3.3 Chemistry of the p-block

Unit 3

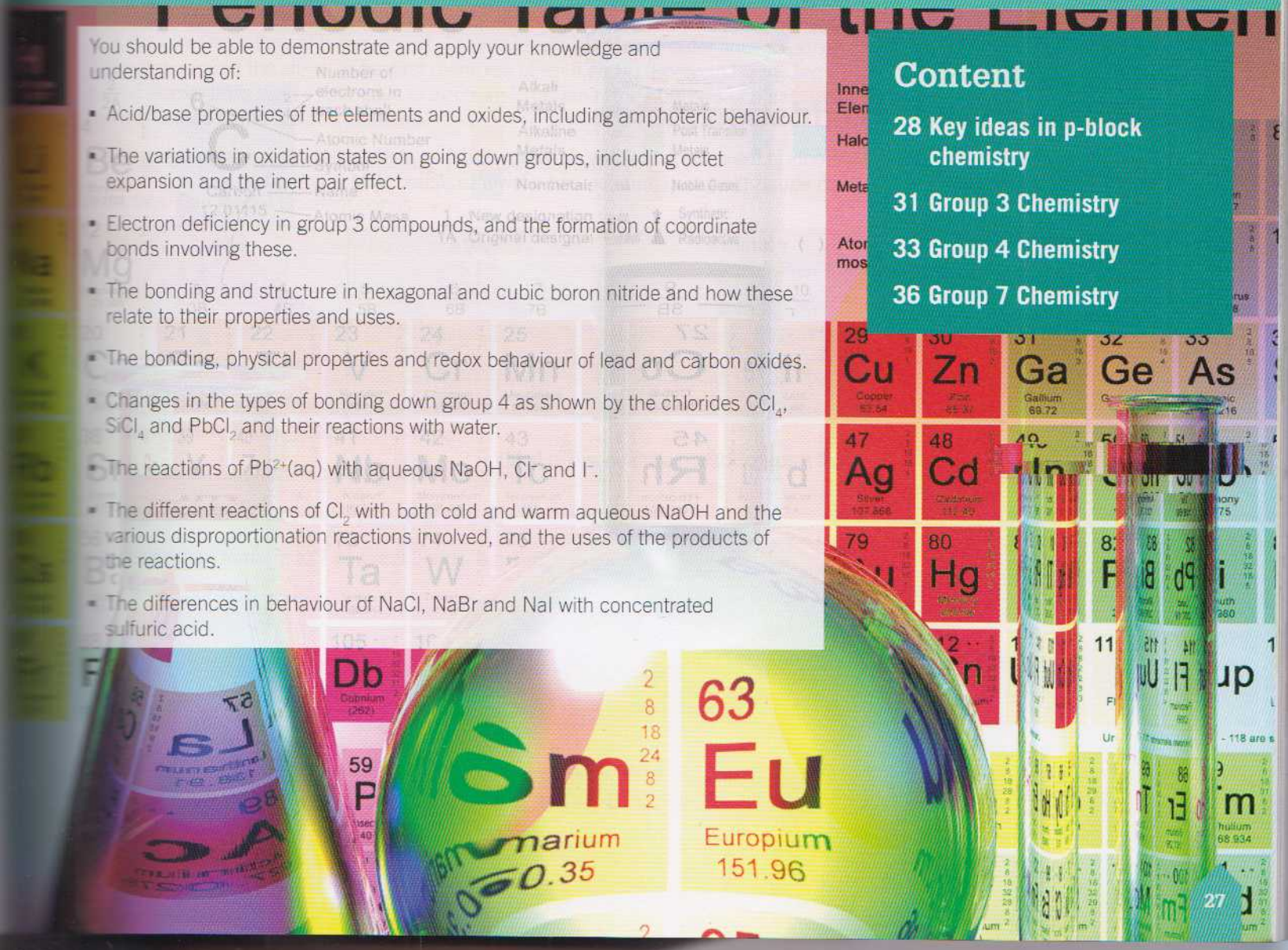
The periodic table is the greatest tool available to a chemist. Patterns and similarities in behaviour across periods and down groups allow chemists to make predictions. The explanations for these patterns have led to many of the significant ideas in chemistry.

The p-block makes up a significant part of the periodic table, from group 3 to group 0. Like all groups in the periodic table, there are similarities between the elements in a group; however, the p-block also shows patterns with significant differences. The differences we see in some fundamental properties of these elements, such as the metal/non-metal behaviour or their common oxidation states can make elements in the same group behave very differently.

You should be able to demonstrate and apply your knowledge and understanding of:

- Acid/base properties of the elements and oxides, including amphoteric behaviour.
- The variations in oxidation states on going down groups, including octet expansion and the inert pair effect.
- Electron deficiency in group 3 compounds, and the formation of coordinate bonds involving these.
- The bonding and structure in hexagonal and cubic boron nitride and how these relate to their properties and uses.
- The bonding, physical properties and redox behaviour of lead and carbon oxides.
- Changes in the types of bonding down group 4 as shown by the chlorides CCl_4, $SiCl_4$ and $PbCl_2$ and their reactions with water.
- The reactions of $Pb^{2+}(aq)$ with aqueous NaOH, Cl^- and I^-.
- The different reactions of Cl_2 with both cold and warm aqueous NaOH and the various disproportionation reactions involved, and the uses of the products of the reactions.
- The differences in behaviour of NaCl, NaBr and NaI with concentrated sulfuric acid.

Content



Link The chemistry of group 7, part of the p-block, was discussed in AS Topic 1.6 on pages 59–60 of the AS book.

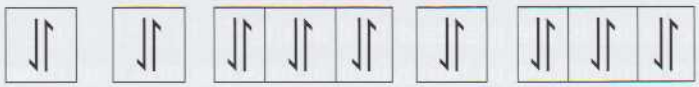
YOU SHOULD KNOW ›››

››› the most common oxidation states for the p-block elements in groups 3, 4 and 5

››› the most stable oxidation state for the p-block elements, especially those in group 4

Key ideas in p-block chemistry

The p-block elements are called this as their outer electrons are located in p sub-shells (2p, 3p, 4p, etc.). You need to be able to write the electronic configurations for these p-block elements in the second and third periods, i.e. those with outer electrons in the 2p or 3p sub-shells.



Every p-block element has a full s sub-shell in their outer shell, with between 1 and 6 further electrons in their p sub-shell.

- Group 3 atoms have 1 electron in their p sub-shells, i.e. outer electrons are s^2p^1.
- Group 4 atoms have 2 electrons in their p sub-shells, i.e. outer electrons are s^2p^2.
- Group 5 atoms have 3 electrons in their p sub-shells, i.e. outer electrons are s^2p^3.
- Group 6 atoms have 4 electrons in their p sub-shells, i.e. outer electrons are s^2p^4.
- Group 7 atoms have 5 electrons in their p sub-shells, i.e. outer electrons are s^2p^5.

The division of the outer electrons into s-electrons and p-electrons has a substantial effect on the chemistry of these elements, and so it is important that you can differentiate between these sets of electrons.

