

Shipwrecks, Corrosion and Conservation

1.1.1 Anions – chlorides, sulfates, carbonates, bromides, hydrogen carbonates

Cations – sodium, magnesium, calcium, potassium

1.1.2

Word	Meaning
Mineral	An element or compound found in soil or rocks
Leaching	The process of water seeping through rocks and soil dissolving minerals from the rocks and soil
Terrestrial	Of land
Hydrothermal vent	An opening in the sea floor releasing a spring of hot water
Mid-ocean ridge	Undersea mountain range formed by magma rising from the mantle where tectonic plates are moving apart

1.1.3 Rainwater seeps over or through the earth dissolving minerals and carrying them via ground water or rivers to the oceans. This is a major source of replenishment of salts in the ocean. The ions dissolved vary according to the composition of the rocks.

1.1.4 At mid-ocean ridges, cooling rocks crack, allowing water to sink into the rocks. The rocks heat the water and rock minerals dissolve in it. This water, saturated with minerals, returns to the ocean through springs in the sea floor. These are called hydrothermal vents, literally, hot water vents.

1.2.1 Oxidation means a reaction in which electrons are lost or given up.

Reduction is a reaction in which electrons are gained.

1.2.2 One species accepts the electrons which are given up by another species. Hence oxidation/reduction reactions are really electron transfer reactions. For example, when an active metal such as magnesium is in contact with a less active metal such as silver, the active metal will lose electrons and the less active metal will take up the electrons.



1.2.3 $\text{Mg(s)} \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{e}^{-}$ and $2\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{H}_2(\text{g})$. The electrons are transferred from magnesium atoms (Mg) to hydrogen ions (H^{+}).

1.3.1 (a) Electrolytes are liquids which can conduct electricity because they have ions free to move. They can be solutions of ionic compounds, molten metals or molten ionic compounds, e.g. sea water, potassium nitrate solution, molten sodium chloride.

- (b) (i) no light, 0 current (or very close)
(ii) light glows, current shown on microammeter

1.3.2 Electrons can be transferred in electrolytes as they can conduct electricity. Therefore redox reactions can occur as the electrons are transferred from one species in the liquid to another.

1.4.1 While studying the effects of static electricity on muscle contraction using dissected frog's legs, Galvani observed that the electricity caused the muscle to contract. He also noticed that the muscle contracted when two different metals were in contact with both the spinal cord and the leg muscle of the frog. He suggested that this was due to electricity generated by the frog.

1.4.2 Volta investigated Galvani's effect further and realised that the current was generated by the metals, not the dead animal. This made the important connection between chemical reactions and electricity. Volta then developed the first battery, a 'voltaic pile' made of alternating zinc and copper discs with an electrolyte solution in between. This enabled landmark experiments to be carried out by Davy on the effects of electricity on chemicals.

1.4.3 Davy used Volta's device to pass electricity through compounds. This caused the decomposition of some compounds previously classified as elements, e.g. water and sodium chloride. Active metals such as sodium, potassium, calcium, strontium, barium and magnesium were discovered. Davy suggested that the forces holding atoms together were electrical in nature. Davy also made important discoveries in electrochemistry that led to corrosion protection for ships' hulls.

1.4.4 Faraday carried on from Davy's work. Faraday quantified electrolysis by relating the quantity of electricity used in electrolysis to the valency and mass of the element produced. He formulated laws of electrolysis. He also developed the terminology used today – words such as electrolytes, ion, anion and cation.

- 1.4.5** In an exam you would first describe the work of each scientist (see above) and then analyse their contributions, e.g. Each of these scientists advanced the knowledge and understanding of electrochemistry and the nature of matter. Galvani's and later Volta's experiments led to the development of the first device for generating a continuous electric current and to the connection made by Volta between chemical reactions and electricity. Davy then examined decomposition by electrolysis and discovered several active elements. Faraday quantified the relationship between electricity and chemical reactions. This further showed the relationship between electricity and chemical bonds. At this time, the structure of the atom was not known, however, this early work on the electrical nature of matter and the relationship between electricity and matter was the first step in our understanding of electron transfer reactions.

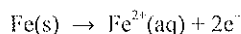
1.5.1

Name	Significance of work to electrochemistry
Luigi Galvani	His work on the effect of electricity on frog muscle contraction provided the basis for Volta's later discoveries. His accidental discovery of muscle contraction when different metals were used in contact with the dissected frog was the basis for the development of the battery (which uses electron transfer reactions).
Alessandro Volta	Was the first to generate electricity from a chemical reaction. Established the connection between chemistry and electricity and developed a primitive battery called a voltaic pile.
Humphry Davy	Used Volta's voltaic pile to decompose compounds, discovered new elements in this way and first suggested the connection between chemical bonds and electricity.
Michael Faraday	Continued Davy's work on electrolysis, establishing that the electricity was actually used in the chemical decomposition and developed the quantitative laws governing electrolysis. Related charge used to product formed.

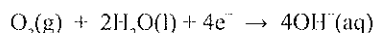
- 2.1.1** Rusting is the slow oxidation of iron, as it reacts with oxygen and water, to form hydrated iron oxide. The rust which forms is a brown, crumbly, porous compound.

- 2.1.2** Iron in contact with oxygen and water. (High humidity in the air is sufficient moisture for rusting.) A warm temperature and a neutral or acidic pH are also necessary.

- 2.1.3** (a) Iron is oxidised to iron(II) ions (ferrous ions), losing electrons.



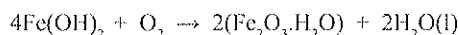
- (b) Oxygen is reduced, gaining electrons, reacting with water to form hydroxide ions.



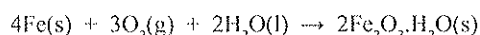
- (c) $2\text{Fe(s)} + \text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)} \rightarrow 2\text{Fe}^{2+}(\text{aq}) + 4\text{OH}^{-}(\text{aq})$

The ferrous and hydroxide ions form iron(II) hydroxide. $\text{Fe}^{2+} + 2\text{OH}^{-} \rightarrow \text{Fe(OH)}_2(\text{s})$

Further oxidation of Fe^{2+} to Fe^{3+} occurs, with reduction of oxygen.

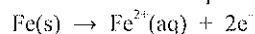


The overall equation for the formation of rust can then be written as:

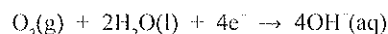


- (d) Rust is hydrated iron(III) oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) where x is commonly equal to 1 or 2.

