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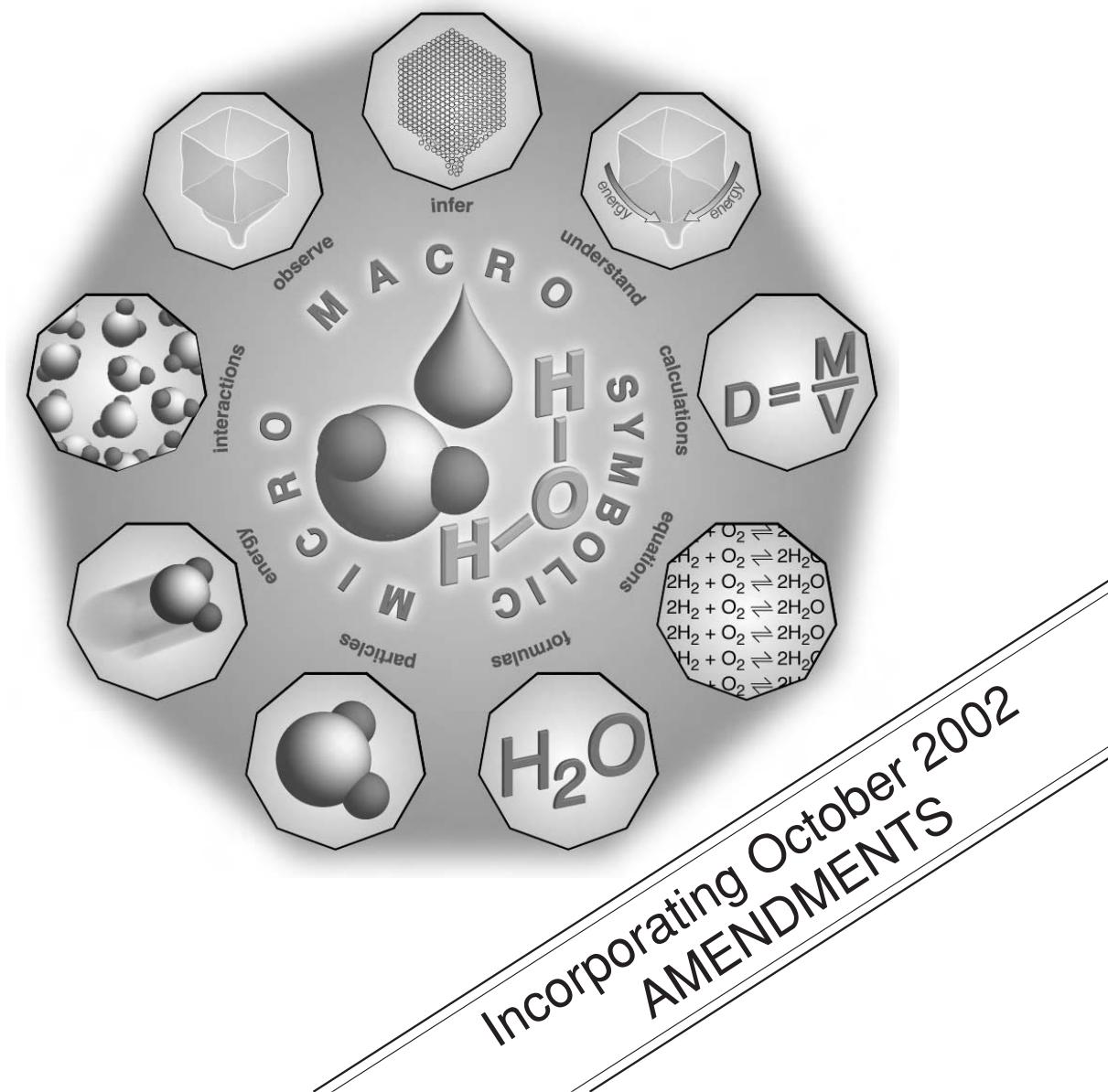
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Shipwrecks, corrosion and conservation



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understand



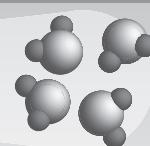
SYMBOLIC

H_2O formulas
equations
calculations



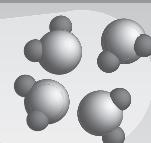
MICRO

particles
energy
interactions



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Module overview

The extracts below are from the Chemistry Stage 6 Syllabus © Board of Studies NSW, November 2002. The most up-to-date version can be found at http://www.boardofstudies.nsw.edu.au/syllabus_hsc/index.html

‘Electrochemistry plays an important part in both theoretical and practical chemistry. Since the discovery of its theoretical basis, knowledge and understanding of the reactions involved have greatly increased. Today electrochemistry is used in a wide range of applications, from space travel to pacemakers to the mobile phone battery.’

The study of electrochemistry is only two hundred years old. Observations of its effects in frog’s legs by Galvani led to experimentation and the building of the first electric battery by Volta. Davy used an electric battery to decompose compounds and produce previously unknown elements such as sodium and potassium. Faraday established the quantitative basis of electrochemistry and summarised this in his laws of electrolysis. Imagine what the world would be like without the work of these pioneers. Think about how your daily life would change if there were no batteries available at all!

‘The ocean represents a massive electrolyte and the effects of the saline environment can be investigated and analysed from the perspective of prevention of corrosion and its effects. The salvaging of iron ships that have sunk into deep-water environments requires consideration of the effects of anaerobic environments on corrosion. Conservation of salvaged artefacts can require electrolytic reactions.’

The saline environment is the salt water of oceans, able to conduct electric currents. The conductivity of this electrolyte increases the extent of corrosion of metal atoms to metal ions. The conservation of objects salvaged from iron ships in deep water requires a comprehensive knowledge and understanding of chemistry.

Part 1 revises and extends concepts studied in the Preliminary *Metals* module and the electrochemistry part of the HSC module *Production and*

identification of materials. Part 2 covers the ocean as a massive electrolyte, Part 3 corrosion of metals and alloys and Part 4 ways of protecting metals from the marine environment. Part 5 deals with the rate of corrosion and ocean depth and Part 6, methods for conservation and restoration of salvage from shipwrecks.

The emphasis in this module is on Prescribed Focus Areas 1, 3 and 5.

Word and balanced formulae equations of chemical reactions are to be constructed as they are encountered.

Indicative time

This module is designed to take a minimum of thirty hours. There are a number of practical activities that need to be set up and observed over a few weeks. Organising materials and equipment for carrying out all these activities could take additional time but in doing so you will better understand the type of work chemists do.

Resources

Materials and equipment and some estimates of time over which the activity needs to be run are listed below. Access to a computer and the worldwide web is important for the study of modern chemistry.

An important skill to develop in chemistry is planning ahead and thinking things through before carrying out the action. Make sure the resources you need are available when you start an activity.

If the activity needs to be left for a lengthy period of time make sure the equipment is protected and unlikely to be interfered with by animals or small children. Label all equipment and chemicals with appropriate warning signs.

You will need access to the worldwide web for some of the activities and exercises. **www access is needed for all parts except Part 1.**

For Part 1 you will require:

- a variety of metals such as steel paper clip, brass drawing pin, copper wire, iron nail, zinc galvanised nail, silver plated cutlery, nickel plated jewellery
- an electrolyte solution to place the metals in eg. vinegar (5%w/w acetic acid solution) or a salt solution (make about 5%w/w salt).

- multimeter or voltmeter able to measure to at least 0.2 V DC (direct current)
- sodium chloride (table salt)
- copper sulfate (available from some plant nurseries and hardware stores)
- broad range pH indicator solution such as universal indicator or red cabbage solution
- two graphite rods (wooden pencils sharpened at both ends or long pencil ‘leads’ or graphite rods obtained from the centre of 1.5 V dry cells – that is, ordinary batteries but not the alkaline type)
- three glass containers or transparent plastic containers such as beakers, of at least 100 mL volume
- two electrical leads with crocodile/alligator clips on the end (if you can’t get suitable clips you could join the wires to the graphite or copper with adhesive tape making sure you have metal to metal/graphite contact)
- a source of low voltage (up to 10 V) direct current (DC) such as a 9 V battery or transformer rectifier unit
- the CuSO₄(aq) solution in a container from the last activity
- two pieces of flat copper each 4 to 10 cm² in area (can be obtained from plumbing shops, some hardware shops, some craft shops supplying jewellery materials); minimise handling of the flat surfaces and, if necessary, clean with some emery paper or steel wool
- [Optional: Access to a balance measuring to 0.01g for weighing the electrodes before and after electrolysis. Paper towelling/filter paper to gently dry electrodes]
- electrolysis equipment for one of the electrolyses you have already carried out; an electrolysis where the rate of reaction is obvious is best
- a willingness to experiment and improvise (change, adjust and substitute equipment)

For Part 2 you will require:

- access to a computer so that you can use an internet search engine or data stored on a CDROM or **DVD** to find out information about Galvani, Volta, Davy and Faraday

For Part 3 you will require:

- steel wool (also called iron wool) – not the type with added soap
- 6 iron nails (clean and shiny and without coatings of other metals)

- 8 glass test tubes or plastic tubes, six with air tight stoppers or corks
- a transparent container such as a beaker of 250 mL to 1000 mL capacity able to hold two test tubes vertically upside down
- emery paper
- salt (NaCl) solution
- epsom salt ($MgSO_4$) solution
- cooking oil
- moisture absorbent such as silica gel or $CaCl_2$ – often found in newly opened electrical goods, shoes or pharmaceuticals
- access to a gas supply such as through a gas tap, from a LPG cylinder or a butane gas filler can
- iron
- an identified form of steel such as mild steel or stainless steel (the iron and the steel should have similar surface areas, masses and shapes). Panelbeaters and welders often have mild steel offcuts.
- containers and chemicals such as salt suitable for encouraging the corrosion of the iron and the identified form of steel
- a way of comparing the rate of corrosion – this could involve quantitative measurements or qualitative observations.

For Part 4 you will require:

- at least three different metals/alloys preferably in the same form such as wire, sheet, nails of similar dimensions
- equipment and chemicals to compare the corrosion rates of the different metals/alloys
- access to a computer connected to the internet
- pieces of iron
- coatings such as water based paint, oil based paint and rust preventing paint.

For Part 5 you will require:

- at least two different metals
- vinegar, table salt solution and washing soda solution
- thermometer.

For Part 6 you will require:

- access to a food freezer or freezing compartment of a refrigerator
- pieces of fruit or salad

Additional resources

- Budinski, KG and MK. (1999). *Engineering materials: properties and selection*. Prentice Hall.
- Harrington, Roy (Ed.). (1992). *Marine Engineering*. Society of Naval Architects and Marine Engineers.
- Millero, Frank J. (1996). *Chemical oceanography*. CRC Press
- Pearson, Colin (Ed.). (1987). *Conservation of Marine Archaeological Objects*. Butterworths.
- Taggart, R (Ed.). (1980). *Ship design and Construction*. Society of Naval Architects and Marine Engineers.

Icons

The following icons are used within this module. The meaning of each icon is written beside it.



The hand icon means there is an activity for you to do. It may be an experiment or you may make something.



You need to use a computer for this activity.



Discuss ideas with someone else. You could speak with family or friends or anyone else who is available. Perhaps you could telephone someone?



There is a safety issue that you need to consider.



There are suggested answers for the following questions at the end of the part.



There is an exercise at the end of the part for you to complete.



You need to go outside or away from your desk for this activity.

