# Option: Shipwrecks, Corrosion and Conservation

## 1. The chemical composition of the ocean implies its potential role as an electrolyte.

### *Students learn to:*

- The ocean has a large amount of **positive and negative ions** dissolved in it (mainly $NaCl$), 3.5% by mass or a 0.5 molL$^{-1}$ solution with a pH of 8, and thus acts as an **electrolyte**. These minerals originate from two main sources:
  - **Terrestrial leaching** or **chemical weathering** is where rain water **percolates** through rocks and soils as it runs over the land to get to the ocean. In doing so, it **dissolves many ions** from the land in the percentage breakdown depending on their **solubility** where they are transported to the ocean. These include sodium, calcium, magnesium, chloride and sulfate. **Acid rain** also dissolves carbonates and some nitrates and phosphates are acquired from **decaying organic matter**. **3 billion metric tons** of ions are transported this way every year.
  - **Hydrothermal vents** (pictured right) are caused by **mid-ocean ridges** where **tectonic activity** between plates occurs. This allows water to percolate to magma which **superheats the water** making minerals **highly soluble** then forcing it back out into the ocean. The majority of these minerals are **deposited** around the vent but many are **dispersed** throughout the oceans thus they **contribute significantly** to ion concentrations.
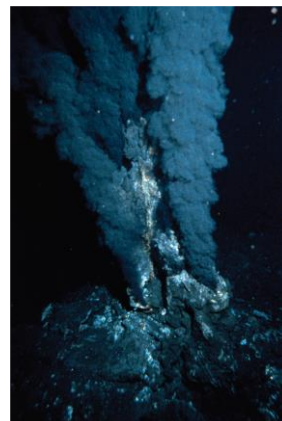
  This **ionic balance** is maintained by salt spray, mineral deposition and organic processes.
- An **oxidation-reduction reaction** is a chemical reaction that involves the **transfer of electrons**, also known as a **redox reaction**. **Oxidation Is Loss** of electrons whilst **Reduction Is Gain** and both must occur **simultaneously**. Thus, the role of electron transfer defines redox reactions.
- Redox must occur in contact or can occur separately where the electrons are transferred through a **conductor** (a metal). The corresponding charge inequities balanced by **ions in a solution**. Thus if an **electrolyte** is present, redox often occurs **spontaneously** as the charge build up does not limit it.

### *Students:*

- Four men were crucial in our understanding of electron transfer reactions:
  - **Luigi Galvani:** (1737-1798) In 1791, Galvani published a paper where he stated how **dissected frogs legs** could be made to contract using **static electricity**. He also discovered that when frog spines were hung from **copper** hooks attached to an **iron** railing, continual contractions occurred. He concluded that muscle issue must hence contain an inherent *animal electricity* the drove biological functions. Whilst he was incorrect, his theories sparked the **investigation of electrics** and the galvanometer and galvanic cell are named in his honour.
  - **Count Alessandro Volta:** (1745-1827) was a physicist who was interested in Galvani's work but disagreed with his **interpretation**. Volta thought the electricity originated from an **electrical interaction** between the **metals** and these two interpretations competed for a few years. However Volta triumphed with his creation of the V**oltaic Pile** (right) where alternating silver and zinc plates separated by cloth/cardboard soaked in electrolyte solution generated a DC current. This was the first **battery** thus Volta's contribution was significant to **electrochemistry** and the Volt is named in his honour.
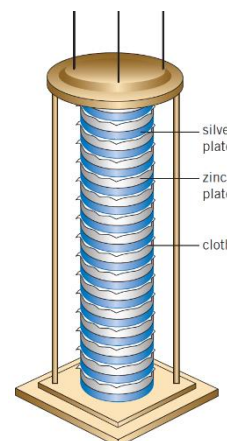
- o **Sir Humphry Davy:** (1778-1829) was a highly acclaimed chemist who achieved across a range a chemical areas. In electrochemistry, Davy experimented with the Voltaic pile and realised that the electricity was coming from a **chemical reaction** rather than just the **contact between the metals** as Volta hypothesised. Davy continued to **decompose** many materials and isolate new elements with **electrolysis** however it was not realised until later that electrolysis was a redox reaction.
- o **Michael Faraday:** (1791-1867) was assistant to Davy and during his **electrolysis experiments** developed his laws of electrolysis. These surmised that the **quantity of substance** evolved at the electrode during electrolysis was **directly proportional** to the charge passed through, where $Q = It$. His second law stated how the for elements of the same valency masses evolved in a ratio proportional to their atomic masses and thus **electrolysis was a molar effect** (although such terminology had not bee developed). These theories are important as the **quantified electrolysis** although Faraday's greatest contribution to science was his laws on electromagnetism.

The above experiments helped **Arrhenius** to develop an accepted **theory on electrolysis** and contributed largely to the advanced understanding we now have of **electron transfer reactions**. Although they did not directly contribute, they were the essential first steps to **achieved understanding**.

## 2. Ships have been made of metals or alloys of metals.
*Students learn to:*

- **Active metals** are metals that **readily oxidise** but do so in a way that allows the **reaction to continue**. Iron is an example as it's oxidised form **does not adhere** to the metal it came from, forming **porous flakes** that fall off continuing the corrosion process. Thus active metals will **continue to corrode** due to the nature of their oxidised form. **Passivating metals** however develop an **oxidised form** that prevents the oxidant from further corroding the metal. Aluminium is an example where the aluminium oxide **adheres strongly** to the metal which forms a **protective layer** preventing the oxide from further interacting with the metal. This oxide layer can be **removed by scraping** as it causes the metal to **lose its lustre** however a new layer will reform. Thus **self passivating metals** will not continue to corrode as the corrosion process **prevents further corrosion**.



aluminium oxide
water / oxygen
aluminium
$2Al(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(s)$

hydrated iron(III) oxide
water / oxygen
iron
$4Fe(s) + 3O_2(g) + 2H_2O(l) \longrightarrow 2Fe_2O_3.H_2O(s)$