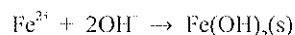
- 2.1.4** An electrochemical process occurs. Iron atoms are oxidised releasing electrons. This area is called the anode.



These electrons are transferred through the drop of water. Oxygen from the atmosphere takes up these electrons and is reduced. This area is called the cathode.



The ferrous and hydroxide ions come together and form iron(II) hydroxide.



This model only shows the formation of iron(II) hydroxide. Fe^{2+} is further oxidised to Fe^{3+} forming the hydrated iron(III) oxide which makes up rust. (See Question 2.1.3(c).)

- 2.2.1** Water reacts with oxygen forming hydroxide ions in the cathodic reaction. Water also acts as an electrolyte, transferring electrons from anode to cathode. This is done more efficiently when water has dissolved ions in it such as in sea water.

- 2.2.2** Oxygen is reduced in the cathode reaction. It is the electron acceptor and is thus essential for rusting to occur.

- 2.2.3** Acidic pH accelerates rusting as H^{+} ions accept electrons readily, forming hydrogen atoms. High pH (alkaline conditions) inhibits rusting by inhibiting the reduction of oxygen to hydroxide ions.

- 2.2.4** Temperature increase causes rates of chemical reactions to increase as collisions between reactants become stronger and more frequent. Rusting is a chemical reaction so rusting rate increases with increases in temperature.
- 2.2.5** Less active metals increase the rate of corrosion of iron as an electrochemical cell is set up in which iron is the anode and hence will oxidise faster. For example, iron alloyed with tin or copper will rust more quickly than pure iron. However, if iron is alloyed with more active metals such as zinc or manganese, the iron becomes more resistant to corrosion. The more active metal is oxidised in preference to the iron. The presence of non metals such as silicon can accelerate rusting by causing internal stresses in the iron metallic lattice. This weakens the structure of the iron so that oxidation occurs more readily. Since steels are impure forms of iron, they tend to corrode more readily than pure iron unless other elements such as chromium are alloyed in to prevent corrosion.
- 2.2.6** (a) Independent variable – presence or absence of salt in water.
Dependent variable – rate of formation of rust, i.e. amount of rust formed in a given time.
Controlled variables – type, size and cleanliness of nails, volume of liquid, containers, surrounding conditions, e.g. temperature.
- (b) Rust will be observed sooner on the nail in salt water. At the end of the week there will be more rust on the nail in A (salt water) than in B (fresh water).
- (c) Set up a number of identical nails in the same conditions at the same time or repeat the experiment a number of times.
- (d) Set up a dry test tube containing an identical nail plus silica gel or calcium chloride to absorb any moisture. Stopper the test tube. This is the control.
- 2.2.7** (a) Various, e.g. Anodes occur at the ends of the nails and at the site of bending.
Oxidation occurs at the ends of the nails and at the site of bending (stress).
Agar acted as an efficient electrolyte, allowing the transfer of electrons from anodes to cathodes.
- (b) Phenolphthalein turns pink in basic solution. Reduction of oxygen at the cathode produces hydroxide ions that turn phenolphthalein pink.
$$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$$
- (c) At anodes Fe is oxidised as follows: $\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$
The Fe^{2+} ions turn the potassium ferricyanide solution blue.
- 2.3.1** The natural deterioration of a material due to its reaction with the environment.
- 2.3.2** (a) Various, e.g. Cast iron and mild steel or stainless steel. Cast iron has about 3% carbon and small quantities of silicon and manganese. Mild steel has about 0.1-0.3% carbon and various amounts of other alloyed elements whereas stainless steel has at least 10.5% chromium as well as small amounts of other elements.
- (b) Various, e.g. Samples should be in water or in a moist environment and exposed to the air. Samples should initially be free of surface corrosion and the same size and shape. Whatever the conditions used, the iron and steel samples should be in the same environment and left for the same time.
- (c) Various depending on samples used, e.g. Stainless steel did not rust whereas iron rusted. Or cast iron did not rust as fast as the mild steel.
- (d) Various, e.g. Chromium (in stainless steel) is a passivating metal and protects stainless steel from rusting. Mild steel will rust due to stress on its lattice structure caused by the presence of impurities. Very pure iron will rust very slowly as no other metal ions are present to form a galvanic cell. Cast iron will not rust as fast as steel because the high carbon content tends to form a protective graphite layer whereas the steel has many alloyed elements that can weaken its structure.
- (e) For an experiment to be considered reliable, it should contain duplicate or triplicate test samples and be performed many times. If your experiment was performed only once without duplicates the results should not be judged very reliable.
- 2.4.1** (a) Steel is iron with < 2% carbon and different amounts of other alloyed metals such as manganese, chromium, nickel, tungsten molybdenum and others.
- (b) Steel has many uses, e.g. in household appliances, construction, cars, ships. Each different use requires different properties and thus different types and percentages of other added metals. For example, chromium is added to prevent corrosion, manganese increases strength and malleability.

- 2.4.2 (a) The less carbon the more malleable the steel. The higher the carbon content, the less malleable, but the steel is stronger and harder.
- (b) (i) Can be made into plates, shaped and welded so is used for ship's hulls and cars.
- (ii) Used for small tools where strength and hardness are important, e.g. hammers, axes.

2.4.3 Steel is an alloy, which is a mixture of metals, so changes in composition affect its properties. Mild steel tends to corrode relatively quickly whereas the addition of more than 10.5% chromium to this steel makes stainless steel which is corrosion resistant and has a shinier appearance. Small changes in carbon content also determine the malleability of the steel.

2.5.1 Various, e.g:

Composition	Properties	Uses
Stainless steels have >10.5% chromium content, also possibly nickel, manganese, silicon and < 0.3% carbon.	Corrosion resistant, hard and strong, pleasing appearance. Very malleable.	Sinks, cutlery, electrical appliances.
High carbon steels (0.6-1.3% carbon) and < 4% chromium.	Increased hardness, resistant to wear and abrasion.	Tools such as axes, hammerheads. Gears and axles.
Steel with added tungsten and cobalt.	Very hard steels, resistant to abrasion, can withstand heat.	High-speed cutting and drilling tools.
Steel with molybdenum alloyed.	Malleability increased, easily welded, strong and hard.	Pressure vessels, construction industry.

2.5.2 Stainless steel is corrosion resistant because the alloyed Cr is a passivating metal and forms a thin, invisible, inert film of chromium oxide on the surface of the steel. If damaged, the film quickly re-forms.