Glossary

The following words, listed here with their meanings, are found in the learning material in this module. Most of them appear bolded the first time that they occur in the learning material.

active metal	metal that reacts readily
anaerobic	without oxygen or air
anode	electrode at which oxidation occurs
anodic	like an anode
artefact	object made by human hand
biocide	chemical that kills a living thing
biofilm	thin layer of microbes; commonly called a slime layer
cathode	electrode at which reduction occurs
cathodic	like a cathode
cathodic protection	supply of electrons to a metal to prevent it oxidising to metal ions
chronology	order of past events
concretion	solid formed from liquid materials
conservation	the act of saving or preserving
corrosion	deterioration of any material or its properties because of chemical reaction with its environment
differential aeration	exposure of different parts of a metal surface to different concentrations of air (and therefore oxygen) leading to galvanic corrosion
DVD	digital versatile disk
electrolyte	liquid substance or solution through which ions can move
electrolytic	electrochemical cell changing electrical energy to chemical energy
electrophoresis	motion of particles in a fluid under the influence of an electric field
encrustation	crust or coat on the surface of an object
galvanic	electrochemical cell changing chemical energy to electrical energy

galvanic corrosion	corrosion caused by formation of a galvanic cell
galvanising	covering a metal with a layer by dipping the metal into molten zinc
hydrogenase	enzyme which changes hydrogen gas to hydrogen ions and electrons
hydrothermal vents	openings in the ocean floor out of which hot water containing dissolved minerals passes
impressed current	method of inhibiting corrosion of metal by connection to negative terminal of a DC supply
inert electrode	electrode made of material which does not react eg. platinum, graphite
in situ	Latin for 'at the original site'
leaching	removal of soluble substances from a material as a solvent passes through
metabolism	chemical reactions in a living thing
microbiologically induced corrosion	corrosion produced by activity of microbes
non-passivating metal	metal which does not have a protective oxide layer
oxidation	reaction involving loss of electrons
passivating metal	metal coated with a tenacious oxide layer that protects and results in less metal reactivity than expected
reduction	reaction involving gain of electrons
reduction potential	voltage required for a reduction to occur compare to the standard hydrogen electrode
restoration	the act of bringing back to original condition
sacrificial anode	metal which oxidises before a less active metal that it is attached to
saline	salty
salinity	g of salt per kg of water
salvage (noun)	ship or cargo saved from the sea
salvage (verb)	the act of saving something from a shipwreck
stabilise	to maintain at current condition
steel	iron containing 0.1 to 1.5% carbon

sulfate reducing
bacteria (SRB)

anaerobic bacteria that reduce sulfate ions to
hydrogen sulfide

voltaic cell

alternative name for galvanic cell



Shipwrecks, corrosion and conservation

Part 1: Oxidation-reduction reactions

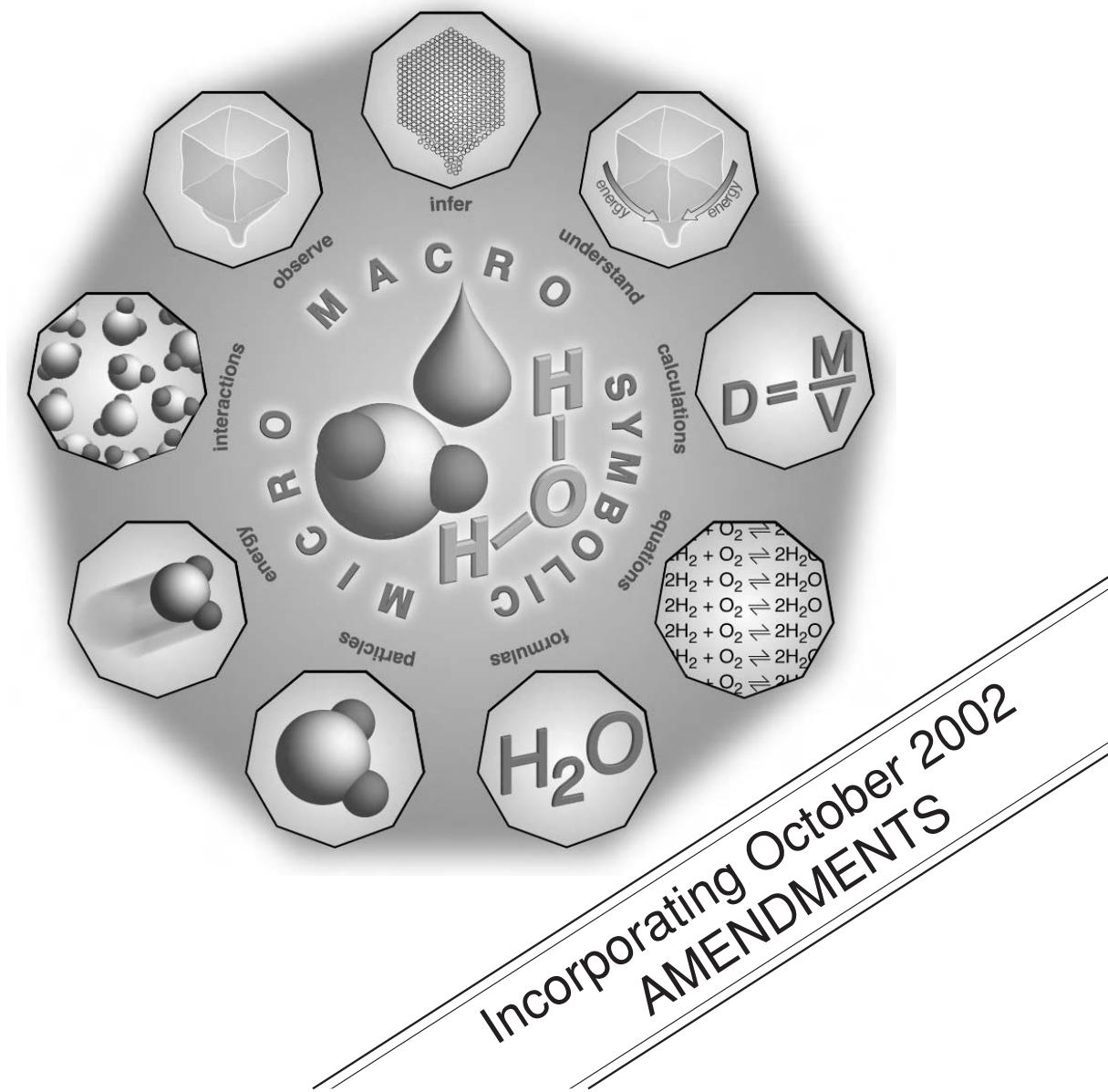
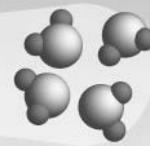


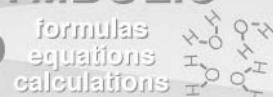
Table of standard potentials and half equations

oxidant	+ electron(s)	\rightleftharpoons	reductant	E^\ominus (volts)
Li^+	+ e^-	\rightleftharpoons	Li	-3.04
K^+	+ e^-	\rightleftharpoons	K	-2.94
Ca^{2+}	+ $2e^-$	\rightleftharpoons	Ca	-2.87
Na^+	+ e^-	\rightleftharpoons	Na	-2.71
Mg^{2+}	+ $2e^-$	\rightleftharpoons	Mg	-2.36
Al^{3+}	+ $3e^-$	\rightleftharpoons	Al	-1.68
H_2O	+ e^-	\rightleftharpoons	$1/2\text{H}_2(\text{g}) + \text{OH}^-$	-0.83
Zn^{2+}	+ $2e^-$	\rightleftharpoons	Zn	-0.76
Fe^{2+}	+ $2e^-$	\rightleftharpoons	Fe	-0.44
Cd^{2+}	+ $2e^-$	\rightleftharpoons	Cd	-0.40
Ni^{2+}	+ $2e^-$	\rightleftharpoons	Ni	-0.24
Sn^{2+}	+ $2e^-$	\rightleftharpoons	Sn	-0.14
Pb^{2+}	+ $2e^-$	\rightleftharpoons	Pb	-0.13
H^+	+ e^-	\rightleftharpoons	$1/2\text{H}_2(\text{g})$	0.00
Cu^{2+}	+ $2e^-$	\rightleftharpoons	Cu	0.34
$1/2\text{O}_2(\text{g}) + \text{H}_2\text{O}$	+ $2e^-$	\rightleftharpoons	2OH^-	0.40
Cu^+	+ e^-	\rightleftharpoons	Cu	0.52
$1/2\text{I}_2(\text{aq})$	+ e^-	\rightleftharpoons	I ⁻	0.62
Fe^{3+}	+ e^-	\rightleftharpoons	Fe^{2+}	0.77
Ag^+	+ e^-	\rightleftharpoons	Ag	0.80
$1/2\text{Br}_2(\text{aq})$	+ e^-	\rightleftharpoons	Br ⁻	1.10
$1/2\text{O}_2(\text{g}) + 2\text{H}^+$	+ $2e^-$	\rightleftharpoons	H_2O	1.23
$1/2\text{Cl}_2(\text{aq})$	+ e^-	\rightleftharpoons	Cl ⁻	1.40
$1/2\text{F}_2(\text{g})$	+ e^-	\rightleftharpoons	F ⁻	2.89

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Introduction

The electrochemical cells involved in the corrosion and the conservation of shipwrecks use reactions known as electron transfer or oxidation-reduction reactions. A knowledge and understanding of these electrochemical cells and the factors affecting their reactions provides a firm foundation for preventing corrosion and for successful conservation.

In *Part 4* of the HSC core module *Production of materials* you studied galvanic cells, electrochemical cells in which chemical energy changed to electrical energy. In this part you will study electrochemical cells where electrolysis changes electrical energy into chemical energy. Corrosion of metals involves galvanic cells while the restoration of metals for conservation involves electrolytic cells.

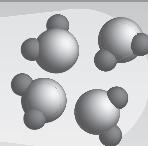
In Part 1 you will be given opportunities to learn to:

- describe, using half equations, what happens at the anode and cathode during electrolysis of selected aqueous solutions
- describe factors that affect an electrolysis reaction
 - effect of concentration
 - nature of electrolyte
 - nature of electrodes.

In Part 1 you will be given opportunities to:

- plan and perform a first-hand investigation and gather first-hand data to identify the factors that affect the rate of an electrolysis reaction.

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Oxidation-reduction (redox) revision

In the Preliminary course module *Metals* and the HSC core module *Production and identification of materials* you have already studied electron transfer reactions. Electron transfer reactions are also called oxidation-reduction or redox reactions.

In this module you will study:

- the corrosion of metal atoms in shipwrecks by oxidation in galvanic cells that form naturally in sea water
- the restoration of metal atoms in salvaged objects by reduction in electrolytic cells created in conservation laboratories.

But, before you begin, you need to revise your understanding of important terms.



Match the following terms, listed alphabetically, with the definitions in the table: anion, anode, cathode, cation, electrode, electrolyte, electrolytic, galvanic, oxidant, oxidation, redox, reductant, reduction.

Term	Definition
	positive ion
	negative ion
	reaction involving loss of electron(s)
	reaction involving gain of electron(s)
	reaction involving both loss and gain of electron(s)
	electrochemical cell changing chemical energy to electrical energy
	electrochemical cell changing electrical energy to chemical energy

	liquid substance or solution through which ions can move
	metal or graphite which transfers electrons in or out of an electrolyte
	oxidising agent; chemical species that causes oxidation (loss of electrons) while itself undergoing reduction
	reducing agent; chemical species that causes reduction (gain of electrons) while itself undergoing oxidation
	electrode at which oxidation occurs
	electrode at which reduction occurs

Check your answers.

Each year huge amounts of energy are expended in the extraction of metals (metal atoms) from metal ores (containing metal ions).

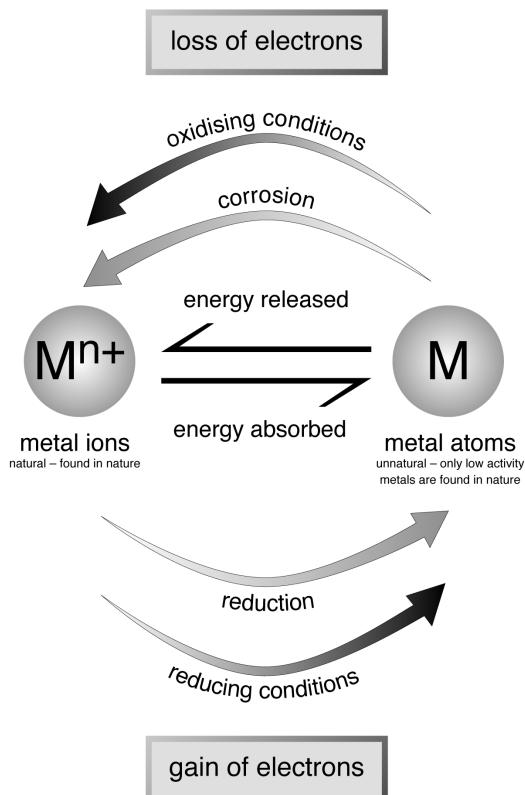
Billions of dollars are spent each year in preventing corrosion of metals. The Sydney Harbour Bridge has a permanent crew of painters working to minimise rusting of the steel bridge.



It has been estimated that 20% of the world's annual production of iron goes into replacing rusted metal. Estimate the average lifetime of an iron atom before it is oxidised to an iron ion.

Check your answer.

The very useful metals that are extracted from metal ores can be regarded as temporarily available to humans. In metal corrosion these atoms are oxidised and returned to their more natural, lower energy form as ions.



Galvanic and electrolytic cells

When comparing galvanic and electrolytic cells it is important that you realise that they carry out opposite processes. A galvanic cell uses a redox reaction that occurs spontaneously to change chemical energy to electrical energy. An electrolytic cell changes electrical energy to chemical energy in a change that does not occur spontaneously.