- With the **industrial revolution**, iron has become more readily available. Most ships today are built out of **iron** or the **carbon alloy steel** because of the **large ore deposits**, **economical extraction**, and its easily **workable properties** such as their relative hardness, are mechanically strong, can be worked various structures and can be welded. Not the entirety of the ship will be made out of iron, but the **hull** and any **large components** will be.
- **Steel** is an alloy of **iron and carbon** that contains **less than 2%** carbon with small amounts of other metals and silicon. The **percentage breakdown** of steel greatly effects its **properties**. If there are lots or **carbon atoms in the lattice**, this increases the **hardness and brittleness** as the lattice has increased difficulty sliding over itself smoothly with the **irregularities**. The carbon may also form **cathodic sites** accelerating the **corrosion process**. Thus the percentage carbon of steel directly **determines its properties**. Stainless steel works by containing a high enough concentration of chromium that it forms a **passivating layer**, protecting from corrosion whilst maintaining its lustre.
- **Rusting** is specifically the **corrosion of metallic iron** to $Fe^{3+}$. The net reaction is $4Fe_{(s)} + 3O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Fe_2O_3 \cdot H_2O_{(s)}$ and produces the brown, soft and porous **hydrated iron oxide**. As an active metal, this allows the water and oxygen to migrate down and continue the reaction with the iron oxide eventually **flaking off**. Thus two elements are essential to rusting apart from an anode and cathode, **oxygen and water** (acting as an electrolyte); without these it cannot occur. **Pits or ruts** in the iron act as a
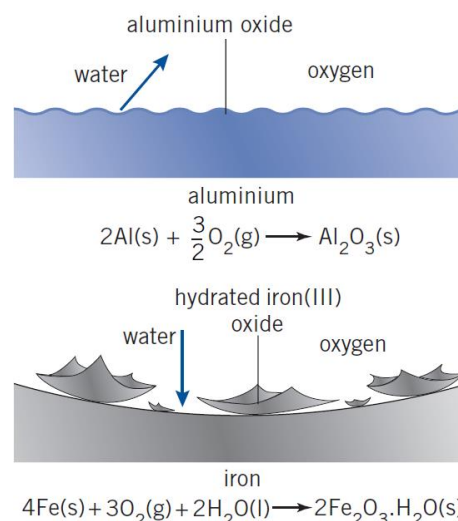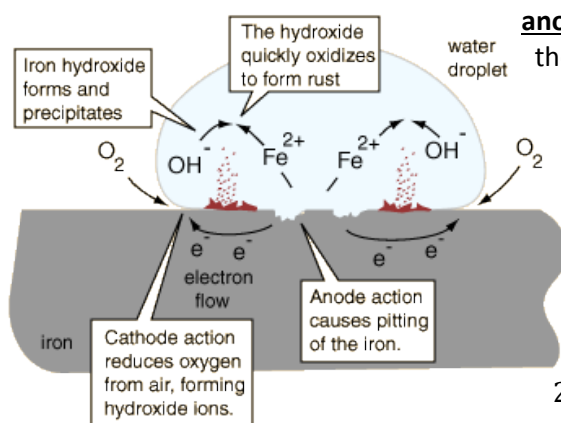
**anode** because it is easier for the ions to escape and the water as the electrolyte has a gre**ater surface area**. The **oxidation half reaction** is $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$ and occurs at anodic sites. **Impurities in the iron** act as **cathodic sites** where the electrons reduce oxygen in the presence of water (a thin film is best as oxygen has low solubility) to form **hydroxide** as in the **reduction half equation**, $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$. This gives an overall reaction of $2Fe_{(s)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Fe(OH)_{2(s)}$ When the iron and hydroxide ions meet, they **precipitate** and are further oxidised to **iron (III)** in the overall reaction $4Fe(OH)_{2(s)} + O_{2(g)} \rightarrow 2Fe_2O_3 \cdot H_2O_{(s)} + 2H_2O_{(l)}$.
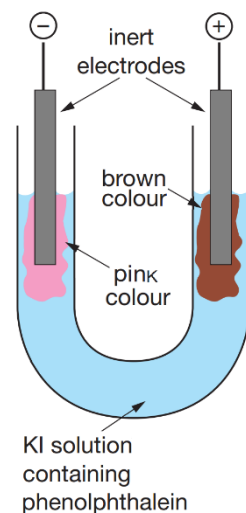
## *Students:*

- **Practical Investigation – Corrosion of Iron vs Stainless Steel. Aim:** to compare the rate of corrosion of iron and stainless steel. **Independent Variable** – alloy percentage breakdown; **Dependent Variable** – the rate of corrosion. **Method:** submerge a piece of mild steel (closest to pure iron available) and stainless steel of equal size and shape in a brine solution (to increase corrosion to a measurable rate) with small level of potassium ferrycyanide. Leave for 2 hours and observe changes. **Results:** If blue is present, rusting has occurred. The iron should be significantly rusted whilst the stainless steel should have minimal to no signs of corrosion. Thus, the iron corrodes much faster than the stainless steel.