2.6.1 Iron (in the form of steel alloys).

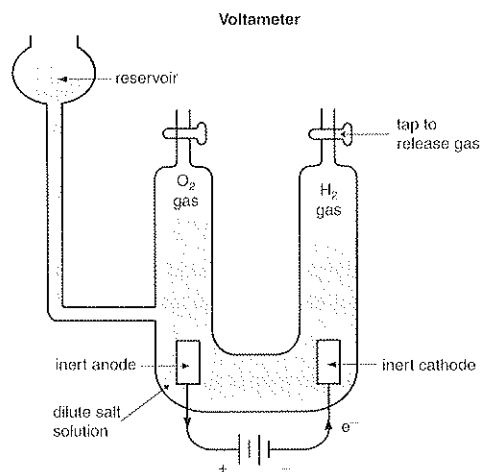
2.6.2 Strong, hard, malleable; can be made into plates and welded; less dense than iron; can be made relatively corrosion resistant by the use of alloyed elements.

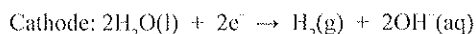
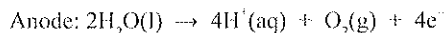
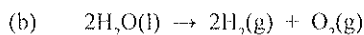
2.6.3 Anchors and chains can be made of iron as cast iron is very hard and strong.

- 2.7.1 (a) Active metals react chemically much faster than unreactive metals and will corrode rapidly. Passivating metals do not normally corrode (although they may be active) as they form a passive, protective oxide film on the surface of the metal. Aluminium is an active metal, but unlike other active metals such as magnesium and zinc, it will not corrode as it is also a passivating metal. Chromium and tungsten are also passivating metals.
- (b) Active metals react readily with the environment such as with oxygen to form oxides. If the metal forms an oxide that adheres to the surface forming a thin, inactive, non-porous coating over the metal, then the metal will be protected from corrosion by this barrier. These are called passivating metals. If the oxide formed does not adhere or is porous, e.g. rust forming on iron, the metal will not be protected and will continue to corrode as there will not be a barrier between the metal and the environment.

3.1.1 Electrolysis is the decomposition of a substance by passing electric current through it. Chemical reactions occur due to a voltage being applied.

3.1.2 (a)



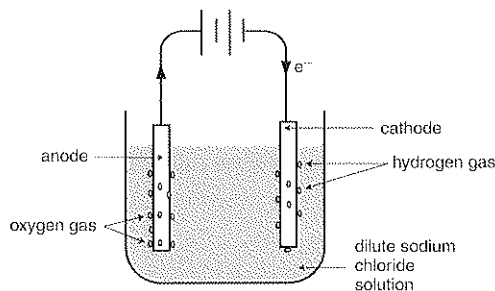


3.1.3 A container with an electrolyte and two electrodes. The electrodes are connected by an external circuit containing a power source such as a battery. The positive terminal is the anode. The negative terminal is the cathode.

3.1.4 (a) Oxidation occurs and electrons are released.

(b) Reduction occurs and electrons are taken up.

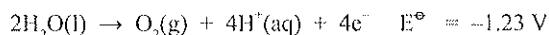
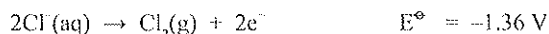
3.1.5 (a) Electrolysis of dilute sodium chloride solution:



(b) (i) oxygen, hydrogen

(ii) chlorine gas, hydrogen and sodium hydroxide

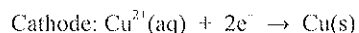
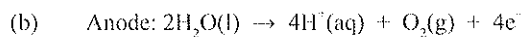
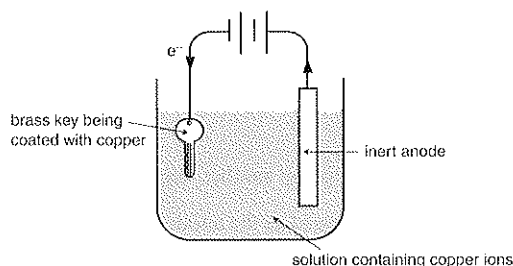
(c) At the anode, two reactions are possible, the oxidation of water to produce oxygen and the oxidation of chloride ions to produce chlorine. The voltages required for these half reactions are very similar at standard conditions of 1 mol L^{-1} electrolyte concentration. Both reactions tend to occur.



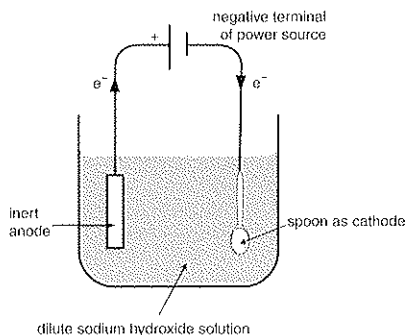
However, if the electrolyte concentration is very dilute oxygen predominates whereas, with concentrated solution, chlorine is formed. Therefore the electrolyte concentration determines the product formed at the anode.

3.1.6 Various, e.g. to decompose compounds and thus extract elements, e.g. electrolysis of molten sodium chloride to form sodium and chlorine; the refining of metals such as aluminium and copper; electroplating, e.g. covering iron with zinc, silver or gold; cleaning corroded artefacts.

3.1.7 (a) Electroplating an object with copper:



3.1.8 (a) Electrolytic cell for cleaning a corroded silver spoon:



- (b) At low voltage, the silver ions on the surface of the spoon would be reduced to silver and the sulfide ions released from the surface. $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$

This helps to restore the surface of the spoon. With higher voltage, hydrogen bubbles will be produced from the reduction of water at the cathode and this can loosen difficult to remove silver sulfide from the surface.

3.1.9 The possible anode reactions would be:

- oxidation of the Cu anode
- oxidation of the electrolyte
- oxidation of the water.

With standard conditions, the redox table of electrode potentials can be used to predict the reaction. The reaction that will proceed first is the one requiring the lowest input of electrical energy. This is the one with the lowest numerical value of E^\ominus . However, non-standard conditions would change the electrode potentials.

- 3.2.1 (a) When the concentration of the electrolyte is not 1 mol L^{-1} the electrode potentials are different and the redox table cannot be used to predict the reactions occurring. The concentration can determine the anode product. If the possible reactions have similar E^\ominus values, both reactions may occur, depending on concentration., e.g. in electrolysis of dilute NaCl, water is oxidised producing O_2 , in conc. NaCl (brine), Cl^- ions are oxidised to Cl_2 and in between, both Cl_2 and O_2 will be formed.

- (b) The more concentrated the electrolyte, the faster the rate of reaction as the electrolyte becomes a better conductor of electricity.

