



## The Chemistry of Aluminium

To succeed in this topic you need to understand:

- the principles of oxidation and reduction (covered in Factsheet 11);
- salt hydrolysis (covered in Factsheet 85);
- deprotonation (covered in Factsheet 88).

After working through this Factsheet you will:

- know to have revised the extraction of aluminium;
- know how and why aluminium is recycled;
- understand its amphoteric behaviour;
- understand why some of its compounds are covalent;
- know the principal reactions of aluminium;
- understand its aqueous chemistry;
- know the chemistry of its principal compounds.

Aluminium (atomic number = 13) is the most abundant metal in the Earth's crust. It is the second element of Group 3 of the Periodic Table, although its chemistry has much in common with that of beryllium at the head of Group 2.

**Remember** - The head element of a group of the Periodic Table often resembles the second element of the one to the right of it. The similarities are known as *diagonal relationships*.

Aluminium is a p-block element (i.e. one formed by the filling of p-orbitals) and has the electronic configuration  $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$ . It forms only one stable ion,  $Al^{3+}$ , by the loss of all three outer shell electrons.

### Occurrence

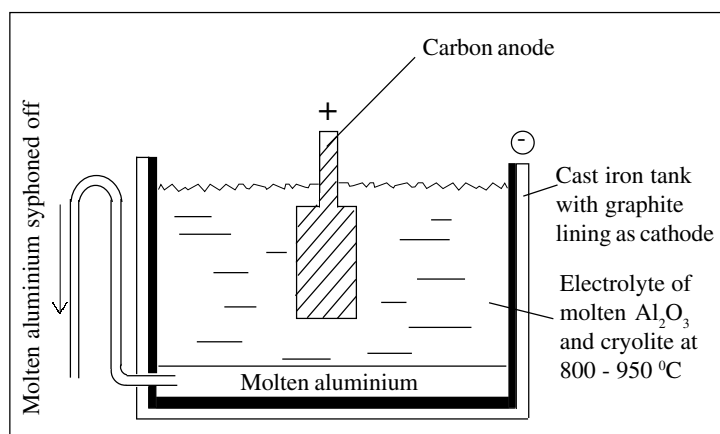
The only commercial ore is *bauxite*,  $Al_2O_3 \cdot 2H_2O$ , found mainly in Jamaica. The main impurities are  $SiO_2$  and  $Fe_2O_3$  which gives it a red brown colour. Before aluminium is extracted by electrolysis, the  $Fe_2O_3$  must be removed, otherwise the product is an Al/Fe alloy with poor resistance to corrosion. The purification of bauxite is described in Factsheet 80.

### Extraction

Aluminium is a very reactive metal near the top of the electrochemical series. A lot of energy is released when it is converted into its oxide: a similar amount of energy is therefore needed to reconvert the oxide to the metal. That is why  $Al_2O_3$  cannot be reduced by carbon: not enough energy is available as C is converted to CO. Electrolytic reduction has to be used instead, because this allows unlimited energy to be supplied. Even so, a huge amount of electricity is needed.

Purified  $Al_2O_3$  is dissolved in molten cryolite,  $Na_3[AlF_6]$ , at  $\sim 900^\circ C$  and electrolysed in a cast iron cell with a graphite lining (Fig. 1).

Fig. 1 The cell for the extraction of aluminium



In an examination, you could be awarded marks for the following details.

- Cryolite is used as a *flux*, i.e. a substance that allows aluminium oxide to be obtained in the molten state at a temperature well below its melting point of  $2045^\circ C$ .

**Exam Hint** - Do not say: 'It lowers the m.p. of  $Al_2O_3$ ', because  $Al_2O_3$  (like all solids) has a fixed melting point. Better to say that a mixture of  $Al_2O_3$  and cryolite has a lower m.p. than  $Al_2O_3$  alone.

- The cathode is the graphite cell lining.
- Several carbon rods are used as anodes.
- The voltage is very low (about 6 V) but the current is enormous (about 100 000 A).
- The electrode reactions are:  
Cathode  $Al^{3+} + 3e^- \rightarrow Al$   
Anode  $2O^{2-} \rightarrow O_2 + 4e^-$
- The anodes burn away in the liberated  $O_2$  and have to be replaced periodically. Heat from the burning anodes helps to keep the electrolyte molten.
- Fresh bauxite is added from time to time.
- Conditions are adjusted so as to minimise decomposition of cryolite.

