Reactivity series of Metals

Sacrificial anodes work because zinc is more reactive than iron, but how did the engineers know to use zinc rather than e.g. copper?

Would it work if the pipes were made of titanium rather than iron?

Could aluminium be used for galvanising iron?

We need to put the metals in reactivity order. How can we do this?
Key ideas: redox

We already know of oxidation as the addition of oxygen and reduction as removal of oxygen, but this only one definition.

A substance is oxidised if it loses electrons, and reduced if it gains electrons:

\[
\begin{align*}
\text{Oxidation} & \quad \text{Is} \quad \text{Loss} \\
\text{Reduction} & \quad \text{Is} \quad \text{Gain}
\end{align*}
\]

Because when one substance loses electrons, another has to gain them, these are redox reactions.

We can also define a **reducing agent** as a substance that causes another substance to gain electrons or lose oxygen, and an **oxidising agent** as a substance that causes another substance to lose electrons or gain oxygen.
1. Reactions of metals with water

Reactive metals undergo a redox reaction with cold water. We have already seen this with the Group 1 metals, where we established the order:

\[
\text{potassium} \succ \text{sodium} \succ \text{lithium}
\]

e.g. \[2 \text{Li} (s) + 2 \text{H}_2\text{O} (l) \rightarrow 2 \text{LiOH} (aq) + \text{H}_2(g)\]

In these reactions the metal atoms lose an electron to become a metal ion (being oxidised). The water is therefore the oxidising agent. The water loses oxygen (is reduced).

Practical work:
establish the reactivity order for lithium, magnesium and calcium by reacting similar size pieces with cold water.
Conclusions:
Calcium reacts exothermically with cold water, producing hydrogen gas. The reaction is less vigorous than that between lithium and water.

$$2\text{Ca}_\text{(s)} + 2\text{H}_2\text{O}_\text{(l)} \rightarrow 2\text{Ca(OH)}_\text{2(aq)} + \text{H}_2\text{(g)}$$
calcium          water          calcium hydroxide                hydrogen

Magnesium hardly reacts with cold water at all – the reaction is extremely slow. We can see that the order is

lithium \(>\) calcium \(>\) magnesium

Other metals such as iron, zinc, copper, silver and gold also do not react with cold water, and so are less reactive than calcium.
2. Reactions of metals with dilute acids

It is **too dangerous** to react the very reactive metals, potassium, sodium, lithium and calcium with acids.

Reactions with dilute sulphuric or hydrochloric acid can be used to establish the reactivity order for magnesium, aluminium, zinc, iron and copper.

e.g. \[ \text{Mg}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{MgSO}_4(aq) + \text{H}_2(g) \]

The magnesium atoms are **oxidised**, losing electrons to become metal ions. The acid is the **oxidising agent** that causes this to happen. The \(\text{H}^+\) ions in the acid gain an electron each (**reduction**) to become hydrogen atoms in a hydrogen molecule.
Practical:

React magnesium, aluminium, zinc, iron and tin with dilute sulphuric or hydrochloric acid. Note your observations.

If no reaction (or very slow) with cold dilute acid, warm (but don’t boil) the acid and note how this affects the reaction.

In what ways was your practical work not fair tests to put these metals in reactivity order?
Conclusions:
Magnesium reacts vigorously with cold dilute acid. The reaction is exothermic, and hydrogen is given off:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Aluminium reacts slowly with cold acid, but after warming reacts very vigorously:

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

Zinc and iron react slowly with cold acid, but more rapidly on warming:

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$
$$Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$$

Copper does not react with these acids even when warmed.
Order: magnesium > aluminium > zinc > iron > copper
3. Displacement reactions of metals with metal oxides

Reactions with water and acids only work for metals which are more reactive than hydrogen. As an alternative we can use displacement reactions.

These reactions are also redox reactions. The more reactive metal is oxidised and the less reactive metal reduced.

\[
\text{Mg} + \text{ZnO} \rightarrow \text{MgO} + \text{Zn} \\
\text{MgO} + \text{Zn} \rightarrow \text{Mg} + \text{ZnO}
\]

Magnesium wins the ‘tug-of-war’
Example: The Thermit Reaction

This reaction shows that aluminium is more reactive than iron. It is of practical use as it is used to make molten iron for welding rails together.

\[
2\text{Al}_\text{(s)} + \text{Fe}_2\text{O}_3\text{(s)} \rightarrow \text{Al}_2\text{O}_3\text{(s)} + 2\text{Fe}_\text{(l)}
\]

aluminium   iron(III) oxide   aluminium oxide   iron

The iron is displaced from its oxide by the more reactive aluminium. Aluminium is oxidised to aluminium oxide. Iron(III) oxide is reduced to iron.
4. Displacement reactions of metals with metal salts

A more reactive metal will **displace** a less reactive metal from a solution of one of its salts.