Consequently the electrodes are allocated different signs:

Galvanic cell anode – cathode +

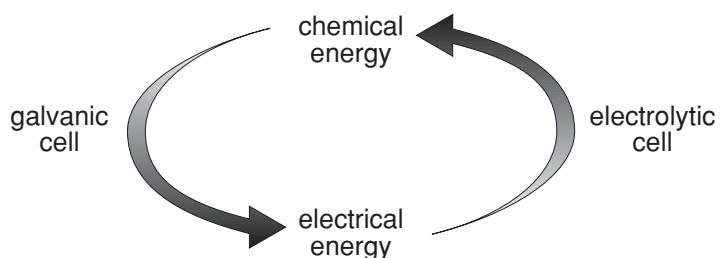
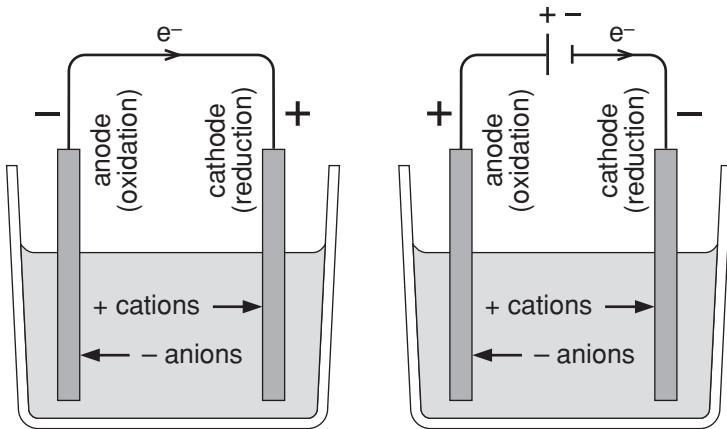
Electrolytic cell anode + cathode –

In both types of cells:

- positive cations always move to the cathode because that is where the negative electrons arrive to carry out reduction
- negative anions always move to the anode because that is where oxidation occurs leading to loss of negative electrons from the electrode to the external circuit.

galvanic cell

electrolytic cell



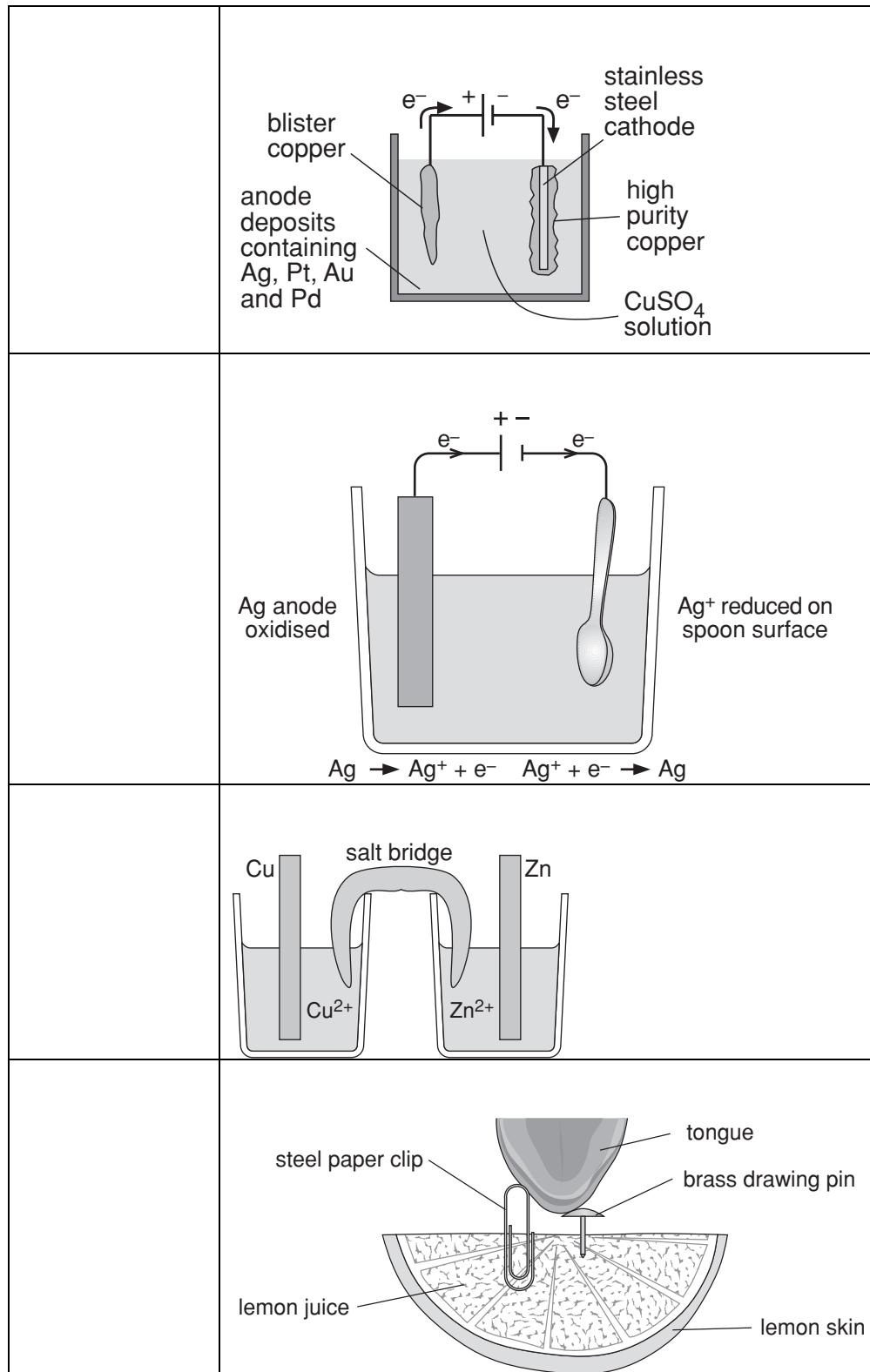
Note that while the current in the wires of the external circuit consists of moving electrons, electrons cannot move through the liquid electrolyte. Current in the electrolyte of the internal circuit consists of moving cations and anions.

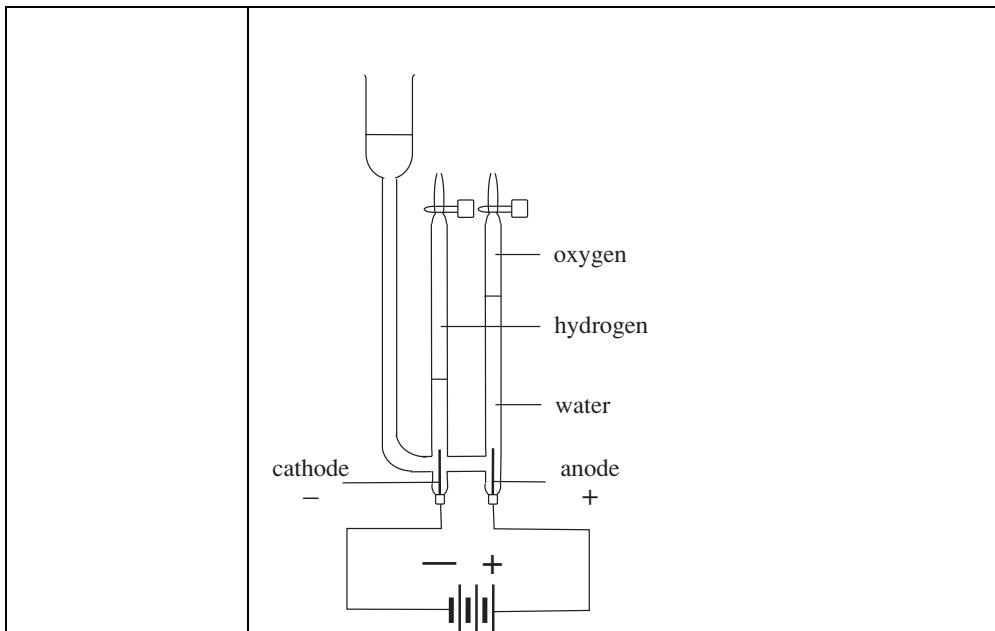
Distinguishing between cells



Use the features in the previous diagrams to identify the electrochemical cells below as galvanic or electrolytic.

Cell type	Cell diagram





Check your answers.

You may find these mnemonics or memory aids useful:

OIL RIG –Oxidation Is Loss of electrons; Reduction Is Gain of electrons.

AN OX – Anode is where Oxidation occurs;

RED CAT – Reduction occurs at the Cathode.

Calculating cell potential from two half equations



A table of standard potentials includes half equations and potentials for electrochemical reactions. The potential (voltage) of a cell can be calculated from this table. A table of standard potentials is provided on the inside cover of this part.

The half equations in this table are given as reduction potentials. As you read the equation from left to right (as you do in the English language), the gain of electrons shows you that reduction is occurring.

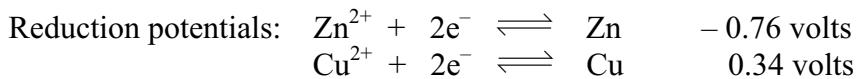
You can still use the table to write oxidation equations. First you need to decide which part of the cell underwent oxidation (if two metals are involved this is usually the more active metal). Then reverse the reduction equation for this part so that it represents oxidation. Whenever the half equation is reversed the sign of the potential also is reversed.

Note that when the shorthand notation $\text{Zn} | \text{Zn}^{2+} \parallel \text{Cu}^{2+} | \text{Cu}$ is used for an electrochemical cell:

- \parallel represents a salt bridge
- $|$ represents a phase change such as from solid to solution
- the oxidation (anode) is written on the left; the reduction (cathode) is written on the right.



Consider the cell $\text{Zn} | \text{Zn}^{2+} \parallel \text{Cu}^{2+} | \text{Cu}$



- 1 Consider the two metals. Which is the more active? _____
- 2 Write the half equation for the more active metal as an oxidation and change the sign of the potential value.

- 3 Write the half equation for the less active metal as a reduction and give the potential value.

- 4 Add the two half equations and their potentials. This will give the full equation and the cell potential.

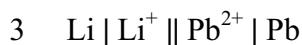
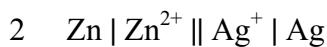
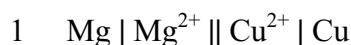
Check your answers.

If the potential of a cell is positive, you can predict that the cell will react spontaneously. The cell will release electrical energy at that voltage if the solutions are approximately one molar concentration. The cell is galvanic.

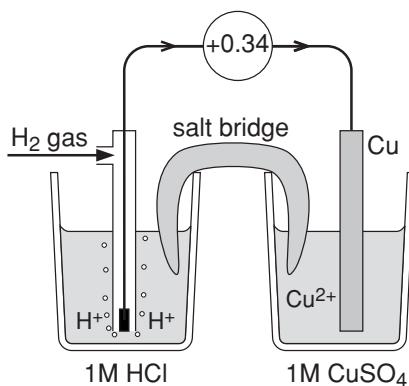
If the potential is negative then you can predict the reaction will not occur spontaneously. No electrical energy is released.



Use the table of standard potentials and half equations on the inside cover to predict the full equation and potential for the following electrochemical cells.



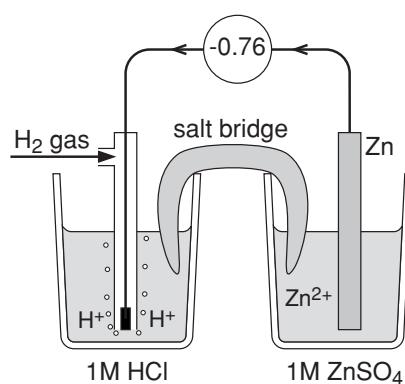
Check your answers.



This cell is represented as $\text{Pt}[\text{H}_2(\text{g})] | 2\text{H}^+ \parallel \text{Cu}^{2+} | \text{Cu}$ because the platinum, Pt, is an **inert electrode** in contact with hydrogen gas. The hydrogen gas is oxidised to hydrogen ions. This half cell is called the standard hydrogen electrode.



- 1 Describe, in words, what happens in the following electrochemical cell.



- 2 Describe using half equations, potentials and a full equation what is happening in the cell.

- 3 Write out the shorthand notation for this cell.

Check your answers.



Complete Exercises 1.1 and 1.2.

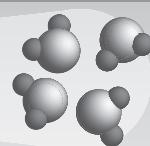
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Electrolytic cells

Investigating electrolysis



What you will need:

- sodium chloride (table salt)
- copper sulfate (available from some plant nurseries and hardwares)
- broad range pH indicator solution such as universal indicator or red cabbage solution
- two graphite rods (wooden pencils sharpened at both ends or long pencil ‘leads’ or graphite rods obtained from the centre of 1.5 V dry cells – that is, ordinary batteries but not the alkaline type)
- three glass containers or transparent plastic containers such as beakers, of at least 100 mL volume
- two electrical leads with crocodile/alligator clips on the end (if you can’t get suitable clips you could join the wires to the graphite or copper with adhesive tape making sure you have metal to metal/graphite contact)
- a source of low voltage (up to 10 V) direct current (DC) such as a 9 V battery or transformer rectifier unit.