**Exam Hint** - If you're asked about the siting of an aluminium smelter, remember that the most important requirement is a plentiful supply of relatively cheap electricity, usually from a near-by hydroelectric or nuclear power station. Another consideration is proximity to a port, for importing bauxite.

### Recycling of aluminium

Scrap aluminium (especially from drinks cans) is cut up and melted down, after any steel has been removed with a magnet. Recycling has four advantages:

- It requires far less energy than electrolysis of bauxite.
- It conserves limited reserves of bauxite.
- Tipping in landfill sites is reduced.
- Unlike the electrolysis of bauxite, it does not produce carbon dioxide - a greenhouse gas.

**Exam Hint** - Do not simply say that 'Recycling of aluminium is cheaper' without explaining why.

### Uses of aluminium

- For the manufacture of aircraft, because of its low density and resistance to corrosion.
- For overhead power transmission cables, because of its high electrical conductivity and low density.
- For saucepans, because of its high thermal conductivity and resistance to corrosion.
- For foil and drinks cans, because of its malleability and resistance to corrosion.

Corrosion resistance is due to a very thin protective film of oxide that immediately forms on the surface whenever aluminium is exposed to the air. Unlike rust (on iron), this does not flake off. The thickness of the oxide layer, and hence the resistance to corrosion, can be increased electrolytically. So-called *anodised aluminium* is used for making window frames.

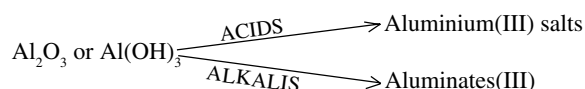
### Chemical properties

Aluminium is described as a 'weak metal'. This does not mean that it is mechanically weak (even though it does have a low tensile strength) but that it has some of the characteristics of non-metals.

- Aluminium is a weak metal because:**
- its oxide and hydroxide are amphoteric, i.e. they have both basic and acidic character;
  - it is chemically attacked by alkalis, e.g.  $\text{NaOH(aq)}$ ;
  - some of its compounds are covalent.

### Amphoteric character

Aluminium oxide and aluminium hydroxide dissolve in both acids and alkalis:

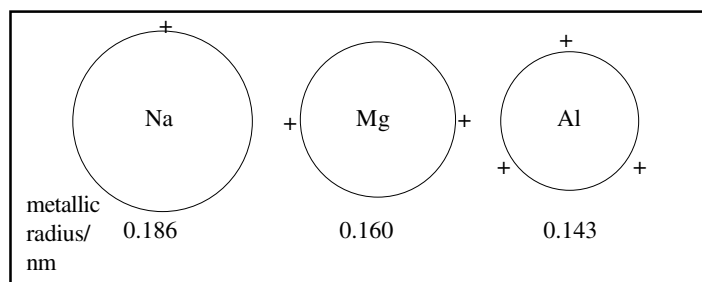


Aluminates, i.e. salts with aluminium in the anion, are also produced when aluminium dissolves in alkalis. Few other metals behave in this way.

**Remember - Well known weak metals are: Al, Zn, Cr, Sn, Pb, Be.**

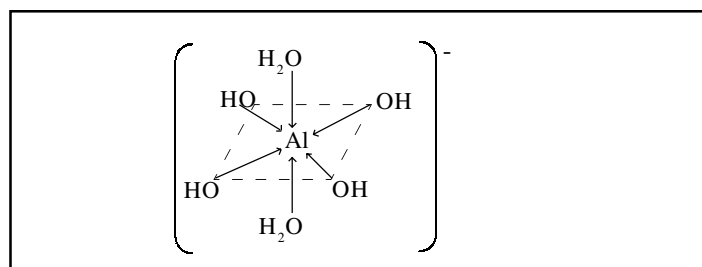
So why aluminium? The key to amphoteric behaviour lies in the very high charge density on the surface of the aluminium ion.