- 3.2.2 The ions in the electrolyte can be reduced or oxidised in electrolysis. Therefore the nature of the electrolyte affects the products. In molten electrolytes with inert electrodes, only one product will be possible at each electrode, e.g. for the electrolysis of molten potassium bromide, the products will be potassium and bromine. However, if the electrolyte is an aqueous solution the water may react and the products will vary depending on the electrode potential of the possible half reactions.

- 3.2.3 (a) The area of the electrode in contact with the electrolyte affects the rate of reaction. The greater the area, the faster the reaction rate.
- (b) Also the distance apart affects rate. The closer the electrodes are to one another, the faster the reaction rate.
- (c) The composition of the electrodes is important to the products formed as the anode may oxidise in preference to the electrolyte, e.g. Pt, stainless steel or graphite electrodes are inert and will not affect the products, but metals such as zinc, nickel, copper, iron may be oxidised.

- 3.3.1 (a) Various, e.g. You may have varied the electrolyte concentration, the shape and distance apart of the electrodes, the voltage applied.
- (b) Various, e.g. a suitable cell would be a beaker containing CuSO_4 solution, with graphite electrodes, connected to a power pack.

3.3.2 (a) Various, e.g. electrolyte concentration.

1. Half fill the beaker with $0.1 \text{ mol L}^{-1} \text{ CuSO}_4$ solution. 2. Place electrodes in the solution 5 cm apart to a depth of 5 cm. 3. Apply 6 V for 1 minute. 4. Observe and record the copper deposit on the cathode using a + to ++++ system. 5. Repeat using $0.5 \text{ mol L}^{-1} \text{ CuSO}_4$ solution, $1.0 \text{ mol L}^{-1} \text{ CuSO}_4$ solution and $2.0 \text{ mol L}^{-1} \text{ CuSO}_4$ solution.

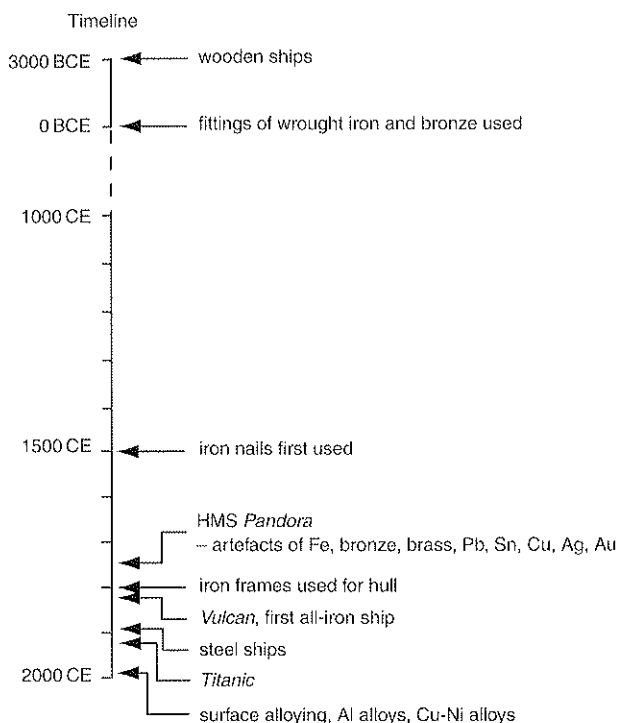
(b) The dependent variable is what is being measured or observed. In this case it is the quantity of copper deposited on the cathode in a given time. It is being judged subjectively using a 4-point scale.

(c) Various depending on the factors investigated, e.g. Increasing the concentration of the electrolyte, led to an increase in the rate of electrolysis as shown by the increase in electrical conductivity of the solution.

3.3.3 Various, e.g.

Factor investigated	Hypothesis
Varying electrolyte concentration	As electrolyte concentration increases, the rate of deposition of copper will increase.
Varying voltage	As voltage increases (e.g. from 2 V to 10 V) the rate of copper deposited will increase.
Varying area of electrode immersed	The greater the area immersed in the electrolyte, the greater the rate of copper deposited.
Varying the distance apart of the electrodes	As the distance between the electrodes increases, the rate of copper deposited will decrease.

4.1.1



4.1.2 Iron was available – it was one of the earliest metals discovered, it is abundant in the Earth’s crust and is extracted relatively easily by heating its ore. Iron’s properties are suitable – it is a strong, hard metal, which can be welded and shaped. As it became readily available by 1800 it became the metal of choice for ship construction.

4.1.3 The technology to alloy metals led to larger, faster and stronger ships. The *Titanic* was constructed of steel and was considered ‘state of the art’ for its time. However, the steel alloy used in the *Titanic* had a higher content of phosphorus and sulfur than later alloys and this made it more brittle at low temperatures. There have been improvements in steel alloys since that time, including the use of aluminium, chromium, titanium and nickel. Corrosion resistant alloys of copper-nickel are one of the latest developments.

Improved technology and materials have led to ships which are lighter, stronger, more corrosion resistant, safer and more economical.

- 4.2.1 (a) Various, e.g. Gather samples of different metals and alloys possibly suitable for marine use. Samples could include mild steel, stainless steel, copper, brass, aluminium, cast iron, copper-nickel alloy. All samples should be the same size and shape. Samples could be placed half submerged in containers of sea water, left for the same time in the same environment and then observed for corrosion.
- (b) Various. Make detailed observations of the surface of the metals, noting pitting, discolouration, signs of a deposit of a corrosion product. Tabulate your observations. Rate the samples in order of degree of corrosion.

4.2.2 Corrosion occurs rapidly when galvanic cells are set up. Metals in a marine environment readily form electrochemical cells with the sea water as electrolyte. Oxygen is dissolved in sea water. Thus water and oxygen are in close contact with metal. Also the metals in ships are subjected to mechanical stress and stress points can easily become electrode sites. Numerous cells can form on the surface of a piece of metal and the metal at anode sites will corrode rapidly.

4.3.1 Ship hulls are in an environment where they are very susceptible to corrosion. The presence of salt water, oxygen, mechanical stress and alloyed metals in the steel producing irregularities in the crystal structure of the metal all increase the likelihood of corrosion. Electrochemical cells form which hastens corrosion.

4.3.2 Steels can be made more corrosion resistant by including corrosion-resistant or passivating metals in the steel. Alloys which resist corrosion are those with a high percentage of chromium, nickel, manganese and/or molybdenum. Although these alloys have improved corrosion resistance, they still need further protection.

