## The Reactivity Series and Corrosion of Metals

K Potassium mo Na Sodium mo Ca Calcium rea Mg Magnesium Al Aluminium C *Carbon* Zn Zinc Fe Iron Sn Tin Pb Lead H *Hydrogen* Cu Copper Ag Silver lear

The higher the metal in the series, the more reactive it is ie the faster, more vigorous and more exothermic the reaction.

- At a more theoretical level,
  - the more reactive a metal, the greater tendency it has to form its positive ion.
- This also implies that the reverse reaction becomes more difficult ie the more reactive a metal, the more difficult it is to extract from its ore and the metal is also more susceptible to corrosion with oxygen and water.
- The reactivity series can be established by observation of the reaction of metals with water, oxygen or acids (and also from simple cell experiments).
- A metal in the series, can displace any metal below it in the series, from the less reactive metal's oxide, chloride or sulphate compound.
  - eg on heating the mixture of magnesium powder and black copper(II) oxide, white magnesium oxide is formed with brown bits of copper:
    - $Mg_{(s)} + CuO_{(s)} = > MgO_{(s)} + Cu_{(s)}$
  - or adding a metal to a salt solution eg adding magnesium to blue copper(II) sulphate solution, the blue colour fades as colourless magnesium sulphate is formed and brown bits of copper metal form a precipitate:
    - $Mg(s) + CuSO_{4(aq)} = > MgSO_{4(aq)} + Cu(s)$
    - The electron transfer **redox theory** behind displacemet reactions is explained later.
- Some general word equations where the metal does react:
  - (a) **metal + cold water => metal hydroxide + hydrogen** (metals above aluminium)
  - (b) heated metal + steam => metal oxide + hydrogen (for metals above tin?)
  - (c) metal + acid => metal salt + hydrogen
    - if the metal is at least as reactive as lead (see reactivity series list above left)
    - and hydrochloric acid makes a metal chloride
    - and **sulphuric** acid makes a metal **sulphate**
    - reactions with nitric acid are complex, the nitrate is formed BUT the gas is rarely hydrogen, and more often an oxide of nitrogen (not usually studied at GCSE level these days).
- Within the general Reactivity or Activity Series of Metals there are some Periodic Table Trends ...
  - Down Group 1 (I) the "Alkali Metals" the activity increases Cs > Rb > K > Na > Li
    - Down Group 2 (II) the activity increases eg Ca > Mg
    - On the same period, the Group 1 metal is more reactive than the group 2 metal, and the group 2 metal is more reactive than the Group 3 metal, and all three are more reactive than the "Transition Metals". eg Na > Mg > AI (on Period 3) and K > Ca > Ga > Fe/Cu/Zn etc. (on Period 4)
- The reactivity of a metal has an important bearing on the method by which a <u>metal is extracted</u> from its ore. Since
  prehistoric times, as technology has improved more and more, all metals can now be extracted and comments on
  when the metals were first isolated and used are added in the table below. If the metal is above carbon, it cannot be

extracted by carbon reduction and must be usually extracted by electrolysis.

- Two non-metals, carbon and hydrogen, are included in the table for comparison, and are important chemical reference points concerning the method of metal extraction and reactivity towards acids
  - Metals above carbon cannot usually be extracted by carbon or carbon monoxide reduction and are usually extracted by electrolysis
  - Metals below carbon in the series can be extracted by heating the oxide with carbon or carbon monoxide.
  - Metals below hydrogen will not displace hydrogen from acids and can be extracted by heating the oxide in hydrogen.