**Fig. 2 To illustrate the high surface charge density on the  $\text{Al}^{3+}$  ion**



$\text{Al}^{3+}$  is a tiny ion (Fig 2) with three positive charges distributed over its small surface area. Consequently, whenever  $\text{Al}^{3+}$  is in the presence of  $\text{OH}^-$  ions, lone pairs of electrons in the outer shell of the O atoms are attracted so strongly that coordinate (or dative covalent) bonds are formed and a complex ion is produced. Figure 3 shows the hydroxo-complex obtained by dissolving Al,  $\text{Al}_2\text{O}_3$  or  $\text{Al(OH)}_3$  in aqueous sodium hydroxide.

**Fig. 3 The diaquatetrahydroxoaluminate(III) ion**



'Sodium aluminate' in solution is therefore a complex salt.



It is named systematically as sodium diaquatetrahydroxoaluminate(III). On evaporating a solution to dryness, water is driven off to leave a solid residue of the simple salt, sodium aluminate,  $\text{NaAlO}_2$ .

### Covalent compounds

Most binary compounds of aluminium, i.e. those derived from aluminium and one other element, are covalent. There are two reasons for this.

- The large amount of energy needed to convert an aluminium atom to an  $\text{Al}^{3+}$  ion (Table 1). The formation of covalent compounds rather than ionic ones is therefore favoured.

**Table 1 Energy required to convert gaseous metal atoms to ions**

Change	Energy/kJ mol <sup>-1</sup>
$\text{Na(g)} \rightarrow \text{Na}^+(\text{g})$	494
$\text{Mg(g)} \rightarrow \text{Mg}^{2+}(\text{g})$	2186
$\text{Al(g)} \rightarrow \text{Al}^{3+}(\text{g})$	5137

However, binary compounds which contain **anions** of high surface charge density are ionic. A notable example is  $\text{Al}_2\text{O}_3$ . Such compounds have a lattice energy which is high enough to give a stable ionic structure, i.e. the energy *released* when gaseous ions join together to give the crystal lattice more than compensates for the energy *required* to form the ions.

- Anions, unless they are particularly small, are *polarisable*, i.e. their electron clouds are not rigidly held by their nuclei and can be distorted by  $\text{Al}^{3+}$ , a cation of high surface charge density with exceptional polarising power. Consequently, the bond pair of electrons ceases to be located at the anion (as in  $\text{NaCl}$ ) but occupies a position between the two nuclei: the essential condition for covalency.

**Remember - According to Fajans' rules, ionic bonding in a compound  $\text{A}^+ \text{B}^-$  tends towards covalency when:**

- $\text{A}^+$  is small;
- the charge on  $\text{A}^+$  is high;
- $\text{B}^-$  is large.

### Reactions with non-metals

Aluminium reacts with most non-metals on heating to give binary compounds with names ending in -ide, e.g. aluminium oxide,  $\text{Al}_2\text{O}_3$ ; aluminium chloride,  $\text{AlCl}_3$ ; aluminium sulphide,  $\text{Al}_2\text{S}_3$ .

### Reactions with acids

Aluminium dissolves readily in hydrochloric acid to give a solution of aluminium chloride plus hydrogen. On crystallising the solution,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  is obtained. *Anhydrous* aluminium chloride is prepared by using hydrogen chloride gas (see below).

**Exam Hint - Anhydrous aluminium chloride cannot be prepared by heating crystals of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ . Thermal decomposition leads to the formation of  $\text{Al}_2\text{O}_3$ ,  $\text{HCl}$  &  $\text{H}_2\text{O}$ .**

There is no reaction with dilute sulphuric acid, because of the protective oxide film on the surface, but with concentrated sulphuric acid oxidation-reduction occurs to give  $\text{Al}_2(\text{SO}_4)_3 + \text{SO}_2$ . With nitric acid, of any concentration, aluminium is rendered *passive*, i.e. inert.  $\text{HNO}_3$ , a powerful oxidising agent, increases the thickness of the surface oxide film.

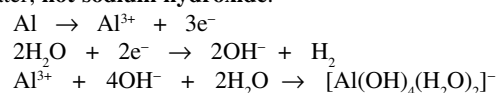
### Reaction with alkalis

Aluminium dissolves readily in dilute aqueous sodium hydroxide.

