

WJEC Chemistry A-Level

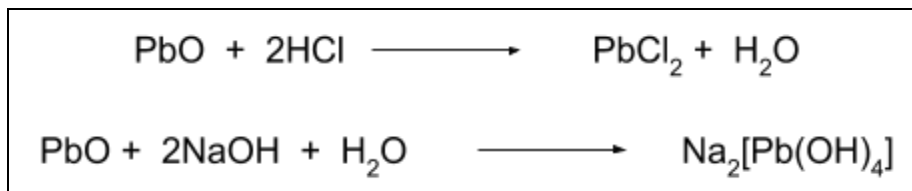
PI2.1: Chemistry of the p -block

Detailed Notes

English Specification

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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 **BF₃** with only **6 electrons** in its valence shell, and similarly aluminium is found in **AlCl₃** 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 **SF₆**. In this compound, sulfur has 12 valence electrons.

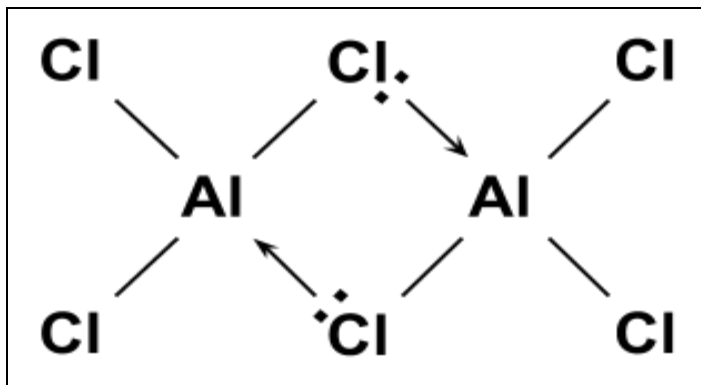




Aluminium Hexachloride

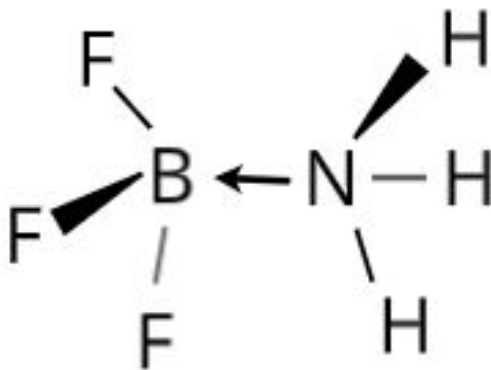
Aluminium hexachloride, Al_2Cl_6 , is a **donor-acceptor dimer**, made up of two separate, identical molecules linked together by two **dative bonds**. Two atoms of chlorine share their lone pair of electrons with two atoms of aluminium to form the dative bonds.

Example:



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

Ammonia boron trifluoride is also a **donor-acceptor dimer**, made up of BF_3 and 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.



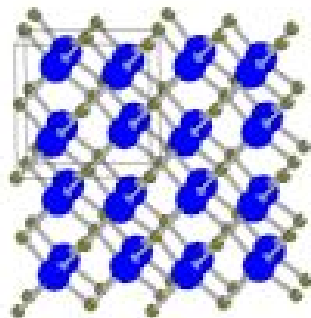
Boron Nitride

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



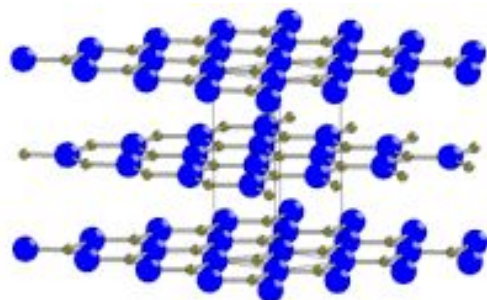
carbon atoms in diamond. The lone pair of electrons on nitrogen are accepted by boron to form a **coordinate bond**, producing a giant 3D covalent lattice.



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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**.



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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

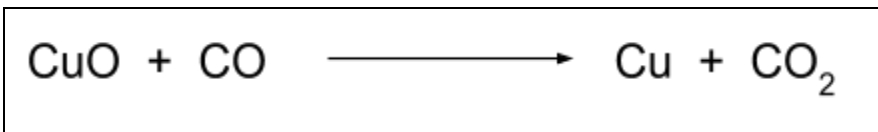
The group IV elements tend to form compounds in the **oxidation state of +4**, such as CCl_4 or SiCl_4 . However, stability of the **+4** oxidation state **reduces down the group**, whilst stability of the **+2** oxidation state **increases down the group**. This is due to the inert pair effect, as explained further up the page.



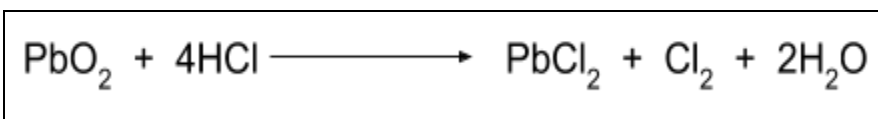


This trend can be demonstrated with a series of reactions that use CO and Pb(IV) as the reducing and oxidising agents.