<b>METAL</b> in decreasing reactivity order	<b>Reactivity and Reactions</b>
Caesium CS	<ul> <li>Burns vigorously with a blue flame when heated in air to form the white powder caesium oxide.</li> <li>4Cs(s) + O<sub>2</sub>(g) ==&gt; 2Cs<sub>2</sub>O(s)</li> <li>Because it is extremely reactive, it explodes with cold water forming the alkali caesium hydroxide and hydrogen gas.</li> <li>2Cs(s) + 2H<sub>2</sub>O(t) =&gt; 2CsOH(aq) + H<sub>2</sub>(g)</li> <li>Caesium was first extracted in 1860 by electrolysis of the molten chloride CsCl.</li> </ul>
Rubidium Rb	<ul> <li>Burns vigorously with a red flame when heated in air to form the white powder rubidium oxide.</li> <li>4Rb(s) + O<sub>2(g)</sub> ==&gt; 2Rb<sub>2</sub>O(s)</li> <li>Extremely reactive, can ignite in air, it explodes with cold water forming the alkali rubidium hydroxide and hydrogen gas.</li> <li>2Rb(s) + 2H<sub>2</sub>O(I) =&gt; 2RbOH(aq) + H<sub>2(g)</sub></li> <li>Rubidium was first extracted in 1861 by electrolysis of the molten chloride RbCl.</li> </ul>
Potassium K	<ul> <li>Burns vigorously with a lilac flame when heated in air to form the white powder potassium oxide.</li> <li>4K(s) + O<sub>2(g)</sub> ==&gt; 2K<sub>2</sub>O(s)</li> <li>The reaction of potassium with water - the reaction is the same as for sodium (full description below) BUT it is faster and more exothermic AND so the hydrogen is ignited to give a purple or lilac flame. The hydrogen flame is coloured by the excitation of potassium atoms in the very hot flame. The very rapid reaction with cold water forms the alkali potassium hydroxide and hydrogen gas.</li> <li>2K(s) + 2H<sub>2</sub>O(I) =&gt; 2KOH(aq) + H<sub>2</sub>(g)</li> <li>Potassium was first extracted in 1807 by electrolysis of the molten chloride KCI. [top]</li> </ul>

Sodium Na	<ul> <li>Burns vigorously with a yellow flame when heated in air to form the white powder sodium oxide.</li> <li>4Na(s) + O<sub>2(g)</sub> ==&gt; 2Na<sub>2</sub>O(s) (also forms Na<sub>2</sub>O<sub>2</sub>)</li> <li>The reaction of sodium with water: the sodium melts to a silvery ball and fizzes as it spins over the water. The rapid exothermic reaction produces a colourless gas which gives a squeaky pop! with a lit splint (hydrogen). Universal indicator will turn from green to purple/violet as the strong alkali sodium hydroxide is formed. The initially sodium floats because it is less dense than water.</li> <li>2Na(s) + 2H<sub>2</sub>O(I) =&gt; 2NaOH(aq) + H<sub>2(g)</sub></li> <li>Sodium was first extracted in 1807 by electrolysis of the molten chloride NaCI</li> </ul>
Lithium Li	<ul> <li>Burns vigorously with a red flame when heated in air to form the white powder lithium oxide.</li> <li>4Li(s) + O<sub>2(g)</sub> ==&gt; 2Li<sub>2</sub>O(s)</li> <li>Quite a fast reaction with cold water forming the alkali lithium hydroxide and hydrogen gas. For full description see sodium above, but the reaction is not as fast.</li> <li>2Li(s) + 2H<sub>2</sub>O(t) =&gt; 2LiOH(aq) + H<sub>2(g)</sub></li> <li>Lithium was first extracted in 1821 by electrolysis of the molten chloride LiCl.</li> </ul>
Calcium Ca	<ul> <li>Burns with a brick red flame when strongly heated in air to form the white powder calcium oxide.</li> <li>2Ca(s) + O<sub>2(g)</sub> ==&gt; 2CaO(s)</li> <li>Quite reactive with cold water forming the moderately soluble alkali calcium hydroxide and hydrogen gas.</li> <li>Ca(s) + 2H<sub>2</sub>O(t) =&gt; Ca(OH)<sub>2(aq/s)</sub> + H<sub>2(g)</sub></li> <li>Very reactive with dilute hydrochloric acid forming the colourless soluble salt calcium chloride and hydrogen gas.</li> <li>Ca(s) + 2HCl(aq) =&gt; CaCl<sub>2(aq)</sub> + H<sub>2(g)</sub></li> <li>Not very reactive with dilute sulphuric acid because the colourless calcium sulphate formed is not very soluble and coats the metal inhibiting the reaction.</li> <li>Ca(s) + H<sub>2</sub>SO<sub>4(aq)</sub> =&gt; CaSO<sub>4(s)</sub> + H<sub>2(g)</sub></li> <li>Calcium was first extracted in 1808 by electrolysis of the molten chloride CaCl<sub>2</sub>.</li> </ul>