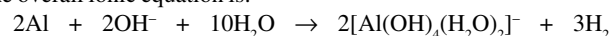
#### Practical 1 - The action of $\text{NaOH(aq)}$ on aluminium

Cautiously warm a piece of aluminium foil with dilute  $\text{NaOH(aq)}$  in a boiling tube. Test the gas evolved with a lighted spill.

This is a redox reaction in which hydrogen is produced by the reduction of water; **not sodium hydroxide**.



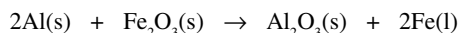
The overall ionic equation is:



**Remember -  $\text{OH}^-$  serves only as a ligand; it is not the oxidant!**

**The thermite reaction**

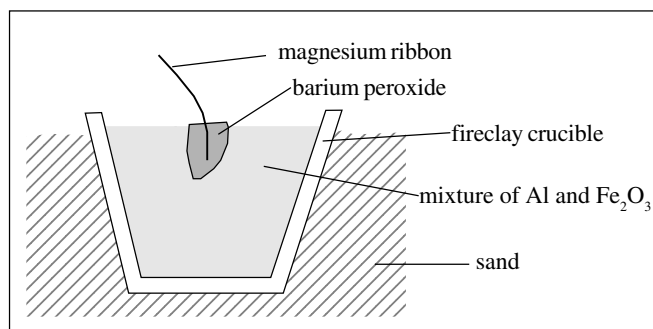
A strongly exothermic redox reaction occurs between powdered aluminium and iron(III) oxide to give aluminium oxide and molten iron:



**This so-called ‘thermite reaction’ should be performed, with appropriate safety precautions, only by a teacher.**

**Demonstration - The thermite reaction**

Set up the apparatus as shown in the following diagram.



Ignite the fuse of magnesium ribbon in barium peroxide with a Bunsen burner and **stand well back**. When the reaction has subsided, observe **with goggles** molten iron in the bottom of the crucible.

The thermite reaction is applied for welding in restricted places, e.g. for making continuously welded railway track. It can also be adapted to prepare other metals below aluminium in the electrochemical series, e.g. chromium, by using  $\text{Cr}_2\text{O}_3$  instead of  $\text{Fe}_2\text{O}_3$ .

**Aqueous chemistry of aluminium****Hydrolysis of aluminium salts**

Aluminium salts are strongly acidic in solution due to hydrolysis.

**Practical 2 - Hydrolysis of aluminium salts**

Dissolve a few crystals of an aluminium salt in water and measure the pH of the solution with universal indicator or a test paper.

The reason is that the hydrated aluminium ion,  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ , present in all solutions, is a Brønsted-Lowry acid capable of donating protons to molecules of solvent water:

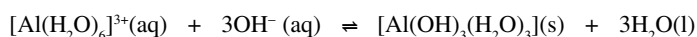


Consequently,  $[\text{H}_3\text{O}^+(\text{aq})] > [\text{OH}^-(\text{aq})]$ , i.e. the solution is acidic. Refer to Factsheet 85 for details

**Deprotonation (acid-base reactions)****Practical 3 - Aluminium salt solutions with NaOH(aq) and  $\text{NH}_3(\text{aq})$** 

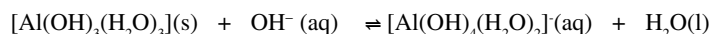
Pour a few  $\text{cm}^3$  of a solution of an aluminium salt into a test tube and add dilute  $\text{NaOH}(\text{aq})$ , dropwise with shaking, until it is eventually present in excess. Observe the formation of a white precipitate, which dissolves in excess reagent to give a colourless solution. Repeat the experiment with dilute  $\text{NH}_3(\text{aq})$  in place of  $\text{NaOH}(\text{aq})$ .

The white precipitate is hydrated aluminium hydroxide, which is formed in a *deprotonation* reaction. Protons are lost from coordinated water molecules of hydrated aluminium ions and transferred to hydroxide ions:

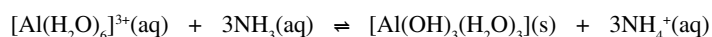


Because  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  behaves as an acid on the Brønsted-Lowry theory (i.e. proton donor), while  $\text{OH}^-$  is a base, this can also be described as an acid-base reaction.