Example: If we dip a zinc strip in copper sulphate solution, copper metal is deposited on the zinc.

\[
\text{Zn}_\text{(s)} + \text{CuSO}_4\text{(aq)} \rightarrow \text{ZnSO}_4\text{(aq)} + \text{Cu}_\text{(s)}
\]

The copper has been displaced from the salt solution by the zinc. The zinc atoms have **lost electrons** to become zinc ions, and the copper ions in the solution have **gained electrons** to become atoms of copper metal.

This method **does not work** for reactive metals such as calcium or sodium. Why?
Practical - Try the following reactions:

Magnesium ribbon in lead nitrate solution
Copper wire in silver nitrate solution
Copper wire in lead nitrate solution
Iron nails in copper sulphate solution

What can you conclude from each experiment, in terms of the relative reactivities of the two metals?
Results:
Magnesium ribbon in lead nitrate solution:
Obs: Crystals of lead are seen growing on the magnesium
Reaction: \[ \text{Mg} (s) + \text{Pb(NO}_3\text{)}_2(aq) \rightarrow \text{Mg(NO}_3\text{)}_2(aq) + \text{Pb} (s) \]
Conclusion: Mg is more reactive than Pb

Copper wire in silver nitrate solution:
Obs: Crystals of silver are seen growing on the copper wire
Reaction: \[ \text{Cu} (s) + 2\text{AgNO}_3(aq) \rightarrow \text{Cu(NO}_3\text{)}_2(aq) + 2\text{Ag} (s) \]
Conclusion: Cu is more reactive than Ag

Copper wire in lead nitrate solution:
No reaction – Cu must be less reactive than Pb

Iron nails in copper sulphate solution:
Obs: A coating of copper is deposited on the iron nails
Reaction: \[ \text{Fe} (s) + \text{CuSO}_4(aq) \rightarrow \text{FeSO}_4(aq) + \text{Cu} (s) \]
Conclusion: Fe is more reactive than Cu
Why are these reactions also **redox** reactions?

Oxidation is loss of electrons  
Reduction is gain of electrons

Look at the reaction below:

\[ \text{Zn}(s) + \text{CuSO}_4(aq) \rightarrow \text{ZnSO}_4(aq) + \text{Cu}(s) \]

What is the charge on the zinc ion in \(\text{ZnSO}_4\)?  
What has happened in terms of electrons to the zinc in the reaction?  
Why is this oxidation?  
What is the charge on the copper ion in \(\text{CuSO}_4\)?  
What has happened in terms of electrons to the copper in the reaction?  
Why is this reduction?  
What is the reducing agent in this reaction?
Why are these reactions also redox reactions?

Oxidation is loss of electrons
Reduction is gain of electrons

Look at the reaction below:

$$\text{Zn}_\text{(s)} + \text{CuSO}_4\text{(aq)} \rightarrow \text{ZnSO}_4\text{(aq)} + \text{Cu}_\text{(s)}$$

- The zinc ion in ZnSO$_4$ has a 2+ charge
- In the reaction, Zn loses two electrons:  $\text{Zn} - 2\text{e}^- \rightarrow \text{Zn}^{2+}$
- The zinc atom has been oxidised by losing electrons
- The copper ion in CuSO$_4$ has a 2+ charge
- The copper ion gains two electrons:  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
- The copper ion has been reduced by gaining electrons.
- The zinc caused the copper ions to be reduced, so the zinc is the reducing agent.
The iron forms $\text{Fe}_2\text{O}_3$ when it rusts. Each Fe atom loses 3 electrons to become $\text{Fe}^{3+}$:

$$\text{Fe} - 3e^- \rightarrow \text{Fe}^{3+}$$

The zinc atoms prevent this by supplying electrons to turn the $\text{Fe}^{3+}$ ions back into Fe:

$$\text{Zn} - 2e^- \rightarrow \text{Zn}^{2+} \quad \text{(oxidation)}$$

and

$$\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe} \quad \text{(reduction)}$$

So sacrificial protection is also a redox reaction

Overall: $3\text{Zn} + 2\text{Fe}^{3+} \rightarrow 3\text{Zn}^{2+} + 2\text{Fe}$
Extracting and using metals

Only the most unreactive metals such as gold and platinum are found as native metals.

All the other metals we use are extracted from their ores by redox reactions.
Definition: An ore is a rock containing enough of a metal compound for it to be worth extracting the metal from the rock.

The metal compounds in rocks are often metal oxides, sometimes metal sulphides or carbonates.

- **Bauxite** contains aluminium oxide, from which we extract aluminium.

- **Galena** is lead sulphide from which we obtain lead.

- **Iron pyrites** (Fools Gold) is actually iron sulphide, and contains no gold. We normally obtain iron from an ore called **haematite** which contains iron oxide.
Methods for turning the metal compounds in ores into metals depend on how reactive the metal is.

Two methods commonly used are:

1) REDUCTION WITH CARBON
Used for oxides of metals less reactive than carbon – the carbon displaces the metal, becoming oxidised to form carbon dioxide, and the metal oxide is reduced to the metal. Carbon is used because it is cheap and plentiful.