Magnesium Mg	<ul> <li>Burns with a bright white flame when strongly heated in air to form a white powder of magnesium oxide.</li> <li>2Mg(s) + O<sub>2(g)</sub> ==&gt; 2MgO(s)</li> <li>Slow reaction with water forming the slightly soluble alkali magnesium hydroxide and hydrogen gas.</li> <li>Mg(s) + 2H<sub>2</sub>O(I) =&gt; Mg(OH)<sub>2(aq/s)</sub> + H<sub>2(g)</sub></li> <li>With steam, the reaction is faster with heated magnesium and the white neuroder magnesium oxide is formed with the hydrogen</li> </ul>
	<ul> <li>Magnesium will burn with a bright white flame in steam, if previously ignited in air!</li> <li>Mg(s) + H<sub>2</sub>O(g) =&gt; MgO(s) + H<sub>2</sub>(g)</li> <li>In fact it will even burn in carbon dioxide forming black specks of carbon!</li> <li>2Mg(s) + CO<sub>2</sub>(g) ==&gt; 2MgO(s) + C(s)</li> <li>Very reactive with dilute hydrochloric acid forming the colourless soluble salt magnesium chloride and hydrogen gas.</li> <li>Mg(s) + 2HCl(aq) =&gt; MgCl<sub>2</sub>(aq) + H<sub>2</sub>(g)</li> <li>Very reactive with dilute sulphuric acid forming colourless soluble magnesium sulphate and hydrogen.</li> <li>Mg(s) + H<sub>2</sub>SO<sub>4</sub>(aq) =&gt; CaSO<sub>4</sub>(s) + H<sub>2</sub>(g)</li> <li>Magnesium was first extracted in 1808 by electrolysis of the molten chloride MgCl<sub>2</sub>.</li> </ul>
Aluminium Al	<ul> <li>Surface goes white when strongly heated in air to form aluminium oxide. Theoretically its quite a reactive metal but the oxide layer as an inhibiting effect. This is why it appears to be less reactive than its position in the reactivity series of metals would predict.         <ul> <li><b>4Al</b>(s) + <b>3O</b><sub>2</sub>(g) ==&gt; <b>2Al</b><sub>2</sub><b>O</b><sub>3</sub>(s)</li> </ul> </li> <li>Aluminium has no reaction with water or steam due to a protective aluminium oxide layer of Al<sub>2</sub>O<sub>3</sub>. [note: Chromium behaves chemically in the same way, forming a protective layer of chromium(III) oxide, Cr<sub>2</sub>O<sub>3</sub>, and so its anti-corrosion properties are used in stainless steels and chromium plating]</li> <li><b>The thermit reaction</b>: However the true reactivity of aluminium can be spectacularly seen when its grey powder is mixed with brown iron(III) oxide powder. When the mixture is ignited with a magnesium fuse (high activation energy!), it burns very exothermically in a shower of sparks to leave a red hot blob of iron and white aluminium oxide powder.</li> </ul>
	<ul> <li>aluminium + iron(III) oxide ==&gt; iron + aluminium oxide</li> <li>2Al<sub>(s)</sub> + Fe<sub>2</sub>O<sub>3(s)</sub> ==&gt; Al<sub>2</sub>O<sub>3(s)</sub> + 2Fe<sub>(s)</sub></li> <li>Slow reaction with dilute hydrochloric acid to form the colourless soluble salt aluminium chloride and hydrogen gas.</li> <li>2Al<sub>(s)</sub> + 6HCl<sub>(aq)</sub> =&gt; 2AlCl<sub>3(aq)</sub> + 3H<sub>2(g)</sub></li> <li>The reaction with dilute sulphuric acid is extremely slow to form colourless aluminium sulphate and hydrogen.</li> <li>2Al<sub>(s)</sub> + 3H<sub>2</sub>SO<sub>4(aq)</sub> =&gt; Al<sub>2</sub>(SO<sub>4</sub>)<sub>3(aq)</sub> + 3H<sub>2(g)</sub></li> <li>Aluminium was first extracted in 1825 by electrolysis of its molten oxide Al<sub>2</sub>O<sub>3</sub>.</li> </ul>
(Carbon C, a non- metal)	Elements <b>higher</b> than carbon ie aluminium or more reactive, must be extracted by <b>electrolysis</b> (or displacing it with an even more reactive metal). Metals <b>below it</b> , ie zinc or a less reactive, can be extracted by <b>reducing</b> the hot metal oxide <b>with carbon</b> . [top]