4.3.3 Surface alloying is a recent development in which a protective metal is bound strongly into the surface layers of the steel. This provides a cheaper product than the same metal alloyed into the whole structure. When chromium is surfaced alloyed into steel it is strongly bound so that its oxide is not affected by chloride ions in the sea water and the chromium is less polluting to the environment.

4.3.4 (a) Paints and other coatings keep oxygen and water away from the metal. Since water and oxygen are required for corrosion, the metal will not corrode.

(b)

Advantages	Disadvantages
<ul style="list-style-type: none"> Can be coloured and attractive Relatively cheap Effective when maintained 	<ul style="list-style-type: none"> Need to be regularly maintained so that chips and scratches are repaired. Corrosion would proceed rapidly under the paint if scratches were not repaired. Difficult to maintain on underwater structures. Needs dry docking. Can leach out chemicals and pollute the environment.

4.3.5 A recent development in coatings is the paint called Rustmaster. This paint forms a polymer layer that is impervious to air and water. It also develops an interlayer between the polymer and the metal. This interlayer prevents the movement of ions so that electrochemical cells cannot be set up. Such paints are a big improvement as they are more effective, durable and do not pollute the water.

4.4.1 (a) Various. A variety of paints, lacquers and oils could be coated on identical iron samples. Uncoated samples should be included as a control. All samples should be left in the same environment for the same period of time and the corrosion on the coated samples compared with the unprotected samples.

(b) Various. For the experiment to be valid, the unprotected samples needed to have rusted. These uncoated samples allow you to check that the corrosion really is prevented by the coatings.

4.4.2 Various. As long as the coatings remained intact, the coated samples would not have rusted. Without being used, all samples would protect equally, however, if samples were constantly exposed to wear, some coatings may be less effective.

4.4.3 (a) This is called galvanising and is an effective protection. Even if the coating of zinc is damaged, the zinc (being a more active metal) will be oxidised in preference to the iron.

(b) Tin is an effective coating as long as it remains intact. It keeps water and oxygen away from the iron. However, tin is a less active metal than iron. So, if the tin coating is damaged, an electrochemical cell will be set up, with iron as the anode, and the iron will rust rapidly.

4.4.4 (a) Unpainted samples of the steel treated the same and kept in the same place for the same time. These samples would be used for comparison.

(b) Same steel used for all samples, same thickness of paint coating, shaken in the same way, kept in the same environment including the same temperature for the same period.

(c) Samples with coating A showed no difference in the amount of corrosion between the shaken and unshaken coated samples. Also the shaken samples showed no sign of chips or scratches. However, the unpainted control samples had corroded. There was more corrosion evident on samples painted with B and C.

4.5.1

Metals	Standard potentials from table	Metal which will corrode
Mg, Fe	Mg -2.36 V, Fe -0.44 V	Mg
Zn, Ag	Zn -0.76 V, Ag 0.80 V	Zn
Sn, Fe	Sn -0.14 V, Fe -0.44 V	Fe
Cu, Zn	Cu 0.34 V, Zn -0.76 V	Zn

4.5.2 The metal with the lowest standard potential will corrode.

4.5.3 Any unprotected, weak spot in the metal can form a galvanic cell. There are many cells set up in any sheet of metal. The electrons pass from anode to cathode site and a film of moisture completes the circuit by allowing ion flow. Where two different metals are in contact the more active metal will be the anode.

4.6.1 The process of protecting iron structures from corrosion by making the iron structure become the cathode in an electrochemical cell.

4.6.2 (a) The iron is the cathode. Reduction occurs at the cathode. Oxygen is reduced at the cathode. However, if any Fe ions are present they will be quickly reduced back to Fe metal. $O_2(aq) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

(b) The metal forming the anode is oxidised. This may be Mg or Zn. If the anode is inert, water is oxidised.
 $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

4.6.3 (a) Marine: ship hulls, oil rigs, metal pylons on bridges and wharves.

Wet terrestrial: underground fuel tanks, steel pipes and pylons in wet terrestrial environments.

(b) Various, e.g.

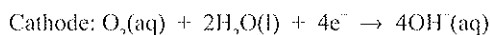
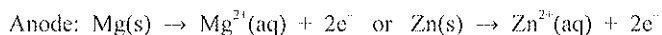
Advantages	Disadvantages
Effective	Corrosion is rapid if galvanic cell is lost.
Long lasting	
Relatively inexpensive	
Easily maintained	

(c)

Protection by painting	Cathodic protection
Maintenance. Paint layer needs to cover all the hull and to be intact, hence regular maintenance needed. Ship needs to be dry docked for maintenance. Thus maintenance may be expensive.	Maintenance of galvanic cell is required, but is inexpensive and can be done without dry docking. May require a zinc plate to be replaced regularly or a small current to be continually supplied.
Corrosion occurs if paint layer is damaged.	Loss of galvanic cell results in corrosion.
Water is polluted as paint deteriorates.	Water is polluted with sacrificial anode, not with impressed current.

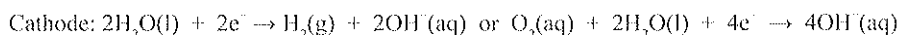
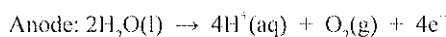
4.7.1 (a) Metals which are more active than iron (stronger reductants) are attached to the iron structure in order to set up a galvanic cell. They are corroded away in preference to the iron and need to be regularly replaced. Mg and Zn commonly used.

(b) A galvanic cell is set up with the Mg or Zn as the anode and the iron structure as the cathode. The Mg or Zn is oxidised and corroded away while the iron is protected by the excess electrons at the cathode. Oxygen is reduced at the cathode. If oxygen is limited, such as in waterlogged soils, water may be reduced at the cathode.



4.7.2 (a) An electrical circuit is attached to the steel or iron structure using an inert anode. A small voltage is applied continuously. The steel structure is the cathode.

(b) The steel structure has a supply of electrons which prevent the Fe from corroding. Water or oxygen is reduced at the cathode and water is oxidised at the anode.



4.7.3 Both methods are very effective. Sacrificial anode requires regular maintenance to replace the anode whereas an impressed current only needs a constant voltage to be supplied. The anode material is released to the environment in a sacrificial anode system whereas an impressed current is non-polluting. An impressed current system is more expensive initially, but both are cheap to maintain.

4.7.4 Galvanised iron is iron with a layer of zinc covering it and protecting the iron. If the zinc layer is damaged, exposing the iron, the zinc and iron form a galvanic cell with the iron as cathode. Hence the iron is protected from corrosion as in cathodic protection.

4.8.1 (a) Ship hulls are normally protected by sacrificial anodes as are rudders and propellers. Accessible steel structures use sacrificial anodes.

