

3

Covalent and dative bonding

- 1 Draw dot-and-cross diagrams for the following compounds, showing electrons in the outer energy level only.
(a) Cl_2 (b) O_2 (c) CO_2 (d) CH_4 (e) HCN (f) C_2H_4 (g) F_2O (h) H_2O_2
- 2 When ammonia (NH_3) forms a compound with boron trifluoride (BF_3), a dative bond is formed. Write out the electron arrangements for nitrogen and boron and draw dot-and-cross diagrams for NH_3 and BF_3 ; use these to show how the bond is formed.
- 3 Draw dot-and-cross diagrams to show how the following molecules are formed and then, alongside, draw structural formulae for the molecules, using lines to represent covalent bonds and an arrow to represent a dative bond.
(a) The ammonium ion, NH_4^+ (b) nitric acid, HNO_3 (c) carbon monoxide, CO
- 4 Repeat the instructions of Question 3 for the following more difficult examples.
(a) Dinitrogen monoxide, N_2O (there are two possible answers).
(b) The aluminium chloride dimer, Al_2Cl_6 , which exists in the gas phase.
(c) The beryllium chloride dimer, Be_2Cl_4 , which exists in the gas phase.
(*Hint:* In parts (b) and (c) there are no bonds between the aluminium atoms or the beryllium atoms.)
- 5 Draw dot-and-cross diagrams for the following ions, using a small triangle to show the electron(s) that have been gained:
(a) The hydroxide ion, OH^-
(b) The carbonate ion, CO_3^{2-}
(c) The hydrogen carbonate ion, HCO_3^-
(d) The hydrogen sulphide ion, HS^-
- 6 In all the above examples, the atoms either have eight electrons in their outer energy level (they have completed their octet) or two electrons. In the following the central atom has to 'expand its octet' in order to form the required number of bonds. Draw dot-and-cross diagrams for:
(a) Phosphorus pentachloride, PCl_5
(b) Sulphur hexafluoride, SF_6
(c) The sulphate ion, SO_4^{2-}
(d) The phosphate ion, PO_4^{3-}
- 7 Explain the following covalent bond energies of the Group 7 halides:

Bond	Bond energy/ kJ mol^{-1}
H-F	562
H-Cl	431
H-Br	366
H-I	299

3

Shapes of molecules

- 1 What is the theory governing the shapes of molecules?
- 2 'Electron regions' can be single bonds, multiple bonds (double or triple) or lone pairs of electrons. Put these three in order of increasing repelling power (i.e. put the weakest at the top of the list).

3 Use the following list of compounds for this question:

CCl_4 , BF_3 , NH_3 , SO_2 , CO_2 , F_2O , PCl_5 , SF_6

Choose from the list an example of:

- (a) A tetrahedral molecule.
- (b) A V-shaped molecule with one lone pair of electrons on the central atom.
- (c) A V-shaped molecule with two lone pairs of electrons on the central atom.
- (d) An octahedral molecule.
- (e) A trigonal planar molecule.
- (f) A pyramidal molecule.
- (g) A linear molecule.
- (h) A trigonal bipyramidal molecule.

In all cases, give the electron arrangement of the central atom (in box formation) to show how the shape is worked out, draw the molecule and give the bond angles.

4 Work out the shape of the ethene molecule, C_2H_4 , and give the bond angles with an explanation.

5 Work out the shape of the following molecules. In each case name the shape (with respect to bonding pairs), draw the structure and show the bond angles.

- (a) PCl_3
- (b) BrF_3
- (c) SbCl_5
- (d) IF_4^-
- (e) SO_3^{2-}

3

Giant covalent bonding

1 Draw a section of the lattice of diamond and graphite.

2 Use your drawings to answer the following questions:

- What is the coordination number of carbon in each case?
- Explain why diamond is used for cutting and drilling but graphite is used as a lubricant.
- Explain why diamond is an electrical insulator but graphite is an electrical conductor.
- Despite the fact that graphite contains weak van der Waals bonds, it has a very high melting point. Why is this the case?
- Explain why diamond has a density of 3.51 g cm^{-3} , whereas for graphite the figure is 2.25 g cm^{-3} .
- What do the following bond lengths suggest about the nature of the bonding in graphite?