What you will do:

- 1 Prepare solutions of dilute NaCl(aq) [about 1% NaCl], saturated NaCl(aq) [about 25% NaCl], and dilute CuSO₄(aq) in the three containers.
- 2 Attach one end of each graphite rod to leads connected to the DC source. Make sure the graphite rods do not touch one another – this can produce a short circuit that flattens the battery.
- 3 Insert about half of each graphite rod into the container of dilute NaCl(aq) making sure the graphite rods do not touch. List any

changes you observe (into the preliminary observations table, below in the results section) during the electrolysis.

- 4 From your preliminary observations (what you detect with your senses) make preliminary inferences (what you think happens).
- 5 Now make a fresh solution of dilute NaCl(aq), add some broad range indicator solution and repeat the electrolysis. Do any changes in pH that you observe agree or disagree with your preliminary inferences? If need be, add to the modified inferences part of the results table.
- 6 Repeat steps 3, 4 and 5 using saturated NaCl(aq) instead of dilute NaCl(aq). If you note a new odour, try to work out which electrode, the positive anode or negative cathode, the odour is coming from by gentle waving the gas above the electrode towards your nose. Just take a small sniff of gas into your nose then quickly breathe out without taking the gas sample into your throat or lungs.
- 7 Repeat steps 3 and 4 (but not 5) using CuSO₄(aq) with the graphite electrodes. Remember graphite is usually an inert electrode material that does not react during electrolysis. The graphite is simply an inert electrical conductor suitable for allowing electric current to enter and leave a solution without the electrode reacting with the solution.
- 8 The NaCl solutions can be discarded down a sink but keep the copper sulfate solution for the next activity.

Results:

	dilute NaCl(aq)	saturated NaCl(aq)	CuSO ₄ (aq)
Preliminary observations			
Preliminary inferences			
pH change observations			
Modified inferences			



Conclusions:

Describe, using half equations selected from the table of standard potentials on the inside cover, what happens at the anode and cathode during electrolysis of the three aqueous solutions.

- Dilute NaCl(aq):

- Saturated NaCl(aq):

- CuSO₄(aq):

Check your answers.

Electrolysis using an active electrode



The graphite electrodes you used in the last activity were inert. The graphite did not react with any of the solution or any of the products of electrolysis. In this activity you should be able to observe electrode material actively involved in the electrolysis.

What you will need:

- the CuSO₄(aq) solution in a container from the last activity
- two pieces of flat copper each 4 to 10 cm² in area (can be obtained from plumbing shops, some hardware shops, some craft shops supplying jewellery materials). Minimise handling of the flat

surfaces and if necessary clean with some emery paper or steel wool. Put a mark on one so you can distinguish the two electrodes.

- two electrical leads with crocodile/alligator clips on the end
- a source of low voltage (up to 10 V) direct current (DC) such as a 9 V battery or transformer rectifier unit
- [Optional: Access to a balance measuring to 0.01 g for weighing the electrodes before and after electrolysis. Paper towelling/filter paper to gently dry electrodes.]

What you will do:

- 1 [Optional: Weigh the electrodes before and after electrolysis.]
- 2 Connect the clips to the top of the flat copper pieces. Insert the copper half into the solution making sure the metal parts of the crocodile/alligator clips are not in the solution.
- 3 Connect the leads to the source of DC and observe for at least ten minutes. Record any changes you can observe then leave the electrolysis on for hours or even overnight. Make sure the equipment is left in a safe place away from animals and small children.

Results:

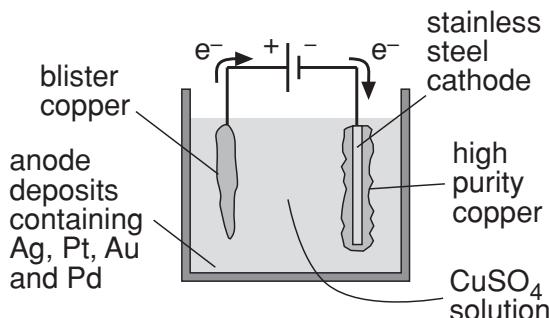
- 1 Make sure your results compare the copper anode and copper cathode noting any changes in surface appearance or thickness. Use the mark to distinguish which was the anode and which the cathode.

- 2 [Optional: Record masses of electrodes before and after electrolysis and calculate any mass changes].

Conclusion:



Compare your activity with the electrolytic refining of copper.



Check your answer.

Factors that affect the rate of electrolysis



In this activity you are going to perform a first-hand investigation and gather first-hand data to identify the factors that affect the rate of one of the electrolysis reactions you have already carried out. Certain approaches will be suggested to you but in implementing these you may need to improvise and solve problems.

What you will need:

- electrolysis equipment for one of the electrolyses you have already carried out; an electrolysis where the rate of reaction is easily noticeable is best
- a willingness to plan ahead, experiment and improvise (change, adjust and substitute equipment).

What you will do:

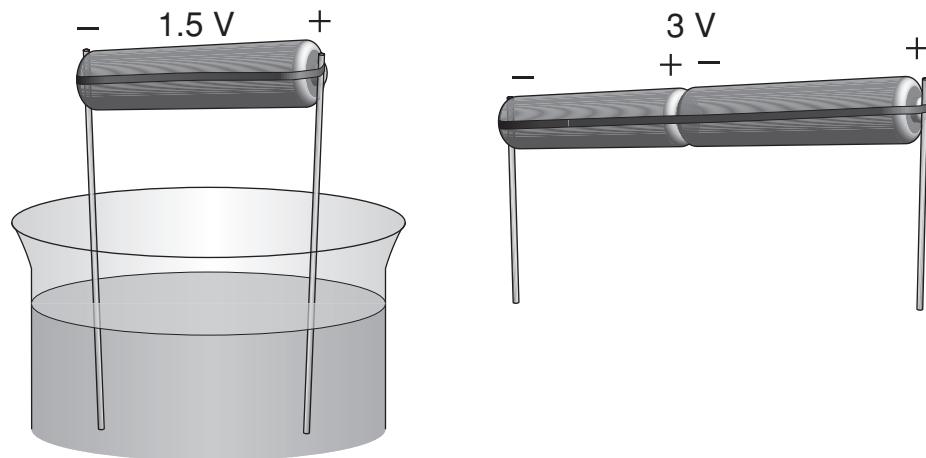
Change each of the following factors and see if there is any change in rate of electrolysis.

- Area of electrode immersed in the electrolyte.
- Distance apart of electrodes (but make sure electrodes do not touch).

- Concentration of the electrolyte.
- Applied voltage.

If you do not have a DC source with different voltages you can obtain different voltages by joining batteries in the ways illustrated below.

More than one battery can be held together by rubber bands; long pencil ‘leads’ or pieces of fuse wire can be used as electrodes.



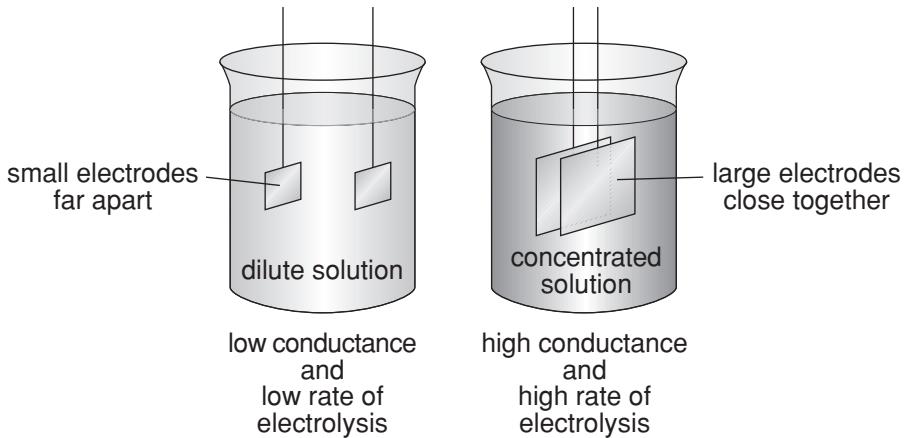
Conclusions:



Complete the following sentences by striking out the underlined words that are inappropriate:

- 1 As the area of electrode immersed in the electrolyte increases more/less reaction can occur. Increasing the surface area in the electrolyte increases/decreases the number of places where reaction can occur.
- 2 The further apart the electrodes are, the more/less reaction occurs. As the distance between the electrodes increases there is a longer length of solution between the electrodes and this increases/decreases the electrical resistance of the solution. This reduced the electrical conductivity and rate of flow of electric charge.
- 3 The higher the concentration of electrolyte the more/less reaction occurs. High concentrations provide more/fewer ionic particles present to conduct electricity and to react.
- 4 The higher the applied voltage the more/less reaction occurs. The higher the voltage or ‘electrical pressure’ the higher/lower the current that flows between the electrodes.

Check your answers.



-  1 When you carried out the two electrolyses of NaCl(aq) you used the same electrodes, the same electrolyte but at different concentrations. Outline the differences produced by using a higher concentration of electrolyte.

- 2 When you carried out the electrolysis of CuSO₄(aq) you used graphite electrodes and copper electrodes. Compare the differences produced by using different electrodes.

Check your answers.

Summary of factors affecting electrolysis

- The greater the area of electrode immersed in the electrolyte the greater the rate of electrolysis.
- The further apart electrodes are, the less the rate of electrolysis.
- The greater the concentration of the electrolyte the greater the rate of electrolysis.
- The greater the voltage applied the greater the rate of reaction; higher voltages can also lead to more than one reaction occurring.
- The nature of the electrodes – inert electrodes such as graphite or platinum do not react but active electrodes such as copper can.
- Most importantly, the nature of the electrolyte. The electrolyte supplies the chemicals to be oxidised or reduced. These form the products of the reaction.

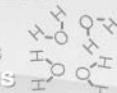
Predicting products of electrolysis

If the voltage is increased until electrolysis starts in a cell, a table of potentials can be used to predict the first reaction and its products.

Metals of low activity are easiest to reduce. Metals with positive E^\ominus values, such as copper and silver, have ions which are easily reduced, such as in electrolysis of copper sulfate and in silver electroplating.

Water is reduced to hydrogen gas and hydroxide ions at just under -1 V . The ions of metals with E^\ominus values above -1 V such as Al^{3+} , Mg^{2+} and Na^+ are not reduced in aqueous solution. The water requires a lower voltage to be reduced and so will be reduced first.

Bromide and iodide ions are oxidised before water molecules are oxidised to oxygen and hydrogen ions. Whether chloride ions are oxidised or water is oxidised depends on the concentration of chloride ions. In dilute NaCl(aq) water is oxidised. In saturated NaCl(aq) where the chloride concentration is much higher and the concentration of water is less the chloride ions are oxidised first. Fluoride ions are never oxidised. Nitrate ions and sulfate ions are also too stable to be oxidised.

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Suggested answers

Oxidation-reduction (redox) revision

Term	Definition
cation	positive ion
anion	negative ion
oxidation	reaction involving loss of electron(s)
reduction	reaction involving gain of electron(s)
redox	reaction involving both loss and gain of electron(s)
galvanic	electrochemical cell changing chemical energy to electrical energy
electrolytic	electrochemical cell changing electrical energy to chemical energy
electrolyte	liquid substance or solution through which ions can move
electrode	metal or graphite which transfers electrons in or out of an electrolyte
oxidant	oxidising agent; chemical species that causes oxidation (loss of electrons) while itself undergoing reduction
reductant	reducing agent; chemical species that causes reduction (gain of electrons) while itself undergoing oxidation
anode	electrode at which oxidation occurs
cathode	electrode at which reduction occurs

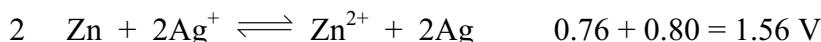
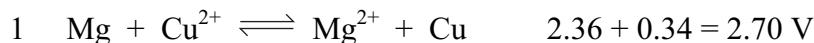
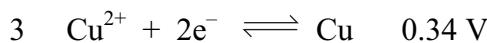
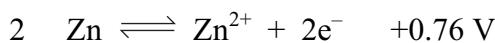
Twenty per cent of annual iron production is to replace rusted metal. If no rusted iron was replaced, after five years 100% of the annual iron production would be needed to replace all the rusted iron. So, the average lifetime of an iron atom before it is oxidised to an iron ion would be about five years.

Galvanic and electrolytic cells

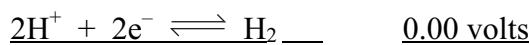
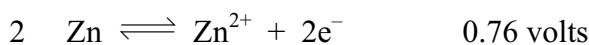
- galvanic cell producing 0.76 volts
- electrolytic cell used to purify copper
- electrolytic cell used to silver plate a spoon
- galvanic cell using copper and zinc half cells
- galvanic cell of steel and brass in a lemon juice electrolyte
- electrolytic cell (commonly called a voltameter) to decompose water.