- For **rusting to occur**, **oxygen** to eventually oxidise the iron and **water**, both to act as an electrolyte and facilitate the reaction, must be present or rusting cannot occur. Other **factors accelerate the rusting** process. **Salt water** results in an increased **strength of the electrolyte** allowing ions to flow more freely and often which speeds up the reaction. **Acidic environments** also increase the rusting process, not only because the **hydronium ions** improve the electrolyte but because, $H_2CO_3$ in particular, react with the $Fe$, $Fe(OH)_2$, and the $Fe_2O_3$, breaking down the lattice structure and **shifting the equilibrium** generating more rust products. **Impure iron** corrodes faster than pure iron because the **impurities act as cathodic sites** for oxygen reduction. If the iron is under **mechanical stress**, like on sharp points/edges, bends or riveted joins, the individual $Fe$ atoms are **less strongly bound** to the lattice due to the **distortion** of the lattice. This makes it easier for them to break free, promoting rusting. Finally, if the iron is in contact with a **less active metal**, it will act as an **anode** to protect the other metal, establishing a **galvanic cell** and hastening corrosion.

| Substance | Structure | Properties | Uses |
|---|---|---|---|
| Pure Iron | 100% Fe | Soft/malleable, corrodes slowly | Not widely commercially used. |
| Mild Steel | <0.2% C | Soft/malleable, cheap, rapid co | Cars, pipes, nuts/bolts, roofs, shipbuilding |
| Structural Steel | 0.3-0.6% C | Hard/malleable, high tensile strength, corrodes rapidly. | Beams, girders, railways, reinforcing for buildings, ship building. |
| Tool Steel | 0.9-2% C | Very hard and strong. Wear resistant. | Tools, knife blades, machinery. |
| Pig Iron (cast iron) | 3-4% C, 1% Mn, Si | Hard/brittle, corrodes rapidly | Casting engine block, fire hydrants, building decoration. |
| Stainless Steel | 10-20% Cr, 5-20% Ni | Hard, high polish, extremely corrosion resistant | Food processing machinery, kitchen sinks, cutlery, surgical and dental equipment. |
| Chromium | 2-5% Cr | Hard, strong, resists corrosion | Aeroplanes, vehicles, gears, tools. |
| Nickel | 15-25% | Strong, dense, ductile, no corr. | Heavy vehicles, gears, crankshafts. |
| Tungsten/ Cobalt | 12-20% W, 2-5% Co | Hard (at high temp), high abrasion. | Drill bits, high speed cutting implements. |
| Vanadium | 0.5% V | High strength/ shock resistant. | Bearings, tools, axels. |

# 3. Electrolytic cells involve oxidation-reduction reactions.

## *Students learn to:*

- **Electrolysis** is the **non-spontaneous decomposition** of an **electrolyte** by a pair of **endothermic chemical reactions** that occur on the **electrodes**. A **DC current** is established, and the current is carried through the electrolyte by the ions, **no electrons move.** Thus the ions migrate to the electrodes where the electrons must be **relieved** or **donated** which occurs by **endothermic redox**. For electrolysis to occur, the **voltage must be higher** than the cell voltage, which according to the potentials table, is **always negative** (not spontaneous). **An-ox** and **Red-cat** still hold for determining the electrodes. In general terms (noting all standard potentials are **reduction half equations**), the *higher* (more positive) the standard potential of the half equation, the *harder it is to oxidise the anion*. This applies inversely, the *lower* (more negative) the standard potential of the half equation, the *harder it is to reduce the cation*. Taking, for example, the electrolysis of **potassium iodide** solution in a U-tube (right), the bromine oxidises before the water (generating brown $Br_2$) as it has a lower potential (by 0.13 V) whilst the water is reduced before the potassium generating hydrogen gas and hydroxide ions (basic response to indicator). Similarly water can be electrolysed into its constituents.

- There are many types of **electrolysis** but **three factors** that determine them. Generally if common sense is applied, all is good (note $NO_3^-$ and $SO_4^{2-}$ do not generally undergo oxidation as they are too stable):
  - The **concentration of the electrolyte** will effect what is electrolysed in a solution. Generally, if the electrolyte is **more concentrated** it is **more likely** to discharge to relieve the 'pressure' than if dilute. For example, the electrolysis of a $NaCl$ solution. Since the standard anode potentials are **relatively close** (1.23 V for water, 1.36 V for chlorine), if there are **high concentrations** of chlorine than its **oxidation is favoured**, despite being a higher potential. Obviously as it is oxidised and the concentrations change, the situation will change too.
  - The **nature of the electrolyte** also effects the electrolysis. If the electrolyte is a **molten salt** (often required to isolate the more active metals), then there is no water and the ions have **no choice** but to undergo electrolysis. However in **aqueous electrolytes**, if the ions are too costly to electrolyse the **water will decompose** instead. Although the ions **still travel** (and more ions are generated by the electrolysis), they are not ultimately decomposed at the electrode.
  - The **nature of the electrode** depends greatly on what **products are produced**. If the aim is to decompose the electrolyte, the **electrodes must be inert** (common are graphite or platinum) as to not interfere with the reaction, merely providing an **interface** for the reaction. This is because if the electrodes are **metallic**, they may **undergo oxidation** themselves and dissolve into solution, eroding the electrode. Whilst maintaining the ionic balance, this can affect the electrolysis. For the metals **less reactive** than water, this will result in **electroplating** on the cathode. Ie the anode is oxidised into solution and then deposited on the cathode, which explains behind silver plating.
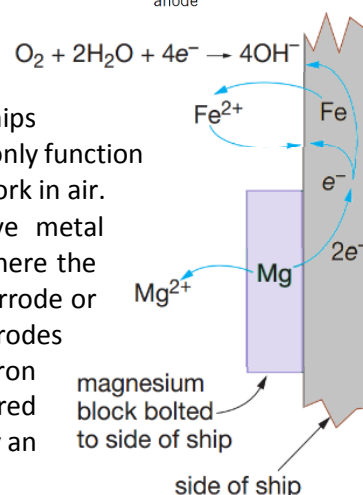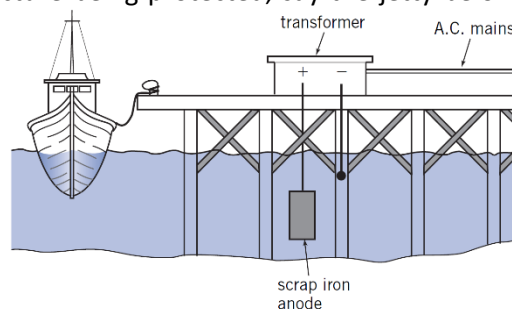
## *Students:*

