

# WJEC Chemistry A-level

## 3.3: Chemistry of the $p$ -block

Detailed Notes

Welsh Specification

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## p-Block Elements

The p-block of elements consists of the **six columns** to the **right hand side** of the periodic table, starting from boron.

	1 1A																		18 8A	
1	1 H 1.0079																			2 He 4.0026
2	3 Li 6.94	4 Be 9.0122																		
3	11 Na 22.990	12 Mg 24.305																		
4	19 K 39.098	20 Ca 40.078																		
5	37 Rb 85.468	38 Sr 87.62																		
6	55 Cs 132.91	56 Ba 137.33																		
7	87 Fr 223.02	88 Ra 226.03																		

	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 146.92	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu 239.05	95 Am 241.06	96 Cm 244.06	97 Bk 249.08	98 Cf 252.08	99 Es 252.08	100 Fm 257.10	101 Md 258.10	102 No 259.10	103 Lr 262.11

s     
  p     
  d     
  f

[https://commons.wikimedia.org/wiki/File:Subshells\\_of\\_Orbitals.jpg](https://commons.wikimedia.org/wiki/File:Subshells_of_Orbitals.jpg)

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Each of the **p-block elements** has the outermost electrons held in the **p-orbital**. These electrons are typically lost to form **positively charged cations**, that increase in stability down a group.

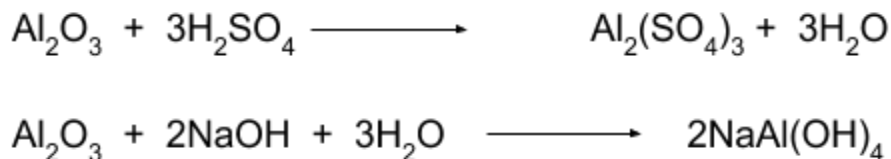
### Amphoteric Nature

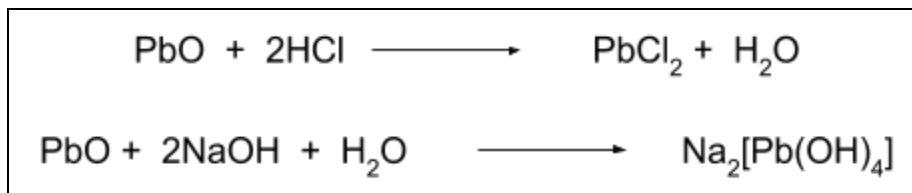
The bonding of some of the p-block elements and their ions means they are **partially ionic and covalently bonded**. This is best demonstrated by aluminium and lead.

The different types of bonding give rise to **amphoteric nature**, where the ions can react both as an **acid** and as a **base**. It will react as both to form a **salt and water** in neutralisation reactions.

The  $\text{Al}^{3+}$  ions present in **aluminium oxide** and the  $\text{Pb}^{2+}$  ions present in **lead oxide** demonstrate this amphoteric nature in their reactions with acids and bases.

Example:





### Inert pair effect

As you descend **Groups 3, 4 and 5**, there is an **increasing stability** of the **inert pair cations**. This means that down the groups, the ..... This is due to the **inert pair effect** which refers to the idea that **lower valencies** become **more stable** as the group is descended.

The **inert pair effect** is the tendency of the two electrons in the **outermost atomic s-orbital**,  $s^2$ , to remain **unshared** in compounds of elements from Groups 3, 4 and 5. The d-orbital and f-orbital do **not effectively shield** the inert pair of electrons, so the **inert pair** remains **strongly attracted** to the **nucleus**, and so is not involved in the **formation of bonds**.

Consider **Group 4**. Elements further down the group are increasingly found in the **+2 oxidation state**, such as in lead oxide (PbO). This is due to the order in which electrons are lost from the outer orbitals, leaving behind '**inert pairs**' of electrons from the  $s^2$  level. As you go down the Group, there is an increasing tendency for the  $s^2$  pair not to be used in bonding. Therefore, stability of the **+4** oxidation state **reduces down the group**, whilst stability of the **+2** state **increases down the group**.