Calculating cell potential from two half equations

1 zinc

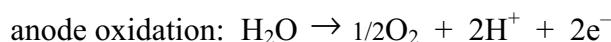


1 Zinc in the electrode oxidises releasing zinc ions into solution. Electrons pass from the zinc electrode through the external circuit to the platinum, attracting H^+ and forming H_2 gas. Negative ions pass from the hydrogen half cell to the zinc half cell while positive ions move in the opposite direction.



Electrolytic cells

- Dilute NaCl(aq) :



small number of gas bubbles; indicator shows pH changes to acid
cathode reduction: $\text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^-$

larger number of hydrogen gas bubbles; pH changes to basic

[Note that in water and aqueous solutions water molecules can act either as a reductant $\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$ OR as an oxidant $\text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^-$]

- Saturated NaCl(aq):

anode oxidation: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

strong smell of chlorine gas around anode; pH changes to acid (as some of the chlorine dissolves in water forming acid)

cathode reduction: $\text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^-$

about same amount of gas but no smell; pH changes to basic

- CuSO₄(aq):

anode oxidation: $\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$

small number of gas bubbles

cathode reduction: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

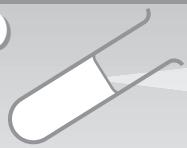
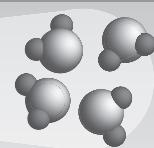
copper coats the part of the cathode in the solution.

The copper connected to the positive terminal loses mass and becomes thinner in both situations. The copper sheet used is very unlikely to contain precious metals and to leave anode deposits. The copper sheet connected to the negative terminal increases in mass and becomes thicker in both situations.

Factors that affect the rate of electrolysis

- 1 As the area of electrode immersed in the electrolyte increases more/less reaction can occur. Increasing the surface area in the electrolyte increases/decreases the number of places where reaction can occur.
- 2 The further apart the electrodes are, the more/less reaction occurs. As the distance between the electrodes increases there is a longer length of solution between the electrodes and this increases/decreases the electrical resistance of the solution. This reduced the electrical conductivity and quantity of electric charge that can flow.
- 3 The higher the concentration of electrolyte the more/less reaction occurs. High concentrations provide more/fewer ionic particles present to conduct electricity and to react.

- 4 The higher the applied voltage the more/less reaction occurs.
The higher the voltage or ‘electrical pressure’ the higher/lower the current that flows between the electrodes.
- 1 The higher concentration of electrolyte increased the rate of reaction and changed the products produced. When the NaCl concentration is higher more Cl^- ions are present and these are oxidised to Cl_2 gas. When the NaCl concentration is lower there are many more water molecules at the electrode surface and these are oxidised to O_2 gas and hydrogen ions.
- 2 When graphite electrodes are used oxidation at the anode is of water to O_2 gas and hydrogen ions. The graphite electrode does not change in size. When a copper anode is used the copper atoms in the anode oxidise before the water in the solution does. The anode becomes thinner. The intensity of the blue colour of the copper sulfate solution decreases when graphite electrodes are used as copper ions are reduced but not replaced. When copper electrodes are used each copper ion from solution gaining two electrons and depositing on the cathode is replaced by a copper ion forming at the anode.

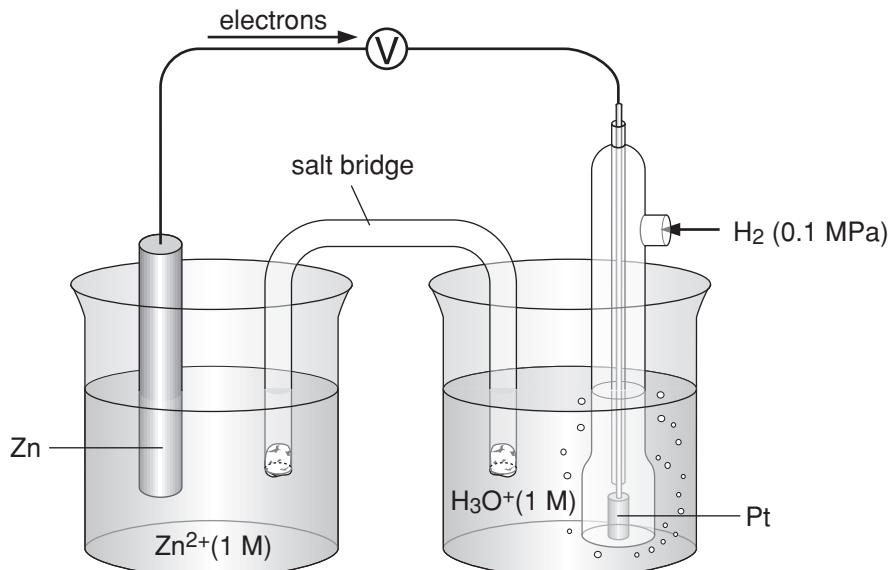
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Exercises – Part 1

Exercises 1.1 to 1.2

Name: _____

Exercise 1.1: What type of cell is this?



- a) Is this a galvanic or an electrolytic cell? Justify your answer.

- b) Use the table of reduction potentials to explain why electron flow is in the direction shown rather than the opposite direction.

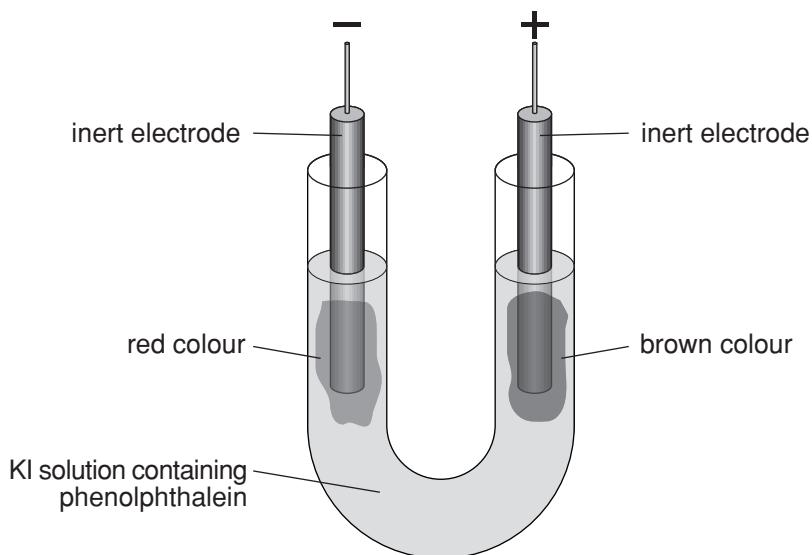
- c) Predict and explain what would happen if the salt bridge was removed.

- d) Represent this electrochemical cell in shorthand notation.

- e) Use the table of standard reduction potentials to calculate the voltage of this cell.

- f) Identify the anode and indicate whether it is positive or negative.

Exercise 1.2: What type of cell is that?



- a) Is this a galvanic or an electrolytic cell? Justify your answer.

- b) Describe the electron flow in the electrodes and the ion flow in the solution.

- c) Predict and explain what would happen if the wire to one of the electrodes was cut so no electricity could flow.

- d) Identify the anode and indicate whether it is positive or negative.

- e) Give the anode and cathode half equations.

- f) Use the table of standard reduction potentials to calculate the voltage needed for this cell to undergo chemical change.



Shipwrecks, corrosion and conservation

Part 2: The ocean electrolyte

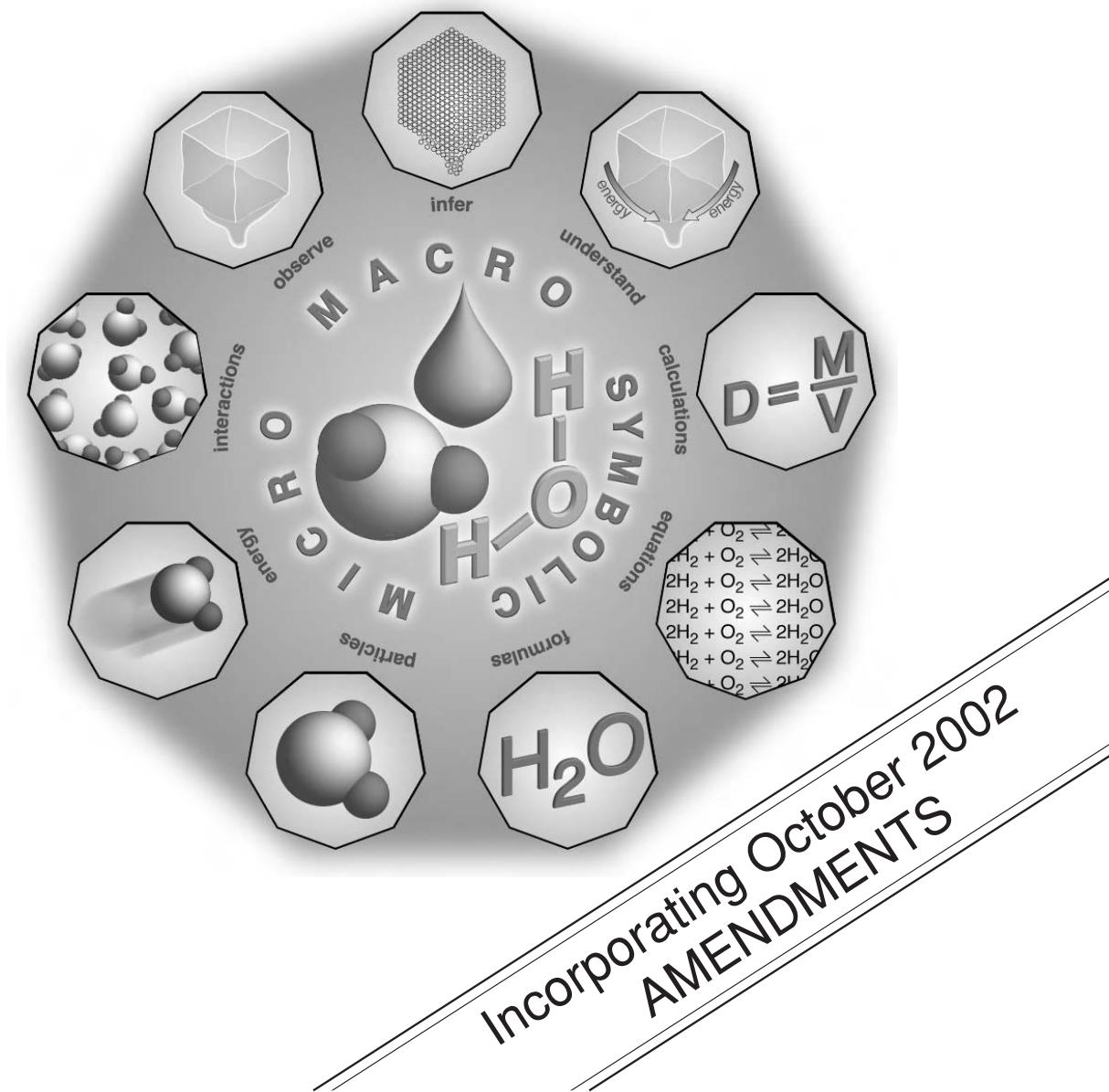
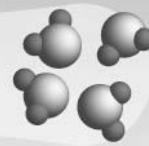


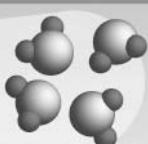
Table of standard potentials and half equations

oxidant	+ electron(s)	\rightleftharpoons	reductant	E^\ominus (volts)
Li^+	$+ \text{e}^-$	\rightleftharpoons	Li	-3.04
K^+	$+ \text{e}^-$	\rightleftharpoons	K	-2.94
Ca^{2+}	$+ 2\text{e}^-$	\rightleftharpoons	Ca	-2.87
Na^+	$+ \text{e}^-$	\rightleftharpoons	Na	-2.71
Mg^{2+}	$+ 2\text{e}^-$	\rightleftharpoons	Mg	-2.36
Al^{3+}	$+ 3\text{e}^-$	\rightleftharpoons	Al	-1.68
H_2O	$+ \text{e}^-$	\rightleftharpoons	$1/2\text{H}_2(\text{g}) + \text{OH}^-$	-0.83
Zn^{2+}	$+ 2\text{e}^-$	\rightleftharpoons	Zn	-0.76
Fe^{2+}	$+ 2\text{e}^-$	\rightleftharpoons	Fe	-0.44
Cd^{2+}	$+ 2\text{e}^-$	\rightleftharpoons	Cd	-0.40
Ni^{2+}	$+ 2\text{e}^-$	\rightleftharpoons	Ni	-0.24
Sn^{2+}	$+ 2\text{e}^-$	\rightleftharpoons	Sn	-0.14
Pb^{2+}	$+ 2\text{e}^-$	\rightleftharpoons	Pb	-0.13
H^+	$+ \text{e}^-$	\rightleftharpoons	$1/2\text{H}_2(\text{g})$	0.00
Cu^{2+}	$+ 2\text{e}^-$	\rightleftharpoons	Cu	0.34
$1/2\text{O}_2(\text{g}) + \text{H}_2\text{O}$	$+ 2\text{e}^-$	\rightleftharpoons	2OH^-	0.40
Cu^+	$+ \text{e}^-$	\rightleftharpoons	Cu	0.52
$1/2\text{I}_2(\text{aq})$	$+ \text{e}^-$	\rightleftharpoons	I ⁻	0.62
Fe^{3+}	$+ \text{e}^-$	\rightleftharpoons	Fe^{2+}	0.77
Ag^+	$+ \text{e}^-$	\rightleftharpoons	Ag	0.80
$1/2\text{Br}_2(\text{aq})$	$+ \text{e}^-$	\rightleftharpoons	Br ⁻	1.10
$1/2\text{O}_2(\text{g}) + 2\text{H}^+$	$+ 2\text{e}^-$	\rightleftharpoons	H_2O	1.23
$1/2\text{Cl}_2(\text{aq})$	$+ \text{e}^-$	\rightleftharpoons	Cl ⁻	1.40
$1/2\text{F}_2(\text{g})$	$+ \text{e}^-$	\rightleftharpoons	F ⁻	2.89

