar 	Trigonal planar 	 120°	SO_3, BH_3, NO_3^-
Four electron clouds, each containing a bonding pair of electrons. No lone pairs.	Tetrahedral 	Tetrahedral 	109.5° 	CH_4, NH_4^+, SO_4^{2-}, PO_4^{3-}

Pairs of electrons	Arrangement of electron pairs around central atom of molecule	Shape of molecule	Bond angle	Examples
Four electron clouds – three bonding pairs and a lone pair.	Tetrahedral 	Trigonal pyramidal. The lone pair is not 'visible', so the molecule is not tetrahedral, it is trigonal pyramidal. 		NH_3, PH_3, SO_3^{2-}
Four pairs of electrons – two bonding pairs and two lone pairs.	Tetrahedral 	Bent. The lone pairs force the bonds into a tetrahedral shape, but the lone pairs are not visible, so the molecule looks bent (not tetrahedral). 		H_2O, H_2S, SCl_2

QUESTIONS

1. Use molecular model kits to determine the shape of the following molecules, then based on these models:
   - Draw their Lewis electron dot structures.
   - Identify the bonding and non-bonding electron pairs and work out the electron geometry.
   - Identify the shape of the molecule.

   (a) Hydrogen sulfide.
   (b) Ammonia.
   (c) Phosphorus trichloride.
   (d) Oxygen.
   (e) Tetrachloromethane.
2. Use three-dimensional perspective diagrams to compare the shapes of molecules for three different-shaped molecules, all with four pairs of electrons around the central atom as follows.
   (a) Four pairs of bonding electrons.
   (b) Three pairs of bonding electrons and one lone pair.
   (c) Two pairs of bonding electrons and two lone pairs.
3. Based on the number of atoms in the molecule, you might expect water and carbon dioxide to have the same shaped molecules. Identify the shapes of these molecules and explain why they are different.
4. The following molecules all contain one or more polar bonds. Use arrows to show dipoles, any net dipole force for each molecule and state whether each substance will have polar or non-polar molecules.
   (a) 
   (b) 
   (c) $H^{\delta+}-C\equiv N^{\delta-}$
   (d) 
   (e) 
   (f) 
5. Check your knowledge with this quick quiz.
   (a) What is the shape of all diatomic molecules?
   (b) A flat, two-dimensional triangular shape is described as ....
   (c) How many triangular shaped faces make up a tetrahedron?
   (d) Identify the shape of a water molecule.
   (e) Which has the stronger repelling force, a bonding pair of electrons or a non-bonding pair?
   (f) What is another term for a pair of electrons which is not involved in bonding with another atom?

(b) Three of the compounds, H_2S, H_2Se and H_2Te show an increase in boiling point (from about −60 to −40, to 0°C) with increase in size of the molecule. Water does not fit this trend – its boiling point is much higher than would be expected based on size of the molecules alone.

(c) H_2Te, H_2Se and H_2S all have low boiling points (approximately 0°C, −40°C and −60°C respectively) but water has a much higher boiling point than would be expected (100°C). All four compounds, H_2Te, H_2Se, H_2S and H_2O have dispersion forces and dipole-dipole intermolecular forces attracting their molecules. These are weak forces, so a small rise in heat is able to break these bonds and allow them to move more freely so that a change of state occurs. Water would have not only these forces, but also hydrogen bonds. Hydrogen bonds are attractive forces between a hydrogen atom in one molecule and an oxygen atom in an adjacent molecule. Hydrogen bonding would cause a higher boiling point because to break these stronger hydrogen bonds more energy would be needed – the boiling point would be higher.

5. Various, e.g.
- The boiling points of these compounds are relatively low – most are below zero Celsius.
- Boiling points decrease as you move up the group from HI to HBr to HCl.
- Hydrogen fluoride (HF) has the highest boiling point and is an exception to the trend of boiling point decreasing as you go up the group.
- As you go up the group, the molecules get smaller. Smaller molecules have weaker dispersion forces.
- If HF followed the trend, its boiling point would be about −100°C, but instead it is much higher at about 20°C.
- As the boiling point of HF is higher than expected, its bonding must be stronger than in the other compounds shown in the graph. As hydrogen fluoride contains hydrogen and fluoride, it would have intermolecular hydrogen bonds, between H in one molecule and F in an adjacent molecule. These bonds would be in addition to the dispersion forces and dipole-dipole forces found in all the compounds.
- The other three compounds, HI, HBr and HCl, contain hydrogen, but they do not have O, F or N atoms, so they cannot form hydrogen bonds. They would only have dispersion forces and dipole-dipole forces between their molecules.
- This difference in bonding would account for hydrogen fluoride having a higher boiling point than the other compounds on the graph.