- **Practical Investigation – Investigating Electrolysis. Aim:** to identify the factors affecting the rate of electrolysis. **Independent Variable** – various; **Dependent Variable** –rate of electrolysis. **Method:** set up a beaker of $CuSO_{4(aq)}$ solution with two electrodes connected to a variable DC power supply. Hence vary; the *concentration* of the solution, the *surface area* of the electrodes, the *voltage*, and the *distance* between the electrodes. Observe any changes. **Results:** the current is the only thing affecting electrolysis, **higher current results in faster electrolysis**. Thus **conductance** of the cell affects the rate; greater surface area of electrodes increases conductance, as does the concentration of the electrolyte, whilst greater distances decreases the rate due to an increase in resistance. We must also note that an increased voltage to increase current may also allow unwanted reactions to occur.
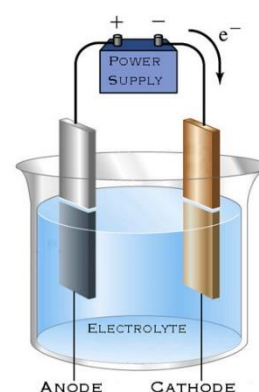
## 4. Iron and steel corrode quickly in a marine environment and must be protected.
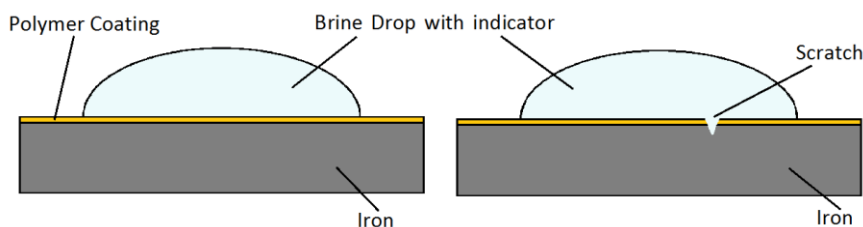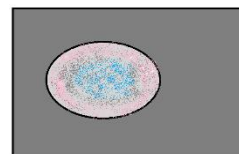
*Students learn to:*

- As there are many different **requirements and accelerators** for rusting, metal hulls and other structures can be protected using the following methods:
    - **Corrosion Resistant Metals** are often used and are **alloys of normal steel.** High concentrations of chromium (10-20%) and nickel (5-20%) in low carbon steel (structural, tool) are just enough to provide a **self-passivating** layer such that the iron resists corrosion, known as **stainless steels**. Steels can be more rust resistant in **acidic environments** when 0.25-8% **molybdenum** is included in the alloy. If **copper** is alloyed in mild steel, this also reduces corrosion.
    - **Surface Alloys** are where only the **very top layer** of an iron structure is alloyed. This is achieved with a **laser** which quickly heats up the top millimetre, melting it and alloying **powdered metals** or ceramic powder to be added forming an alloy. As the iron cools, the alloy is **fused** into the structure so there is no gaps for oxygen or water to intrude letting the alloys resist corrosion.
    - **New Paints** are protective coats that come in a variety of forms. **Protective metal coatings** is a common form, **Galvanised steel** is steel coated with a layer of zinc, which as **self passivating** forms a corrosion resistant layer but also acts as a **sacrificial anode** if scratched. **Tin plating** provides similarly but acts as a cathode in the event of being scratched whilst **chromium plating** is using to plate inert metals onto steel for jewellery, etc. Other coatings include oils, grease, paints, varnishes, enamels, glass, plastics and **polymer-based paints** which all act to prevent water and oxygen from contacting the steel, although also fail if scratched. Most paints today are a **variety of different techniques** to achieve the best protection. Often the polymers adhere to the metal making it a tough resistive coat.
- If you can't do this, be concerned. The **lower one** on the potentials table will act as the **cathode**, the **higher the anode.** Thus if connected as an **electrochemical cell,** the **anode will corrode** whilst the **cathode will be reinforced** or fine. Simple.
- **Cathodic protection** is used for larger structures as it can be **more reliable and cheaper** than galvanising every surface. There are two types, applied voltage or sacrificial anode. In **applied voltage cathode protection**, a **small DC voltage** is applied such that the structure being protected, say the jetty below, becomes the cathode whilst some scrap pig iron or **platinum plated titanium** (inert), insulated from the structure, is used as the anode. Applied voltage protection is also used on **underground tanks** and **pipelines** as well as ships and marine structures. **Sacrificial anodal protection** works similarly by using a **more active metal**, like Mg or Zn to establish an **electrochemical cell**. Thus the **active metal corrodes preferentially** to the iron in the same way as above. Only metals that are sufficiently active to protect the hull whilst having still **surviving long enough** are useful, metals like potassium, barium or calcium would not be efficient enough. The sacrificial anode also only protects iron around **a metre away** so large ships or structures **need multiple anodes**. Both forms of cathodic protection only function if the two metals are **connected by a electrolyte**, say water, so don't work in air.



$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

- By forming an **electrode potential**, whether this be by the active metal combination or by an applied voltage, a **galvanic cell is** established where the water acts as the **salt bridge**. This means the more active metal will corrode or the voltage will **supply electrons to the iron** such that any iron that corrodes is **precipitated** back onto the structure as pictured right. Thus the iron remains protected whilst the voltage or active metals supplies the required electrons for the **oxygen to undergo reduction**; the iron remains as only an interface and doesn't participate in the reaction.

