3 Chemical bonding

This topic introduces the different ways by which chemical bonding occurs and the effect this can have on physical properties.

3.3 Intermolecular forces, electronegativity and bond properties ☐

INTERMOLECULAR FORCES

3 Chemical bonding

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	Learning outcomes Candidates should be able to:
3.3 Intermolecular forces, electronegativity and bond properties	a) describe hydrogen bonding, using ammonia and water as simple examples of molecules containing N–H and O–H groups b) understand, in simple terms, the concept of electronegativity and apply it to explain the properties of molecules such as bond polarity (see also Section 3.3(c)), the dipole moments of molecules (3.3(d)) and the behaviour of oxides with water (9.2(c)) c) explain the terms *bond energy*, *bond length* and *bond polarity* and use them to compare the reactivities of covalent bonds (see also Section 5.1(b)(ii)) d) describe intermolecular forces (van der Waals' forces), based on permanent and induced dipoles, as in, for example, $CHCl_3$(l); Br_2(l) and the liquid Group 18 elements

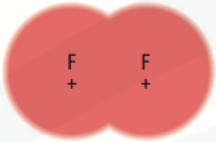
BOND POLARITIES

The example in which two hydrogen atoms bond is simple because both atoms are the same.

Also, each one has a single proton and a single electron, so the attractions are easy to identify.

However, many covalent bonds form between two different atoms.

These atoms often have different attractions for shared electrons.



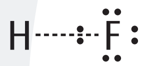
electrons symmetrically distributed in covalent bond

BOND POLARITIES

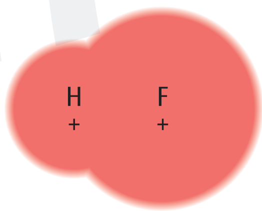
Now consider a diatomic molecule composed of two different elements; HF is a common example.

It has been experimentally shown that the electrons in the H—F bond are not equally shared; the electrons spend more time in the vicinity of the fluorine atom.

This is because fluorine is a more electronegative element than hydrogen.



electrons lie, on average, closer to F



$^{\delta+}H — F^{\delta-}$

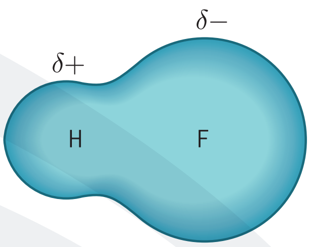
POLAR BONDS

Polar covalent bond is the preferred term for a bond made up of unequally shared electron pairs.

One end of the bond (in this case, the F atom) is more electron rich (higher electron density), hence, more negative.

The other end of the bond (in this case, the H atom) is less electron rich (lower electron density), hence, more positive.

These two ends, one somewhat positive and the other somewhat negative may be described as electronic poles, hence the term polar covalent bonds.



POLAR BONDS

In a polar covalent bond, the shared electrons, which are in a molecular orbital, are more likely to be found nearer to the atom whose electronegativity is higher.

This unequal distribution of charge makes the bond polar covalent.

To emphasize the dipole nature of the HF molecule, the formula can be written as $H^{\delta+}\ F^{\delta-}$. The symbol δ means partial.

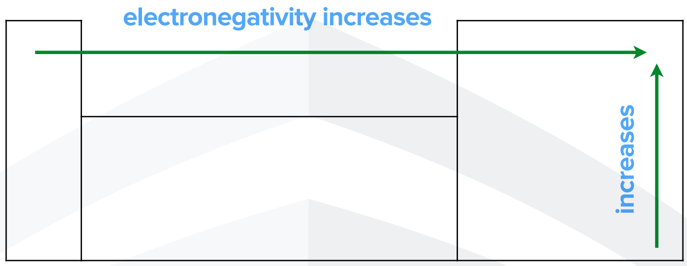
With polar molecules, such as HF, the symbol δ+ is used to show a partial positive charge on one end of the molecule.

Likewise, the symbol δ− is used to show a partial negative charge on the other end.

ELECTRONEGATIVITY

Electronegativity is a measure of the ability of an atom to attract electrons in a chemical bond. Elements with high electronegativity have a greater ability to attract electrons than do elements with low electronegativity.

The four most electronegative elements are F, O, N, Cl.