Zinc Zn	<ul> <li>Surface goes white when strongly heated in air to form zinc oxide (yellow when hot).</li> <li>2Zn(s) + O2(g) ==&gt; 2ZnO(s)</li> <li>No reaction with cold water.</li> <li>When the metal is heated in steam zinc oxide and hydrogen are formed.</li> <li>Zn(s) + H2O(g) =&gt; ZnO(s) + H2(g)</li> <li>Quite reactive with dilute hydrochloric acid forming the colourless soluble salt zinc chloride and hydrogen gas.</li> <li>Zn(s) + 2HCl(aq) =&gt; ZnCl2(aq) + H2(g)</li> <li>Quite reactive with dilute sulphuric acid forming the colourless soluble salt zinc sulphate and hydrogen gas.</li> <li>Zn(s) + H2SO4(g) =&gt; ZnSO4(s) + H2(g)</li> <li>Quite reaction is catalysed by adding a trace of copper sulphate solution)</li> <li>Zinc can be extracted by reducing the hot metal oxide on heating with carbon</li> <li>ZZnO(s) + C(s) =&gt; ZnS(s) + CO2(g)</li> <li>A zinc coating (galvanising) is used to protect iron from rusting. The more reactive zinc oxidises 1<sup>st</sup>. Blocks of zinc attached to steel are used as 'sacrificial corrosion'.</li> <li>Zinc was known and used in India and China before 1500 so it must have been extracted like copper or iron by carbon reduction of the oxide, sulphide or carbonate. [top]</li> </ul>
Iron Fe	<ul> <li>Surface goes dark grey-black when strongly heated in air to form a tri-iron tetroxide. When steel wool is heated in a bunsen flame it burns with a shower of sparks - large surface area - increased rate of reaction - so even moderately reactive iron has its moments!</li> <li>3Fe(s) + 2O<sub>2(g)</sub> ==&gt; Fe<sub>3</sub>O<sub>4(s)</sub></li> <li>No reaction with cold water (rusting is a joint reaction with oxygen).</li> </ul>
	<ul> <li>When the metal is heated in steam an iron oxide (unusual formula) and hydrogen are formed. This oxide is 'technically' diiron(III)iron(II) oxide!!!!</li> <li>3Fe(s) + 4H<sub>2</sub>O(g) =&gt; Fe<sub>3</sub>O<sub>4</sub>(s) + 4H<sub>2</sub>(g)</li> <li>Slow reaction with dilute hydrochloric acid forming the soluble pale green salt iron(II) chloride and hydrogen gas.</li> <li>Fe(s) + 2HCl(aq) =&gt; FeCl<sub>2</sub>(aq) + H<sub>2</sub>(g)</li> <li>Slow reaction with dilute sulphuric acid forming the soluble pale green salt iron(II) chloride and hydrogen gas.</li> </ul>
	<ul> <li>Fe(s) + H<sub>2</sub>SO<sub>4</sub>(g) =&gt; FeSO<sub>4</sub>(s) + H<sub>2</sub>(g)</li> <li>Iron can be extracted by reducing the hot metal oxide on heating with carbon monoxide formed from carbon in the blast furnace eg</li> <li>Fe<sub>2</sub>O<sub>3</sub>(s) + 3CO(g) =&gt; 2Fe(s) + 3CO<sub>2</sub>(g)</li> <li>Fe<sub>3</sub>O<sub>4</sub>(s) + 4CO(g) =&gt; 3Fe(s) + 4CO<sub>2</sub>(g)</li> <li>For the past 2500 years. iron has been extracted from pre-historic times using charcoal (C). Known in Anglo-Saxon as 'iron' and in Roman times in Latin as 'ferrum' hence the Fe symbol! [top]</li> </ul>