Study point

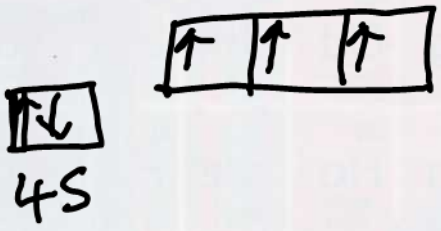
It is easier to learn the patterns in oxidation states rather than learn each element separately. For all elements, the highest oxidation state equals the group number, with a second oxidation state two lower in many cases.

Oxidation states

Elements in the p-block typically show two oxidation states – the maximum oxidation state which equals the group number, and a lower oxidation state which is two less.

Group 3		Group 4		Group 5	
B	**3**	C	2, **4**	N	**3, 5**
Al	**3**	Si	**4**	P	**3, 5**
Ga	1, **3**	Ge	2, **4**	As	**3**, 5
In	**1**, 3	Sn	2, **4**	Sb	**3**, 5
Tl	**1**, 3	Pb	**2**, 4	Bi	**3**, 5

(Most stable oxidation state shown in **bold**)



Inert pair effect

The stability of the lower oxidation states becomes greater down the group, as is shown above. This tendency of the heavier elements to form the lower oxidation state is called the **inert pair effect**. For an element in group 4, the outer electronic configuration is:

- When the element has an oxidation state of 4, it involves all four electrons.
- When the element has an oxidation state of 2, the inner two electrons do not become involved, and this ns^2 pair is called the *inert pair*.

The trend for the ns^2 electron pair to become an inert pair occurs in groups 3, 4 and 5 of the periodic table. It is only the lower members of these groups that show this tendency to lower oxidation states: +1 for group 3; +2 for group 4 and +3 for group 5. In groups 3 and 4, the lower oxidation state is not observed in the first two members of each group (with the exception of +2 in carbon monoxide), but in group 5 the upper members (nitrogen and phosphorus) exhibit the lower oxidation state more frequently.

Octet expansion

There are significant differences seen between the first members of the p-block groups and the lower members of these groups. The maximum number of outer shell electrons that can surround the atoms in the first members of each group (Boron to Neon, 2nd period elements) is eight – four pairs of electrons. This limits the numbers of bonds that can be formed in the first row elements:

- Boron: Can form 3 covalent bonds and is electron deficient.
- Carbon: Can form 4 covalent bonds.
- Nitrogen: Can form 3 covalent bonds and one lone pair.
- Oxygen: Can form 2 covalent bonds and two lone pairs.

The other members of each group (3rd period and below) have access to d-orbitals that are not present in the second shell. This allows them to '**expand** their **octet**' which means every electron in the outer shell can be used to form a covalent bond as there is no longer a limit of 8 electrons in the outer shell. This affects the numbers of bonds that can be formed for elements in groups 5, 6 and 7:

- Phosphorus: can form 5 covalent bonds, e.g. PCl_5.
- Sulfur: can form 6 covalent bonds, e.g. SF_6.
- Chlorine: can form up to 7 covalent bonds, e.g. ClO_4^-.

Key Terms

Inert pair effect is the tendency of the s^2 pair of electrons in an atom to stay paired leading to a lower oxidation state.

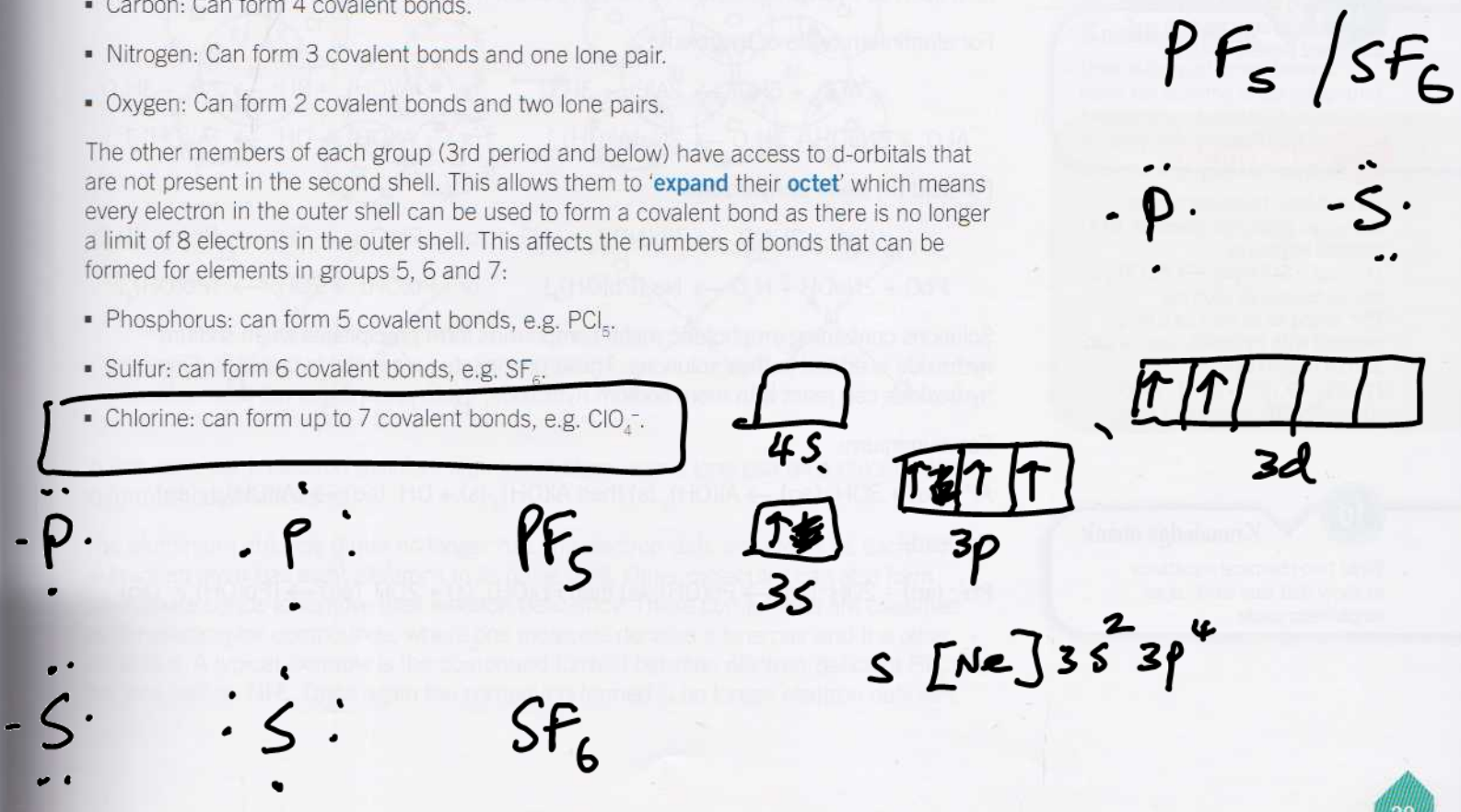
Octet expansion is the ability of some atoms to use d-orbitals to have more than 8 electrons in their valence shell.