Electronegativity increases across a period and decreases down a group

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BOND POLARITIES

Non-polar bond

- Similar atoms have the same electronegativity
- They will both pull on the electrons to the same extent
- The electrons will be equally shared

Polar bond

- Different atoms have different electronegativities
- One will pull the electron pair closer to its end
- It will be slightly more negative than average, δ-
- The other will be slightly less negative, or more positive, δ+
- A dipole is formed and the bond is said to be polar
- Greater electronegativity difference = greater polarity

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MOLECULAR POLARITY

The electronegativity difference between two atoms covalently bonded together results in the electrons lying more towards one atom than the other. We call such a bond polar.

However, whether an overall molecule is polar also depends on the shape of the molecule.

The polarity of molecules is distinct from the polarity of individual bonds; a non-polar molecule may have polar bonds.

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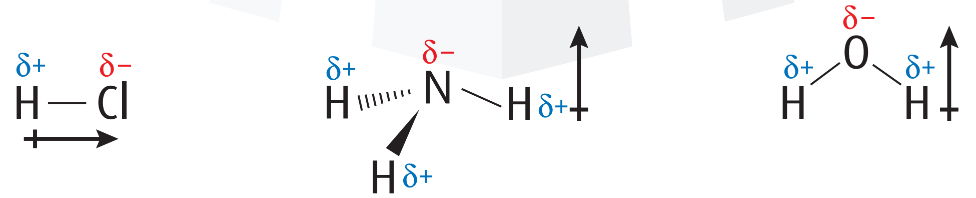
POLAR MOLECULES

For a molecule to be polar it must have a positive end to the molecule and a negative end. For instance, HCl, NH_3 and H_2O are all polar.

These molecules all have an overall dipole moment, and the arrow indicates the direction of the dipole moment.



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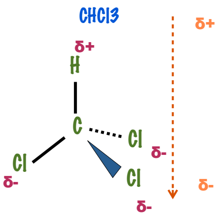
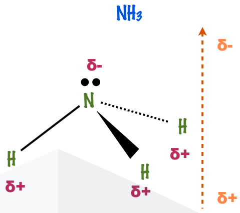
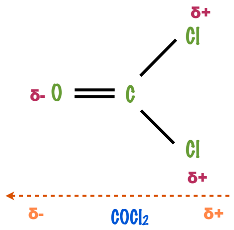
POLAR MOLECULES



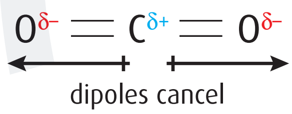




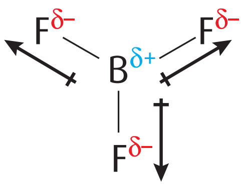
NON-POLAR MOLECULES

Although individual bonds may be polar, the overall molecule may be non-polar if, owing to the symmetry of the molecule, the dipole moments of the individual bonds cancel out.

CO_2 is a non-polar molecule. Each C–O bond is polar, because oxygen is more electronegative than carbon, but overall the dipoles cancel so that there is no overall dipole moment and the molecule is non-polar.

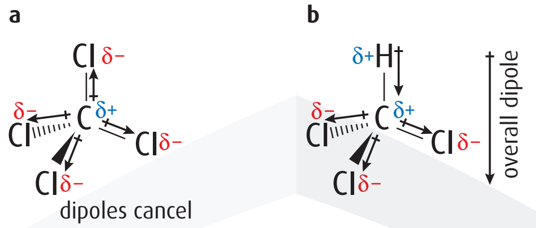


BF_3 is also non-polar. Again, each individual bond is polar but the dipoles cancel.



NON-POLAR MOLECULES

In contrast, a molecule containing polar bonds may be either polar or non-polar depending on the relative arrangement of the bonds and any lone pairs of electrons, e.g. CCl_4 is non-polar, but $CHCl_3$ is polar.



a CCl_4 is non-polar because the individual dipoles cancel. **b** $CHCl_3$ is polar because the dipoles do not cancel; there is a positive end to the molecule and a negative end. Although the C in $CHCl_3$ is shown as δ+, it is not as positive as the H (as C is more electronegative than H); therefore, the C is slightly negative compared with the H, although it is positive overall in the molecule.

