

Shapes of molecules and ions

Valence-shell electron-pair repulsion theory

The shape of a molecule is determined by several factors:

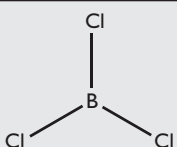
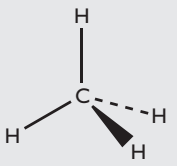
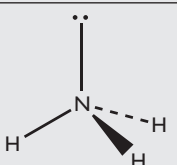
- The number of electron pairs around the atom of interest, both lone pairs and bond pairs.
- The electrons arrange themselves as far apart as possible.
- Lone pair–lone pair repulsions are greater than lone pair–bond pair repulsions, which in turn are greater than bond pair–bond pair repulsions. The repulsions between electrons modify the bond angles. Thus in methane the H–C–H angle is 109.5° , in ammonia the H–N–H angle is 107° and in water the H–O–H angle is 104° .

The shapes of analogous molecules can be predicted from those given above. The shape of methane (CH_4) is the same as that of silane (SiH_4), phosphine (PH_3) has a similar shape to ammonia (NH_3) and the shape of water (H_2O) is similar to that of hydrogen sulfide (H_2S).

A double or triple bond is stereochemically equivalent to a single bond.

Species with single bonds only

The arrangement of the bonds depends on the number of electron pairs in total. The name of the shape depends on the position of the atom centres only.

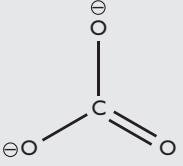
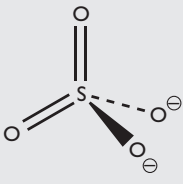
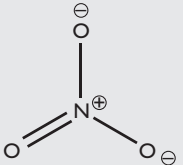
Name	Formula	Bond pairs	Lone pairs	Shape	Structure
Beryllium chloride	BeCl_2	2	0	Linear	$\text{Cl}-\text{Be}-\text{Cl}$
Boron trichloride	BCl_3	3	0	Trigonal planar	
Methane	CH_4	4	0	Tetrahedral	
Hydrogen chloride	HCl	1	3	Linear	$\text{H}-\text{Cl}$
Ammonia	NH_3	3	1	Pyramidal	

Name	Formula	Bond pairs	Lone pairs	Shape	Structure
Ammonium ion	NH_4^+	4	0	Tetrahedral	
Water	H_2O	2	2	Bent	
Phosphorus pentachloride (gas phase only — the solid is PCl_4^+ and PCl_6^- ions)	PCl_5	5	0	Trigonal bipyramidal	
Sulfur hexafluoride	SF_6	6	0	Octahedral	

Species with double bonds

Stereochemically a double bond is equivalent to a single bond.

Name	Formula	Single bonds	Double bonds	Lone pairs	Shape	Structure
Carbon dioxide	CO_2	0	2	0	Linear	$\text{O}=\text{C}=\text{O}$
Sulfur dioxide	SO_2	0	2	1	Bent	
Sulfite ion	SO_3^{2-}	2	1	1	Pyramidal	

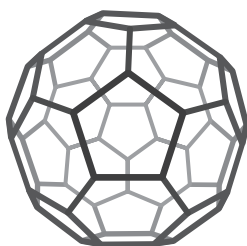
Name	Formula	Single bonds	Double bonds	Lone pairs	Shape	Structure
Carbonate ion	CO_3^{2-}	2	1	0	Trigonal planar	
Sulfate ion	SO_4^{2-}	2	2	0	Tetrahedral	
Nitrate ion	NO_3^-	1	2	0	Trigonal planar	

Diamond, graphite and the fullerenes

Diamond has layers of hexagonal rings that are puckered, not flat: each carbon atom is bonded to four others throughout the lattice by covalent bonds. Diamond is a poor electrical conductor because it has no delocalised electrons. It is a good thermal conductor, since the stiff lattice readily transmits vibration. It has a high melting temperature (c. 3800°C).

Graphite has layers of flat hexagons with the fourth bond delocalised along the plane of the carbons. Bonds between layers are van der Waals and therefore weak. Graphite is a stack of giant molecules. It is a good electrical conductor parallel to the planes but a poor thermal conductor. It sublimes at 3730°C.

Buckminsterfullerene (C_{60}) was discovered in the late 1990s. It is a sphere of pentagons and hexagons, exactly like a football. It is red and soluble in organic solvents.



C_{60}

Related to fullerenes are carbon nanotubes, which are tubular structures, made from carbon hexagons with diameters from one to several nanometres. Their structure is like a roll of wire netting. They can be capped at each end with a hemisphere of carbon atoms to make nanometre-sized capsules. Much research is being conducted to develop these tiny capsules so that they can deliver drugs and other treatments to tumour cells with great precision, avoiding damage to healthy tissue. Another potential application is in building electronic devices even smaller than those presently available.