The colourless solution formed with excess  $\text{NaOH}(\text{aq})$  is sodium diaquatetrahydroaluminate(III), formed in a further deprotonation reaction:



With aqueous ammonia the reaction is:



Practical 3 shows that the precipitate does not dissolve in excess reagent. Further deprotonation does not occur because  $\text{NH}_3$  is a weaker base than  $\text{OH}^-$ .

**Important compounds of aluminium****Aluminium oxide,  $\text{Al}_2\text{O}_3$** 

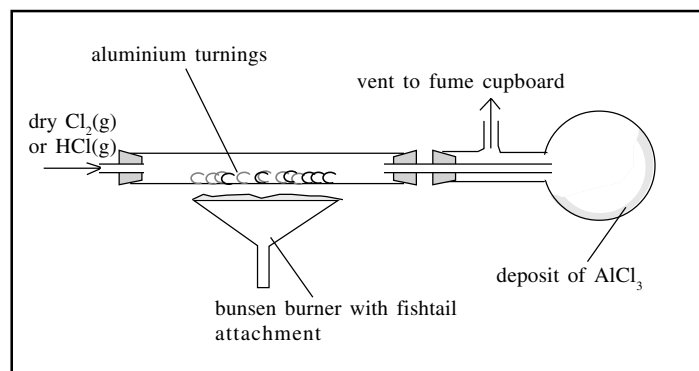
This compound, which occurs naturally in bauxite, can be prepared in the pure state by heating aluminium hydroxide:



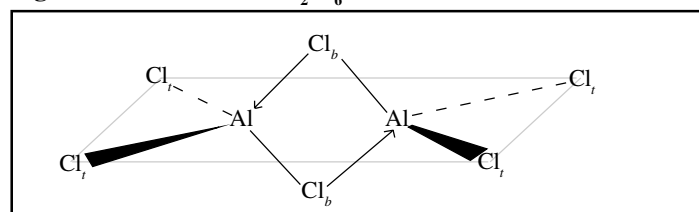
Like  $\text{Al}(\text{OH})_3$ ,  $\text{Al}_2\text{O}_3$  is amphoteric, but is more resistant than the hydroxide to attack by dilute reagents.

**Aluminium chloride,  $\text{AlCl}_3$** 

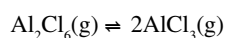
Anhydrous aluminium chloride is prepared by passing **dry** chlorine or hydrogen chloride over heated aluminium in the type of apparatus shown in Fig. 4.

**Fig. 4 Preparation of anhydrous aluminium chloride**

Solid aluminium chloride has a complex polymeric structure (not required at A-level). On heating, it sublimes at  $\sim 200^\circ\text{C}$  to give a dimer,  $\text{Al}_2\text{Cl}_6$ , shown in Fig. 5.

**Fig. 5 The structure of  $\text{Al}_2\text{Cl}_6$** 

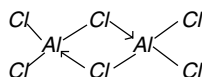
Between  $200^\circ\text{C}$  and  $400^\circ\text{C}$  the dimer dissociates into monomeric molecules:



A dimer can be formed by coordination between two  $\text{AlCl}_3$  molecules because:

- every Cl atom has lone pairs of electrons in its outer shell;
  - every Al atom has a vacant orbital in its outer shell to accept a lone pair.
- In a molecule of  $\text{Al}_2\text{Cl}_6$  the four terminal chlorine atoms ( $\text{Cl}_t$  in Fig. 5) lie at the corners of a rectangular plane which includes both aluminium atoms. The bridging chlorine atoms ( $\text{Cl}_b$ ) lie above and below the plane respectively. This means that the distribution of bonds about each Al atom is roughly tetrahedral.

**Exam Hint** - Do not draw molecules of  $Al_2Cl_6$  as follows, because this implies a planar structure.



### Lithium tetrahydridoaluminate(III), $Li[AlH_4]$

This compound, commonly known as 'lithium aluminium hydride', is made by reacting  $LiH$  and  $AlH_3$  together in dry ether. It is one of the most powerful reducing agents there is, with two principal uses.