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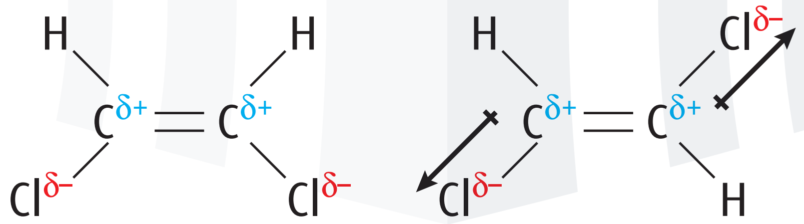
DIPOLE MOMENTS



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SKILL CHECK 1

Decide whether the following bonds are polar or non-polar. if the bond is polar, state which is the δ+ atom, and explain whether or not the molecule is polar:

A C-O as in CO_2

B C-I as in CH_3I

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SKILL CHECK 2

Predict which of the following bonds are polar, and, if polar, in which direction the electrons are pulled:

a. O—S b. Cl—Cl c. C—N d. I—Cl

Predict whether each of the following molecules is polar:

a. BCl_3 b. HCl c. NH_3 d. $SiCl_4$

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SKILL CHECK 3

Predict whether each of the following molecules is polar:

a. CO_2 **b**. BrCl **c**. SCl_2 **d**. CS_2

Using the shapes drawn on slide 48 to 51, predict whether each of the following molecules is polar:

a. CF_4 **b.** Cl_2O **c**. PF_3 **d**. NCl_3 **e**. $SiCl_4$ **f.** SO_3

INTERMOLECULAR FORCES

Intermolecular forces are weak attractive forces between molecules.

These forces determine such properties as the solubility of one substance in another and the freezing and boiling points of liquids.

Without intermolecular forces there could be no molecular liquids or solids.

INTERMOLECULAR FORCES

Weak intermolecular forces arise from electrostatic attractions between dipoles, including attractions between:

- Molecules with permanent dipoles such as hydrogen chloride
- A permanent dipole in one molecule and a dipole induced in a neighbouring molecule, such as the attraction between iodine and water
- Temporary dipoles are created fleetingly in non-polar atoms or molecules

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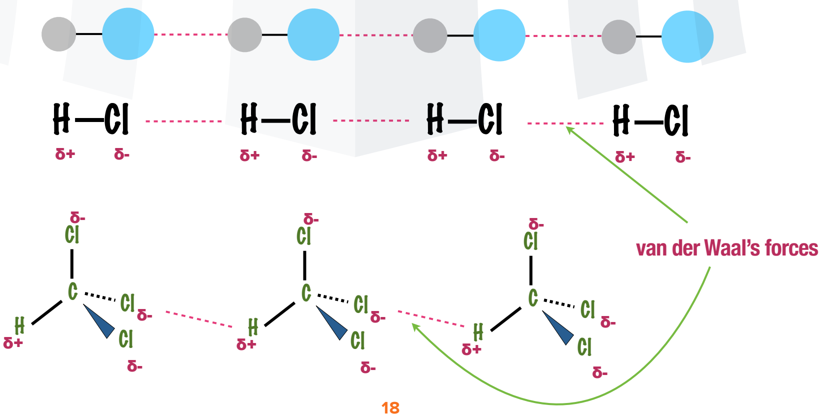
VAN DER WAALS' FORCES DUE TO PERMANENT DIPOLES

Van der Waal's forces due to permanent dipoles are interactions between polar molecules - the positive end of one molecule attracts the negative end of a neighbouring molecule.



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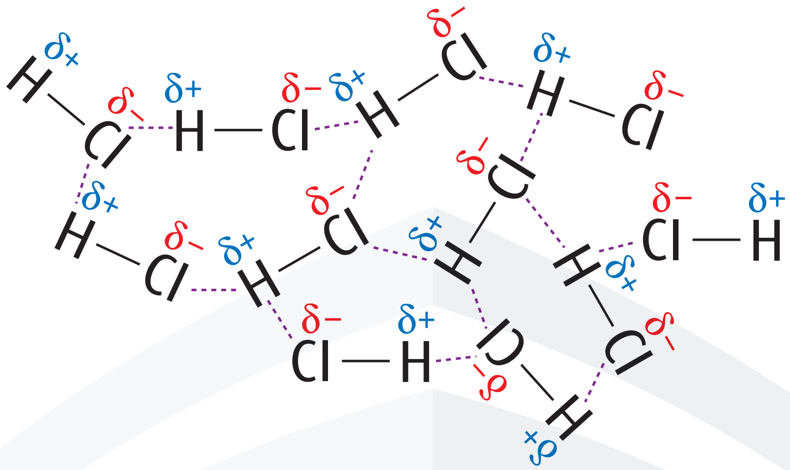
VAN DER WAALS' FORCES DUE TO PERMANENT DIPOLES