Intermediate bonding and bond polarity

Electronegativity and polarity

Ionic and covalent bonds are extremes. Ionic bonding involves complete electron transfer and covalent bonding involves equal sharing of electrons in pairs. In practice, bonding is intermediate between these two forms in most compounds, with one type being predominant.

Electronegativity

The attraction a bonded atom has for electrons is called its **electronegativity**. There are several electronegativity scales, the commonest being the Pauling scale. Fluorine is the most electronegative element with a value of 4, caesium the least at 0.7. There are no units.

- Atoms with the same electronegativity bond covalently with equal sharing of electrons.
- Atoms with different electronegativity form:
 - polar covalent bonds if the difference is not too large — up to about 1.5
 - ionic bonds if the difference is more than about 2

Polarity

Cations can distort the electron clouds of anions (which are generally larger). This distortion leads to a degree of electron sharing and hence some covalence in most ionic compounds.

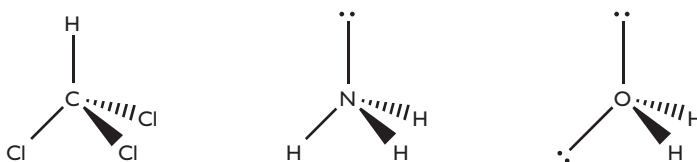
- Small cations with a high charge (2+ or 3+) have a high charge density. They can polarise anions and have therefore a high polarising power.
- Large anions do not hold on to their outer electrons very tightly, so they can be easily distorted. Such ions are polarisable.
- Magnesium chloride (MgCl_2) has a polarising cation but a not very polarisable anion. There is some covalent character in the compound, but much more in magnesium iodide (MgI_2) since the large I^- ion is highly polarisable.

Polarity in molecules

A molecule may have polar covalent bonds, but will not be polar overall if the bond polarities cancel because of the shape of the molecule. Thus boron trifluoride (BF_3) has polar bonds but no overall polarity because the trigonal planar shape means the bond polarities cancel. The same is true for the tetrahedral carbon tetrachloride (CCl_4). Ammonia (NH_3) has polar bonds and is polar overall because its pyramidal shape does not cause the individual polarities to cancel.



These molecules have polar bonds, but the polarities cancel overall because of the symmetry of the molecule.



These molecules also have polar bonds, but the individual polarities do not cancel so the molecules are polar overall.

Intermolecular forces

Types of intermolecular force

There are several types of intermolecular force. They depend to some extent on the distortion of the electron distribution of one molecule by another. At close range there are also repulsive forces in action. In decreasing order of strength, the attractive forces are:

- hydrogen bonds
- permanent dipole–permanent dipole forces
- permanent dipole–induced dipole forces
- temporary dipole–induced dipole forces

The last two forces are often referred to generically as **van der Waals** forces.

Hydrogen bonds

Hydrogen bonds are electrostatic bonds between a hydrogen atom covalently bonded to an electronegative atom (N, O or F) and another N, O or F atom, usually on a different molecule. The hydrogen is made highly δ^+ and thus is attracted to a *lone pair*

of electrons on the electronegative atom, which is δ^- . The three atoms involved in the bond are collinear.

Hydrogen bond strength in hydrogen fluoride (HF) is around 150 kJ mol^{-1} , but most others are between 60 and 20 kJ mol^{-1} . Hydrogen bonding is responsible for the high boiling temperatures of NH_3 , H_2O and HF compared with the other hydrides in their groups and for the high solubility of alcohols and sugars in water. The hydrogen bonds formed between the solute and the water are of similar strength to the hydrogen bonds in water itself.

Permanent dipole–permanent dipole forces

Polar molecules attract via their permanent dipoles. Polar molecules have higher boiling temperatures than non-polar molecules of similar size.

Permanent dipole–induced dipole forces

These forces arise where a polar molecule distorts the electron density on a non-polar molecule, giving rise to a temporary dipole that attracts the permanent dipole. The strength of this force depends on the polarisability of the non-polar molecule, which generally increases with increasing numbers of electrons in the molecule.

Temporary dipole–induced dipole forces

These are sometimes called **London** forces. They are the only interaction in non-polar molecules or in single atoms such as the monatomic inert or noble gases. These forces arise from a temporary dipole inducing a complementary dipole in an adjacent molecule. These dipoles are always shifting, but are induced in phase and give a net attraction. Their strength depends on the polarisability of the molecule.