Bond	Length
C–C (graphite)	0.143 nm
C–C (diamond)	0.154 nm
C=C (ethene)	0.134 nm

3 Both silicon and carbon are in Group 4 of the Periodic Table, but their oxides have quite different properties.

- Draw a small section of the lattice of silicon dioxide and draw a diagram of the carbon dioxide molecule.
- Use your answer to (a) to explain why:
 - Carbon dioxide is quite soluble in water, but silicon dioxide does not dissolve in water.
 - Silicon dioxide melts at 1610°C whereas carbon dioxide melts at -56°C (at 5.2 A pressure).
 - Neither compound conducts electricity when solid, but carbon dioxide does conduct when dissolved in water.

3

Intermolecular bonding

1 The table gives the boiling points of some organic compounds.

Alkane	Formula	Relative molecular mass	Boiling point/K
Butane	$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$	58	273
Pentane	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	72	309
2,2-Dimethylpropane	$\text{C}(\text{CH}_3)_4$	72	283
Propanone	CH_3COCH_3	58	329
Chloroethane	$\text{CH}_3\text{CH}_2\text{Cl}$	64.5	285
Bromoethane	$\text{CH}_3\text{CH}_2\text{Br}$	109	311
Iodoethane	$\text{CH}_3\text{CH}_2\text{I}$	156	345

In your answers to the following questions, explain the origin of the intermolecular forces involved and express yourself clearly.

- Why does pentane have a higher boiling point than butane?
- Despite having the same relative molecular mass, why does 2,2-dimethylpropane boil at a lower temperature than pentane?
- Despite having the same relative molecular mass, why does propanone boil at a considerably higher temperature than butane?
- Bearing in mind your knowledge of the electronegativities of the halogens, why might you expect the boiling points of the halogenoalkanes (chloroethane, bromoethane, iodoethane) to increase in the opposite direction to the one shown in the table?
- Why do the boiling points of the halogenoalkanes increase in the direction shown?

- 2
- Look up the boiling points of the Group 4 hydrides and sketch a graph of boiling point (on the y-axis) against relative molecular mass (on the x-axis) of the different hydrides.
 - Look up the boiling points of the Group 6 hydrides and plot them on the same axes.
 - Explain fully the shapes of the two graphs.

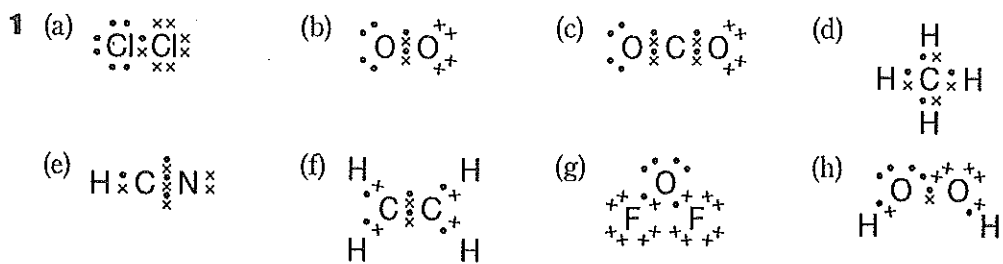
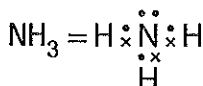
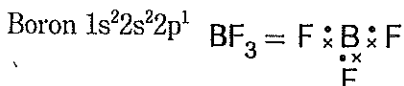
- 3
- Using your knowledge of intermolecular attractions, explain the following observations:
- Ethanol mixes with water in all proportions and there is virtually no temperature change on mixing.
 - With ethanol and cyclohexane, there is little mixing and there is a drop in temperature when the two liquids are added together.