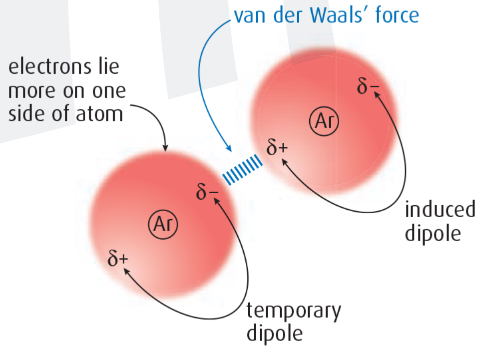
VAN DER WAALS' FORCES IN NON-POLAR MOLECULES

Intermolecular forces also exist in non-polar molecules. Van der Waal's forces due to induced dipoles are the intermolecular attraction resulting from the uneven distribution of electrons and the creation of temporary dipoles.

Because electrons move quickly in orbitals, their position is constantly changing; at any given instant they could be anywhere in an atom.

The possibility will exist that one side will have more electrons than the other.

This will give rise to a dipole.



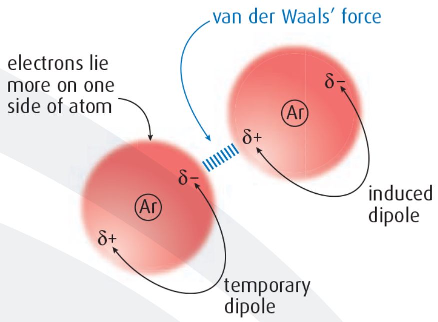
VAN DER WAALS' FORCES DUE TO INDUCED DIPOLES

Consider liquid argon. The electrons in an atom are in constant motion, and at any one time the electrons will not be symmetrically distributed about the nucleus.

This results in a temporary (instantaneous) dipole in the atom, which will induce an opposite dipole in a neighbouring atom.

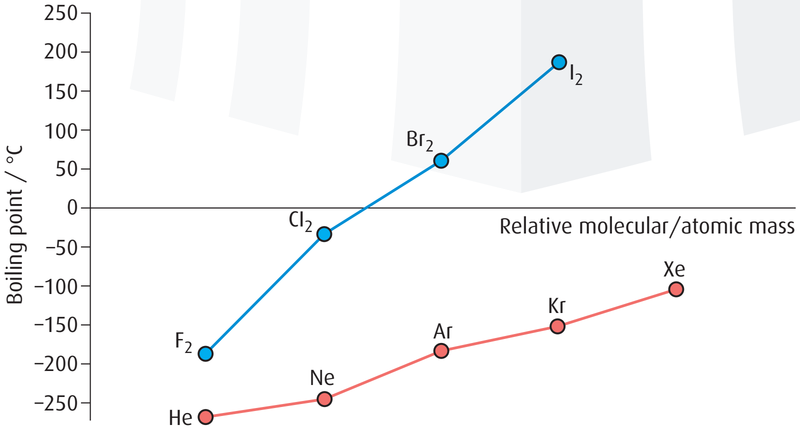
These dipoles will attract each other so that there is an attractive force between atoms.

Although the dipoles are constantly disappearing and reappearing, the overall force between the argon atoms is always attractive, because a dipole always induces an opposite one.

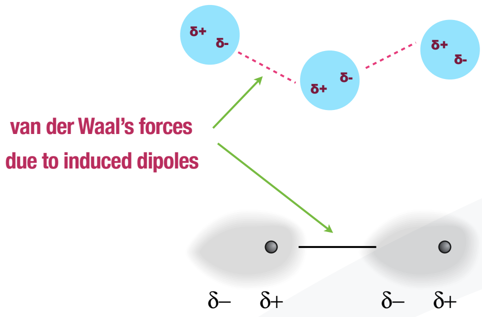


VAN DER WAALS' FORCES DUE TO INDUCED DIPOLES

In general, van der Waals' forces get stronger as the number of electrons in a molecule increases. As the number of electrons increases, the relative molecular mass also increases, resulting in an increase in the strength of van der Waals' forces.