Structures that are buried such as fuel storage tanks and pipelines use impressed currents. Modern naval vessels may have built-in impressed current systems.

(b) Various, e.g. Ship hulls have zinc plates attached as these are cheaper to set up than impressed currents and can be easily replaced as the zinc is used up. Similarly other structures with access use sacrificial anodes.

However, underground structures require impressed current systems because the anodes could not be reached to replace them whereas an electric current can be easily monitored and maintained from the surface.

High-tech modern ships may use impressed current as it is cheaper to install such a system during ship building and the ship will not be out of action for replacement of zinc plates.

For the chemistry of sacrificial anodes and impressed currents see answers to 4.7.1 (b) and 4.7.2 (b).

5.1.1 Solubility of gases decreases as temperature increases.

5.1.2 Forward reaction is exothermic. By Le Châtelier's principle, if temperature is increased, then the reverse reaction will be favoured as this will minimise the change. Therefore CO_2 will be released from solution (become less soluble) as temperature rises. Conversely, when the temperature drops, the forward reaction is favoured, so more CO_2 will dissolve.

5.1.3 As temperature rises, the solubility of salts increases. More solid will dissolve in hot water than in cold water.

5.1.4 More salt dissolves as the temperature is increased. However, the difference is very slight with NaCl. For 100 mL of solution only an extra 0.3 g dissolves when the temperature increases from 0°C to 20°C . Therefore temperature affects the concentration of NaCl in water only very slightly.

5.1.5 Pressure has little effect on the solubility of salts. With gases, increased gas pressure above the water increases the solubility of the gases especially CO_2 , but increased pressure due to water depth increases solubility of gases only slightly.

5.2.1 Atmospheric gases are dissolved at the water surface in contact with the air. Wind and waves increase the aeration of the surface layers. Phytoplankton in the surface layers where light penetrates use CO_2 for photosynthesis and release O_2 to the water. Animals and plants both, during the process of respiration, remove O_2 dissolved in the water and release CO_2 .

5.2.2 Gases diffuse slowly to the lower depths from the surface. Ocean currents may play a role.

5.2.3

Gas	Concentration in the atmosphere	Concentration in the ocean
Oxygen	21%	Much lower concentration in water than in air. Slightly soluble. Below the light zone (about 100 m) it is less as animals use the oxygen in respiration. At great depths the conditions are largely anaerobic.
Nitrogen	78%	Much less in water than in air. Nitrogen is not very soluble in water. Very little is found at any depth.
Carbon dioxide	0.04%	Concentration in water is much greater than in air. CO_2 reacts with water and is much more soluble than O_2 or N_2 . Concentration increases with depth due to lower temperature.

5.3.1 (a) Temperature decreases with depth. At about 1000 m it is about 4°C and remains near freezing below this.

(b) Pressure increases with depth. For every 100 m depth, pressure increases by about 100 kPa.

5.3.2 Oxygen has highest concentration in the upper layers due to diffusion from the air and photosynthesis in the light zone. Oxygen is slightly soluble in water and may be up to about 1.2 mg/100 mL at the surface. Below the light zone (about 100 m) it is only about 0.1 mg/100 mL as living things use the oxygen in respiration. At depth, conditions are largely anaerobic except if cold ocean currents bring in water with oxygen.

5.3.3 Nitrogen is less soluble in water than oxygen.

- 5.3.4** (a) Carbon dioxide is very soluble in water while oxygen is only slightly soluble in water.
 (b) CO_2 is very soluble in water and reacts with water.

$$\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{CO}_3(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) \rightarrow 2\text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$$
 CO_2 continuously dissolves from the surface and is also produced from animal and plant respiration so carbonates and hydrogen carbonates are two of the more common anions in sea water.
- 5.4.1** Temperature drops with depth to about 4°C. Low temperatures decrease reaction rate. Thus low temperatures at great depths will cause slow reaction rates.
- 5.4.2** Since corrosion is a chemical reaction, the low temperatures at depth would inhibit corrosion. Corrosion would be very slow.
- 5.4.3** As temperature increases, the rate of corrosion increases, but when the temperature exceeds 40°C the rate of corrosion decreases. The initial increase in rate of corrosion occurs because increasing temperature causes faster chemical reactions (harder and more frequent collisions). However, increase in temperature of the water also causes the solubility of gases to decrease. By about 40°C, the concentration of oxygen dissolved in the salt water is too low for corrosion to occur.
- 5.5.1** (a) Rust would be present in containers with iron and steel in solution – the largest amount in B, then C with least in A. Copper would show little if any corrosion in all solutions.
 B – with the highest $[\text{O}_2]$ would corrode the fastest as O_2 is needed for corrosion. The samples with less O_2 would show little corrosion.
 The steel and iron samples would corrode faster than the copper because copper is an unreactive metal. The composition of the steel would determine which sample, iron or steel, corroded the fastest.
 (b) The sample with salt solution left exposed to the air. This would contain normal levels of O_2 and would be used to compare to the reduced O_2 and O_2 saturated samples.
 (c) Metal samples should be the same size and thickness, kept in the same temperature and under the same conditions and in salt solutions of the same concentration.
- 5.5.2** (a) Iron and steel in the most concentrated salt solution would corrode the fastest as this would be the best electrolyte so it would carry electrons from anode to cathode sites most efficiently. Copper samples would be least corroded as copper is less active than iron.
 (b) Identical samples of iron, steel and copper in distilled water.
 (c) Oxygen levels, temperature, left for the same time, samples the same size.
- 5.5.3** Various, e.g.
 1. Place 6 identical sized samples of iron, steel and copper into separate Petri dishes with 20 mL of 1% salt solution in each dish. Mark the level of the liquid. Cover the dishes.
 2. Place 2 of these Petri dishes with each metal or alloy into the fridge, at room temperature and into an incubator at 50°C.
 3. Leave all samples for one week, checking each day for evaporation of water. Top up samples to the 20 mL mark with distilled water as water evaporates.
 4. Examine each sample for signs of corrosion after one week and record observations in a table.
- 5.6.1** Temperature – near freezing; Pressure – very high (100 kPa for each 100 m depth); Light – total blackness; Salt concentration – only slightly higher than at the surface; Oxygen concentration – no oxygen or very little oxygen.
- 5.6.2** Corrosion would be inhibited due to lack of oxygen and the near freezing temperatures. Oxygen is needed for rusting and reaction rates are decreased at low temperatures.