Stretch & Challenge

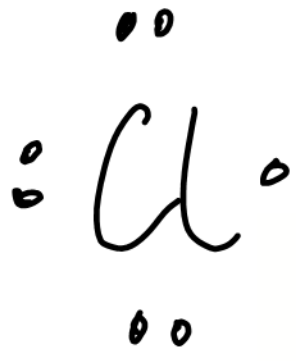
What causes the inert pair effect?

For a group 4 atom to form four bonds, the pair of s electrons must be unpaired, which requires energy to move an electron from the s to p sub-shell. This becomes more difficult down the group.

The unpairing energy must come from the energy released when bonds are formed and as you go down the group, the bonds get weaker, so less energy is released as they form. For the lowest members of the group, the energy released by making two extra bonds is not enough to balance the energy needed to move an electron from the s to p sub-shell.



HCl



Chloric(VII) acid

+7 -2

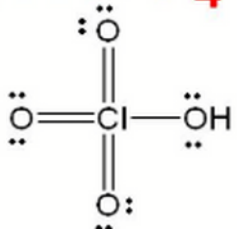
ClO_4^-

(+7) -8 = -1

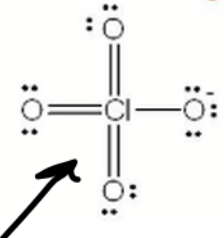
Chlorate (VII)

ClO_4^-

c) $HClO_4$



ClO_4^-



Chlorine uses all 7 electrons

+5

$HClO_3$

Chloric (V) acid

+1

$HClO$

Chloric(1) acid

Metallic properties

In the p-block the elements at the top of each group are non-metals, such as boron, carbon or nitrogen, whilst the elements at the bottom of each group are metals such as thallium, lead or bismuth. This change in properties leads to the characteristic zig-zag line between metals and non-metals.

1	2											3	4	5	6	7	0
		H															He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Metals												*Some metals and non-metals*				*Non-metals*	

This change in metallic character has a significant effect on the bonding and properties of the p-block compounds.

Stretch & Challenge

The change from non-metal to metal on going down the group is linked to the ionisation energy of the elements. Ionisation energy decreases on going down a group so it is easier for the atoms to form positive ions. This allows the atoms to contribute to ionic bonding with non-metals and helps the elements form metallic bonding, as the atoms form positive ions and a sea of delocalised electrons easily.

Key Term

Amphoteric materials react with both acids and bases.

Study point

When learning the equations for the reactions of acids and alkalis with amphoteric metals, remember that the equations for all metals forming +2 ions have similar formulae and the same balancing numbers. You do not need to learn each metal separately, as zinc, lead (II) and tin (II) will behave similarly

Amphoteric behaviour

Many p-block elements form **amphoteric** oxides, and these are typically metals close to the line separating metals and non-metals. They show both acidic and basic properties. To show amphoteric behaviour, we must show that an element or its compounds react with both acids and bases. Typically this would be to show the material reacting with an acid such as hydrochloric or nitric acid and sodium hydroxide:

For aluminium oxide or hydroxide:

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ or $Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$

$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$ or $Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$

For lead (II) oxide or hydroxide:

$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O$ or $Pb(OH)_2 + 2H^+ \rightarrow Pb^{2+} + 2H_2O$

$PbO + 2NaOH + H_2O \rightarrow Na_2[Pb(OH)_4]$ or $Pb(OH)_2 + 2OH^- \rightarrow [Pb(OH)_4]^{2-}$

Solutions containing amphoteric metal compounds form precipitates when sodium hydroxide is added to their solutions. These precipitates are metal hydroxides. Since the hydroxides can react with more sodium hydroxide, these precipitates will then redissolve:

For aluminium:

$Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$ then $Al(OH)_3(s) + OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$

For lead:

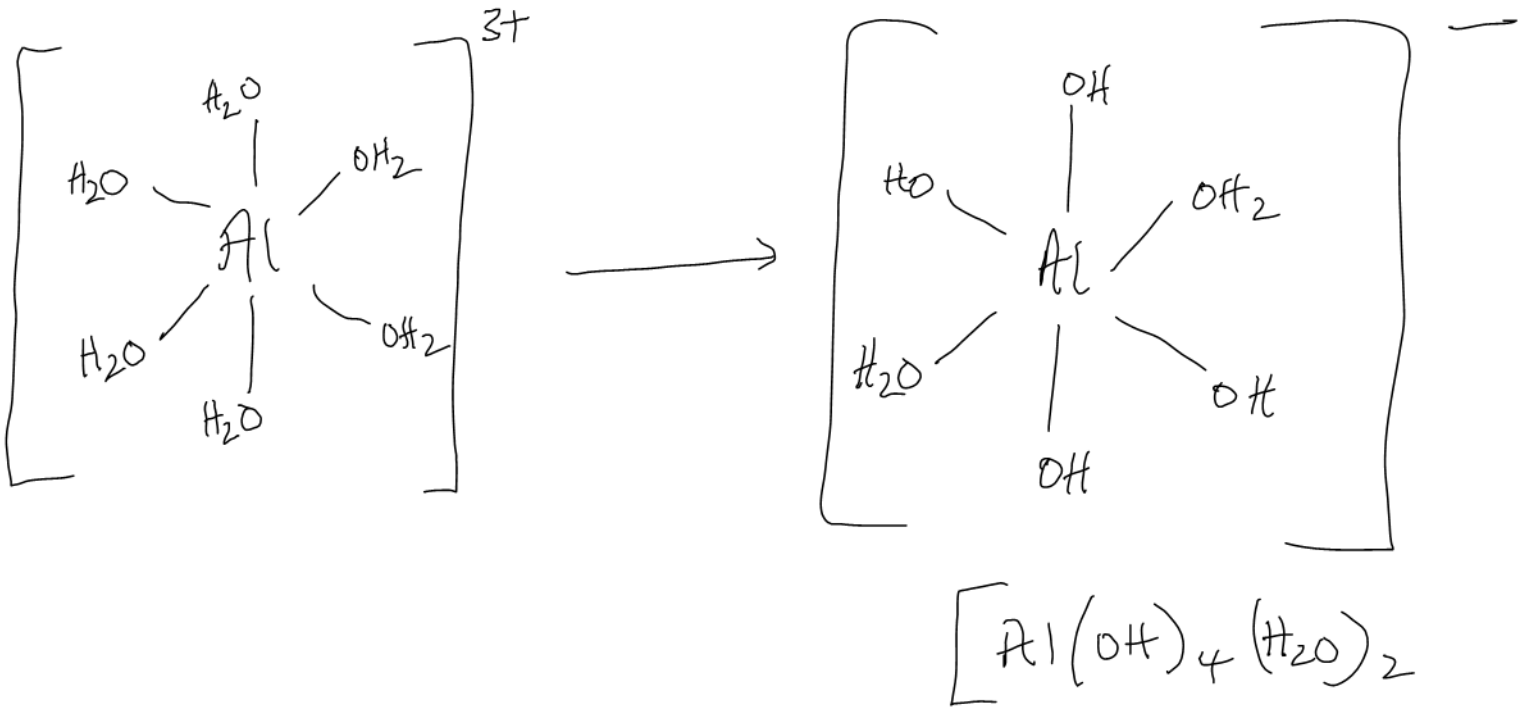
$Pb^{2+}(aq) + 2OH^-(aq) \rightarrow Pb(OH)_2(s)$ then $Pb(OH)_2(s) + 2OH^-(aq) \rightarrow [Pb(OH)_4]^{2-}(aq)$