Properties of materials

Intermolecular forces (including those between ions or atoms — but be clear which you are talking about) determine the physical properties of a substance such as its melting and boiling temperatures, hardness and density. The forces between particles in liquids are similar to those in solids, but because of thermal agitation they are less directional.

Change of state

In solids the particles vibrate about a mean position in the crystal lattice. Heating increases the amplitude of the vibration until a point where the interparticular forces are overcome and the lattice collapses — the solid melts. Just above the melting temperature, liquids often have considerable order to their structure; further heating causes movement over increasing distances, until the temperature is such that the vapour pressure of the liquid is the same as the external pressure. At this temperature the interparticular forces are overcome and the liquid boils.

Noble gases

The only interatomic forces are dispersion (London) forces arising from the limited movement of electrons within the atom. The smaller the atom, the less the movement

and so the weaker the attractions. This is reflected in their boiling temperatures:

Element	He	Ne	Ar	Kr	Xe	Rn
Boiling temperature/K	4	27	87	121	165	211

Hydrides of group 4

- None of the elements in group 4 is electronegative enough to give hydrogen bonding.
- The hydrides have covalent intramolecular bonds, intermolecular bonds being van der Waals (London-type) forces.
- The more electrons, the greater the attraction. The boiling temperatures are:

Hydride	Methane (CH ₄)	Silane (SiH ₄)	Germane (GeH ₄)	Stannane (SnH ₄)
Boiling temperature/K	109	161	183	221

Hydrides of groups 5–7

Nitrogen, oxygen and fluorine are electronegative enough to give hydrogen bonding in their hydrides. Therefore, for molecules of their size, these hydrides have much higher boiling temperatures than would be expected from van der Waals interactions alone. The remaining hydrides have both dipole–dipole and van der Waals interactions and in every case the latter dominate. The boiling temperature therefore increases with increasing size of the hydride.

Group 5

Hydride	NH ₃	PH ₃	AsH ₃	SbH ₃
Boiling temperature/K	240	185	218	256

Group 6

Hydride	H ₂ O	H ₂ S	H ₂ Se	H ₂ Te
Boiling temperature/K	373	212	232	269

Group 7

Hydride	HF	HCl	HBr	HI
Boiling temperature/K	293	188	206	238

Alkanes

The intermolecular forces in the non-polar alkanes are temporary dipole–induced dipole. The forces increase in strength with increasing numbers of electrons in the molecules and decrease in strength the further apart the molecules are. There is an increase in both the melting and the boiling temperatures of the straight-chain alkanes as the chain length, and hence the number of electrons, increases. The values for the melting temperature of the solids are less regular at first because of differences in the crystal packing. The values in the table below are given to three significant figures.

Alkane	Methane	Ethane	Propane	Butane	Pentane	Hexane
Melting temperature/K	91.1	89.8	83.4	135	143	178
Boiling temperature/K	109	185	231	273	309	342

Effect of branching

Since the strength of the intermolecular forces falls off rapidly with increasing distance, the melting and boiling temperature of branched-chain isomers of the alkanes are generally lower than those of the straight-chain compound (compare pentane and 2-methylbutane below). However, 2,2-dimethylpropane is a symmetrical molecule and can pack well both in the crystal lattice and in the liquid, so its values are much higher than those of 2-methylbutane.

The following table compares the melting and boiling temperatures of the three isomers of C_5H_{12} .

Alkane	Pentane	2-methylbutane	2,2-dimethylpropane
Melting temperature/K	143	113	257
Boiling temperature/K	309	301	283

Volatility of alkanes and alcohols

An alcohol is less volatile (i.e. has a higher boiling temperature) than an alkane of similar size. Alcohols are strongly hydrogen-bonded, whereas alkanes are non-polar and have only London forces between their molecules. These London forces are much weaker than hydrogen bonds.

Alkane	Ethane (CH_3CH_3)	Propane ($CH_3CH_2CH_3$)	Butane ($CH_3CH_2CH_2CH_3$)
Boiling temperature/K	185	231	273
Alcohol	Methanol (CH_3OH)	Ethanol (CH_3CH_2OH)	Propan-1-ol ($CH_3CH_2CH_2OH$)
Boiling temperature/K	338	352	371

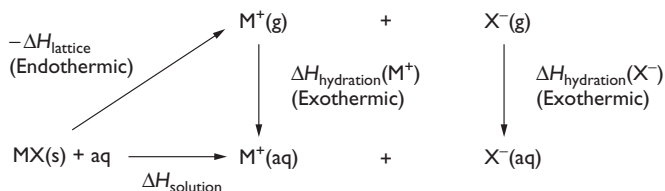
Solute, solvent and solubility

The solubility of a substance in a given solvent depends on the enthalpy (heat energy) and entropy changes of the dissolving process. Entropy is considered at A2 in Unit 4, so solubility is discussed here only in terms of enthalpy, but you should remember that the full story is more complex.