Tin Sn	<ul> <li>Slow reaction when heated in air to form white tin(IV) oxide or tin dioxide</li> <li>Sn(s) + O<sub>2(g)</sub> ==&gt; SnO<sub>2(s)</sub></li> <li>No reaction with cold water or when heated in steam.</li> <li>Very slow reaction with dilute hydrochloric acid forming the slightly soluble tin(II) chloride and hydrogen gas.</li> <li>Sn(s) + 2HCl<sub>(aq)</sub> =&gt; SnCl<sub>2(aq)</sub> + H<sub>2(g)</sub></li> <li>Very slow reaction with dilute sulphuric acid forming the colourless slightly soluble tin(II) sulphate and hydrogen gas.</li> <li>Sn(s) + H<sub>2</sub>SO<sub>4(g)</sub> =&gt; SnSO<sub>4(s)</sub> + H<sub>2(g)</sub></li> <li>Tin can be extracted from its oxide by heating with carbon. Tin has been known from pre-historic times. Known in Anglo-Saxon as 'tin' and in Latin - 'stannum' hence the symbol Sn! [top]</li> </ul>
Lead Pb	<ul> <li>Slow reaction when heated in air to form red/yellow lead(II) oxide and tri-lead tetroxide</li> <li>2Pb(s) + O2(g) ==&gt; 2PbO(s)</li> <li>and 3Pb(s) + 2O2(g) ==&gt; Pb<sub>3</sub>O<sub>4</sub>(s)</li> <li>No reaction with cold water or when heated in steam.</li> <li>Very slow and effectively no reaction with dilute hydrochloric acid or dilute sulphuric acid.</li> <li>Lead can be extracted from its oxide by heating with carbon. Probably used from pre-historic times and known in Anglo-Saxon as 'lead' and in Latin 'plumbum' hence the symbol Pb! [top]</li> </ul>
Hydrogen H non-metal	Non of the metals below hydrogen can react with acids to form hydrogen gas. They are least easily corroded metals and partly accounts for their value and uses in jewellery, electrical contacts etc. [top]
Copper Cu	<ul> <li>Surface blackens when strongly heated in air to form copper(II) oxide.</li> <li>2Cu(s) + O<sub>2(g)</sub> ==&gt; 2CuO(s)</li> <li>No reaction with cold water or when heated in steam.</li> <li>No reaction with dilute hydrochloric acid or dilute sulphuric acid.</li> <li>Copper can be extracted by reducing the hot black metal oxide on heating with carbon</li> <li>2CuO(s) + C(s) =&gt; 2Cu(s) + CO<sub>2(g)</sub></li> <li>The elemental metal can be found 'native' and was probably first used over 6000 years ago in Turkey by literally beating it out of rocks and into shape (malleable at room temperature!) - no high temperature technology used or available. It has been extracted by carbon reduction of a copper mineral for at least 3000 years. Latin 'cuprum' meaning Cyprus?, anyway that's why its symbol is Cu! [top]</li> </ul>

	No reaction when heated in air.
Silver Ag	<ul> <li>No reaction with cold water or when heated in steam.</li> <li>No reaction with dilute hydrochloric acid or dilute sulphuric acid.</li> <li>Silver can be extracted by BUT can be found 'native' as the element because it is so unreactive. It has been used from prehistoric times in jewellery for 4000 years at least. In Anglo-Saxon it was 'siolfur' meaning 'silver in nature' and in Latin 'argentum' hence its symbol Ag. [top]</li> </ul>
Gold Au	<ul> <li>No reaction when heated in air</li> <li>No reaction with cold water or when heated in steam.</li> <li>No reaction with dilute hydrochloric acid or dilute sulphuric acid.</li> <li>Gold can be readily extracted from its ores easily by reduction BUT it is usually found 'native' as the element because it is so unreactive and has been used from pre-historic times in jewellery for at least 6000 years. Known in Anglo-Saxon as 'gold'. Gold is rather a soft metal and is 'hardened' by alloying with other metals - pure gold is 24 carat - 22, 18, 15, 12 and 9 carat gold are legalised, meaning it has that carat number/24 as parts of gold as a measure of its purity and value! [top]</li> </ul>
Platinum Pt	<ul> <li>No reaction when heated in air.</li> <li>No reaction with cold water or when heated in steam.</li> <li>No reaction with dilute hydrochloric acid or dilute sulphuric acid.</li> <li>It seems ironic that despite its apparent lack of 'reactivity' it is a very potent catalyst eg catalytic converter in cars.</li> <li>Spanish 'platina' meant 'silvery in nature'. Like gold, it is a very rare metal but was known by pre-Columbian South American Indians and brought to Europe in about 1750. It is used in expensive jewellery, laboratory ware (eg inert crucible container) and catalytic converters in car exhausts. [top]</li> </ul>