Stretch & Challenge

All acid-base reactions can be treated as reversible reactions, so a reaction written as $Pb^{2+}(aq) + 2OH^-(aq) \rightarrow Pb(OH)_2(s)$ can be treated as showing Pb^{2+} acting as an acid, as it is reacting with hydroxide ions. It can also be treated as $Pb(OH)_2 \rightarrow Pb^{2+} + 2OH^-$, which shows $Pb(OH)_2$ acting as a base.

10 Knowledge check

Write two chemical equations to show that zinc oxide is an amphoteric oxide.



$$\left[Al(OH)_4(H_2O)_2\right]^-$$

Group 3 chemistry

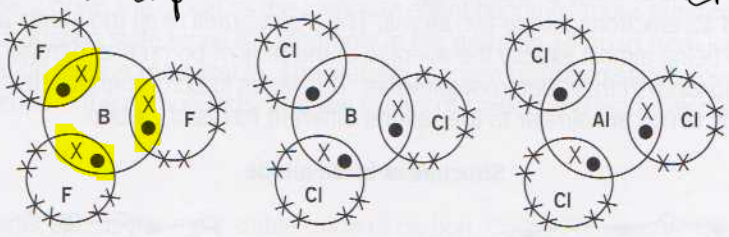
The two most common elements in group 3 are the first two in this group: boron and aluminium. These elements have very different physical properties as one is a non-metal and the other is a metal. Although aluminium is a metal, it has a relatively high electronegativity so some of its compounds are covalent and show some similarities to analogous compounds of boron.

YOU SHOULD KNOW ›››

- ››› the effects of electron deficiency on the compounds of group 3 elements
- ››› the bonding, structure and properties of the allotropes of boron nitride

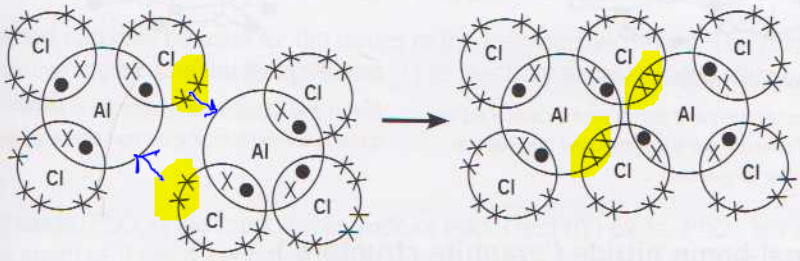
Electron deficiency

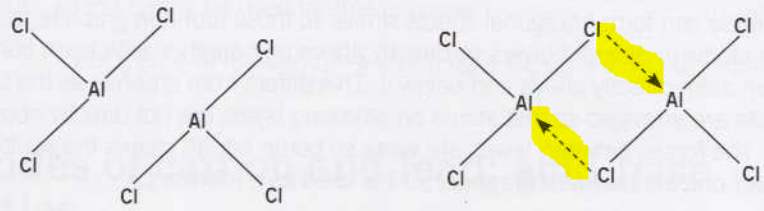
An electron-deficient atom is one that does not have a full outer shell, i.e. has fewer than eight electrons in its outer shell. When elements in group 3 form compounds, they commonly form three covalent bonds such as in BF_3, BCl_3 and $AlCl_3$. In each of these cases the three electrons from the group 3 atom (shown as dots below) form covalent bonds with halogen atoms.



BF_3 BCl_3 $AlCl_3$

To fill their outer shell, these atoms will often form co-ordinate bonds to gain extra electron pairs (they are ***electron acceptors***). This may be done by reacting with other compounds, or by forming dimers, as in the case of $AlCl_3$ in the gas phase, which forms Al_2Cl_6 dimers:





In this case, each electron deficient aluminium atom uses a lone pair on a chlorine atom to form a coordinate bond.

The aluminium chloride dimer no longer has any electron-deficient atoms as each aluminium atom has eight electrons in its outer shell. Other molecules can also form co-ordinate bonds to remove their electron deficiency. These compounds are classified as donor-acceptor compounds, where one molecule donates a lone pair and the other accepts it. A typical example is the compound formed between electron-deficient BF_3 and the lone pair on NH_3. Once again the compound formed is no longer electron deficient.

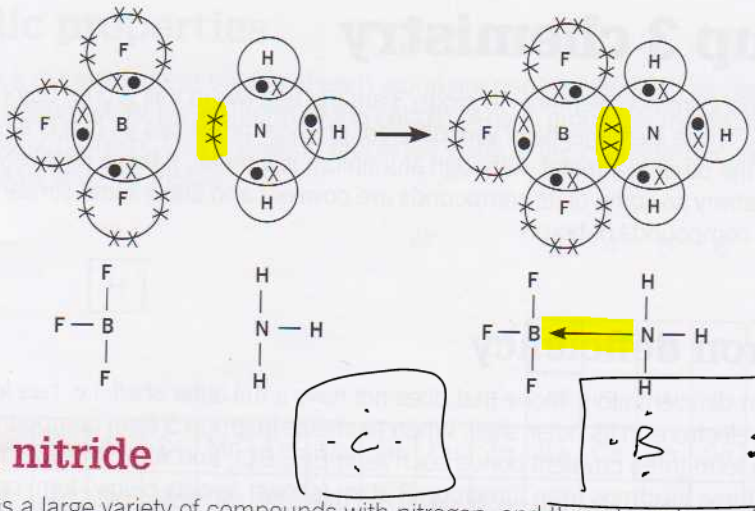
Exam tip

When discussing electron deficiency in group 3 compounds, always be specific about the atom that is electron deficient. Writing 'Aluminium chloride is electron deficient' does not identify the aluminium atom as the source of the electron deficiency.

Link The formation of coordinate bonds in compounds such as these is included in AS Topic 1.4 on page 47 of the AS book.

Knowledge check 11

Draw a dot-and-cross diagram to show the bonding in the compound formed when boron trichloride (BCl_3) is mixed with phosphine (PH_3).



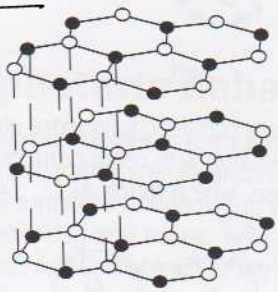
Exam tip

When discussing the structures of BN and the allotropes of carbon, focus on the requirements of the question. These may ask you to focus on similarities or differences in structures or properties, and if you try to simply repeat everything you know about these substances, you may not address the specific points required.