VAN DER WAALS' FORCES DUE TO INDUCED DIPOLES



	Electrons	b.p. / °C
NOBLE GASES		
He	2	-269
Ne	10	-246
Ar	18	-186
Kr	36	-152
ALKANES		
CH_4	10	-161
C_2H_6	18	-88
C_3H_8	26	-42

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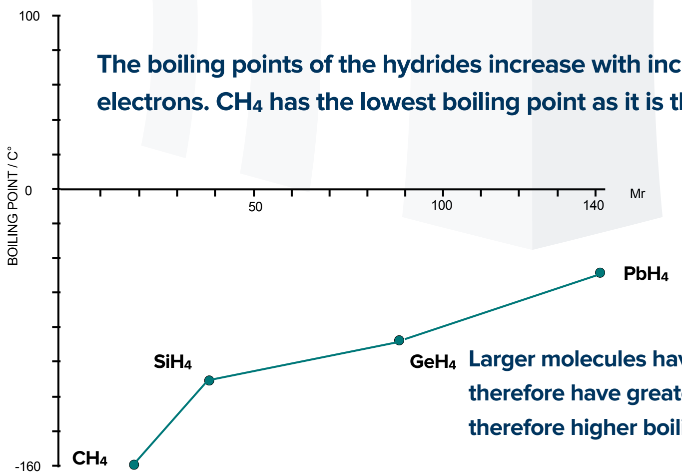
EXAMPLES OF VAN DER WAAL'S

BOILING POINTS OF HYDRIDES OF GROUP 14

The boiling points of the hydrides increase with increasing number of electrons. CH_4 has the lowest boiling point as it is the smallest molecule.



Larger molecules have more electrons and therefore have greater intermolecular forces and therefore higher boiling points.

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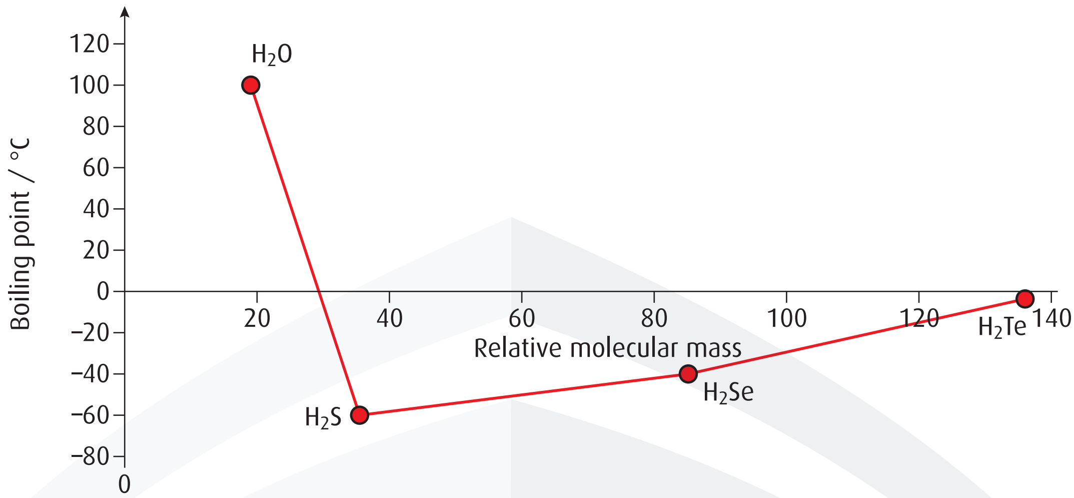
HYDRIDES OF GROUP 16