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Introduction

About 3.5% of the mass of ocean water is dissolved substances, mostly positive and negative ions from salts. The ions are free to move in this aqueous solution. So, ocean water is an electrolyte, able to conduct electricity. The ability of ocean water to carry an electric current enables oxidation-reduction (redox) reactions to occur involving dissolved gases, water and metal parts of shipwrecks. These reactions involve electron transfer from the place where oxidation occurs, usually a metal, to the place where reduction occurs – a non-metal, non-metal compound or metal of lower activity. Although called electron transfer reactions the movement of charge in solution is carried out by movement of ions. The ions can be cations deficient in electrons (positive ions) or anions carrying excess electrons (negative ions). Electrons do not actually move through water by themselves.

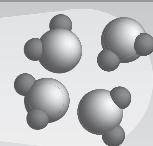
In Part 2 you will be given opportunities to learn to:

- identify the origins of the minerals in oceans as:
 - leaching by rainwater from terrestrial environments
 - hydrothermal vents in mid-ocean ridges
- outline the role of electron transfer in oxidation-reduction reactions
- identify that oxidation-reduction reactions can occur when ions are free to move in liquid electrolytes
- describe the work of Galvani, Volta, Davy and Faraday in increasing understanding of electron transfer reactions.

In Part 2 you will be given opportunities to:

- process information from secondary sources to outline and analyse the impact of the work of Galvani, Volta, Davy and Faraday in understanding electron transfer reactions.

Extracts from *Chemistry Stage 6 Syllabus* © Board of Studies NSW, November 2002. The most up-to-date version can be found on the Board's web site at http://www.boardofstudies.nsw.edu.au/syllabus_hsc/index.html

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Galvani, Volta, Davy and Faraday

These four scientists made important contributions to our understanding of electron transfer reactions.



Use an Internet search engine or data stored on a CD-ROM or **DVD** to find out the impact of these four scientists on chemical reactions involving electricity. If you do not have access to digital data sources then use textbooks or encyclopedias to read about these scientists' contributions.

Make brief notes for each scientist in the spaces below.

Luigi Galvani (1737-1798)

Alessandro Volta (1745-1827)

Humphry Davy (1778-1829)

Michael Faraday (1791-1867)



Matching exercise. Match the statements below with the scientist whose work is described. Put numbers for contributions under names in the table.

- 1 generated an electric current in frog legs using two different metals
- 2 carried out quantitative research into electrochemistry
- 3 investigated electrolysis of water
- 4 built the first battery from a pile of two different metals separated by materials soaked in salt solution
- 5 this scientist was an apprentice to Humphry Davy and was considered to be Davy's 'greatest discovery'
- 6 explained his observations by saying that animal tissue contained a fluid which he called 'animal electricity'
- 7 alerted scientists to an interesting phenomenon but contributed little to scientific understanding of what is happening
- 8 made the prototype of equipment which provides the energy for most portable appliances today
- 9 discovered potassium and sodium by carrying out electrolysis of hydroxides
- 10 first person to use the terms electrolyte, electrode, anode, cathode, ions, anion and cation
- 11 probably died young because he, like many nineteenth century chemists, smelt and tasted all new chemicals that he investigated
- 12 unit of potential difference named after this scientist
- 13 electrochemical cells that release electrical energy are usually named after this scientist
- 14 total charge on a mole of electrons is named after this scientist
- 15 developed a safety lamp that provided light but did not cause gas explosions in coal mines

Scientist	Galvani	Volta	Davy	Faraday
Contributions				

Check your answers.

You have processed information about the work of Galvani, Volta, Davy and Faraday. Now concentrate on how their work increased understanding of electron transfer reactions.



Insert the name of one of these four scientists after each of the following concepts of electron transfer reactions. The concepts are listed in chronological order, that is, in order of when they happened.

Two different metals generate an electric current in animal tissue	
pairs of different metals separated by salt solution generate an electric current	
the electricity that comes from an electric cell or battery is produced by chemical reactions	
the electrical energy from a battery can be used to decompose substances that are difficult to decompose by heat	
the amount of substance produced in electrolysis is proportional to the amount of electricity that flows	
in electrolysis the anion particles go to the anode while cation particles go to the cathode	

Check your answers.

Galvani and Volta contributed to the development of the first electrochemical cells able to change chemical energy to electrical energy. Today these cells are usually called galvanic cells but can also be called voltaic cells. Galvani made the initial observations that two different metals could generate electricity but Volta first developed a way of supplying electricity from chemicals.

Davy and Faraday showed how galvanic/voltaic cells could be used to further understanding of chemistry. Davy contributed to our understanding of how electrical energy could be used to cause chemical changes in electrolytic cells while Faraday provided suitable terms, quantitative laws and particle theory explanations.

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Why are the oceans salty?

The two main origins of minerals in ocean water are:

- leaching by rainwater from terrestrial environments
- hydrothermal vents in mid-ocean ridges.

Leaching is the removal of soluble substances from a material as a solvent passes through. Rainwater moving through soil and rock layers dissolves soluble substances such as sodium chloride. The water is carried down by gravity, in rivers or through the ground, to the low-lying parts of the earth's surface – the oceans.

Most rainwater is acidic to some extent. The hydrogen ions in acid rain can react with carbonate ions and phosphate ions in insoluble materials forming water soluble hydrogen carbonate and hydrogen phosphate ions.



Write balanced equations for the formation of water soluble ions from CO_3^{2-} and PO_4^{3-} ions.

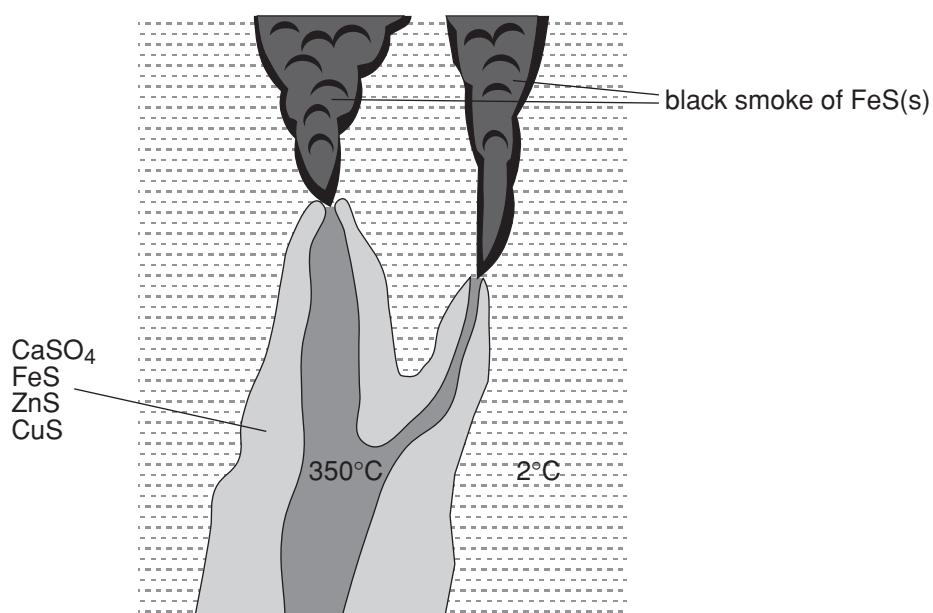
Check your answers.

Hydrothermal vents are openings in the ocean floor near underwater volcanic activity. Sea water passes down into rocks near the vents where it is heated and dissolves salts. Hydrothermal vents release hot water, rich in mineral salts, into cold sea water. The lower temperature causes some of the dissolved salts to come out of solution forming mineral deposits on the ocean floor. Other dissolved salts remain in solution and are added to the sea water. The hot water released from the vents is much less dense than surrounding cold water and rapidly rises, dispersing the mineral salts.

The sulfur dioxide and hydrogen chloride gases released through these vents increase the concentration of sulfate ions and chloride ions in sea water. Chemical reactions can lead to the removal of magnesium ions and sulfate ions while adding lithium and rubidium ions.

The rate of movement of water through the newly formed basaltic ocean crust in mid-ocean ridges is equivalent to the entire volume of the ocean's water every five million to ten million years. This movement, coupled with dissolution and precipitation of ionic compounds in water, may have kept the composition of sea water fairly constant over many years.

Structures called smokers are formed around the vents by precipitation of salts. Black smokers which are the hottest precipitate black iron(II) sulfide FeS. White smokers emit cooler water which precipitates white compounds of barium, calcium and silicon.



Structure of a typical black smoker.



<http://www.lmpc.edu.au/science>

has:

- an audio interview with Dr. Joanna Parr of the CSIRO Division of Exploration and Mining about her research into mineral rich black smokers in the Bismarck Sea off Papua-New Guinea
- a link to a CSIRO video showing gold rich black smokers

Electron transfer and ion movement

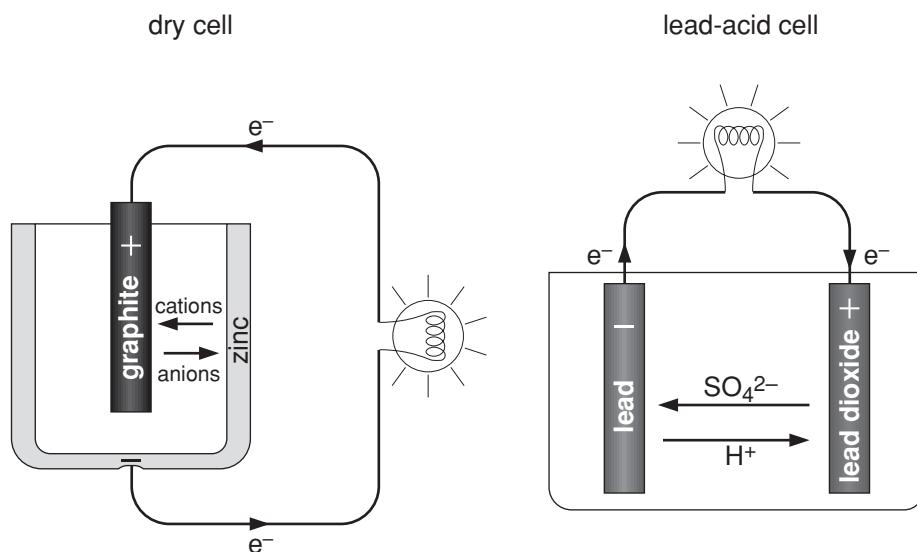
Oxidation-reductions are electron transfer reactions where electrons transfer from one chemical (the reductant) to another (the oxidant).

The two chemicals do not have to be in direct contact. If a conductor is placed between the two, electron transfer takes place through the conductor.

This is what happens when a connection is made between the negative terminal of a battery (the reductant that undergoes oxidation) and the positive terminal of the battery (the oxidant that undergoes reduction).

The conductor allowing transfer of electrons is called the external circuit.

Electron and ion movement in:



For oxidation and reduction to continue the circuit needs to be completed. The movement of ions through an internal circuit within the battery allows oxidation and reduction to occur. Positive cations move towards the terminal accumulating negative electrons while negative anions move towards the terminal that has lost negative electrons.

Water soluble minerals such as sodium chloride provide charged ions that can move easily through sea water. Corrosion reactions are oxidation-reduction reactions that involve electron transfer from metals. These reactions also require the movement of ions in the electrolyte between the anode and cathode and so salty sea water facilitates corrosion.