Boron nitride

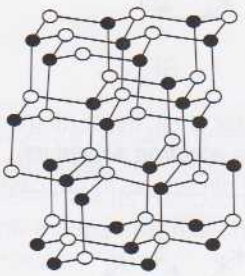
Boron forms a large variety of compounds with nitrogen, and these have been of great interest due to the analogy between the B–N bond and the C–C bond. In each case there are a total of 12 electrons on the two atoms. The atomic radii of all the atoms are similar with carbon being almost exactly the average of the radii of boron and nitrogen, with a similar relationship in their electronegativities. This leads to boron nitride, BN, having several forms which are similar to the several different forms of carbon.

Structure of boron nitride



(a) Hexagonal boron nitride

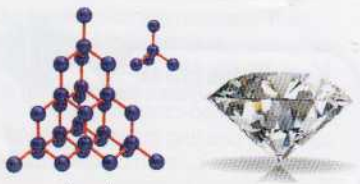
Layers where nitrogen and boron atoms combined in a hexagonal network are superimposed and have a structure similar to graphite.



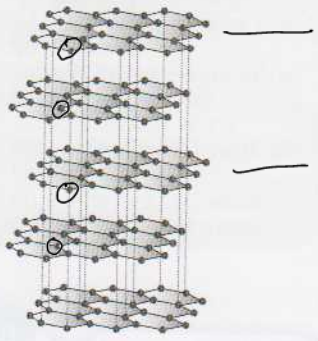
(b) Cubic boron nitride

Boron and nitrogen atoms combine three-dimensionally replacing carbon atoms in diamond.

Link The structures of diamond and graphite are included in AS Topic 1.5 on page 54 of the AS book.



diamond



graphite

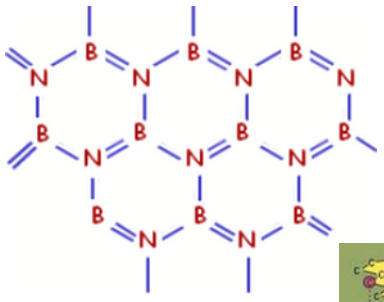
Hexagonal boron nitride ('graphite structure')

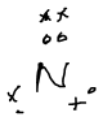
Boron nitride can form hexagonal sheets similar to those found in graphite, but in this case the atoms in different layers lie directly above one another, with each boron having a nitrogen atom directly above and below it. This differs from graphite as the layers in graphite are arranged so that atoms on adjoining layers are not directly above one another. The forces between layers are weak so boron nitride shares the ability for layers to slip over one another with graphite, so it is used as a lubricant.

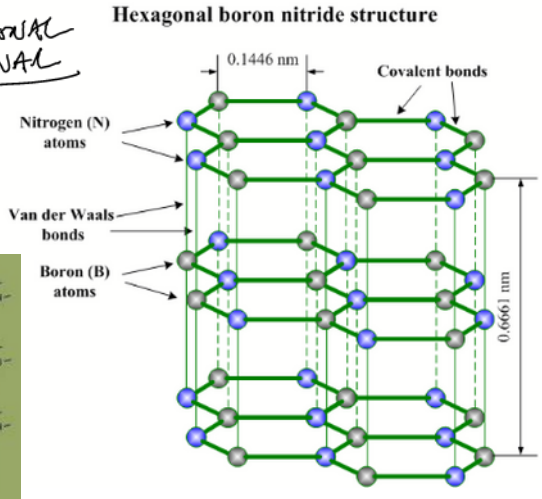
The electrical properties of boron nitride are very different from graphite as there are no delocalised electrons present, with electrons localised as lone pairs on nitrogen atoms. The B–N bonds are polar due to the different electronegativities of the two atoms. This makes BN an insulator and leads to its use in electronics as a substrate for semiconductors, microwave-transparent windows, and a structural material for seals, electrodes and catalyst carriers in fuel cells and batteries.

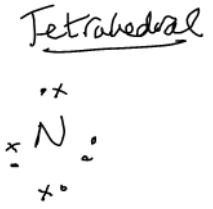
Cubic boron nitride ('diamond structure')

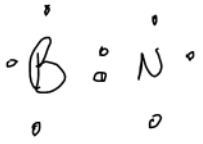
Like diamond, cubic boron nitride is extremely hard with a high melting point as covalent bonds must be broken to break or melt the solid. This leads to its use as a wear-resistant coating or an industrial abrasive.

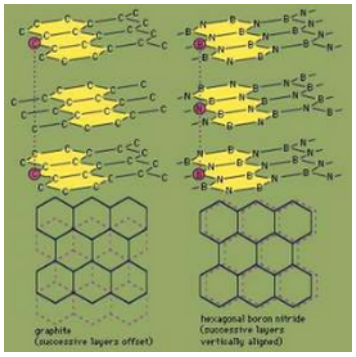


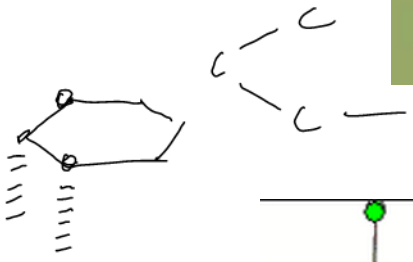


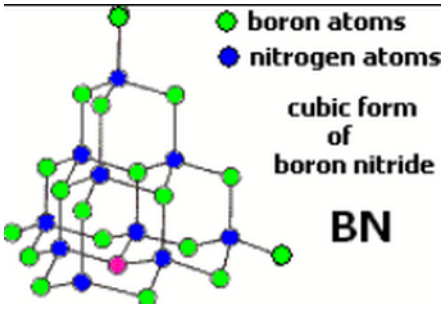


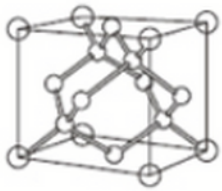
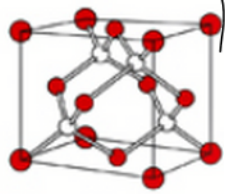










	Diamond	CBN
Crystal Structure (Cubic Crystal)		
Molecular Formula	C	BN
Lattice Constant Å	3.567	3.615
Density g/cm³	3.514	3.480

Group 4 chemistry

Group 4 contains a range of metals and non-metals, with most being familiar names to chemists and non-chemists alike. Indeed most of the elements in this group have been known for a very long time with carbon, tin and lead known for thousands of years. The changes from the top to the bottom of the group are amongst the most significant of all the groups in the periodic table. The first element, carbon, is a non-metal which forms a huge range of covalent compounds with the carbon showing a +4 oxidation state, whilst the heaviest stable member of the group, lead, is a metal which generally forms ionic compounds with the +2 oxidation state being most stable.