## *Students:*

- Since the first ship was built, there has been a focus on finding **stronger and more resistant materials** to be used in the ship building process. **Organic materials** were used for a long time however ocean organisms attacked and degraded the material. The earliest boats were made with only **animal skins, bamboo, logs or reeds**; basically what was available to people, but it was only until 1000 BC that the first **long distance boats** were made by the **Phoenicians**. They created the **first wooden planked boats** which were held together with metals using **copper alloy nails** and **fasteners**. The **Greeks and Romans** used **iron** over the weaker copper, and it was the **Europeans** who added decking, more masts, and fore and aft castles. By the 11$^{th}$ century, **primal knowledge of metallurgy** was beginning and thus **many nails**, etc. were manufactured. As wood became scarce in the 17$^{th}$ century, **lead and copper sheeting** was attached to the wooden hulls to prevent **biofouling** which was replaced with a **bronze alloy** developed as it was cheaper, stronger and thinner. Throughout the **Industrial Revolution** of the 18$^{th}$ century, up to 90% were converted to **full iron ships** including structure and sheeting. Iron was used as there are **large, common ore deposits** easily accessible and it was **much stronger** and **more resistant** to attack and more **workable**. However it needed consistent **dry docking** to remove rusting. The invention of **carbon steels** solved many of the problems with conventional iron making ships **stronger** and hence **lighter**. By the 20$^{th}$ century, **corrosion resistant alloys** where common along with cathodic protection, etc. Fibreglass and aluminium is employed on smaller boats today.

- **Practical Investigation – Metal Corrosion for Ship Use. Aim:** to compare the corrosion rate in electrolyte of a variety of metals and alloys to identify the best for use in marine vessels. **Independent Variable** – the type of metal tested, **Dependent Variable** – the rate of corrosion. **Method:** Add 10 drops of **phenolphthalein** to 100 ml of brine. Combine 4 drops of this solution and 3 drops of **potassium ferricyanide**, $K_3Fe(CN)_6$, on section of mild steel, stainless steel, aluminium tiny alloy, and ship brass. Time how long it takes for both blue and pink colours to develop. **Results:** the **mild steel**, used in the framework and body of iron ships, takes about 2 minutes for both colours to appear, relatively fast corrosion rate. The **stainless steel**, used in high oxygen areas like propellers and above water accessories, had no detectable colour or corrosion after 30 minutes. The **aluminium alloy** used in smaller boats like tinnys had no noticeable corrosion after 30 minutes. The **marine brass** (90% Cu, 10% Ni) stayed pink after 1 minute but no blue (no iron ions). Thus, without taking into account feasibility, all boats should be made of aluminium.



- **Practical Investigation – Corrosion Protection for Metals. Aim:** to compare the effectiveness of different protections used to coat metals like iron to prevent corrosion. **Independent Variable** – coating type, **Dependent Variable** – corrosion rate. **Method**: Coat three pieces of mild steel with spray on **polymer coating, glavnising coating, and adhering oil**. Include a pieve of **tin can.** Also place a scratch in each coated material. Repeat steps above with seperatre drops on both perfect and scratched surface. If so desired, **magnesium and copper strips** can be wrapped around an iron nail to establish cathodic protection **Results:** for each perfect coating, there is no noticeable change. For a polymer, oil and tin coat, the scratch breaches the protection allowing rust to occur as seen from pink and



blue. However for the galvanised iron, there is no blue but lots of pink as the zinc is undergoing preferential corrosion. In the cathodic protection, the magnesium acts similarly to the galvanising whereas the copper accelerates the rusting as it makes the iron the anode promoting corrosion.
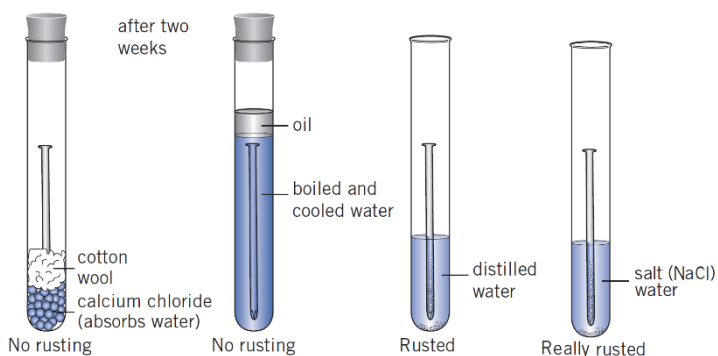
## 5. When a ship sinks, the rate of decay and corrosion may be dependent on the final depth of the wreck.

*Students learn to:*

- Many things affect the solubility of gases and salts. Notably an increase in dissolved salts decreases the solubility of gases. The isolated factors are:
  - o **Temperature:** an increase in temperature decreases the solubility of gases in an electrolyte, ie gases are less soluble in hot solvents. The opposite is true for salts (although there are many exceptions), an increase in temperature generally results in increased solubility for salts.
  - o **Pressure:** an increase in the pressure of the gas in contact with the solvent increases the solubility of that gas, ie the more gas pressing on the water (known as partial pressure), the more gas that dissolves. Pressure however has no noticeable effect of salt solubilities.
- Many non-polar gases are **dissolved in the ocean** but the most common are **carbon dioxide, nitrogen and oxygen** in that order (as below). Although these concentrations vary, considering their **solubility** and **relative atmospheric concentrations** explains this. Although not particularly soluble, both nitrogen and oxygen have high atmospheric concentrations and thus **high partial pressure** resulting in high percentages at the surface. Carbon dioxide has relatively low atmospheric concentration but a **very high gaseous solubility** due to its **acidic equilibrium** and thus is present in much greater percentages than expected.

| Gas | Air % (v/v) | Dissolved % (v/v) | Solubility (molL$^{-1}$) |
|---|---|---|---|
| **Carbon Dioxide** | 78.1 | 16 | 0.73 |
| **Nitrogen** | 20.9 | 48 | 0.012 |
| **Oxygen** | 0.03 | 36 | 0.024 |

- The solubility or **presence of dissolved gases** depends on both **physical and biological processes**. At the surface, oxygen and nitrogen are rich because or **constant aeration** by wave action, etc. Oxygen in particular is produced by the **photosynthesis of phytoplankton** where sunlight is available at the surface so is in greatest concentration there. However **respiration and decomposition** activities use up dissolved oxygen as depth increases with no replenishing so at large depths, there is **next to no oxygen** present. The **reverse is true** for carbon dioxide, as depth increase less $CO_2$ is used in **photosynthesis** but **CO₂ producing respiration** still occurs. With increased depth, pressure increases and temperature decreases so all gases become more soluble. Thus, at great depths, up to **90% of dissolved gases** can be carbon dioxide.
- **Sea water** at great depths is 4°C as this is the **maximum density** of water, any hotter and the water would rise. As a result, this low temperature will largely **inhibit the rate of any chemical reaction** (less activation energy) and thus any **corrosion reaction will be slowed**. This decreased corrosion is also due to **the lack of oxygen** at great depths.