Metals that corrode very slowly in dry air can undergo rapid corrosion in sea water where ions are plentiful and move freely.

Most ion movement in oxidation-reduction reactions occurs in liquid electrolytes where the ions can move freely.

Oxidation-reduction reactions made possible by the free movement of ions in sea water always use a liquid electrolyte – the sea water.

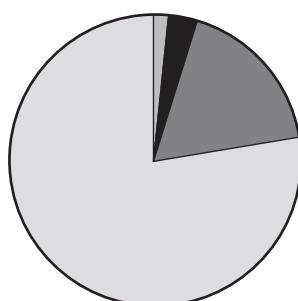
Ions in sea water



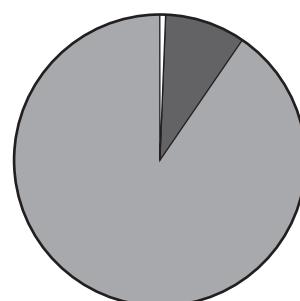
Use the information in the table below to label the pie graphs for the most common ions in sea water. Label each sector of the pie graphs with the formula for the appropriate ion.

Salt ion	% of sea water (mass)	% of total ions (mass)
chloride	1.90	55
sodium	1.06	31
sulfate	0.26	8
magnesium	0.13	4
calcium	0.04	1
potassium	0.04	1
hydrogen carbonate	0.01	–

Cations



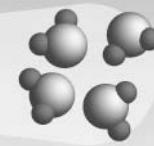
Anions



Check your answers.



Compete Exercise 2.1 and 2.2 now.

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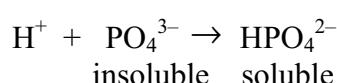
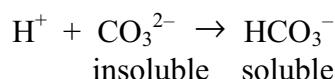
Suggested answers

Galvani, Volta, Davy and Faraday

Scientist	Galvani	Volta	Davy	Faraday
Contributions	1,6,7,13	4,8,12	3,9,11,15	2,5,10,14

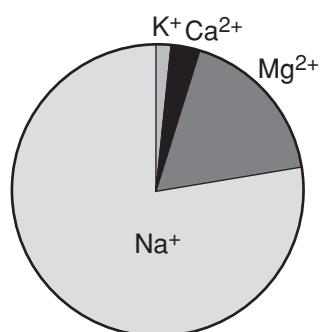
two different metals generate an electric current in animal tissue	Galvani
pairs of different metals separated by salt solution generate an electric current	Volta
the electricity that comes from an electric cell or battery is produced by chemical reactions	Davy
the electrical energy from a battery can be used to decompose substances that are difficult to decompose by heat	Davy
the amount of substance produced in electrolysis is proportional to the amount of electricity that flows	Faraday
in electrolysis the anion particles go to the anode while cation particles go the cathode	Faraday

Why are the oceans salty?

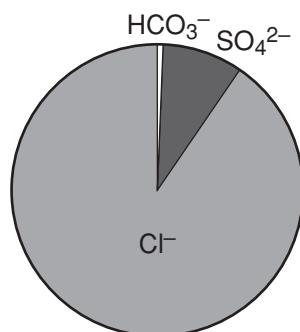


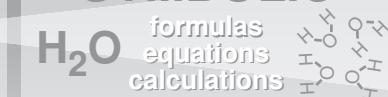
Ions in sea water

Cations



Anions



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Exercises 2.1 to 2.2

Name: _____

Exercise 2.1: Ions in seawater

- a) Complete the formula column for this table of the most common ions in sea water.

Salt ion	Formula	% of sea water (mass)	% of total ions (mass)
chloride		1.90	55
sodium		1.06	31
sulfate		0.26	8
magnesium		0.13	4
calcium		0.04	1
potassium		0.04	1
hydrogen carbonate		0.01	–
bromide		0.01	–

- b) All of these ions except one remain in solution in the ocean for millions of years. The exception is the ion which is amphiprotic and can react with acid or base. Name this ion and write two equations showing how the ion can react.

Exercise 2.2: Gases in sea water

- a) Describe the effect of salts in sea water on the water solubility of gases from the following information. Solubilities are given in millimolar units (millimoles per litre = 10^{-3} mol L⁻¹) mM.

Gas	Water solubility (mM)	Sea water solubility (mM)
nitrogen	823	616
oxygen	456	349
carbon dioxide	23	20

- b) Nitrogen, oxygen and carbon dioxide are all non-polar molecules. Explain why their solubility is affected by the presence of salt ions in water.

- c) Using micro level particle theory, explain the effect of temperature on solubility of gases. The data below is for gas solubility in sea water.

Gas	0°C (mM)	25°C (mM)
nitrogen	616	383
oxygen	349	206
carbon dioxide	20	6

- d) Carbon dioxide is sixty times more soluble in sea water than in the atmosphere. This is because CO₂, unlike N₂ and O₂, chemically reacts with water. Write a series of equilibrium equations showing the reaction of gaseous CO₂ with water and the ions produced in solution by the dissolved carbon dioxide.

- e) One of the ions produced by the solution of CO₂ in water is amphiprotic. This ion and carbonate ions form a buffering system that maintains the pH of sea water in the range 8.0 ± 0.5.

Name the ion and write two equations that show how it acts as a buffer.

- f) Sea water at all depths is saturated with most atmospheric gases except for oxygen and carbon dioxide. Explain how living things in sea water prevent the concentrations of oxygen and carbon dioxide from reaching saturation levels.



Shipwrecks, corrosion and conservation

Part 3: Metal and alloy corrosion

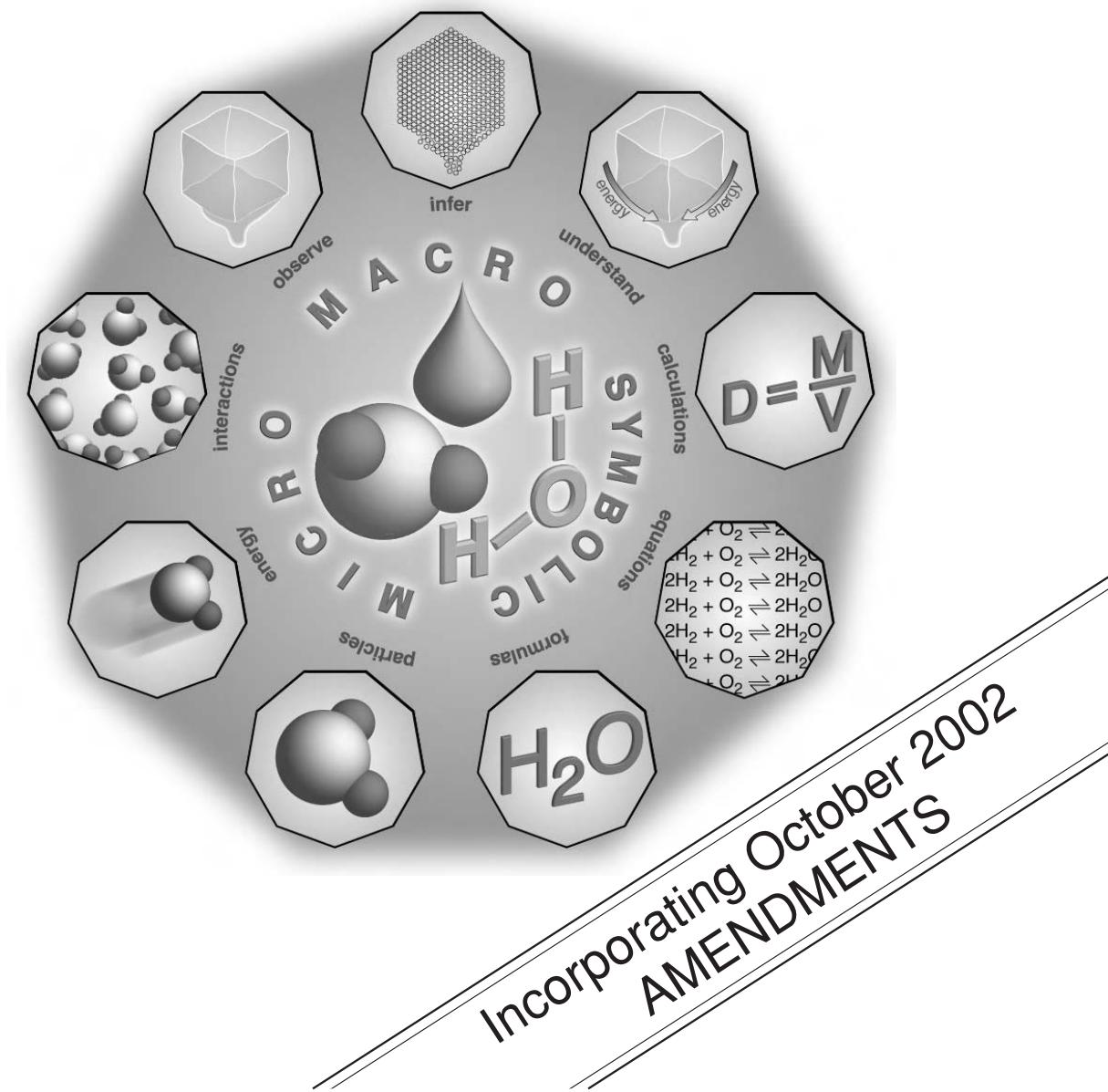
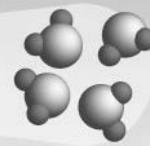


Table of standard potentials and half equations

oxidant	+ electron(s)	\rightleftharpoons	reductant	E^\ominus (volts)
Li^+	+ e ⁻	\rightleftharpoons	Li	-3.04
K^+	+ e ⁻	\rightleftharpoons	K	-2.94
Ca^{2+}	+ 2e ⁻	\rightleftharpoons	Ca	-2.87
Na^+	+ e ⁻	\rightleftharpoons	Na	-2.71
Mg^{2+}	+ 2e ⁻	\rightleftharpoons	Mg	-2.36
Al^{3+}	+ 3e ⁻	\rightleftharpoons	Al	-1.68
H_2O	+ e ⁻	\rightleftharpoons	1/2H ₂ (g) + OH ⁻	-0.83
Zn^{2+}	+ 2e ⁻	\rightleftharpoons	Zn	-0.76
Fe^{2+}	+ 2e ⁻	\rightleftharpoons	Fe	-0.44
Cd^{2+}	+ 2e ⁻	\rightleftharpoons	Cd	-0.40
Ni^{2+}	+ 2e ⁻	\rightleftharpoons	Ni	-0.24
Sn^{2+}	+ 2e ⁻	\rightleftharpoons	Sn	-0.14
Pb^{2+}	+ 2e ⁻	\rightleftharpoons	Pb	-0.13
H ⁺	+ e ⁻	\rightleftharpoons	1/2H ₂ (g)	0.00
Cu^{2+}	+ 2e ⁻	\rightleftharpoons	Cu	0.34
1/2O ₂ (g)+H ₂ O	+ 2e ⁻	\rightleftharpoons	2OH ⁻	0.40
Cu^+	+ e ⁻	\rightleftharpoons	Cu	0.52
1/2I ₂ (aq)	+ e ⁻	\rightleftharpoons	I ⁻	0.62
Fe^{3+}	+ e ⁻	\rightleftharpoons	Fe ²⁺	0.77
Ag^+	+ e ⁻	\rightleftharpoons	Ag	0.80
1/2Br ₂ (aq)	+ e ⁻	\rightleftharpoons	Br ⁻	1.10
1/2O ₂ (g)+2H ⁺	+ 2e ⁻	\rightleftharpoons	H ₂ O	1.23
1/2Cl ₂ (aq)	+ e ⁻	\rightleftharpoons	Cl ⁻	1.40
1/2F ₂ (g)	+ e ⁻	\rightleftharpoons	F ⁻	2.89

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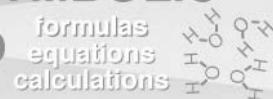
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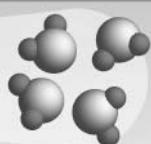


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Introduction

The earliest boats were made from plant and animal materials such as floating logs, matted water reeds and animal hides wrapped around a wooden framework. Wooden boats were fashioned first using tools using stone, then bronze and, later, iron. Thousand years old Viking ships have been found with bronze and wrought iron fittings.

Unfortunately, many woods used in hull construction are attacked by organisms such as marine worms. Lead, copper and brass alloy sheetings were applied to protect wood from attack. In 1824 Humphry Davy showed how attached zinc and iron could protect copper sheeting from corrosion.

About 150 years ago the metal iron became available in sheet form suitable for building ships. Steam powered iron hull ships started to replace wind driven wooden hull sailing ships. About 100 years ago steel hull ships were built with the sheets joined together with rivets. In the last 50 years most ships have been made from steel sheets welded together using flame or electricity. Today small boats are made of composite materials such as reinforced fibreglass but the main shipbuilding materials are metals or alloys, principally steel.