### The Octet Rule

It follows from the octet rule that atoms with an **atomic number below 20** tend to combine so that their **valence shells** each have **8 electrons**. There are some **exceptions** to this rule which occur in three cases: if molecules have an **odd number** of electrons, if molecules contain atoms which have **more than 8** electrons, or if molecules contain atoms with **less than 8** electrons.

Various **Group 3 elements** can form compounds with **fewer than eight electrons** in their valence shells. **Boron** and **aluminium** each only have **three valence electrons**, yet they do not generally bond to gain 5 electrons - indicating that they are an exception to the octet rule. Boron is found in the compound **BF<sub>3</sub>** with only **6 electrons** in its valence shell, and similarly aluminium is found in **AlCl<sub>3</sub>** with only **6 electrons** in its valence shell.

Another exception of the **octet rule** is that elements of **Groups 5, 6 and 7** can form compounds with **more than eight electrons** in their valence shells. For example, consider **SF<sub>6</sub>**. In this compound, sulfur has 12 valence electrons.

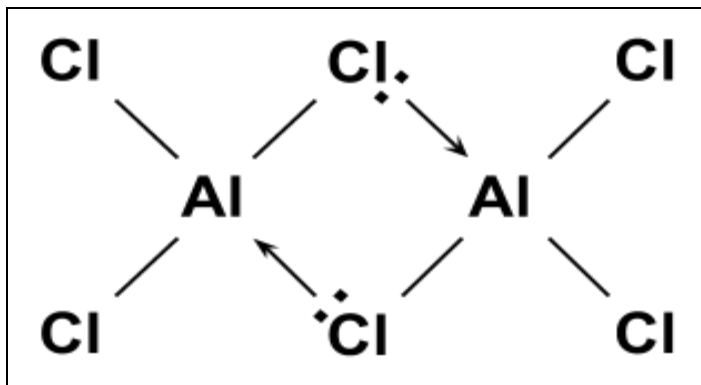




## Aluminium Hexachloride

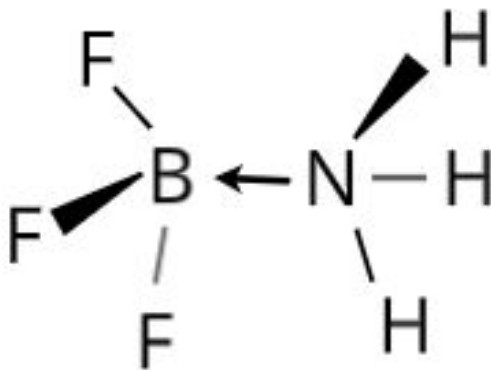
**Aluminium hexachloride**,  $\text{Al}_2\text{Cl}_6$ , is a **donor-acceptor dimer**, made up of two separate, identical molecules linked together by two **dative bonds**. Two atoms of chlorine share their lone pair of electrons with two atoms of aluminium to form the dative bonds.

*Example:*



## Ammonia Boron Trifluoride ( $\text{NH}_3 \cdot \text{BF}_3$ )

**Ammonia boron trifluoride** is also a **donor-acceptor dimer**, made up of  $\text{BF}_3$  and  $\text{NH}_3$ , bonded together by a **coordinate bond**. The **nitrogen** atom has a **lone pair** of electrons which it **donates to the boron** atom, forming a coordinate bond.



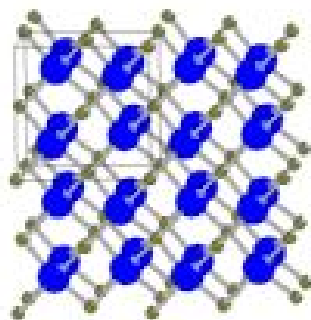
## Boron Nitride

Boron nitride has the **empirical formula BN**. It can form very large compounds in **giant cubic** or **hexagonal** structures.