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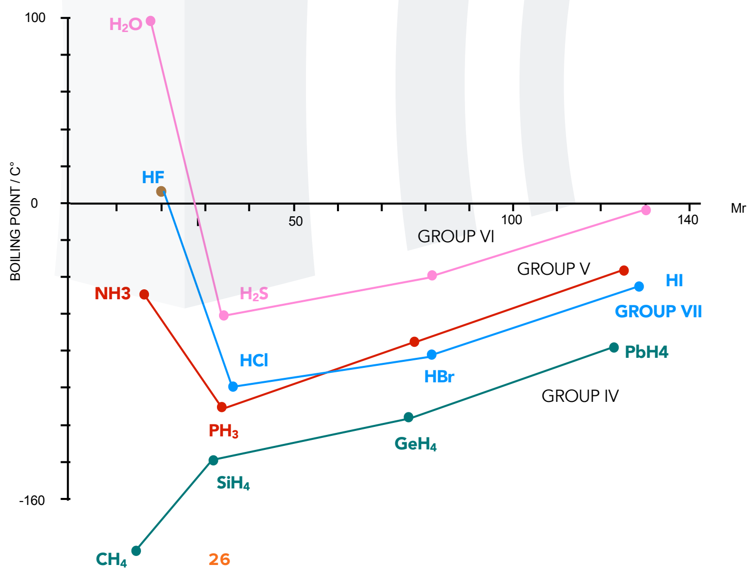
HYDROGEN BONDING

The higher than expected boiling points of NH_3, H_2O and HF are due to intermolecular **HYDROGEN BONDING**



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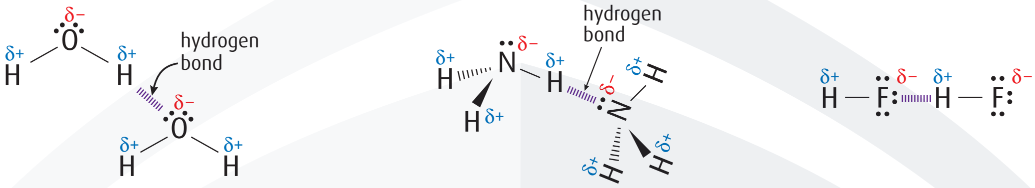
HYDROGEN BONDING

Strong hydrogen bonds can form with a hydrogen atom that is covalently bonded to very electronegative atoms in the upper-right part of the periodic table: nitrogen, oxygen, and fluorine.

When a hydrogen atom bonds to an atom of N, O, or F, the hydrogen atom has a large, partially positive charge.

The partially positive hydrogen atom of polar molecules can be attracted to the unshared pairs of electrons of neighbouring molecules.



HYDROGEN BONDING

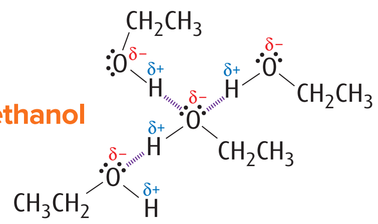
One reason that hydrogen bonds are such strong forces is because the hydrogen atom is small and has only one electron.

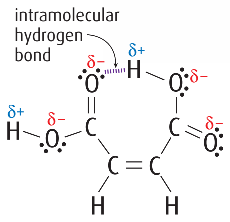
When that electron is pulled away by a highly electronegative atom, there are no more electrons under it. Thus, the single proton of the hydrogen nucleus is partially exposed.

As a result, hydrogen's proton is strongly attracted to the lone pair of electrons of other molecules. The combination of the large electronegative difference (high polarity) and hydrogen's small size accounts for the strength of the hydrogen bond.