2) ELECTROLYSIS
Can be used for any ore, but uses huge amounts of energy, so an expensive process. Therefore usually only used for metals more reactive than carbon.
Extraction and uses of Iron

Reduction is used to extract iron from its ore (haematite) which is mainly iron(III) oxide.

The iron ions are reduced to iron atoms, using carbon. This is oxidised to form carbon dioxide.

$$\text{iron(III) oxide} + \text{carbon} \rightarrow \text{iron} + \text{carbon dioxide}$$

$$2 \text{Fe}_2\text{O}_3(\text{s}) + 3\text{C}(\text{s}) \rightarrow 4 \text{Fe}(\text{l}) + 3 \text{CO}_2(\text{g})$$
The process happens in a **blast furnace**.

**Raw materials:**

**Iron ore** – contains the iron to be extracted

**Coke** – contains the carbon to reduce the iron ore

**Air** – provides oxygen to burn the carbon, which also heats the blast furnace

**Limestone** – is mainly calcium carbonate, which removes the impurities (sand) in the iron ore by reacting to form slag, which floats on the molten iron.
**Blast Furnace reactions**

Firstly the carbon in the coke is **oxidised** by the oxygen in the air to form carbon dioxide. This **exothermic** reaction heats the blast furnace:

\[
C(s) + O_2(g) \rightarrow CO_2(g)
\]

The carbon dioxide reacts with more carbon to form the **reducing agent**, carbon monoxide:

\[
C(s) + CO_2(g) \rightarrow 2CO(g)
\]

The carbon monoxide then **reduces** the iron oxide in the iron ore to iron:

\[
Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)
\]

Meanwhile the calcium carbonate is **thermally decomposed** to calcium oxide. This is a base which **neutralises** the sandy impurities (silicon dioxide, an acidic non-metal oxide) to make calcium silicate:

\[
CaCO_3(s) \rightarrow CaO(s) + CO_2(g)
\]

\[
CaO(s) + SiO_2(s) \rightarrow CaSiO_3(l)
\]

- calcium oxide
- sand
- slag
What comes out:

**Molten iron** – this is cast iron and contains carbon impurities. It is brittle and not yet very useful.

**Slag** – calcium silicate is a waste product, but can be used for road surfacing.

**Carbon dioxide** – produced in several of the reactions in the blast furnace.

**Nitrogen** – left over from the air going into the blast furnace, after the oxygen has been used in reactions.
Extraction of lead from its ore

This is done in two stages. Firstly the lead ore (which is mainly lead sulphide) is heated in air to oxidise it. The products are lead oxide and sulphur dioxide:

\[ \text{PbS}_{(s)} + \text{O}_2(g) \rightarrow \text{PbO}_{(s)} + \text{SO}_2(g) \]

Balance this equation!
The lead oxide is then heated with coke (carbon) in a blast furnace to cause a **displacement reaction** which produces lead and carbon dioxide. This works because carbon is more reactive than lead, so carbon can **reduce** the lead oxide to lead. The carbon gets **oxidised**, so this is also a **redox** reaction.

\[
\text{PbO}_\text{(s)} + \text{C}_\text{(s)} \rightarrow \text{Pb}_\text{(l)} + \text{CO}_2\text{(g)}
\]

Balance this equation!
Practical work:

Use displacement reactions to show that lead and copper are less reactive than carbon:

• Mix the metal oxide and carbon powder thoroughly – use more carbon than metal oxide.

• Heat the mixture strongly in an old test tube (pyrex), for several minutes.

• Allow to cool, then tap the contents of the tube out onto a heatproof mat and look for signs of lead and of copper being formed.
Extraction of Aluminium

Electrolysis is used to extract aluminium from aluminium oxide, because aluminium is more reactive than carbon.

The ionic aluminium oxide is split into its elements, aluminium (a metal) and oxygen (a gas).

$$2 \text{Al}_2\text{O}_3(\text{l}) \rightarrow 4 \text{Al}(\text{l}) + 3 \text{O}_2(\text{g})$$
The aluminium oxide is mixed with cryolite, which acts as a solvent to dissolve the aluminium oxide, and allows the mixture to melt at a lower temperature (about 950°C rather than nearly 2000°C).

This saves some energy costs – although the current required is very high, so the cost of electricity is a major factor.

At the negative electrode, molten aluminium is collected:

\[
\text{Al}^{3+}_{(l)} + 3\text{e}^- \rightarrow \text{Al}_{(l)} \quad \text{REDUCTION}
\]

At the positive electrode, oxygen is formed:

\[
2\text{O}^{2-}_{(l)} - 4\text{e}^- \rightarrow \text{O}_2_{(g)} \quad \text{OXIDATION}
\]

The anodes are made of graphite (carbon) and react with the oxygen, releasing carbon dioxide. This means they get eaten away, and have to be replaced sometimes.