The cubic form of boron nitride consists of alternately linked boron and nitrogen atoms that together form a **tetrahedral bond network**. This network of bonds is similar to that of the



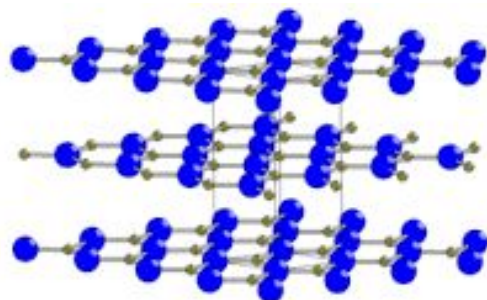
carbon atoms in diamond. The lone pair of electrons on nitrogen are accepted by boron to form a **coordinate bond**, producing a giant 3D covalent lattice.



[https://commons.wikimedia.org/wiki/File:Structures\\_cub\\_hex\\_BN.gif](https://commons.wikimedia.org/wiki/File:Structures_cub_hex_BN.gif)  
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Large covalent structures such as this, make boron nitride **very inert**. The structure also gives boron nitride a **very high melting point** and makes it one of the **hardest** known materials after diamond.

Hexagonal boron nitride has a layered structure, similar to graphite, with layers forming into a **2D giant covalent network**. The alternate boron and nitrogen atoms link together forming **hexagonal rings** in thin layers, held together by **weak intermolecular forces**.



[https://commons.wikimedia.org/wiki/File:Structures\\_cub\\_hex\\_BN.gif](https://commons.wikimedia.org/wiki/File:Structures_cub_hex_BN.gif)  
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The structure and bonding of hexagonal boron nitride, with **smooth, sliding layers** makes it a good **lubricant**. Its structure also allows it to be formed into **nanotubes** which have many uses due to their relative strength and conductivity.

## Group IV Elements

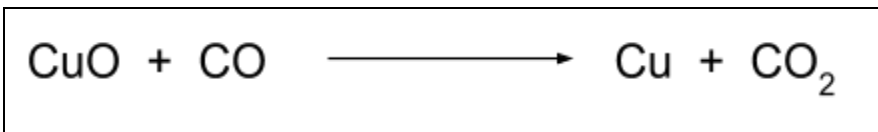
The group IV elements tend to form compounds in the **oxidation state of +4**, such as  $\text{CCl}_4$  or  $\text{SiCl}_4$ . However, stability of the **+4** oxidation state **reduces down the group**, whilst stability of the **+2** oxidation state **increases down the group**. This is due to the inert pair effect, as explained further up the page.



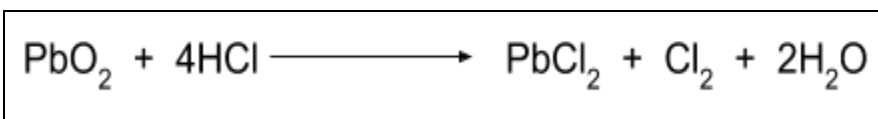


This trend can be demonstrated with a series of reactions that use CO and Pb(IV) as the reducing and oxidising agents.

**Reaction between CO and copper oxide where CO acts as the reducing agent.**

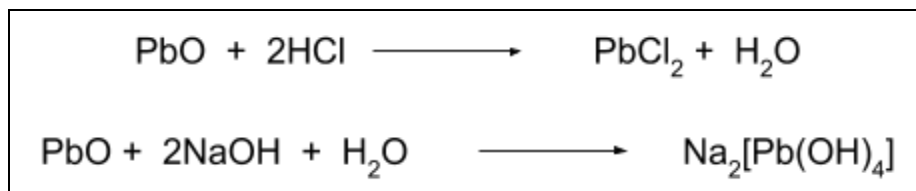


**Reaction between PbO<sub>2</sub> and hydrochloric acid where Pb(IV) acts as the oxidising agent.**

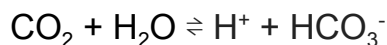


### PbO and CO<sub>2</sub>

PbO is an ionic compound with a relatively large amount of **covalent character** which means it is **amphoteric** and so can act as both an acid and a base.



In comparison, CO<sub>2</sub> has **acidic properties** and the following **equilibrium** is set up in water:



PbO is a **solid** at room temperature, whereas CO<sub>2</sub> is a **gas**. This is because CO<sub>2</sub> is a **simple covalent molecule** so it has **weaker forces** of attraction holding the bonds together.