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

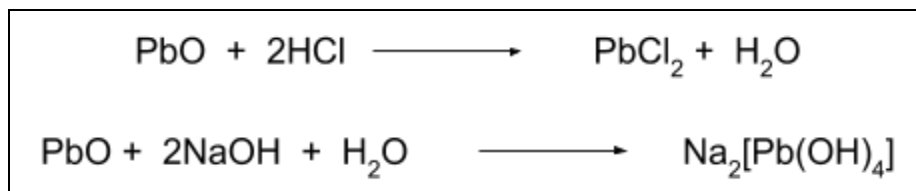


Reaction between PbO₂ and hydrochloric acid where Pb(IV) acts as the oxidising agent.

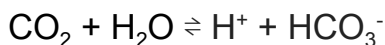


PbO and CO₂

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, CO₂ has **acidic properties** and the following **equilibrium** is set up in water:



PbO is a **solid** at room temperature, whereas CO₂ is a **gas**. This is because CO₂ is a **simple covalent molecule** so it has **weaker forces** of attraction holding the bonds together.

PbO is **insoluble in water** whereas **CO₂** 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** - PbCl₂ is the only exception to this.

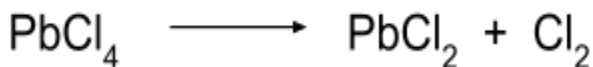
At the top of the group, **carbon and silicon** exist in their **most stable** oxidation state of +4 meaning they don't tend to **break down** into dichlorides. CCl₄ and SiCl₄ are both **simple**





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

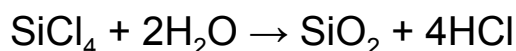
Further down the group, **Lead** can exist in the **+4 or +2 oxidation state** with +2 being much more stable. Therefore, **lead tetrachloride** tends to decompose to produce lead(II) chloride and chlorine gas as these are much more stable products.



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

Group IV Chlorides and water

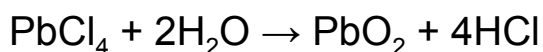
- **Carbon tetrachloride**, CCl_4 , has **no reaction** with water. The reaction does not take place for several reasons. Firstly, the **chlorine** atoms are **very bulky** and the **carbon** atom is comparably very **small**, so the oxygen cannot easily get to the carbon atom. When the carbon gets close 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**, SiCl_4 , reacts **violently** with water to produce **solid white** 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**, PbCl_4 , will also react with water to produce **brown solid** 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.



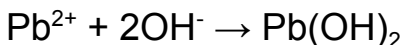


Reactions of Pb^{2+} ions

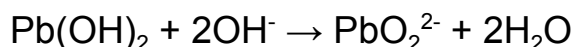
Lead ions can undergo **aqueous reactions with NaOH , Cl^- and I^-** ions to produce aqueous ion solutions.

+ NaOH

If a small amount of sodium hydroxide solution is added to 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:



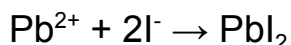
+ Cl^- ions

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



+ I^- ions

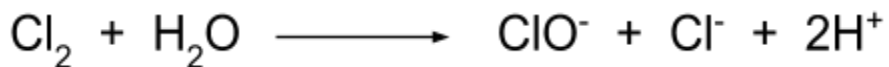
A brown precipitate is produced when Pb^{2+} ions react with potassium iodide:



Chlorine and Chlorate(I)

Chlorine reacts with cold water to produce **chlorate(I) ions (ClO^-)** and **chloride ions**.

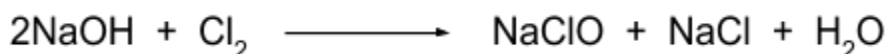
Example:



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 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**.

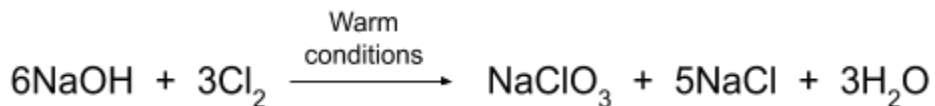
Example:





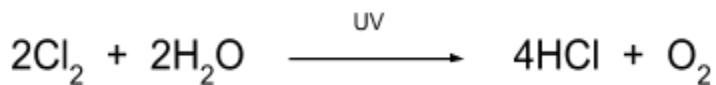
When mixed with **hot, aqueous NaOH**, **chlorate(V)** ions are produced instead. The chlorine is oxidised and reduced to the **-1 and +5** states simultaneously.

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.

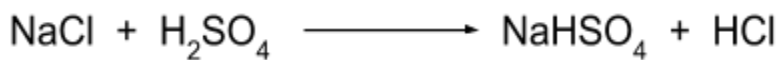
Sodium Halides

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 H_2SO_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.



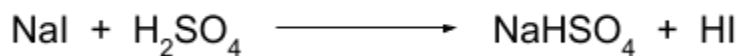


2. Sodium Bromide:



Misty fumes of HBr are produced in the first reaction. **Choking fumes** of SO₂ and **orange fumes** of Br₂ are produced in the second reaction.

3. Sodium Iodide:



Misty fumes of HI are produced in the first reaction. **Choking fumes** of SO₂, **black solid** iodine and **bad-egg smelling** H₂S 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.