3

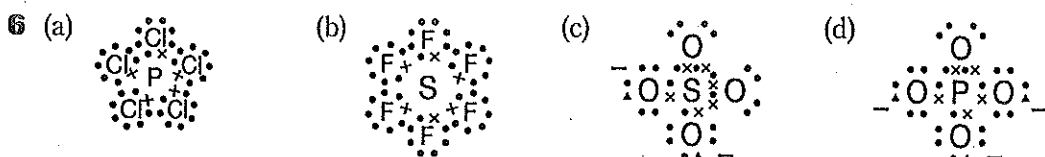
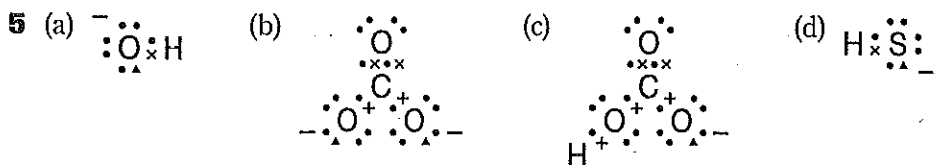
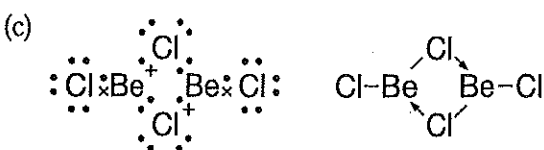
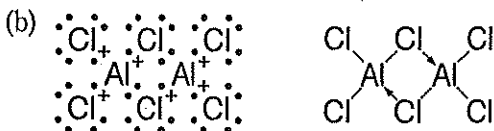
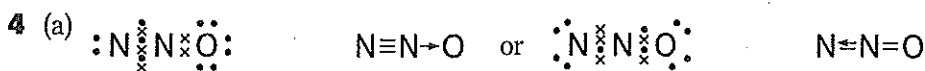
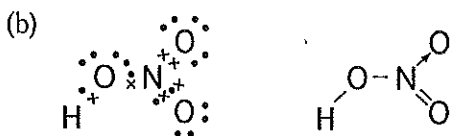
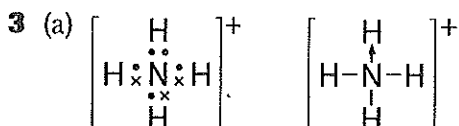
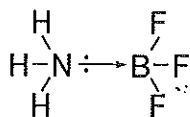
Hydrogen bonding

- 1 Carefully draw a diagram of two methanol molecules and use your diagram to explain fully the origin of the hydrogen bond between the two molecules.
- 2 Given that the electronegativity of nitrogen is the same as that of chlorine (3.0), explain why ammonia forms hydrogen bonds but hydrogen chloride does not.
- 3 How does hydrogen bonding account for the following observations? Use diagrams and drawings of structures to illustrate your answer.
 - (a) Relative molecular mass measurements of ethanoic acid often give the value of 120 despite the fact that the molecular formula of ethanoic acid is known to be $C_2H_4O_2$.
 - (b) Anhydrous calcium sulphate ($CaSO_4$) is much harder and more difficult to cleave than hydrated calcium sulphate ($CaSO_4 \cdot 2H_2O$).
 - (c) In samples of hydrogen fluoride vapour, molecules have been detected with a relative molecular mass of 100.
- 4 Account for the fact that hydrogen fluoride and ammonia can only form, on average, one hydrogen bond per molecule but water can form two. How does this fact lead to an explanation of the structure of ice?
- 5 Write short notes on how hydrogen bonding is significant in the structure of the DNA molecule.

Sheet 1

2 Nitrogen $1s^2 2s^2 2p^3$ Boron $1s^2 2s^2 2p^1$ 

BF_3 is electron deficient and accepts the lone pair from NH_3 with the formation of a dative bond:



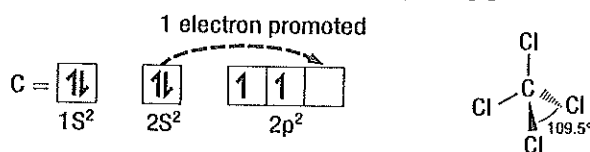
- 7 The distance between the nuclei and the shared pair of electrons increases on descending the table. Therefore the attraction between the positive nuclei and negative electrons decreases, and therefore bond energy decreases.

Sheet 2

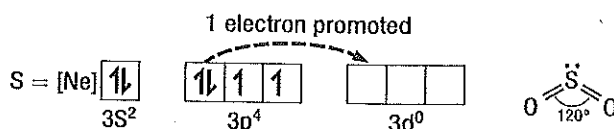
1 The valence shell electron pair repulsion theory (VSEPR): electron regions (lone pairs or bonding pairs) try to keep as far apart as possible; therefore the number of electron pairs determines the shape of the molecule.