YOU SHOULD KNOW › › ›

› › › the properties of the oxides of carbon and lead

› › › the behavior of the chlorides of carbon and silicon

The oxides of carbon and lead: redox properties

The oxidation states shown in group 4 are +2 and +4, with the stability of the +2 oxidation state increasing down the group as the inert pair effect becomes more significant. The most stable oxidation state for all the elements in the group is +4 apart from lead where the +2 oxidation state is most stable. The stability of these oxidation states governs the redox properties of the compounds, and the oxides of carbon and lead exemplify this.

Carbon

Carbon dioxide, CO_2, is the most stable oxide of carbon. Carbon monoxide, CO, is the only stable compound to contain carbon in the +2 oxidation state. CO will act as a reducing agent as it easily becomes oxidised from +2 to +4. Carbon monoxide is used as a reducing agent, especially for extracting metals from their oxides. For example:

Iron: $Fe_2O_3\,(s) + 3CO\,(g) \rightarrow 2Fe\,(s) + 3CO_2\,(g)$

Copper: $CuO\,(s) + CO\,(g) \rightarrow Cu\,(s) + CO_2\,(g)$

This method can only be used for the oxides of the less reactive metals. The oxides of the more reactive metals (anything above zinc in the reactivity series) are too stable, and so will not react.

Lead

Lead (II) oxide, PbO, is the most stable oxide of lead. Lead (IV) oxide, PbO_2, will act as an oxidising agent as it easily becomes reduced from +4 to +2. All lead (IV) compounds are oxidising agents, so PbO_2 may be used for this purpose:

$PbO_2\,(s) + 4HCl\,(conc) \rightarrow PbCl_2\,(s) + Cl_2\,(g) + 2H_2O\,(l)$

The oxides of carbon and lead: acid-base properties

In general we can classify metal oxides as basic oxides and non-metal oxides as acidic oxides. Some metals form amphoteric oxides that can show both acidic and basic properties. The change from non-metal at the top of group 4 to metals at the bottom of the group is reflected in the acid-base properties of the oxides.

Exam tip

When discussing any of the oxides of carbon or lead you must make it totally clear which one you mean. Any reference to lead oxide is unlikely to be specific enough.

Study point

Make sure you are able to write equations to show the redox behaviour of any oxide.

Exam tip

It is not enough to say that an oxide is acidic as it forms acidic solutions, you need to show it reacts with bases. Similarly basic oxides react with acids. You will need to be able to write equations for these reactions.

Stretch & Challenge

Although we focus on carbon and lead here, the patterns are still relevant for the elements in between. The stability of the +2 oxidation state increases down the group; however, it is only lead that has +2 as the most stable oxidation state. In terms of the acid-base properties, both carbon dioxide and silicon dioxide are acidic; however, oxides of germanium, tin and lead are amphoteric.

SiO_2 acidic impurity in iron oxide

$SiO_2 + CaO \rightarrow CaSiO_3$ acid base

Carbon

Carbon dioxide is a colourless gas made up of small covalent molecules. This is an acidic oxide as the oxide is soluble in water to give the very weak acid, carbonic acid: H_2CO_3

$$CO_2\,(g) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)$$

Like all acidic oxides, carbon dioxide will react with alkalis to form a salt. All salts produced in this way are carbonates or hydrogencarbonates:

$$CO_2\,(g) + 2NaOH\,(aq) \rightarrow Na_2CO_3\,(aq) + H_2O\,(l)$$

$$CO_2\,(g) + NaOH\,(aq) \rightarrow NaHCO_3\,(aq)$$

Exam tip

It is not true to say that carbon has no d-orbitals, as all atoms have d-orbitals in higher shells; however, these are not available for use.

Lead

SnO_2 SnO) Basic

Lead (II) oxide, PbO, is an orange solid which contains bonding which is mainly ionic. Lead (II) oxide is an amphoteric oxide, so it reacts with acids and bases:

$$PbO\,(s) + 2HNO_3\,(aq) \rightarrow Pb(NO_3)_2\,(aq) + H_2O\,(l)$$ Acting as base

base

$$PbO\,(s) + 2NaOH\,(aq) + H_2O\,(l) \rightarrow Na_2[Pb(OH)_4]\,(aq)$$ Acting as an acid

acid

12/2/2019.

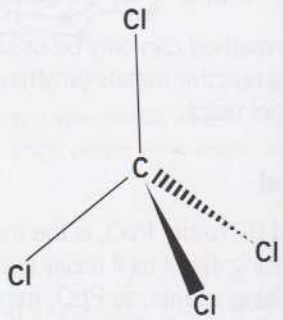
The chlorides of carbon, silicon and lead

Carbon and silicon

The stable chlorides of carbon and silicon are the tetrachlorides, CCl_4 and $SiCl_4$. These are both colourless liquids containing individual covalent molecules. The molecules found in both are tetrahedral, due to the 8 electrons in the valence shell. For CCl_4, the electronic configuration is as shown:

↑ represents an electron from **Carbon**

↓ represents and electron from **Chlorine**



▲ Silicon chloride fumes in moist air as water reacts with it to release acidic HCl fumes.

Key Term

Octet expansion is the ability of an atom to form species with more than eight electrons in the valence shell. These may be stable compounds, such as SF_6, or intermediate stages in a reaction mechanism such as the coordinate bonding of water to $SiCl_4$.

Stretch & Challenge

Energy calculations suggest that carbon tetrachloride should react easily with water to form carbon dioxide; however, the reaction does not occur as it would be too slow – we say that the carbon tetrachloride shows **kinetic stability**.

Reactions with water

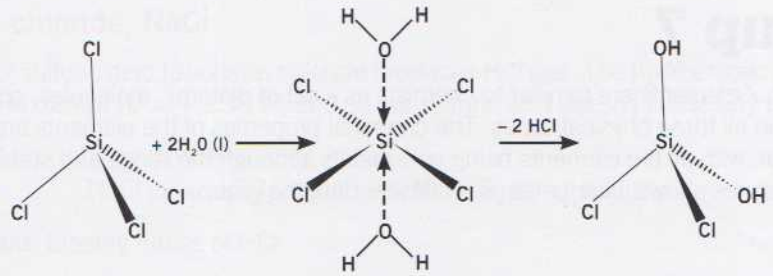
CCl_4 does not react with water as it merely forms a separate layer under the water. The carbon atom cannot combine easily with water molecules. This lack of reactivity is due to the absence of available d-orbitals in the valence shell meaning that the octet cannot be expanded to allow the water molecules to combine with the carbon atom.

→ Silicon tetrachloride, $SiCl_4$, reacts very quickly with water in a hydrolysis reaction. This reaction produces fumes of hydrogen chloride gas, and silicon dioxide, SiO_2, as a solid precipitate. The reaction becomes more vigorous down the group as the bonds in the compound become weaker.

$$SiCl_4\,(l) + 2H_2O\,(l) \rightarrow SiO_2\,(s) + 4HCl\,(g)$$

The reason for the increased reactivity is that silicon possesses available 3d-orbitals in addition to the 3s and 3p orbitals involved in bonding to the chlorine atoms. The lone pairs of the water can form co-ordinate bonds with these empty d-orbitals, giving a complex molecule that can then eliminate two HCl molecules.