*Students:*

- **Practical Investigation- Environment Effects on Corrosion. Aim:** to compare the rate of corrosion varying oxygen concentrations, temperatures, and salt concentrations. **Independent Variable** – oxygen concentration, temperature, salt concentrations, **Dependent Variable –** the rate of corrosion. **Method:** to test oxygen concentrations, set up three test tubes, one with boiled then cooled sea water (removes oxygen) covered with oil, one with normal sea water and one with sea water and 3 drops of hydrogen peroxide ($H_2O_2$). Similarly, for temperature, incubate at 4°, 20° and 40°C in normal sea water. Finally, have one with distilled water, one with normal sea water and one with saturated salt water. Leave all tubes for two weeks and observe. **Results:** oxygen increases corrosion, temperature increased reaction rate and salt increased electrolyte capability.



after two weeks — oil — boiled and cooled water — cotton wool — calcium chloride (absorbs water) — distilled water — salt (NaCl) water — No rusting — No rusting — Rusted — Really rusted

- Use all of the above to **predict corrosion rates** in various situations.

## 6. Predictions of slow corrosion at great depths were apparently incorrect.

*Students learn to:*

The **Titanic** is one of the most famous wrecks sinking on her **maiden voyage in 1912**. It was thought that for the reasons outlined in the last dotpoint that the corrosion of the Titanic would be minimal and the wreck would be in **pristine condition**. However it was found that this was incorrect when she was discovered in 1985.



- Whilst there is little oxygen present, at great depths other methods of corrosion work. **Electrochemical reactions** can still occur. **Acidic environments** promote many types of corrosion and as great depths are highly carbon acidified, this causing corrosion. If **galvanic cells** are established with less active metals that are found on the ship, then this oxidises iron without the need for oxygen. **Anaerobic bacteria** also have major impacts in corroding iron at great depths through **oxygen free corrosion processes**. They are obviously not found in surface waters due to being anaerobic.

- **Sulfate reducing bacteria** (SRB) are one type of corrosion anaerobic bacteria found at great depths known as the *Desulfovibrio* family. They are bacteria that catalyse the **redox of sulfate ions to sulfides** and hydroxides; $4Fe_{(s)} + SO_4{}^{2-}{}_{(aq)} + 5H_2O_{(l)} \rightarrow 4Fe^{2+}{}_{(aq)} + HS^-{}_{(aq)} + 9OH^-{}_{(aq)}$, thus in this neutral reaction one sulfate ion can **oxidise four iron ions**. The iron ions then react with the sulfides and hydroxides to form **insoluble** iron sulfide and iron hydroxide, $4Fe^{2+}{}_{(aq)} + HS^-{}_{(aq)} + 7OH^-{}_{(aq)} \rightarrow FeS_{(s)} + 3Fe(OH)_{2(s)} + H_2O_{(l)}$. Without oxygen, the process proceeds no further and the iron sulfide and iron hydroxide forms rusticles and flakes. These **bacteria congregate** on deep sea wrecks as the normal concentrations of metals is poor. **Acidic environments** also accelerate these processes and generate a **new sulfate reduction reaction**, $SO_4{}^{2-}{}_{(aq)} + 10H^+{}_{(aq)} + 8e^- \rightarrow H_2S_{(aq)} + 4H_2O_{(l)}$. It also accelerates the neutral reaction by **reacting with hydroxide ions** and shifting the equilibrium reaction right. This is just one version of how SRBs work, there are more however we don't know the correct version as they are so hard to study so far down.

- **Acidic environments** accelerate the corrosion process in multiple ways. Firstly, by providing more ions in the **electrolyte solution**, this increases the rate of traditional corrosion. In **non-passivating metals** that don't form an oxide layer, the acid can **directly react** with the metal producing hydrogen gas; $Fe_{(s)} + 2H^+{}_{(aq)} \rightarrow Fe^{2+}{}_{(aq)} + H_{2(g)}$. In **normal oxygenated conditions** hydronium ions increase the **electrode potential** of the reduction of oxygen making it a **better oxidant**, $O_{2(g)} + 4H^+{}_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$. This is a **directly proportional** rate, the lower the pH of the environment, the higher the potential of the reduction half equation thus acidic environments greatly improve corrosion. Acids can also **promote the SRB reaction** as above.