- 2 Single bond–single bond weakest repelling power
 Multiple bond–multiple bond ↓
 Lone pair–lone pair Strongest repelling power

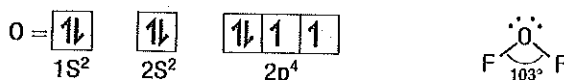
3 (a) CCl_4



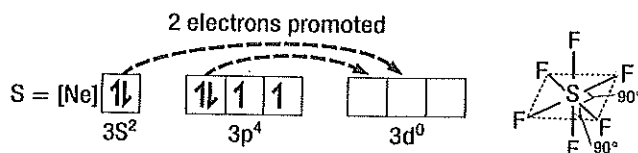
(b) SO_2



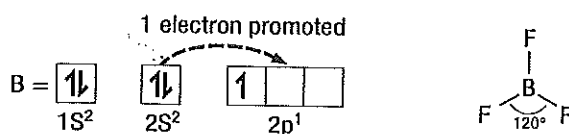
(c) F_2O



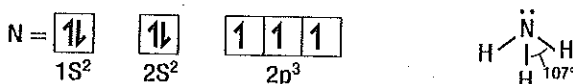
(d) SF_6



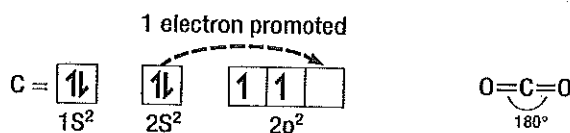
(e) BF_3



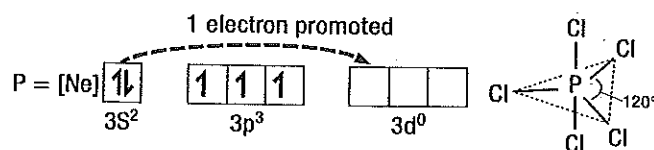
(f) NH_3

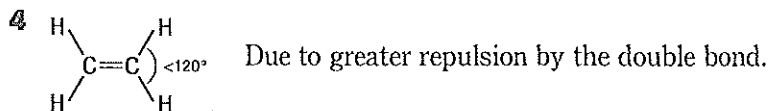


(g) CO_2

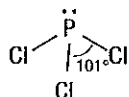


(h) PCl_5

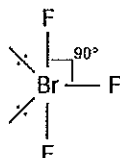




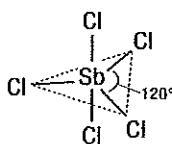
5 (a) PCl_3 = Trigonal pyramidal



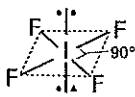
(b) BrF_3 = T-shaped



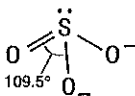
(c) SbCl_5 = Trigonal bipyramidal



(d) IF_4^- = Square planar



(e) SO_3^{2-} = Trigonal pyramidal



Sheet 3

1 Standard diagrams of graphite and diamond.

2 (a) Diamond: 4, graphite: 3.

(b) Diamond has strong covalent bonds throughout the structure, making it hard and strong in all directions. Graphite has strong bonds in planes but weak (van der Waals) attractions between the layers. The layers can slide over each other, enabling it to act as a solid lubricant.

(c) Graphite contains a sea of delocalised electrons between the layers; it conducts because of the movement of these electrons. Diamond does not have any delocalised electrons.

(d) To melt graphite, the strong covalent bonds within the layers need to be broken. This requires a great deal of energy – hence the high melting point (melting requires the disruption of ALL bonds).

(e) The weaker attraction between the layers in graphite means that there is a greater distance between the atoms of different planes than there is between atoms within a given plane; this leads to a slightly lower density than diamond where all bond lengths are the same.

(f) The C–C bond in graphite is intermediate in length between a single and a double due to the delocalisation of electrons within the graphite structure.

3 (a) Diagram of SiO_2 showing diamond-type lattice and standard diagram of the CO_2 linear molecule.