**PbO** is **insoluble in water** whereas **CO<sub>2</sub>** is **soluble** in water. This is because carbon dioxide is a **polar molecule** which attracts water molecules.

### Group IV Chlorides

The type of **bonding** that occurs with the group IV elements varies down the group from carbon to lead. This is best demonstrated with the **group IV chlorides** that all take on a **tetrahedral structure** - PbCl<sub>2</sub> is the only exception to this.

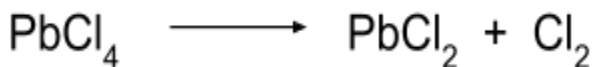
At the top of the group, **carbon and silicon** exist in their **most stable** oxidation state of +4 meaning they don't tend to **break down** into dichlorides. CCl<sub>4</sub> and SiCl<sub>4</sub> are both **simple**





**covalent** molecules held together by **van der waals forces**, meaning they are liquid at room temperature.

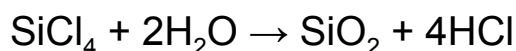
Further down the group, **Lead** can exist in the **+4 or +2 oxidation state** with +2 being much more stable. Therefore, **lead tetrachloride** tends to decompose to produce lead(II) chloride and chlorine gas as these are much more stable products.



Lead(II) chloride is a **white solid** at room temperature and can be considered to have predominantly **ionic character**.

### Group IV Chlorides and water

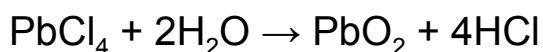
- **Carbon tetrachloride**,  $\text{CCl}_4$ , has **no reaction** with water. The reaction does not take place for several reasons. Firstly, the **chlorine** atoms are **very bulky** and the **carbon** atom is comparably very **small**, so the oxygen cannot easily get to the carbon atom. When the carbon gets close to the chlorine atoms there would also be a lot of **repulsion** due to all the **lone pairs** of electrons. This means that this stage will be very **unstable**, which will give the reaction a **high activation energy**. Another reason why no reaction takes place is that there is **no suitable empty orbital** on the carbon that the oxygen lone pair can bond to.
- **Silicon tetrachloride**,  $\text{SiCl}_4$ , reacts **violently** with water to produce **solid white**  $\text{SiO}_2$  and **misty fumes** of HCl:



This reaction is able to take place because the **silicon** atom is **bigger** than the carbon atom. This gives **more room** around it for the water molecule to attack.

Silicon also has **empty 3d orbitals** available which can accept a lone pair from the water molecule. Therefore, oxygen can bond to the silicon before breaking the silicon-chlorine bond, which makes the process more **energetically favourable**.

- **Lead tetrachloride**,  $\text{PbCl}_4$ , will also react with water to produce **brown solid**  $\text{PbO}_2$  and **misty fumes** of HCl:



This reaction is able to take place due to the **same reasons** as described above for silicon tetrachloride.



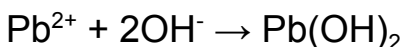


## Reactions of $\text{Pb}^{2+}$ ions

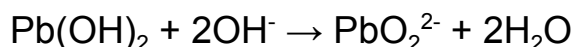
Lead ions can undergo **aqueous reactions with  $\text{NaOH}$ ,  $\text{Cl}^-$  and  $\text{I}^-$**  ions to produce aqueous ion solutions.

### + $\text{NaOH}$

If a small amount of sodium hydroxide solution is added to  $\text{Pb}^{2+}$  ions, a white precipitate of lead(II) hydroxide is produced:



Then, if more sodium hydroxide is added, the precipitate will dissolve to give a colourless solution:



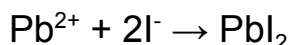
### + $\text{Cl}^-$ ions

A white precipitate is produced when  $\text{Pb}^{2+}$  ions react with dilute hydrochloric acid:



### + $\text{I}^-$ ions

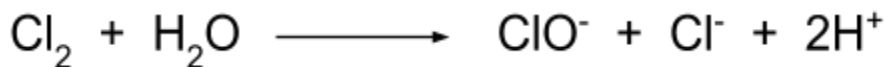
A brown precipitate is produced when  $\text{Pb}^{2+}$  ions react with potassium iodide:



## Chlorine and Chlorate(I)

Chlorine reacts with cold water to produce **chlorate(I) ions ( $\text{ClO}^-$ )** and **chloride ions**.