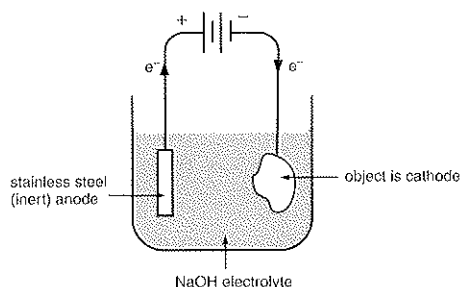
- 6.1.1** (a) Various, e.g. you may have used samples of steel, copper and zinc or other metals available to you. Iron or steel should be one of the metals. The metals need to be placed in a variety of solutions of differing pH, such as $0.1 \text{ mol L}^{-1} \text{ HCl}$, $0.01 \text{ mol L}^{-1} \text{ HCl}$, $0.01 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$, and water. Indicate how you measured the pH of each solution – using an indicator or probe and data logger. Samples would have been left in a warm place for several days before being examined for corrosion. You should indicate how you estimated or measured the rate of corrosion.
- (b) Various, e.g. the rate of corrosion of metals is faster (or slower) in acidic solutions than neutral solutions.
- (c) Your procedure must be designed to provide a fair test of your hypothesis. All variables need to be controlled except for the differing solutions, e.g. metal samples should be the same size and shape, solutions should all contain oxygen and be at the same temperature. If these conditions are met, you can assess your procedure as valid.
- (d) Various, e.g.
The lowest pH (most acidic) solution produced the most corrosion in the same period of time.
 $\text{Fe(s)} + \text{HCl(aq)} \rightarrow \text{FeCl}_2\text{(aq)} + \text{H}_2\text{(g)}$ The neutral solution with copper was not corroded at all. The other metals in water corroded less than the samples in acid.
- 6.1.2** (a) $0.1 \text{ mol L}^{-1} \text{ HCl} - \text{pH} = 1$, $0.01 \text{ mol L}^{-1} \text{ HCl} - \text{pH} = 2$, $0.001 \text{ mol L}^{-1} \text{ HCl} - \text{pH} = 3$ and tap water – $\text{pH} =$ about 7.
- (b) The student's hypothesis is a statement that can be tested experimentally, so it is an acceptable hypothesis. You would not expect the results to support this hypothesis as your experimental results would have shown that corrosion is faster in solutions with lower pH (higher acidity).
- (c) The products of corrosion in acid solution are soluble, therefore rust will not be evident in the solution in acid samples. Corrosion needs to be assessed by examining the surface of the metal for holes and pits etched into the metal. Also any change in size or weight loss would indicate corrosion.
- 6.2.1** Passivating metals such as Al and Cr have a protective coating of the oxide on their surface and these metals will not corrode as long as the coating remains intact.
- 6.2.2** In neutral solutions, the anode reaction is $\text{Fe(s)} \rightarrow \text{Fe}^{2+}\text{(aq)} + 2\text{e}^-$ and the cathode reaction is:
 $\text{O}_2\text{(g)} + 2\text{H}_2\text{O(l)} + 4\text{e}^- \rightarrow 4\text{OH}^-\text{(aq)}$. In acid, the cathode reaction is $2\text{H}^+\text{(aq)} + 2\text{e}^- \rightarrow \text{H}_2\text{(g)}$.
The reduction of H^+ has a lower reduction potential and proceeds more easily than the reduction of oxygen.
Therefore corrosion is accelerated.
- 6.2.3** pH is about 8, so it is basic.
- 6.3.1** Anaerobic bacteria grow wherever the oxygen content is very low and an organic food source is available. They grow in the seabed, utilising organic material, e.g. dead organisms falling from surface layers, as their food source. They do not require oxygen for respiration, but use sulfate ions in the sea water instead. They are able to withstand the low temperatures and high pressures at great depths. They thrive around wrecks where there is a source of organic material such as textiles and wood.
- 6.3.2** Anaerobic bacteria use sulfate ions in sea water for respiration and they thrive around wrecks using organic material such as textiles and wood in the wreck as food.

Electrochemical cells occur as iron and other metals are present in salt water (an electrolyte). They would be slow to operate in the freezing temperatures at great depth, however the growth of anaerobic bacteria stimulates the rate of reaction of the cells by utilising any H_2 produced and providing a source of H_2S to react with any cations.

The reaction of the H_2S with cations produces acid conditions and this further accelerates corrosion. Thus both electrochemical cells and anaerobic bacteria contribute enormously to the rapid corrosion of shipwrecks at depth.
- 6.4.1** $\text{SO}_4^{2-} \rightarrow \text{S} \rightarrow \text{S}^{2-}$ Oxidation number of S in SO_4^{2-} is +6, in S (sulfur atoms) is 0, and in sulfide is -2. Decrease in oxidation number is reduction.
- 6.4.2** $\text{SO}_4^{2-}\text{(aq)} + 10\text{H}^+\text{(aq)} + 8\text{e}^- \rightarrow \text{H}_2\text{S(g)} + 4\text{H}_2\text{O(l)}$

