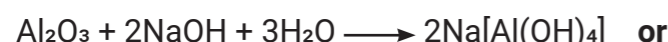


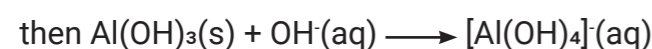
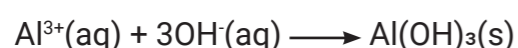
## 3.3 Chemistry of the p-block

### Amphoteric behaviour

Aluminium and lead form amphoteric oxides and hydroxides (they react with both acids and bases). For example:



The reaction of sodium hydroxide with solutions containing metal compounds is used as a test to show if the solution is amphoteric. If the solution forms a precipitate on addition of hydroxide, which is then able to redissolve in excess hydroxide, the compound is amphoteric.



### Inert pair effect

This is the tendency of the outermost  $s^2$  pair of electrons in an atom to remain unshared in compounds, leading to a lower oxidation state.

This occurs in groups 3, 4 and 5. As you go down a group, the tendency increases. Therefore, in Group 3, Tl forms  $\text{Tl}^+$ , in Group 4, Pb forms  $\text{Pb}^{2+}$  and in Group 5, Bi forms  $\text{Bi}^{3+}$ .

### Octet expansion

This is the ability of some atoms to use d-orbitals to have more than 8 electrons in their valence (outer) shell.

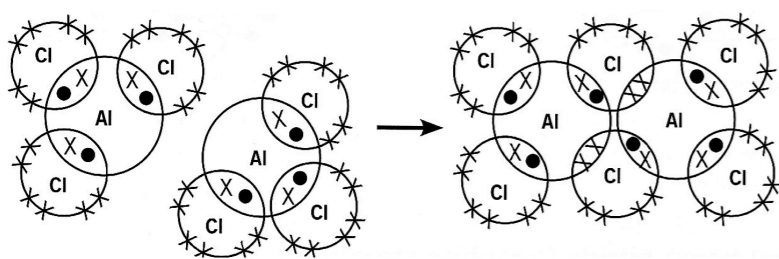
This explains why period 2 elements can only form compounds with eight outer shell electrons, but period 3 elements can form compounds with more than 8 electrons in their outer shell.

For example, nitrogen's only chloride is  $\text{NCl}_3$  but phosphorus can form  $\text{PCl}_3$  or  $\text{PCl}_5$ ; phosphorus has access to d-orbitals, which can accommodate more electrons, so there is no longer a limit of 8 electrons in the outer shell. Nitrogen has no access to d-orbitals so cannot expand its octet.

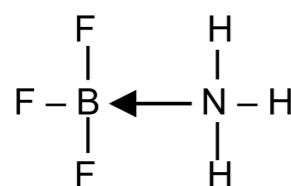
### Electron deficiency in Group 3

An electron-deficient atom is one that does not have a full outer shell i.e. has fewer than eight electrons. When group 3 elements form covalent compounds, they only form 3 covalent bonds. This only gives 6 electrons in the outer shell, which causes electron deficiency.

To fill the shell, they will form **co-ordinate bonds** to gain extra electron pairs. For example, aluminium chloride forms a dimer.



$\text{BF}_3\text{NH}_3$  forms a donor-acceptor compound. The electron deficient  $\text{BF}_3$  accepts a lone pair from the  $\text{NH}_3$ .



### Boron nitride, BN

If you look at the number of electrons in boron + nitrogen and carbon + carbon, you will see that they have the same number, 12. This is known as **isoelectronic**. This leads to BN having several forms that are similar to the different forms of carbon.

### Diamond and cubic BN

Both are extremely hard and have high melting points due to strong covalent bonds between the atoms.

BN is used as a wear-resistant coating.

### Graphite and hexagonal BN

Unlike graphite, the layers in BN are directly above each other, with each B having a N directly above or below it.

There are no delocalised electrons in BN, (the B – N bonds are polar), whilst there are in graphite. So unlike graphite, BN cannot conduct electricity and is used as an electrical insulator.

Forces between layers in both are weak, so layers can slide over one another, making both useful as a lubricant.

### Stability of oxidation states in Group 4

Oxidation states in Group 4 are +2 and +4. The stability of the +2 state **increases** as you go down the group, as the inert pair effect becomes more significant.

Lead's most stable oxidation state is +2, while +4 is the most stable state for the rest of the elements in the group. This is shown by looking at the oxides of carbon and lead.

Since carbon's most stable oxidation state is +4, the most stable oxide of carbon is  $\text{CO}_2$ .

**CO** is easily oxidised to  $\text{CO}_2$  (changes from +2 to +4), so is a **reducing agent**. For example, in the blast furnace



Lead's most stable oxidation state is +2, so the most stable oxide of lead is  $\text{PbO}$ .

**$\text{PbO}_2$**  is easily reduced from +4 to +2, so is an **oxidising agent**.



### Properties of $\text{CO}_2$ and $\text{PbO}$

The properties of the oxides show the change in non-metal at the top of the group to metal at the bottom.

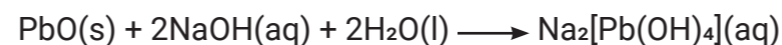
$\text{CO}_2$  is a colourless gas with simple covalent bonding. It is an **acidic oxide**; therefore, it reacts with an alkali to form a salt.