*Students:*

- **Practical Investigation – Acidic Environments and Corrosion. Aim:** to compare the effects of acidic and neutral solutions on the rate of corrosion. **Independent Variable –** the pH of the conditions, **Dependent Variable –** the rate of corrosion. **Method**: establish four test tubes, one with $0.1M\ NaOH$ solution to provide a basic (pH of 13) environment, one with $0.1M\ NaCl$ solution to provide a neutral solution, and two with $0.1M$ and $0.001M$ solutions of $HCl$ to provide two acidic solutions (pH of 1 and 3). Leave for 2 days and qualitatively observe the corrosion. **Results:** the alkaline solution prevents corrosion as $2H_2O_{(l)} + O_{2(g)} + 4e^- \rightarrow 4OH^-{}_{(aq)}$ means that any reduction of oxygen increases salinity which is against Le Chatelier. The neutral environment rusts at a normal rate however the acidic environments increase the rate of corrosion significantly with low pH.
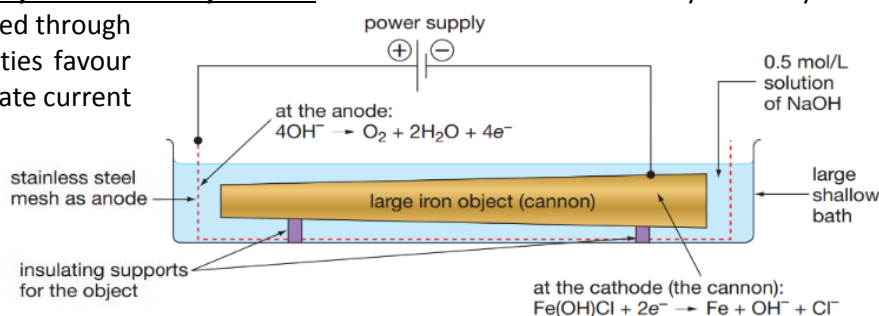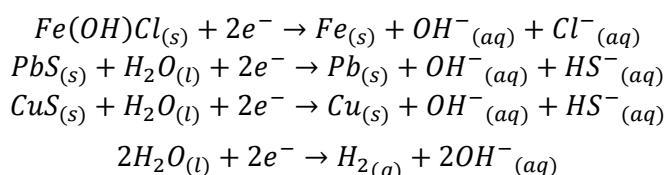
## 7. Salvage, conservation and restoration of objects from wrecks requires careful planning and understanding of the behaviour of chemicals.

*Students learn to:*

- When **artefacts** are **submerged in shipwrecks**, they spend a long time in the presence of seawater. This seawater has a high concentration of **chlorine and sulfate ions** due to their **high solubility** in water and thus these ions have a long time with which to dissolve into the artefact. **Porous or organic materials** like wood and leather will have been saturated with these salts as the water dissolves into **all of their cells**. Any **cellulose** lost by **bacterial activity** will be replaced with water as such **waterlogged timbers** contain up to 850% water when compared with their oven dried weight and as most **organic cells are mainly water**, this fresh water will be replaced by ion saturated seawater. **Metallic artefacts** also have **microscopic pores** where these ions can congregate that are invisible to the naked eye. Any **imperfections** in the metalwork will also enable the ions to penetrate within the metal. Thus **the concentration of chlorides and sulfates** will be large throughout any artefact.

- When **water evaporates**, the remaining water will become more concentrated until it becomes **saturated** at which point any dissolved salts will **precipitate out of solution**. Thus, if an artefact is dried out without being treated, all of the seawater dissolved throughout its structure will **evaporate forming crystals** of salt, the slower the evaporation the larger the crystals. This can be damaging to the structure as the crystals can **deform the artefact** and crack it both on a **cellular and macro level**, especially as without water the artefact will often become **brittle and fragile** with no water to **support the internal structure** of the cell. Thus unless the artefact is treated, it will be **irreparably damaged by drying**.

- For **metallic artefacts**, the salts often bond with the metal to form compounds like $Fe(OH)_{2(s)}$ and insoluble $Fe(OH)Cl_{(s)}$ and are hence difficult to remove. **Electrolysis** can be used to reduce the iron into its metallic form where the anions hence migrate to the anode and thus the salt is removed from the artefact. The **concentration of the chloride ions** in solution is monitored and the electrolyte (NaOH) is **periodically replaced** until the concentration is under **50 ppm**. Thus electrolysis is a method of **removing salt** from artefacts.

- Whilst good at removing salts, **electrolysis** is also used to **stabilise metallic artefacts** made of iron, copper and lead. This is achieved by making the **object the cathode** and then performing electrolysis. Some examples of this **reduction of the metallic corrosion products** appear right. Depending on the voltage applied, the **reduction of water** may also

$$Fe(OH)Cl_{(s)} + 2e^- \rightarrow Fe_{(s)} + OH^-_{(aq)} + Cl^-_{(aq)}$$
$$PbS_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Pb_{(s)} + OH^-_{(aq)} + HS^-_{(aq)}$$
$$CuS_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Cu_{(s)} + OH^-_{(aq)} + HS^-_{(aq)}$$
$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$$

occur. The anode is usually the **stainless steel** dish that the artefact sits in and thus the artefact must be insulated. All variety of oxidations can occur at the anode depending on the voltage however the most common is the **oxidation of water**, as in picture (although this is the oxidation of the hydroxide produced at the cathode which is the same thing). The electrolyte consistently used for this electrolysis is a **2% NaOH solution**. This acts as an ionic electrolyte but also the basicity **inhibits the corrosion** of metals by reducing the oxidising power of the dissolved oxygen. Thus stabilising is achieved by electrolysis and **can take weeks** or years depending on the size of the artefact and the extent of corrosion but cleaning is also a viable outcome. Due to the **hydrolysis of water**, **hydrogen gas** is uniformly evolved over the artefact and this consistent bubbling **mechanically and uniformly cleans** the artefact. The action of any electrolysis is determined by the **current** passed through the artefact, low current densities favour the **reduction of metals**, moderate current densities favour the **removal of chloride** whilst high current densities favour the **vigorous evolution of hydrogen** for cleaning.