(b) (i) SiO_2 is a giant covalent structure. As such, there are no weaknesses within the structure and there is insufficient energy released in the attraction of the lattice to the polar water molecule to enable dissolving to occur. CO_2 contains polar bonds: these attract the polar water molecule enabling CO_2 to dissolve in (and react with) water.

(ii) CO_2 molecules are attracted to each other by weak polar attractions which require little energy to break, whereas SiO_2 requires a great deal of energy to break the covalent bonds throughout its structure.

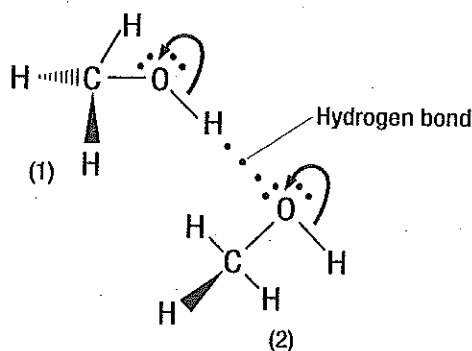
- (iii) Neither contains delocalised electrons which means they do not conduct when solid. When dissolved in water, some of the CO_2 molecules react with the water to form hydrogen carbonate (HCO_3^-) and hydroxonium (H_3O^+) ions; these ions are attracted to the opposite poles of the electricity source and enable the solution to conduct.

Sheet 4

- Pentane has more electrons than butane and therefore a greater induced dipole leading to stronger van der Waals attractions.
 - Despite having the same number of electrons, 2,2-dimethylpropane boils at a lower temperature because it has a branched chain, leading to a lower degree of chain interaction than pentane and less induced dipole attractions.
 - Propanone has permanent dipole attractions between its molecules (due to the polarity of the $\text{C}=\text{O}$ bond); these are stronger than van der Waals and hence the compound boils at a higher temperature than butane.
 - The electronegativities of the halogens are in the order $\text{Cl} > \text{Br} > \text{I}$. It would therefore be expected that chloroethane might have the highest boiling point as it will have the greatest dipole attractions between its molecules.
 - However, boiling points increase with M_r as this is an indication of increasing numbers of electrons and therefore increasing van der Waals attractions.
- Standard graphs of the hydrides. Group 4 hydrides increase in boiling point with increasing M_r due to increasing van der Waals attractions. In Group 6, H_2O has a much greater boiling point as the molecules can hydrogen-bond with each other. The other Group 6 hydrides increase in boiling point with M_r due to increasing van der Waals attractions.
- Both ethanol and water hydrogen-bond as pure liquids. Thus mixing involves breaking hydrogen bonds in order to form new hydrogen bonds with the other molecule. There is therefore little energy change on mixing and, because molecules with similar attractions tend to dissolve in each other, ethanol is soluble in water in all proportions.
 - If ethanol were to mix with cyclohexane, the strong hydrogen bonds between the ethanol molecules would need to be broken, which requires energy. However, the attraction of ethanol to cyclohexane would be by weaker van der Waals forces — there would be little energy release in this and the process would not be energetically viable.

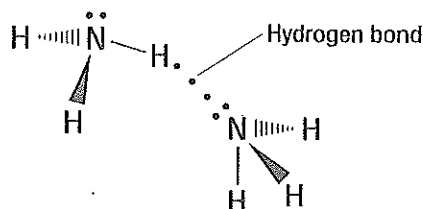
Sheet 5

- 1 Methanol is CH_3OH

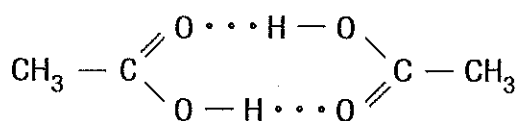


The polarised $\text{O}-\text{H}$ bond in molecule (1), leaves the hydrogen highly $\delta+$ (an exposed proton). This is strongly attracted to the lone pair of electrons on the oxygen of molecule (2) — this constitutes a hydrogen bond.