In general a substance dissolves if the bonds formed between the solute and the solvent are of similar or greater strength than those that are broken between both the solute molecules and the solvent molecules. Thus, for a solute A and a solvent B, the A–B bonds must be similar in strength to, or stronger than, both the A–A bonds and the B–B bonds. The difference between the energy needed to break these bonds is the factor that determines the extent of the solubility.

Ionic compounds

When an ionic compound dissolves in water, the ionic lattice has to be broken up (endothermic process) and the resulting ions are then hydrated (exothermic process). For some compounds where the solubility is controlled mostly by the enthalpy changes, the following Hess's law cycle applies.



If the energy required to break up the lattice is recovered by the hydration of the ions, the compound is soluble, i.e.

$$\Delta H_{\text{solution}} = -\Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}(\text{cation}) + \Delta H_{\text{hydration}}(\text{anion})$$

must be exothermic or only slightly endothermic. (Remember that this applies only where the entropy changes are less important than the enthalpy changes.)

Alcohols in water

An alcohol molecule (ROH) consists of a non-polar alkyl group and a hydroxyl group (–OH) that can hydrogen-bond with water. On dissolving, the –OH group breaks some of the water–water hydrogen bonds and replaces them with alcohol–water hydrogen bonds. The alcohol dissolves if the new alcohol–water bonds formed are strong enough to compensate energetically for the water–water bonds that are broken by the alkyl group (R) occupying space in the liquid water. Alcohols up to C₃ are miscible with water in all proportions. Butan-1-ol and its isomers are partially soluble, dissolving to some extent; alcohols above C₅ are insoluble in water. The long hydrophobic carbon chains disrupt the structure of the water too much.

Larger alcohols dissolve if they have more –OH groups. For example, glucose is a C₆ molecule, but it has 6 –OH groups so it is highly soluble in water.

Polar molecules in water

Hydrogen bonding in water is strong. To overcome this and separate the water molecules a solute has to form strong bonds with water. Polar molecules such as halogenoalkanes are not usually able to form strong enough bonds, so they are not water-soluble.

Non-aqueous solvents: 'like dissolves like'

Since the intermolecular forces in the solute are similar to those between the solvent and to those between solvent and solute in the solution, non-polar solvents such as hydrocarbons (e.g. hexane) dissolve other non-polar substances, such as waxes and fats. In contrast, hydrocarbons do not dissolve sugars, because the hydrogen bonding between the sugar molecules in the solid is too strong to be energetically compensated by any interaction between the non-polar hydrocarbon and the polar sugar molecules.

Redox

Oxidation numbers

Oxidation numbers are used to find the ratio (the stoichiometry) in which the oxidising and reducing agents react. To find the oxidation number of an element in any species, the following rules are used:

- An uncombined element has an oxidation number of zero.
- A simple ion has an oxidation number equal to its charge.
- Oxygen has oxidation number -2 (except in peroxides and superoxides).
- Hydrogen has oxidation number $+1$ (except in metal hydrides).

Example 1

What is the oxidation number of sulfur in sulfur trioxide (SO_3)?

Answer

Oxygen has an oxidation number of -2 , which gives $\text{S}^{x+}(\text{O}^{2-})_3$, so $x = +6$. The oxidation number of S in SO_3 is $+6$.

Example 2

What is the oxidation state of manganese in manganate (MnO_4^-)?

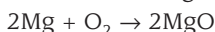
Answer

A similar argument gives $[\text{Mn}^{y+}(\text{O}^{2-})_4]^-$. The oxygen contributes -8 , with -1 charge overall. Thus $y = +7$. The oxidation number of Mn in MnO_4^- is $+7$.

The oxidation number of an atom in a compound is the charge that it would have if the compound were ionic. It is useful because changes in oxidation number indicate that an atom has been oxidised or reduced. Oxidation numbers can be used for simple atoms and ions, molecules or complex ions.

Electron transfer

The reaction of magnesium with oxygen is obviously an oxidation:



- Magnesium is converted into magnesium ions Mg^{2+} , the oxygen to oxide ions O^{2-} .
- A logical extension of this reaction is to say that any reaction converting magnesium to its ion is an oxidation and that **oxidation is electron loss**.
- The reverse process, the acquisition of electrons, is therefore **reduction**.
- **OILRIG**: oxidation is loss, reduction is gain.

An oxidising agent removes electrons from another species, so it gains electrons in a redox process. Similarly, a reducing agent is itself oxidised and therefore loses electrons.