- Reduction of carboxylic acids to primary alcohols, e.g.  $CH_3COOH \rightarrow C_2H_5OH$ . It is the only reducing agent able to do this. The related compound  $Na[BH_4]$  will reduce aldehydes and ketones, but is unable to attack carboxylic acids.
- Preparation of hydrides of non-metals, by reducing the corresponding chlorides, e.g.  $PCl_3 \rightarrow PH_3$ .

### Practice Questions

- Why is it that, although the aqueous chemistry of chromium closely resembles that of aluminium, chromium is classed as a transition element but aluminium is not?
- How does the role of carbon in the extraction of aluminium differ from that of extraction of iron?
- Why cannot aluminium be manufactured by electrolysis of either of the following?
  - Molten aluminium chloride
  - An aqueous solution of aluminium chloride
- Although the re-melting of aluminium drinks cans requires a far smaller amount of energy than obtaining the metal by the electrolysis of bauxite, the **overall** energy saving may be significantly less. Explain this.
- Explain why it is that aluminium fluoride is ionic, whereas aluminium chloride is covalent.
- Aluminium dissolves in aqueous potassium hydroxide to give a colourless solution **A** and a colourless, odourless gas **B**. When **A** is treated with a limited amount of dilute sulphuric acid it gives a white precipitate **C**, which dissolves in excess acid to give a colourless solution **D**.
  - Identify the gas **B**.
  - Write down the formulae of the aluminium-containing species present in **A**, **C** and **D**.
  - Explain how first **C** and then **D** are formed from solution **A**.
- Adding a solution of sodium carbonate to one of aluminium sulphate gives a white precipitate **X** and a colourless, odourless gas **Y**. Predict the identities of **X** and **Y** and suggest how these substances are formed.
- Predict the shape of the  $AlCl_3$  molecule.

### Answers

- By definition, a transition element has partially filled d-orbitals in at least one of its stable ions. Chromium conforms to this definition but aluminium does not.
- In the extraction of aluminium, carbon is used for the electrolysis of the cell. In the extraction of iron, carbon is used as a reducing agent.
- For two reasons. First, aluminium chloride sublimes on heating at normal atmospheric pressure. Second, if it were melted under pressure, the liquid would be a non-electrolyte because aluminium chloride is covalent.
  - Hydrogen ions would be discharged at the cathode in preference to aluminium ions.
- Energy is used in collecting, transporting and sorting scrap cans.
- Two energy changes favour the formation of an ionic structure for  $AlF_3$ : (i) the relatively low bond enthalpy of the F-F bond, and (ii) the high lattice enthalpy of  $AlF_3$ . Also, the  $F^-$  ion is smaller than the  $Cl^-$  ion and therefore less subject to polarisation by the  $Al^{3+}$  cation.
- Hydrogen
  - $A = [Al(OH)_4(H_2O)_2]^-$   
 $B = [Al(OH)_3(H_2O)_3]$ , abbreviated to  $Al(OH)_3$   
 $C = [Al(H_2O)_6]^{3+}$
  - Equilibria exist in solution:
 
$$[Al(OH)_4(H_2O)_2]^- (aq) + H_2O(l) \rightleftharpoons [Al(OH)_3(H_2O)_3](s) + OH^- (aq)$$

$$[Al(OH)_3(H_2O)_3](s) + 3H_2O(l) \rightleftharpoons [Al(H_2O)_6]^{3+} (aq) + 3OH^- (aq)$$
 On adding an acid, these equilibria are disturbed to the RHS by the removal of  $OH^- (aq)$  ions:  $H_3O^+ (aq) + OH^- (aq) \rightarrow 2H_2O(l)$
- X** is aluminium hydroxide; **Y** is carbon dioxide. They are formed by a deprotonation/acid-base reaction.  $CO_3^{2-}$ , which is a base, removes protons from  $[Al(H_2O)_6]^{3+}$  to give  $[Al(OH)_3(H_2O)_3]$ . Acceptance of protons by  $CO_3^{2-}$  ions does not give carbonic acid ( $H_2CO_3$ ) because of its instability but, instead, its decomposition products,  $CO_2 + H_2O$ .
- Trigonal planar, due to equal repulsion between three bond pairs of electrons and the absence of a lone pair of electrons on the Al atom.

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