- 2 Nitrogen is a smaller atom than chlorine. There are therefore fewer electron energy levels between the outer electrons and the nucleus and there is less shielding of the nucleus. The bonding pair in the N-H bond is more attracted to the nitrogen nucleus (the bond is more polar) than is the case in the H-Cl bond. Ammonia can therefore form hydrogen bonds:



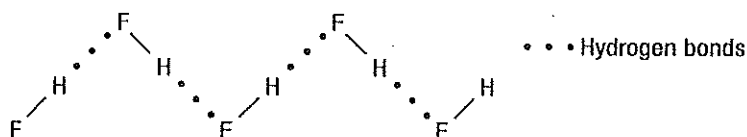
- 3 (a) Ethanoic acid can form a DIMER between its molecules, due to hydrogen bonding.



This leads to the measurements being twice that of the expected value ($C_2H_4O_2 = 60$).

- (b) $CaSO_4 \cdot 2H_2O$ has weaker hydrogen bonds between the layers of ions. These break with only a little force and the structure can be cleaved.
 (c) M_r of HF = 20. Due to hydrogen bonding between HF molecules, in the vapour state it can exist as $(HF)_5$:

i.e.



- 4 Despite having three lone pairs on the fluorine, HF only has *one* hydrogen atom. Likewise, although NH_3 has three hydrogen atoms, there is only *one* lone pair on the nitrogen. These molecules are therefore limited to forming *on average* one hydrogen bond per molecule. However in H_2O there are *two* hydrogens and *two* lone pairs. This enables a water molecule to form on average *two* hydrogen bonds per molecule. The 3-D structure of ice depends on this fact (refer to *Resource Sheet 5*).
- 5 Refer to *Resource Sheet 7* for base-pairs in DNA.

1 What is a covalent bond?

A shared pair
of electrons

2 How is a dative bond (a) different to and (b) the same as a covalent bond?

- (a) Both electrons
originate from one atom.
(b) Once formed it is
indistinguishable from a
normal covalent bond.

3 Draw a diagram to show the dative bonding in carbon monoxide.



4 Name the shape, and give the bond angles, in CH_4 and H_2O .

CH_4 : tetrahedral, 109.5
 H_2O : V-shaped, 105

5 Why are the bond angles for the molecules in Question 4 different?

Lone pairs repel more than
bonding pairs.

6 What is the coordination number of carbon in diamond and graphite?

Diamond: 4
Graphite: 3

7 Why does graphite conduct electricity?

Because it contains a sea of
delocalised electrons.

8 What is meant by electronegativity?

The ability of an atom to
attract the electrons in a
covalent bond.

9 How does the electronegativity of the halogens vary on descending group 7?

It decreases.

10 List the three main types of intermolecular attraction in order of strength.

Hydrogen bonding > dipole-
dipole > van der Waals

11 How does the strength of a hydrogen bond compare to a covalent bond?

It is approximately ten times
weaker.

12 Even though CO_2 has polar bonds, it has no dipole moment. Explain.

The polar bonds act in equal
and opposite directions.

13 List three things which must be present for hydrogen bonding to occur.

- (a) N, O or F atoms.
(b) Attached to a hydrogen
bond.
(c) At least one lone pair on
the N, O or F.

3

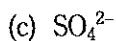
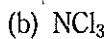
- 1 (a) Draw dot-and-cross diagrams to show the formation of:
 (i) A chlorine molecule (ii) A hydrogen chloride molecule (2)

- (b) Using the above two molecules to illustrate your answer, explain what you understand by the terms:
 covalent bond; polar; electronegativity. (3)

- 2 When ammonia, NH_3 , reacts to form the ammonium ion, a dative covalent bond is formed and the resulting molecular ion is tetrahedral. With the aid of clear diagrams, explain this statement fully. (4)

- 3 For each of the following molecules, draw and name the shape (with respect to bonds formed) and give the bond angles: (8)

- (a) BCl_3



- 4 Draw the shape of the following molecules and state whether or not they have a dipole moment, i.e. whether a stream of the liquid would be deflected by a charged rod: CCl_4 ; CHCl_3 ; CH_2O (6)

- 5 Ethane, C_2H_6 , has a boiling point of 184 K while pentane, C_5H_{12} has a boiling point of 309 K.
(a) What sort of intermolecular attraction will exist between these molecules? Explain its origin. (4)

(b) Explain why their boiling points are different.