## **METAL CORROSION and the RUSTING of IRON**

- **Iron (or steel)** corrodes more quickly than most other transition metals and readily does so in the presence of **both oxygen** (in air) and **water** to form an iron oxide. You can do simple experiments to show that BOTH oxygen and water are needed. Put an iron nail into (1) boiled water in a sealed tube; (2) a tube of air and a drying agent; (3) an open test tube with water. Rusting appears overnight with (3) only.
- **Rusting is speeded up** in the presence of **salt** or acid solutions because of an **increased concentration of ions**. Corrosion is a redox process involving redox electron transfer and ion movement. The rusting metal behaves like a simple cell and more ions enable the current, and hence the electron transfer, to occur more readily.
- Rusting is overall ... Fe<sub>(s)</sub> + O<sub>2(g)</sub> + H<sub>2</sub>O<sub>(l)</sub> ==> Fe<sub>2</sub>O<sub>3</sub>.xH<sub>2</sub>O<sub>(s)</sub> ie rust is a hydrated iron(III) oxide (the equation is not meant to be balanced and the amount of water x is variable, from dry to soggy!).
  - The reaction proceeds via iron(II) hydroxide Fe(OH)2 which is the oxidised further to the



## Fe(OH)<sub>3</sub>

- **Rusting is an oxidation** because it involves iron gaining oxygen (Fe ==>  $Fe_2O_3$ ) or iron atoms losing electrons (Fe  $3e^- ==> Fe^{3+}$ .
- See <u>more examples of oxidation and reduction</u> below.
- The rusting of iron is a major problem in its use as a structural material.
- Iron and steel (alloy of iron) are most easily protected by paint which provides a barrier between the metal and air/water. Moving parts on machines can be protected by a water repellent oil or grease layer.
- This 'rusting' corrosion can be prevented by connecting iron to a more reactive metal (e.g. zinc or magnesium). This is referred to as sacrificial protection or sacrificial corrosion, because the more reactive protecting metal is preferentially oxidised away, leaving the protected metal intact. The picture illustrates what might be seen after a few days.\* Iron or steel can also be protected by mixing in other metals (e.g. chromium) to make non-rusting alloys called stainless steel. The chromium, like aluminium, forms a protective oxide layer.
- \* Theoretically, any iron ions formed by oxidation would be reduced by electrons from the oxidation of the more reactive 'sacrificed' metal.
- Coating iron or steel with a thin zinc layer is called '**galvanising**'. The layer is produced by electrolytic deposition by making the iron/steel the negative cathode or by dipping the iron/steel object in molten zinc (more details). The zinc preferentially corrodes or oxidises to form a zinc oxide layer that doesn't flake off like iron oxide rust does. Also, if the surface is scratched, the exposed zinc again corrodes before the iron and continues to protect it.
- Steel tin cans are protected by relatively unreacted tin and works well as long as the thin tin layer is complete. HOWEVER, if a less reactive metal is connected to the iron, it then the iron rusts preferentially (try scratching a 'tin' can and leave out in the rain and note the corrosion by the scratch!)
- Aluminium does not oxidise (corrode) as quickly as its reactivity would suggest. Once a thin oxide layer of Al<sub>2</sub>O<sub>3</sub> has formed on the surface, it forms a barrier to oxygen and water and so prevents further corrosion of the aluminium.
- Aluminium is a useful structural metal. It can be made harder, stronger and stiffer by mixing it with small amounts of other metals (e.g magnesium) to make alloys.
- **Copper and Lead** are both used in roofing situations because neither is very reactive and the compounds formed do not flake away as easily as rust does from iron. Lead corrodes to a white lead oxide or carbonate and **copper corrodes to form a basic green carbonate** (combination of the hydroxide Cu(OH)<sub>2</sub> and carbonate CuCO<sub>3</sub> eg seen as green roof on buildings).
- Both metals have been used for piping but these days lead is considered too toxic and copper is usually used as the stronger, but equally unreactive alloy with zinc, **brass**. Now of course, most piping is flowing in the plastic direction which doesn't corrode at all!
- The Group 1 Alkali Metals rapidly corrode in air and need to be stored under oil.
- Apart from their structural weakness they would hardly used for any outside purpose!

## DONE