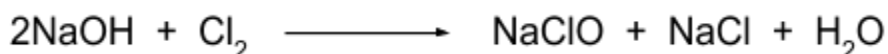
*Example:*



This is a **disproportionation reaction** as the chlorine is both oxidised and reduced. The oxidation state goes from zero to both **+1 and -1**.

Chlorine reacts with both warm and cold sodium hydroxide via disproportionation reactions. When mixed with **cold, aqueous  $\text{NaOH}$** , sodium chlorate(I) and sodium chloride are produced with chlorine in the **+1 and -1** states. Sodium chlorate(I) is a key ingredient in the production of **bleach**.

*Example:*

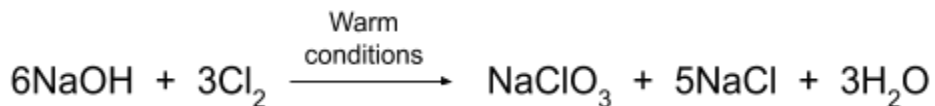






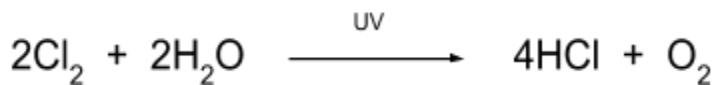
When mixed with **hot, aqueous NaOH**, **chlorate(V)** ions are produced instead. The chlorine is oxidised and reduced to the **-1 and +5** states simultaneously.

*Example:*



In the presence of **UV light**, chlorine decomposes water to produce oxygen and hydrochloric acid. The chlorine is reduced in this reaction.

*Example:*



Chlorine is used in small quantities to kill bacteria in **water treatment processes**. This poses some risks as chlorine can be **toxic**, however, the benefits of clean, treated water outweigh the risks.

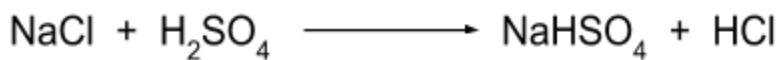
## Sodium Halides

The negative ions of halogens are known as **halide ions**. These ions are **good reducing agents** as they donate electrons to the species being reduced and are themselves oxidised.

This reducing power **increases down the group** as electrons are easier to lose from larger ions due to **shielding** and a **larger atomic radius**.

These redox reactions with  $\text{H}_2\text{SO}_4$  have to be known:

1. Sodium Chloride:



Misty fumes of HCl are observed.

**No further reaction** takes place HCl is not a strong enough reducing agent to reduce the sulfuric acid.



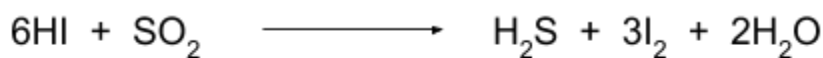
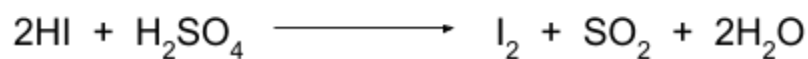
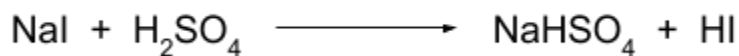


2. Sodium Bromide:



**Misty fumes** of HBr are produced in the first reaction. **Choking fumes** of SO<sub>2</sub> and **orange fumes** of Br<sub>2</sub> are produced in the second reaction.

3. Sodium Iodide:



**Misty fumes** of HI are produced in the first reaction. **Choking fumes** of SO<sub>2</sub>, **black solid** iodine and **bad-egg smelling** H<sub>2</sub>S is produced in the second and third reaction.

The **greater** the reducing power, the **longer** the reaction as the halide is powerful enough to reduce more species.