(2)

6 What kinds of intermolecular attractions would exist in the following molecules? (4)

(a) Trichloromethane CHCl_3

(b) Ethanol $\text{CH}_3\text{CH}_2\text{OH}$

7 Explain fully why ammonia is able to hydrogen bond and draw a diagram of two ammonia molecules to illustrate this bonding. (4)

8 (a) Draw a small section of the lattices of graphite and diamond. (4)

(b) Use your diagrams to discuss the following:

(i) Graphite conducts electricity well but diamond does not.

(8)

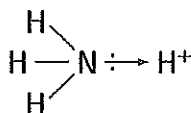
(ii) Graphite has weak forces in its structure but still has a very high melting point.

(iii) Graphite can be used as a lubricant but diamond is used for drill bits.

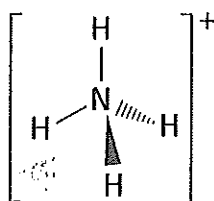
(iv) In the two structures, carbon has a different coordination number.

- 1 (a) Standard dot-and-cross diagrams.
 (b) Covalent bond – a shared pair of electrons. Both the above molecules have a single covalent bond between the atoms. The HCl molecule is polar because the chlorine atom is more electronegative than hydrogen, i.e. the electrons in the covalent bond are not equally shared, they have a stronger affinity for chlorine.

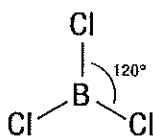
2 A dative bond is formed between the lone pair of electrons on the nitrogen and an H^+ ion.



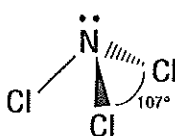
This leads to the formation of NH_4^+ and by the VSEPR theory this molecule has a tetrahedral shape.



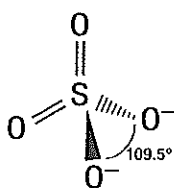
3 (a) Shape = Trigonal planar



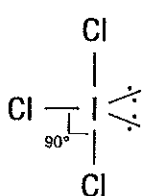
(b) Shape = Trigonal pyramidal



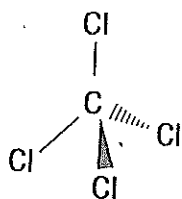
(c) Shape = Tetrahedral



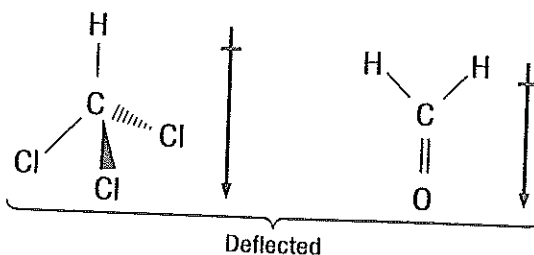
(d) Shape = T-shaped



4



Not deflected



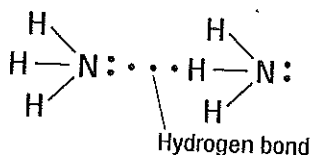
5

- (a) Both molecules have van der Waals attractions. These arise from the fact that electron density is constantly fluctuating within a molecule. One molecule will induce a dipole in a neighbouring molecule and the weak attraction which is produced by this dipole is called a van der Waals attraction. (A diagram could be added to enhance the answer.)
- (b) Pentane has more electrons per molecule than ethane; it is therefore able to establish a greater induced dipole.

6

- (a) Dipole-dipole and van der Waals
 (b) Hydrogen bonding and van der Waals

7



Ammonia can hydrogen-bond because it has a hydrogen atom attached to a lightly electronegative nitrogen atom. The N-H bond is therefore extremely polar, leaving the hydrogen as an exposed proton, which is strongly attracted to the lone pair of electrons on a neighbouring nitrogen.

8

- (a) Standard drawings of the two structures.
- (b) (i) Graphite has a sea of delocalised electrons which enables it to conduct. All the electrons in diamond are involved in covalent bond formation.
- (ii) Melting requires the disruption of all bonds within a structure; although graphite does contain weak van der Waals forces between layers, the bonding within a layer is strong and giant in nature.
- (iii) Weak forces between the layers in graphite enable the layers to slide over each other making it a lubricant. Diamond has no such weaknesses.
- (iv) In diamond, carbon has a tetrahedral structure in which each atom has four neighbours, leading to a coordination number of four. In graphite, each carbon has three neighbours within a plane (coordination number three).