14 Si: $1s^2 2s^2 2p^6 3s^2 3p^2$ 4s 3d



This molecule can then eliminate two more molecules of HCl to leave SiO_2.

You may also see the product of the reaction written as $Si(OH)_4$, with the overall reaction written as:

$$SiCl_4\ (l) + 4H_2O\ (l) \rightarrow Si(OH)_4\ (s) + 4HCl\ (g)$$

Both of these alternatives are acceptable, as the nature of the product formed is not well defined. Hydrated silicon dioxide ($SiO_2.2H_2O$) has the same overall composition as silicon hydroxide ($Si(OH)_4$) and spectroscopic analysis does not distinguish between these.

Lead

Lead (II) chloride is the most stable chloride of lead. It is a white ionic solid made up of Pb^{2+} and Cl^- ions. As it is an ionic compound, it does not react with water, but neither does it dissolve in cold water, although it can be dissolved in hot water. This is in common with most lead (II) compounds, which are insoluble in cold water.

Reactions of solutions of lead (II) compounds, Pb^{2+} (aq)

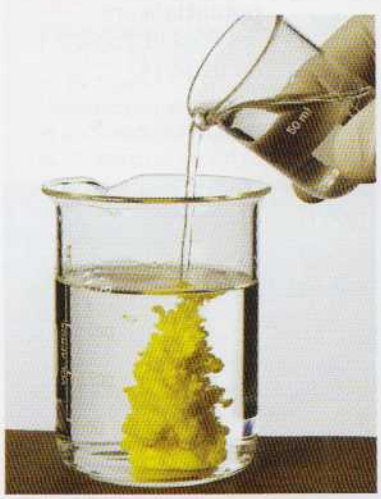
Lead (II) compounds are ionic compounds and practically all of them are insoluble in water. The only two common compounds which dissolve readily in cold water are lead nitrate, $Pb(NO_3)_2$, and lead ethanoate, $Pb(CH_3COO)_2$. The reactions of solutions of these salts with various anions produces a range of precipitates:

Solution added	Anions present	Observation/explanation
NaOH (aq)	OH^- (aq)	An initial white precipitate of $Pb(OH)_2$ is formed: $Pb^{2+}\ (aq) + 2OH^-\ (aq) \rightarrow Pb(OH)_2\ (s)$
excess NaOH (aq)	OH^- (aq)	The white precipitate redissolves in excess OH^- (aq) to form the tetrahydroxoplumbate (II) ion: $Pb(OH)_2\ (s) + 2OH^-\ (aq) \rightarrow [Pb(OH)_4]^{2-}\ (aq)$
HCl (aq)	Cl^- (aq)	A dense white precipitate of lead chloride, $PbCl_2$ is formed: $Pb^{2+}\ (aq) + 2Cl^-\ (aq) \rightarrow PbCl_2\ (s)$
KI (aq)	I^- (aq)	A dense bright yellow precipitate of lead iodide, PbI_2 is formed: $Pb^{2+}\ (aq) + 2I^-\ (aq) \rightarrow PbI_2\ (s)$ **THIS IS A KEY OBSERVATION TO IDENTIFY Pb^{2+} IONS**

Link The reasons for the solubility, or lack of solubility, of ionic compounds are covered in Topic 3.6 on page 62

Exam tip

There are two yellow precipitates that are commonly seen in qualitative analysis. These are silver iodide and lead iodide; however, they are very different colours. The precipitate of lead iodide is often described as bright yellow or canary yellow whilst the precipitate for silver iodide is pale yellow. Whenever a bright yellow precipitate is mentioned in qualitative analysis, this is a good starting point for identifying all solutions present.



▲ Lead iodide precipitate is bright yellow.

YOU SHOULD KNOW ›››

- ››› how the oxidising power of the halogens governs their reactions
- ››› the reactions of sodium halides with concentrated sulfuric acid
- ››› the reactions of chlorine with sodium hydroxide

Group 7

The group 7 elements are familiar to chemists as a set of diatomic molecules, containing elements in all three physical states. The chemical properties of the elements are very similar, with all the elements being non-metals although the range and stability of oxidation states shows clear patterns on descending the group.

The oxidising power of halogens

The halogens have different strengths as oxidising agents, with their oxidising power decreasing down the group. This ability to remove electrons from other species can be measured using the standard electrode potentials for the halogens. The values for chlorine, bromine and iodine are given below.

Reaction			$E^\ominus$ / Volts
Cl_2 (g) + 2e$^-$	⇌	2Cl$^-$ (aq)	+1.36
Br_2 (l) + 2e$^-$	⇌	2Br$^-$ (aq)	+1.09
I_2 (s) + 2e$^-$	⇌	2I$^-$ (aq)	+0.54

- As the value for chlorine is the most positive, it readily gains electrons to form chloride ions, Cl$^-$. This also shows that it is difficult to oxidise chloride ions to chlorine molecules.
- As the value for iodine is the least positive, it gains electrons less readily than bromine and chlorine. This also shows that it is easier to oxidise iodide ions than it is to oxidise bromide or chloride ions.

Example

If we bubble chlorine gas into a solution containing bromide ions, the solution goes orange, showing bromine is being formed.

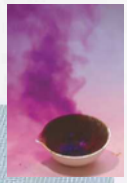
$$Cl_2\ (g) + 2Br^-\ (aq) \rightarrow Br_2\ (aq) + 2Cl^-\ (aq)$$

This occurs because chlorine is a stronger oxidising agent than bromine (it has a more positive standard electrode potential). This means that chlorine is able to oxidise bromide to form bromine molecules.

Exam tip

When discussing the chemistry of the halogens, it is essential to distinguish between a halogen and a halide. Students frequently use these terms interchangeably and they mean different things – a halide is always a negative ion whilst a halogen ion is a positive ion such as I$^+$. If in doubt use the formula each time to make your answer clear.

Link **Standard electrode potentials** are covered in Topic 3.1 on page 14.



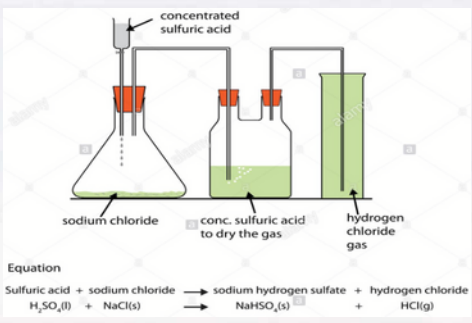
Exam tip

Whenever you are comparing standard electrode potentials use the terms more positive or less negative rather than larger or higher as many standard electrode potentials are negative. It is possible to write that –1.27 V is larger than –0.54 V; however, stating that –1.27 V is more negative than –0.54 V avoids ambiguity.

Reactions of concentrated sulfuric acid with sodium halides

Concentrated sulfuric acid is a strong acid and an oxidising agent. The different ease of oxidising the halide ions means that the reactions undertaken by the different sodium halides are very different. When any sodium halide is added to concentrated sulfuric acid, the hydrogen halide is formed as a steamy gas.