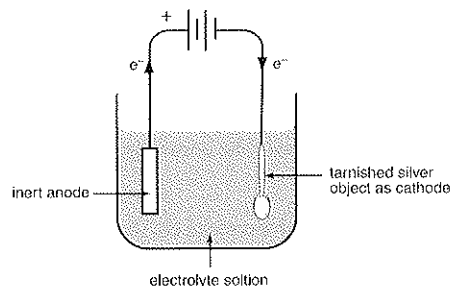
- 6.4.3** (a) Metal cations such as Fe^{2+} react with H_2S : $\text{Fe}^{2+}(\text{aq}) + \text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{FeS}(\text{s}) + 2\text{H}^+(\text{aq})$
- This reaction produces acid and contributes to the acidic microenvironment around wrecks. It also explains the black deposits (sulfides are black) found on metal artefacts in deep wrecks.
- Iron ions will react with water: $\text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Fe}(\text{OH})_2(\text{s}) + 2\text{H}^+(\text{aq})$
- This reaction also contributes to the acid microenvironment. The iron hydroxide then further reacts to form the variety of oxides that make up the rust found on the *Titanic*.
- (b) Acid accelerates corrosion. The cathode reaction is likely to become $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$. The low reduction potential of this reaction causes the galvanic cell to react faster.
- (c) The *Titanic* wreck has deposits of black sulfides on the surface of the metals. These are likely to be caused by the reaction of the metal ions with hydrogen sulfide.
- $\text{Fe}^{2+}(\text{aq}) + \text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{FeS}(\text{s}) + 2\text{H}^+(\text{aq})$
- The iron oxide compounds making up the long rusticles visible around the ship are oxidation products of iron(II) hydroxide produced from reaction of Fe^{2+} with water.
- $\text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Fe}(\text{OH})_2(\text{s}) + 2\text{H}^+(\text{aq})$
- 6.4.4** The lack of oxygen and freezing temperatures at depth led to predictions that steel shipwrecks would be unlikely to corrode. These factors were expected to slow the rate of corrosion. This was shown to be incorrect after the wreck of the *Titanic* was discovered in 1985. The hull and artefacts were badly corroded, showing black metal sulfides and long chains of rust. Research surprisingly showed an acid microenvironment around the wreck and extensive growth of anaerobic bacteria. The chemical processes taking place have been studied in order to explain these observations. The corrosion is believed to be the result of both electrochemical processes and bacterial action.
- 7.1.1** Objects from past human societies. These may be obtained from buried cities, tombs, shipwrecks etc. Examples from shipwrecks would be ships' anchors, bells, cannons, passengers' clothes, jewellery, money, even a button from the uniform of a crew member.
- 7.1.2** Chlorides and sulfates are the most common anions found in sea water. Any object submerged for some time will become saturated with ions from the sea water. This occurs in metal objects, glass objects and organic materials such as leather and textiles.
- 7.2.1** As the solution evaporates, the solutes form crystals.
- 7.2.2** (a) As the object dries out the salts will form crystals. The crystals will grow in size and cause pressure within the structure, weakening the object.
- (b) Ceramic and glass objects may crack and break; leather stains and becomes hard; metal objects corrode more rapidly.
- 7.2.3** Conservators first record information about the site where the artefact was found and its environment. When the object is raised to the surface the procedure is:
- Wash the object free of silt and sand, then store in a slightly basic solution to prevent drying out and halt further corrosion.
 - Remove concretions of calcium carbonate, corrosion products, sand and marine life that may be attached to the surface of the object.
 - Repeated washing in alkaline solutions to desalinate (remove salts).
 - Possible electrolysis to remove deep-seated salts.
 - Stabilise and preserve to protect the object from further corrosion.
- 7.2.4** (a) Desalination
- (b) Monitor the chloride ion concentration in the wash water. This can be done by precipitation with silver nitrate or by using a chloride specific electronic probe. As ions are removed from the object, the chloride ion concentration in successive washes drops.

- 7.3.1** The metal artefact is made the cathode of an electrolytic cell with an inert anode such as stainless steel and a dilute solution of NaOH as electrolyte. A low current draws the negative ions out as they are attracted to the anode. Later, a higher voltage can be used to produce bubbles of H_2 which help to remove any remaining concretions.



- 7.3.2** Anode: $4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$
Cathode: $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$

- 7.4.1** The artefact, such as a piece of cutlery, is made the cathode of an electrolytic cell. An inert anode is used and a suitable electrolyte. The metal is reduced at the cathode, releasing the sulfide anion to move to the anode. Water is oxidised at the anode.



- 7.4.2** Electrolysis can reduce metal ions back to the metal, restoring the structure of the object and releasing the anions which are then removed from the object. The object to be cleaned is made the cathode in the cell and hence the metal ions are reduced. This cleans the object, removing deep-seated corrosion stains. It also stabilises the object as further corrosion is stopped.

7.5.1

Procedure	Outline of method	Example of use
Electrophoresis	Object is placed in an electrolyte between inert electrodes. A small current is applied.	Cleans delicate ceramic and organic materials, e.g. banknotes, leather goods.
Hydrogen furnace reduction	Object is placed in an electrical furnace in an atmosphere of hydrogen. Iron compounds are reduced to iron.	Helps to restore the structure of badly corroded iron objects.
Acid baths	Soak object in a dilute acid bath.	Calcium carbonate deposits can be removed from objects such as wood.
Impregnation of wood with polymers	Wooden object can be soaked in natural plant resins or PEG until the polymer penetrates and sets in the object.	Used to restore strength to wooden objects attacked by micro-organisms, which destroy cellulose in the structure.
Apply wax coating or lacquers	Apply a thin coating of grease, wax or lacquer so that the appearance of the object is not changed.	Preserve objects from further corrosion for display, e.g. in museum.

- 7.6.1**
- Maritime archaeology is the study of marine materials produced by past cultures. It includes discovering, examining, interpreting and conserving marine artefacts and the culture surrounding them.
 - Action taken to clean and stabilise an artefact.
 - Action taken to return an artefact as close as possible to its original condition.

- 7.6.2 Various. There are many suitable projects. The National Maritime museum has many objects from ships involved in exploring and colonising Australia such as the anchor from the *Vernon*, the anchor from the *Sirius*, cannons from the *Endeavour*, many objects from the *Dunbar*. The Western Australian Maritime museum is involved in a project to conserve an engine from a small steamboat called the *Xantho*.

Various, e.g.

	Project 1	Project 2
Details of project	The <i>Batavia</i> – a 17th century trading ship wrecked off the WA coast in 1629. Restoring its timber hull which was water saturated and badly decayed by micro-organisms feeding on cellulose in the wood structure.	The <i>Xantho</i> – a small paddle steamer, made of iron in 1848. Converted to propeller engine in 1871. Wrecked off WA coast 1872. Engine is conserved – only surviving marine engine made at that time.
Wash and clean	Hull raised in sections. Washed until free of sediments.	Engine raised in 1985 using airbags. Stored in dilute NaOH solution. Concretions (about 2 tonnes) removed by careful hammering, chipping and the use of oxyacetylene torch. Then soaked in 5% citric acid with 2% thiourea to remove corrosion products.
Desalinate and stabilise	Desalinated using dilute sodium hydroxide solution for many years.	Engine taken apart and parts desalinated separately by washing with dilute sodium hydroxide for several years. Electrolysis.
Possibly restore	Timbers restored by impregnation with a water soluble wax, polyethylene glycol (PEG) to strengthen timber structure.	
Preserve from further corrosion	Timbers dried and structure rebuilt. Sealed to preserve.	Parts dried and coated with acrylic lacquer to prevent further corrosion. Parts reassembled for display.

- 7.6.3 Objects from past societies are important sources of information about the culture and technology of past human societies. They provide information for historians, but they also help us to analyse our position in the continuum of human existence.
- They provide scientists with valuable information such as the development of metal alloys and their suitability for certain purposes. Information from wrecks such as the *Titanic* has resulted in an increased understanding of the processes of deep sea corrosion and the conditions existing at great depth. An understanding of the behaviour of chemicals in all conditions is one purpose of chemistry.

Notes

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