- There several different procedures that must be followed before an artefact can be put on display. It is also important to recognise the difference between conservation and restoration. Conservation is the treatment of an object to stabilise its condition and inhibit further deterioration. Restoration is the process of returning an object to its original appearance and often involves artificial additions.
    o **General Analysis:** information about the state of the artefact and the **restoration techniques** that are going to be used are recorded as it is crucial future conservationists understand exactly what has been done. This may include **X-ray analysis** of the concretions, etc.
    o **Deconcretion:** whilst at the bottom of the sea floor, organic respiration and activities produced carbon dioxide which reacts with the water $CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons CO_3{}^{2-}{}_{(aq)} + 2H^+{}_{(aq)}$. These carbonate ions then react with spare $Ca^{2+}$ ions to form **calcium carbonate deposits** often mixed with rust products. Combined with **coral growth**, these deposits are known as **concretions** and they can cover the entire artefact and hence must be removed. There are two methods for deconcretion, **percussive deconcretion** is where you basically **bash it carefully off** with a hammer. The concretions generally fall off the artefact leaving the intact iron bare. For less bulky deposits, **acidic deconcretion** is used where dilute acids react with the calcium carbonates as follows; $CaCO_{3(aq)} + 2H^+{}_{(aq)} \rightarrow Ca^{2+}{}_{(aq)} + CO_{2(aq)} + H_2O_{(l)}$. **Hydrochloric or acetic acids** are used and the concretions thus dissolve off the artefact.
    o **Leaching:** is simply the process to remove ions by which the artefact is **submersed in pure water** and the ions slowly **leach or diffuse out** into the water due to **concentration differentials**. The water is periodically replaced. This method can be used **prior to electrolysis** to make large gains and then complete the final desalination with a more expensive but more effective method. Leaching is particularly effective in **organic artefacts** that **cannot be electrolysed**.
    o **Electrolytic Reduction** is a major conservation process and is used to reduce rust products and remove chloride and sulfate ions.
    o **Polyethylene Glycol (PEG):** is a **water soluble wax** that is used to replace water in **waterlogged organic artefacts**. As a polymer, its **molecular weight** determines its properties. However PEG 1500 is used in timber conservation. As it is water soluble, the artefact is soaked in a PEG solution starting at 5-10% and, depending on waterlogging, may end up at 95% PEG. Here, the **wax slowly replaces the water** within the timbers giving it **elastic stability** to retain its original shape when the timber is eventually dried out. The molecular formula of PEG is $HO(CH_2CH_2O)_nH$.
    o **Wax Coating:** provides a **physical barrier coating** the artefact to ensure no further corrosion is possible. PEG 6000 is commonly used as it provides an **opaque solid** that gives the artefact an appealing lacquer whilst protecting it from external attacks.

It is interesting to note that **poisonous metals** like Copper and Lead often protect the timbres or organic material that they corrode with as the form a **natural biocide**.

## *Students:*

- Two **Australian restoration projects** are the restoration of the **HMB *Endeavour* Cannon** and the *Vernon* Anchors. The Endeavour cannon was lost when Captain Cook's Endeavour ran aground on the barrier reef and in an effort to reduce the weight of the ship so they could float off the reef, Cook ordered six of the cannons and other heavy items like ballast **thrown overboard**. The incident was recorded on his charts and in 1969 researchers returned and found all six cannons. They freed them with **explosives** under 200 years of **coral growth** and recovered them leaving the wooden stocks. After recovery the cannons were soaked in **10% formalin as a biocide**. **Percussive deconcretion** was used on the hard coral and **core drilling** of the cannon bores recovered wadding, cannon balls and residue of powder. This was followed by **electrolytic reduction** to preserve any corrosion products and remove excess chloride ions. The process lasted two weeks were the baths were changed until **chloride concentration** reached
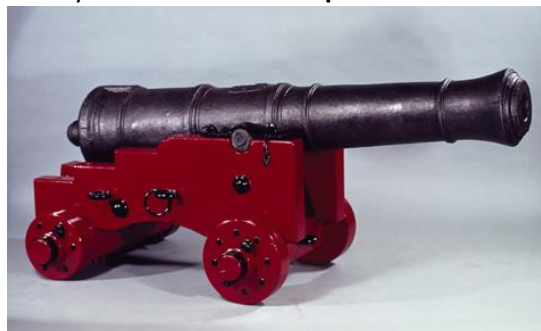
20 ppm. A **current density** of 10 Am$^{-2}$ was used as a moderate density to **maximise desalination** which also assisted in the reduction of rust products. After electrolysis, **prolonged washing** with pure water with chromate ions was implemented, which took 5 months. After this it was **dried** for 48 hours at 120°C then immersed in **molten microcrystalline wax** kept at 135°C for 5 days until no gas bubbles were evident. This wax treatment provides external protection and is **reversible**. The cannon was thus ready to be put on display and was holstered in restored wooden stocks, as pictured.

**The *Vernon* Anchors** were built in 1839 and from 1871 to 1891 their ship was used a **reformatory** for 'wayward and orphaned boys'. The **timber stocks** date to 1905 and were once **sheathed in copper** to protect them, one fluke was bent to avoid damage to the hull. In the conservation process, **electrolytic stabilisation** was not considered for two reasons, it would require the **removal of the timber stocks** which would cause unnecessary damage and as the ship was not sunk, the anchors were in **sufficient condition** that it was not considered necessary to preserve the wrought iron. The preservation process removed the outer corrosion and protective paint by **blasting with copper slag** then surface polished with garnet. The iron was then treated with **zinc epoxy paint**. The timber stocks were saturated with a **zinc napthenate solution** (which retards the growth of organisms such as mould).



There are marked **differences and similarities** in the two processes. Because the cannons were sourced from a **200 year old wreck** and were extensively corroded and coated in deconcretions and because they only consisted of iron, extensive electrolysis and stabilisation was applied. The cannons were also intended to be housed in **non-hostile conditions** in a museum. Thus **more permanent conservation** and less robust techniques were applied and they were also restored to their **previous appearance**. The anchors however had not been subjected to a wreck and thus were in relatively **good condition** not requiring electrolysis. Their conservation techniques are only **temporary** especially as they were to be displayed outside in a **hostile maritime environment** and thus require regular inspection for **potential degradation**.