The sulfuric acid or products formed from it may oxidise the halide in the hydrogen halide to form the halogen if the halide is relatively easy to oxidise. This process becomes easier lower down the group.



Sodium chloride, NaCl

Addition of sulfuric acid to sodium chloride produces HCl gas. The hydrochloric acid is difficult to oxidise ($E^\ominus = +1.36$ V), and so the sulfuric acid doesn't cause any redox reaction.

$$NaCl\ (s) + H_2SO_4\ (conc.) \rightarrow NaHSO_4\ (s) + HCl\ (g)$$

Observations: Steamy fumes of HCl

Knowledge check 12

Use the standard electrode potentials to explain why chlorine is able to oxidise iodide ions and write an equation for this process.

Sodium bromide, NaBr

Addition of sulfuric acid to sodium bromide produces HBr gas.

$$NaBr\ (s) + H_2SO_4\ (conc.) \rightarrow NaHSO_4\ (s) + HBr\ (g)$$

The sulfuric acid oxidises some of the HBr to form brown fumes of Br_2, and SO_2 gas. The hydrobromic acid is slightly easier to oxidise ($E^\ominus = +1.09$ V), and so the sulfuric acid causes the redox reaction below:

$$\overset{-1}{2HBr}\ (s) + \overset{+6}{H_2SO_4}\ (conc.) \rightarrow \overset{+4}{SO_2}\ (g) + \overset{0}{Br_2}\ (g) + 2H_2O\ (l)$$

Sulfur is reduced from +6 in H_2SO_4 to +4 in SO_2.

Bromine is oxidised from –1 in Br^- to 0 in Br_2.

Observations: Steamy fumes of HBr; Orange fumes of Br_2.

Knowledge check 13

Write an equation for the reaction of sulfuric acid with HI producing sulfur and I_2 as significant products, and an equation for sulfuric acid with HI producing H_2S and I_2 as significant products.

▲ The addition of concentrated sulfuric acid to sodium bromide.

Sodium iodide, NaI

Addition of sulfuric acid to sodium iodide initially produces HI gas.

$$NaI\ (s) + H_2SO_4\ (conc.) \rightarrow NaHSO_4\ (s) + HI\ (g)$$

The sulfuric acid easily oxidises the HI ($E^\ominus = +0.54$ V) to form a complex mixture of products including I_2 (s), SO_2 (g) and H_2S (g). The reaction below occurs:

$$2HI\ (s) + H_2SO_4\ (conc.) \rightarrow SO_2\ (g) + I_2\ (s) + 2H_2O\ (l)$$

S is reduced from +6 in H_2SO_4 to +4 in SO_2.

I is oxidised from –1 in I^- to 0 in I_2.

Further reduction of the sulfuric acid to S (O.S. = 0) and H_2S (O.S. = –2) can occur as the HI is a better reducing agent than HBr or HCl.

Observations: Steamy fumes of HI, Purple fumes of I_2 or black solid/brown solution; Smell of rotten eggs (H_2S), yellow solid (S).

Stretch & Challenge

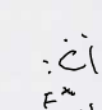
The oxidation states of the halogens studied here reach up to +5; however, it is possible to form compounds with the halogen in a +7 oxidation state such as the perchlorate ion (ClO_4^-). Compounds containing these ions can be very unstable and many are shock sensitive. They decompose explosively to form compounds with the chlorine in a less positive oxidation state.

$$\overset{0}{Cl_2}(g) + H_2O(l) \rightarrow \overset{-1}{HCl}(aq) + \overset{+1}{HClO}$$ chloric(I) acid

Reactions of chlorine with sodium hydroxide

We have already seen the most common oxidation states of the halogens, which are 0 in the element and –1 in the halide ions, but there are many other oxidation states possible including +1 and +5. The higher oxidation states become more stable as you go down the group. Fluorine cannot achieve any of the high oxidation states, but all the other members of the group can form compounds with oxidation states up to +5 with very electronegative elements like oxygen or fluorine. We will examine the chemistry of the ions ClO^- (chlorate (I), + 1 oxidation state) and ClO_3^- (chlorate (V), + 5 oxidation state). These ions are formed by reaction of the elements with an alkali.

ClF_3



Cold dilute NaOH

$$2NaOH + \overset{0}{Cl_2} \rightarrow \overset{-1}{NaCl} + \overset{+1}{NaClO} + H_2O$$

DISPROPORTIONATION — SODIUM CHLORATE(I)

Hot conc. NaOH.

$$6NaOH + 3\overset{0}{Cl_2} \rightarrow 5NaCl + \overset{+5}{NaClO_3} + 3H_2O$$

DISPROPORTIONATION — SODIUM CHLORATE(V)

Key Term

A **disproportionation reaction** is one in which the same element is both oxidised and reduced, forming products containing the element in two different oxidation states.

▲ Bleach is usually a solution of sodium chlorate (I) in water.

Link The use of chlorine in the sterilisation of water on page 60 of the AS book.

When chlorine is bubbled through water, a reversible reaction occurs:

$$Cl_2\,(g) + H_2O\,(l) \rightleftharpoons HCl\,(aq) + HOCl\,(aq)$$

In this reaction, the chlorine is being both oxidised and reduced: the element at the start has an oxidation state of 0. The chlorine in the end has an oxidation state of –1 in HCl, and +1 in HOCl. A process where an element ends up in two different compounds, one with a higher oxidation state and one with a lower is called a **disproportionation reaction**.

This is an equilibrium reaction, and the products are both acids. If we use the alkali sodium hydroxide instead of water, this will force the equilibrium over to the right-hand side:

$$Cl_2\,(g) + 2OH^-\,(aq) \rightarrow Cl^-\,(aq) + OCl^-\,(aq) + H_2O\,(l)$$

The ClO^- ion is stable in the solution at room temperature, but on heating with concentrated sodium hydroxide a further disproportionation reaction occurs:

$$3Cl_2\,(g) + 6OH^-\,(aq) \rightarrow 5Cl^-\,(aq) + ClO_3^-\,(aq) + 3H_2O\,(l)$$

This gives the chlorate (V) ion, where chlorine is in the +5 oxidation state, and to balance this change from 0 → +5 there must be five chlorine atoms undergoing the 0 → –1 change in oxidation state.

Uses of chlorine and chlorate ions

The ions formed above are oxidising agents, being reduced in the process:

$$ClO^-\,(aq) + 2H^+\,(aq) + 2e^- \rightarrow Cl^-\,(aq) + H_2O\,(l)$$

Similarly, elemental chlorine is an oxidising agent:

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

The oxidising power of chlorine and of chlorate ions is the basis of their use in bleaches, which are often labelled with the old name of this chemical, sodium hypochlorite. Bleaching is an oxidation reaction, with the oxidised form of the coloured material or dye being colourless. Similarly the oxidising ability of ClO^- leads to its ability to kill bacteria, as the microbe cells are oxidised. This is the basis of chlorination of water supplies to disinfect them.