6. (a) Low, intermolecular, weak.
(b) Dispersion, dipole-dipole, hydrogen.
(c) Between, higher.

6 Solubility

1. (a) The solute is the substance that gets dissolved, the solvent does the dissolving and the solution is a mixture formed when a solute dissolves in a solvent.
(b) Water can dissolve a wide variety of substances including ionic and polar covalent substances.

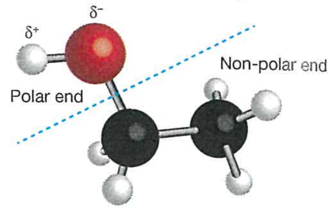
2. (a) Sodium chloride is ionic, and water is polar and has dipoles. The water dipoles can develop attractive forces with the sodium and chloride ions and thus dissolve it. Silicon dioxide is a covalent network structure. It does not form any dipoles and has no ions so there is no attraction to water molecules, it is insoluble.
(b) 'Like dissolves like' is just a saying to help remember which substances dissolve and which do not. It does not provide an explanation. An acceptable answer must mention the type of bonding in each substance involved and explain either how bonds are formed between a solute and a solvent when dissolving occurs, or else why they cannot form (in the case of an insoluble substance).

3. Hydrogen chloride dissolves in water to form ions in solution, which can then carry a charge – it conducts electricity and is called an electrolyte. Sugar molecules spread out through the water, bonding with the water, but no ions are formed so the solution cannot conduct an electric current (it is a non-electrolyte).

4.

Type of chemical	Example (various)	Solubility
Polar molecular compound	Sucrose	Soluble
Molecular element	Oxygen	Slightly soluble
Highly polar molecular compound	Hydrogen chloride	Soluble
Non-polar molecular compound	Hexane	Insoluble
Covalent network structure	Silicon dioxide	Insoluble
Macromolecules	Polyethylene	Insoluble

5. Ethanol is able to dissolve both polar and non-polar substances because its molecule has a polar end and a non-polar end. The ethyl (C_2H_5) group at one end is non-polar, allowing it to attract other non-polar molecules. The hydroxyl (OH) group at the other end is polar and the high electronegativity of oxygen allows it to form hydrogen bonding with molecules containing hydrogen. Ethanol is able to be used as a solvent in cosmetics such as perfumes, food colourings and flavourings, medical products and cleaning agents. Methylated spirits is mainly ethanol with the addition of a toxic substance so it cannot be used as a drink.

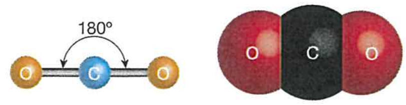


6. (a) Polar. (b) Polar.
(c) Soluble. (d) Insoluble.

7 Shapes of Molecules

1. (a) Water. H:Ö:H (b) In the shape of a tetrahedron.
(c) Bent.
(d) The four pairs of electrons around the oxygen atom are arranged in a tetrahedral shape, but two pairs are lone pairs and these are not involved in bonding so there are no atoms attached to them. The 'visible' parts of the molecule are the oxygen atom and the two hydrogen atoms associated with the bonding pairs. The shape of a molecule is determined by the position of its atoms, in this case an oxygen and two hydrogen atoms. These form a bent shape, so the molecule is bent.

2. (a) Carbon dioxide. :O = C = O:
(b) Carbon dioxide is a linear molecule.



3. (a) A linear molecule has its atoms arranged in a straight line.
(b) A tetrahedron is a type of pyramid with 4 identical triangular faces, 3 faces meeting at each corner or vertex.
(c) A lone pair is a pair of outer shell electrons that are not involved in bonding.

4. Not correct. The shape of the water molecule is bent, but it is the negatively charged electron pairs that repel each other, not the hydrogen atoms.

5. (a) Repel. (b) Tetrahedron.
(c) Bent. (d) Linear.

8 The VSEPR Theory

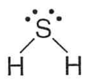
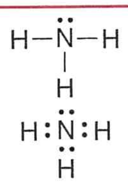
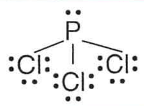
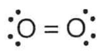
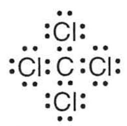
1. (a) According to the VSEPR – valence shell electron pair repulsion – theory the shapes of molecules are determined by the arrangement of its atoms and the arrangement of the atoms in a molecule is influenced by its outer shell electrons. These electron clouds around each atom repel each other, moving as far away from each other as possible while still being attracted to the positive nucleus. A lone pair can repel more strongly than a bonding pair. These forces determine where electrons will be at any moment and thus they determine the arrangement of atoms and the shape of the molecule.