EXAMPLES OF HYDROGEN BONDING

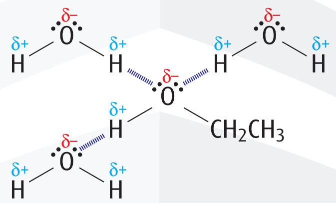
ethanol





but-2-ene-1,4-dioic acid

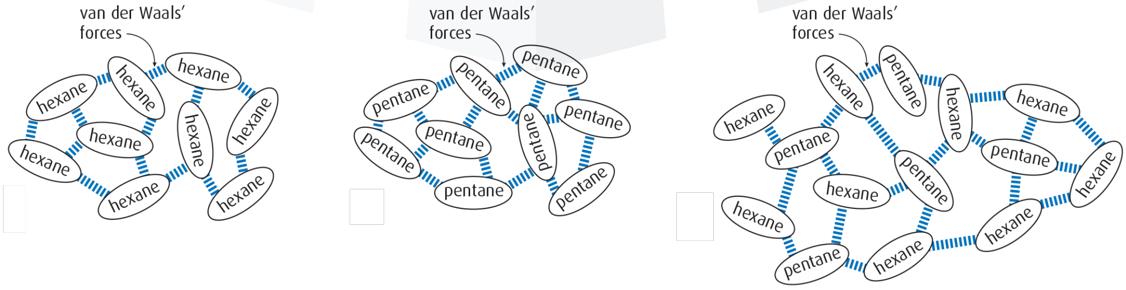
ethanol in water



SOLUBILITY

Generally a substance will dissolve in a solvent if the intermolecular forces in the solute and solvent are similar. E.g. pentane is readily soluble in hexane but not in water.

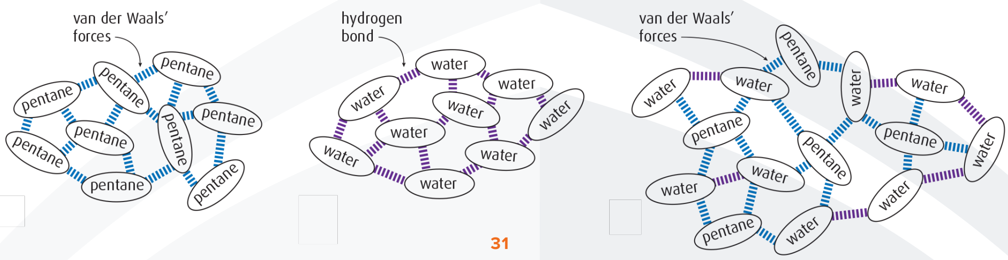
The amount of energy required to break the van der Waals' forces in pure hexane and pure pentane is paid back when van der Waals' forces are formed between the molecules of hexane and pentane



SOLUBILITY

Pentane does not dissolve in water because there is hydrogen bonding between water molecules.

If pentane were to dissolve in water there would be van der Waals' forces between water molecules and pentane. The energy released if van der Waals' forces were to form between water molecules and pentane molecules would not pay back the energy required to break the hydrogen bonds between water molecules, as hydrogen bonds are stronger than van der Waals' forces

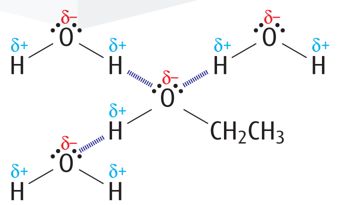


SOLUBILITY

Ethanol (C_2H_5OH) is very soluble in water, because ethanol is able to form hydrogen bonds with the water.

The hydrogen bonding between water and ethanol molecules in the solution releases energy and pays back the energy to break the hydrogen bonds in pure water and pure ethanol.

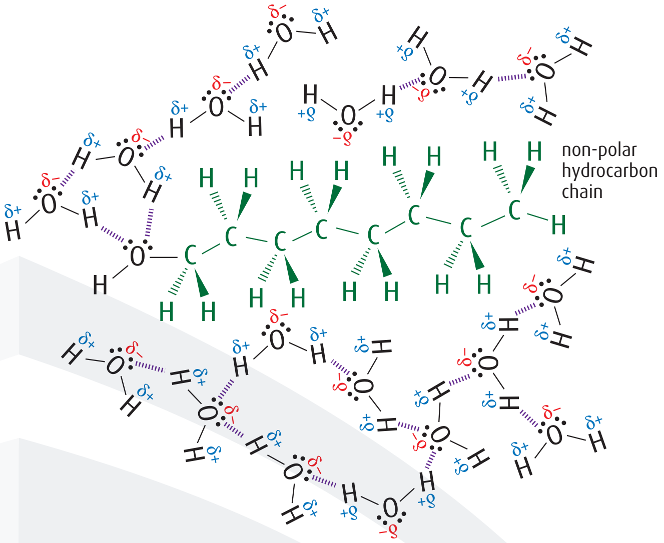
ethanol in water



SOLUBILITY

Octan-1-ol is insoluble in water. Although there is some hydrogen bonding between the O–H group of the alcohol and the water molecules, the long hydrocarbon chain prevents water molecules on either side from hydrogen bonding to each other.