$\text{PbO}$  is an orange solid which contains ionic bonding. It is an **amphoteric oxide**, so reacts with acids and bases.



(most of lead's salts are insoluble, so nitric acid must be used)



### Reactions of Group 4 chlorides with water

The stable chlorides of carbon and silicon are the tetrachlorides. These are **covalently** bonded colourless liquids. The stable chloride of lead is lead(II) chloride. It is an **ionic** solid.

So,  $\text{CCl}_4$  and  $\text{SiCl}_4$  should react with water, but  $\text{PbCl}_2$  will not.

However,  $\text{CCl}_4$  doesn't react with water, it simply forms a separate liquid layer.

$\text{SiCl}_4$  reacts quickly and quite violently with water, forming a white solid of silicon dioxide and cloudy fumes of  $\text{HCl}$ .

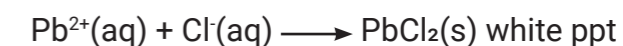
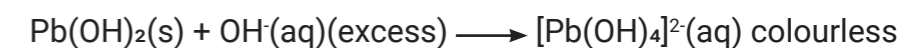


Silicon tetrachloride can react due to the availability of d-orbitals in the silicon atom. They allow a lone pair from oxygen to bond with the  $\text{SiCl}_4$ . These d-orbitals are not available in the carbon atom, so it cannot react.

Lead(II) chloride does not react or dissolve in water, it's insoluble.

### Reactions of $\text{Pb}^{2+}(\text{aq})$

$\text{Pb}^{2+}(\text{aq})$  must be lead(II) nitrate,  $\text{Pb}(\text{NO}_3)_2$  or lead(II) ethanoate,  $\text{Pb}(\text{CH}_3\text{COO})_2$ , since they are the only soluble lead salts.



### Group 7

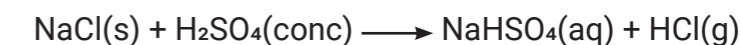
Standard electrode potentials,  $E^\ominus$ , for the halogens, decrease down the group, hence oxidising power decreases down the group.

This means that chlorine is the strongest oxidising agent and iodide ions are the strongest reducing agent.

### Reaction of sodium halides with conc $\text{H}_2\text{SO}_4$

Concentrated sulfuric acid is an oxidising agent. This means that it reacts differently with halide ions depending on the ease of oxidation of the ions.

All of the halides react with sulfuric acid to form  $\text{HCl}$ ,  $\text{HBr}$  or  $\text{HI}$ .



The  $\text{HCl}$  is very difficult to oxidise ( $E^\ominus = +1.36 \text{ V}$ ), so the  $\text{H}_2\text{SO}_4$  doesn't react further. Only steamy fumes ( $\text{HCl}$ ) are seen.

The  $\text{HBr}$  is easier to oxidise ( $E^\ominus = +1.09 \text{ V}$ ), so the  $\text{H}_2\text{SO}_4$  oxidises the  $\text{HBr}$  to  $\text{Br}_2$  ( $\text{Br}^- \rightarrow 0$ ) and is reduced to  $\text{SO}_2$  ( $\text{S} +6 \rightarrow +4$ ).

Steamy fumes ( $\text{HBr}$ ), orange fumes ( $\text{Br}_2$ ) and a choking gas ( $\text{SO}_2$ ) are observed.

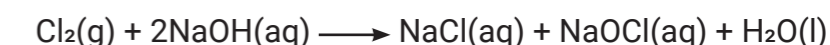
The  $\text{HI}$  is very easy to oxidise ( $E^\ominus = +0.54 \text{ V}$ ), so the  $\text{H}_2\text{SO}_4$  oxidises the  $\text{HI}$  to  $\text{I}_2$  ( $\text{I}^- \rightarrow 0$ ). Since  $\text{HI}$  is a better reducing agent, the  $\text{H}_2\text{SO}_4$  is reduced further to  $\text{S}$  (0) and  $\text{H}_2\text{S}$  (-2).

Steamy fumes ( $\text{HI}$ ), purple fumes ( $\text{I}_2$ ), yellow solid ( $\text{S}$ ) and rotten egg smell ( $\text{H}_2\text{S}$ ) are observed.

### Reaction of $\text{Cl}_2$ with $\text{NaOH}$

Depending on the temperature of the reaction, chlorine can react with dilute sodium hydroxide in one of two ways.

In the cold, they form sodium chloride and sodium chlorate(I).



Chlorine has been oxidised to +1 in sodium chlorate(I) and reduced to -1 in sodium chloride.

This is a **disproportionation** reaction; atoms of the same element are oxidised and reduced to form different products.

When **heated**, sodium chloride and sodium chlorate(V) are formed.



Chlorine has been oxidised to +5 in sodium chlorate(V) and reduced to -1 in sodium chloride.

Again, this is a disproportionation reaction.

### Uses of chlorine and chlorate(I) ions

Chlorine is used in water supplies and chlorate(I) ions are used in bleach. They both work as a disinfectant by killing bacteria, due to their oxidising ability.