(b) The VSEPR theory acts as a model in chemistry. Chemists use it to predict the shape of molecules.

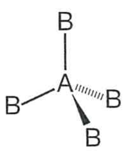
2. A tetrahedron is a pyramid which has 4 identical triangular faces, 3 faces meeting at each corner or vertex. A trigonal pyramid is also a pyramid with a triangular base, with 4 triangular faces with 3 meeting at each corner. However, in the trigonal pyramid the 4 faces are not identical, so the trigonal pyramidal shape is like a flattened tetrahedron.
3. Various.
4. The stable arrangement of electrons in the valence shell is an octet, consisting of eight electrons, arranged as four pairs in a tetrahedral pattern. This is called the noble gas configuration. (An exception is the smallest atoms, with only one shell, which have only one pair of electrons.)
5. (a) GN Lewis.
   (b) Nevil Sidgwick and Herbert Powell.
   (c) Sir Ronald Nyholm and Ronald Gillespie.
6. (a) Valence shell electron pair repulsion theory.
   (b) Pushing apart.
   (c) Non-bonding pairs repel more.
   (d) X-ray crystallography

9 Shapes of Molecules and the VSEPR Theory

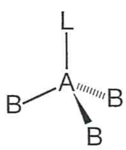
1.

Molecule	Electron dot diagram (all of these different styles are correct for each chemical)	Arrangement of electrons	Shape of molecule
(a) Dihydrogen sulfide (2 bonding pairs and 2 non-bonding (lone pairs)		Tetrahedral	Bent
(b) Ammonia (3 bonding pairs, 1 lone pair)		Tetrahedral	Pyramidal
(c) Phosphorus trichloride (3 bonding pairs, 1 lone pair)		Tetrahedral	Trigonal pyramidal
(d) Oxygen (2 bonding pairs, 2 lone pairs on each oxygen atom)		Trigonal planar	Linear
(e) Tetrachloromethane – previously called carbon tetrachloride (4 bonding pairs around the C atom)		Tetrahedral	Tetrahedral

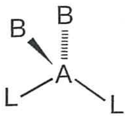
2. In this answer B indicates a bonding pair of electrons with an atom attached and L indicates a lone pair of electrons, not involved in bonding.
   (a) Tetrahedral shaped electron arrangement and tetrahedral shaped molecule.



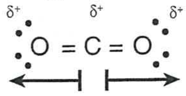
   (b) Tetrahedral shaped electron arrangement and trigonal pyramidal shaped molecule.



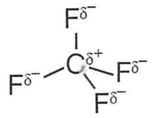
   (c) Tetrahedral shaped electron arrangement and bent shaped molecule.



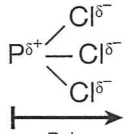
3. Carbon dioxide (CO_2) molecules are linear molecules. There are no lone pairs, just 4 pairs of bonding electrons (two electron clouds) around the central carbon atom – each electron cloud consisting of 2 bonding pairs. The 2 electron clouds repel each other so they are on opposite sides of the central carbon atom. Water (H_2O) molecules also consist of 3 atoms, but there are 2 bonding electron pairs and 2 lone pairs around the oxygen atom. This makes 4 electron clouds, which take up a tetrahedral shape. Because only 2 of the 4 points of the tetrahedron are occupied by atoms, the shape is bent.



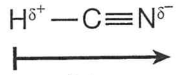
4. (a)



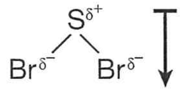
(b)



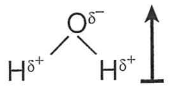
(c)



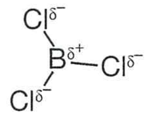
(d)



(e)



(f)



5. (a) Linear.
   (b) Trigonal planar.
   (c) 4
   (d) Bent.
   (e) Non-bonding pair.
   (f) Lone pair.

10 Electronegativity and Polarity

1. (a) Electronegativity is the ability of the atom of an element to attract electrons in a bond.
   (b) The Pauling scale (which varies from 0.7 to 4.0).
   (c) Non-metals are more electronegative than metals – non-metals are better able to attract electrons.
   (d) Fluorine is the most electronegative element (most able to attract electrons).
   (e) ... nent (least able to
2. (a)

Atomic number	Electronegativity
1	2.1
2	0
3	1.0
4	1.5
5	2.0
6	2.5
7	3.0
8	3.5
9	4.0
10	0
11	0.9
12	1.2
13	1.5
14	1.8
15	2.1
16	2.5
17	3.0
18	0
19	0.8
20	1.0