Energy is needed to break the hydrogen bonds between the water molecules, but this is not paid back as only van der Waals' forces form between the water molecules and the hydrocarbon part of the molecule.



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SKILL CHECK 4

Explain why, in comparison with the other group 6 hydrides, water has an anomalous boiling temperature.

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SKILL CHECK 5

State all the forces operating between molecules of:

(a) ammonia, NH_3

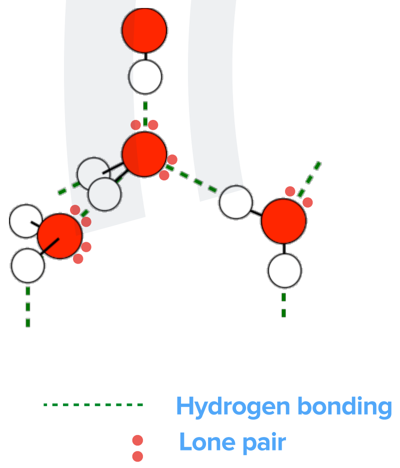
(b) methane, CH_4

(c) oxygen fluoride, OF_2

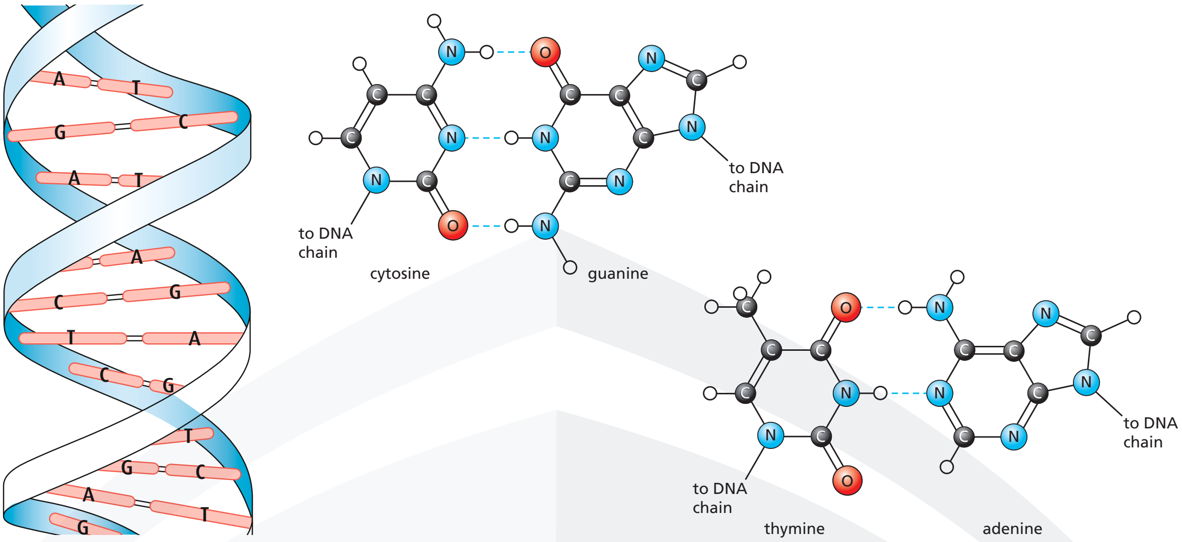
HYDROGEN BONDING IN ICE

- Each water molecule is hydrogen-bonded to 4 others in a tetrahedral formation
- Ice has a “diamond-like” structure
- Volume is larger than the liquid making it less dense
- When ice melts, the structure collapses slightly and the molecules come closer; they then move a little further apart as they get more energy as they warm up

This is why water has a maximum density at 4°C and ice floats.



HYDROGEN BONDING IN DNA



SKILL CHECK 6

What is involved when a hydrogen bond is formed between two molecules?

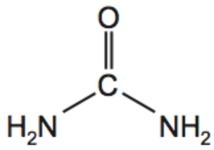
A a hydrogen atom bonded to an atom less electronegative than itself

B a lone pair of electrons

C an electrostatic attraction between opposite charges

SKILL CHECK 7

Which types of intermolecular forces can exist between adjacent urea molecules?



urea

A hydrogen bonding

B permanent dipole-dipole forces

C temporary induced dipole-dipole forces

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