In Part 3 you will be given opportunities to learn to:

- account for the differences in corrosion of active and passivating metals
- identify iron and steel as the main metals used in ships
- identify the composition of steel and explain how the percentage composition of steel can determine its properties
- describe the conditions under which rusting of iron occurs and explain the process of rusting.

In Part 3 you will be given opportunities to:

- identify data, gather and process information from first-hand or secondary sources to trace historical developments in the choice of materials used in construction of ocean-going vessels with a focus on the metals used

- Identify data, select equipment, plan and perform a first-hand investigation to compare the rate of corrosion of iron and an identified form of steel
- Use available evidence to analyse and explain the conditions under which rusting occurs
- gather and process information from secondary sources to compare the composition, properties and uses of a range of steels.

Extracts from Chemistry Stage 6 Syllabus © Board of Studies NSW, November 2002. The most up-to-date version can be found on the Board's web site at
http://www.boardofstudies.nsw.edu.au/syllabus_hsc/index.html

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Historical developments in ocean-going vessels

Developments in metal use



This activity requires you to process information from first-hand or secondary sources. Regard first-hand information as information you gather yourself or organise after talking to people with relevant experience.



For example, the following steps could be taken when gathering and processing information from a primary source.

- Going to a shipping port, ship harbour, dockyard or ship-building enterprise or people who have worked in these areas.
- Discussing the metals used in construction by the enterprise or people over a period of time.
- Organising the information in a systematic way.

Second-hand information is information you gather from:

- printed sources such as texts or encyclopedias
- visual records such as photographs, video, movies
- digital sources such as the internet or a CD-ROM.

Remember to focus on the metals used in constructing ocean-going vessels. Metals that may be important in your gathering of information are lead, copper, iron, aluminium, magnesium, zinc and titanium. Important alloys are steel, bronze and brass.

You may find that the person you talk to only has experience with a small number of metals and alloys – it would be very unusual to find anyone with experience in the full range. Try to find out why a metal/alloy is used for a particular part of an ocean-going vessel.



Report your findings in Exercise 3.1.

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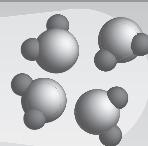
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Iron, steel and rusting

From your investigation of metals used in ocean-going vessels you should realise that iron is the main metal and steel is the main alloy.

Steel is an alloy of iron that typically contains 0.1–1.5% carbon. Pure iron is soft as it has defects that can move easily enabling the iron object's shape to deform. The presence of a small amount of carbon allows formation of small iron carbide crystals (grains). These grains restrict the movement of defects and harden the steel.

The main types of steel used today in ships are:

- mild steel (about 0.2% C) for welded hulls
- structural steel (about 0.5% C) for structural members
- very hard steel (about 1% C) for tools.

Iron used in the past for shipping includes:

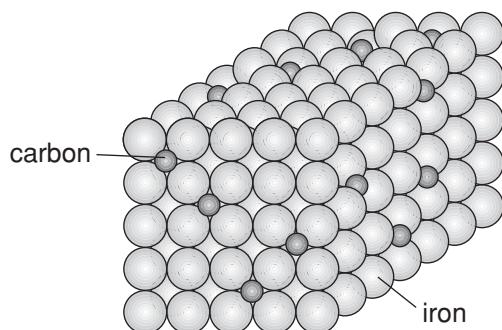
- wrought iron (blacksmith's iron) which has been used for fittings for over 2000 years
- cast iron used for about the last 200 years in engines
- riveted steel hulls used for about 120 years
- welded steel hulls and stainless steel fittings for the last 50 years.

In the Preliminary course module *Metals* you learnt how the iron age developed from the discovery of ways of heating iron oxide with charcoal. The small amounts of tough iron made could be worked into a desired shape by hammering and was called wrought iron. This iron was too valuable for building hulls but could be used for fittings.

The development of charcoal fired furnaces made large amounts of iron available. Liquid iron could be released from the furnace into moulds to form cast iron. Cast iron was harder than wrought iron but brittle and could not be hammered. Cheaper than wrought iron, but being brittle and cracking when hammered into shape, cast iron was unsuitable for building hulls but could be used in engine blocks.

Just over two hundred years ago it was realised that the carbon content of iron determines its toughness and hardness. If the carbon content was kept between 0.1 and 1.5% the product was called steel and was harder and tougher than wrought iron or cast iron.

Carbon distributed throughout the iron structure reduces malleability but increases toughness and hardness. The diagram below is a simplification of the structure of steel showing single carbon atoms amongst the iron. The carbon can also be distributed as aggregations of many carbon atoms (graphite grains) or as an iron carbide compound Fe_3C called cementite. The rate of cooling and physical working (hammering and rolling) of iron also affects properties by determining the size of grains formed.



Simplified structure of steel. Carbon atoms are distributed amongst the iron atoms.

For the next fifty years steel was made by adding carbon to wrought iron. This was expensive so steel was only used in small amounts during the first half of the nineteenth century. Impurities in the steel other than carbon limited its usefulness.

One hundred and fifty years ago the British engineer Henry Bessemer developed the blast furnace to mass produce steel. Blasts of air passed through molten iron provided oxygen. The oxygen reacted with carbon, releasing heat and keeping the iron molten.

Development of ways of removing phosphorus by lining furnaces with limestone dramatically improved the properties of steel. The availability of cheap, quality steel and a structural limitation of about 80 m length in the tallest trees for timber led to the replacement of wooden ships by steel ships.

However, both iron and steel rust.

Investigating rusting



What you will need:

- steel wool (also called iron wool) – not the type with added soap
- 6 iron nails (clean and shiny and without coatings of other metals)
- 8 glass test tubes or plastic tubes, six with air tight stoppers or corks
- a transparent container such as a beaker of 250 mL to 1000 mL capacity able to hold two test tubes vertically upside down
- emery paper
- salt (NaCl) solution
- epsom salt (MgSO_4) solution
- cooking oil
- a moisture absorbent such as silica gel or CaCl_2 – often found in newly opened electrical goods, shoes or pharmaceutical products.
- a gas supply such as through a gas tap, from a LPG cylinder or a butane gas filler can.

What you will do:

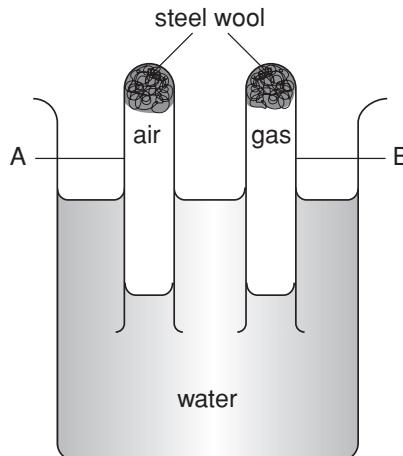
- 1 Place plugs of steel wool in the bottom of two of the test tubes. Turn the test tubes upside down and shake them to make sure the steel wool plugs do not fall out. Add a few drops of water to wet each plug.
- 2 Half fill the transparent container with water
- 3 Place one of the test tubes upside down in the container so that there is air and water in the test tube containing steel wool. This is tube A.



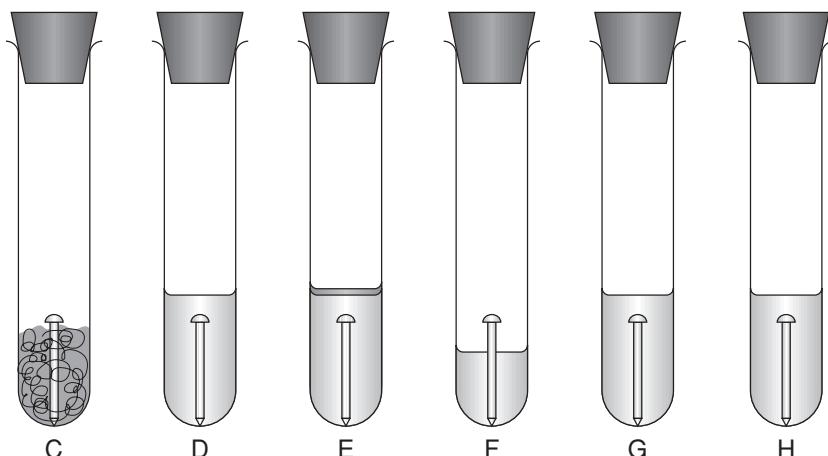
Gas from a gas supply is mostly methane CH_4 with density about 0.6 times that of air. The gas from a LPG cylinder is a mixture of propane and butane with density about 1.5 times that of air. From a butane filler can the gas is butane with density about 2 times that of air.

Explain why a test tube should be upside down when filled with methane but right way up when filled with LPG or butane.

- 4 Fill the other test tube with gas and then immerse it upside down close to the other tube containing steel wool. This is tube B.
- 5 Mark the air/water level on test tube A and test tube B.



- 6 Set up the six test tubes C to H as shown in the diagram and table below.



Test tube	Contents
C	nail is partly covered or surrounded with moisture absorbent
D	nail is completely covered with water
E	water is boiled (this removes air from the water) and while very hot poured in to cover the nail; a few mL of oil is poured onto the water (this prevents air from entering the water).
F	nail is half covered with water
G	nail is completely covered with dilute NaCl(aq)
H	nail is completely covered with dilute MgSO ₄ (aq)

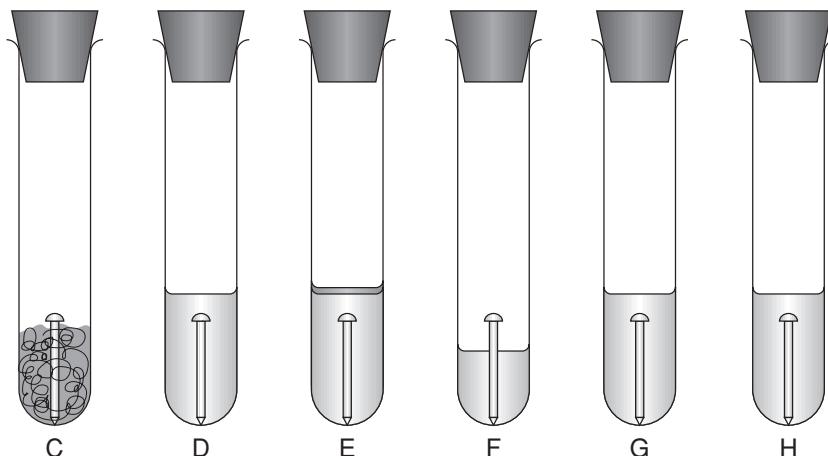
- 7 Observe the test tubes over the next few days and note changes in the results table.

Results:

Complete the table below 2-3 days after setting up the equipment.

Test tube	Observation
A	
B	
C	
D	
E	
F	
G	
H	

Draw the changes in the contents of the test tubes you observed on the diagrams below.



- 1 Is air necessary for rust formation? Justify your answer by explaining which observations from which test tubes led you to your conclusion.



- 2 What part of the air is necessary for rust formation? Justify your answer using your knowledge of the proportions by volume of the main gases in air.

- 3 Is water necessary for rust formation? Justify your answer by indicating which observations led to your conclusion.

- 4 What effect do dissolved salts have on the formation of rust?

- 5 Predict the rate of rusting of an iron ship in salt water compared with fresh water.

Conclusions:

Analyse and explain the conditions under which rusting occurs

Check your answers.

The process of rusting

Corrosion of a metal involves oxidation of metal atoms to metal ions so that the metal structure is broken down.

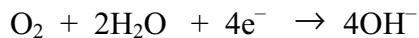
Rusting of iron on the surface of iron or steel is the most common type of corrosion. The iron atoms become part of a layer of hydrated iron(III) oxide. The formula for rust is $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ where x can be from 0.5 to 2 and colour from orange-brown to black colour.

The oxidation of iron occurs first to iron(II) ions.

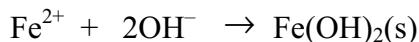


This oxidation causes pitting as iron atoms change to iron(II) ions which can move away in any moisture on the surface of the iron. Because the change is an oxidation, this part of the iron surface where pitting occurs is called the anode.

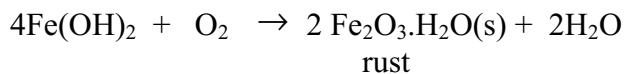
At another part of the iron, non-metal impurities such as carbon can act as a cathode. Electrons released from the oxidation of iron atoms in the anode region can pass through the metal (a good conductor) to the non-metal cathode. At the cathode, oxygen gas and water are reduced by these electrons to form hydroxide ions.



The hydroxide ions formed can move through any moisture on the surface of the iron. When iron(II) ions and hydroxide ions combine in the moisture layer they form insoluble light green iron(II) hydroxide.



Oxygen easily oxidises the iron(II) ions in Fe(OH)_2 to iron(III) ions forming rust.



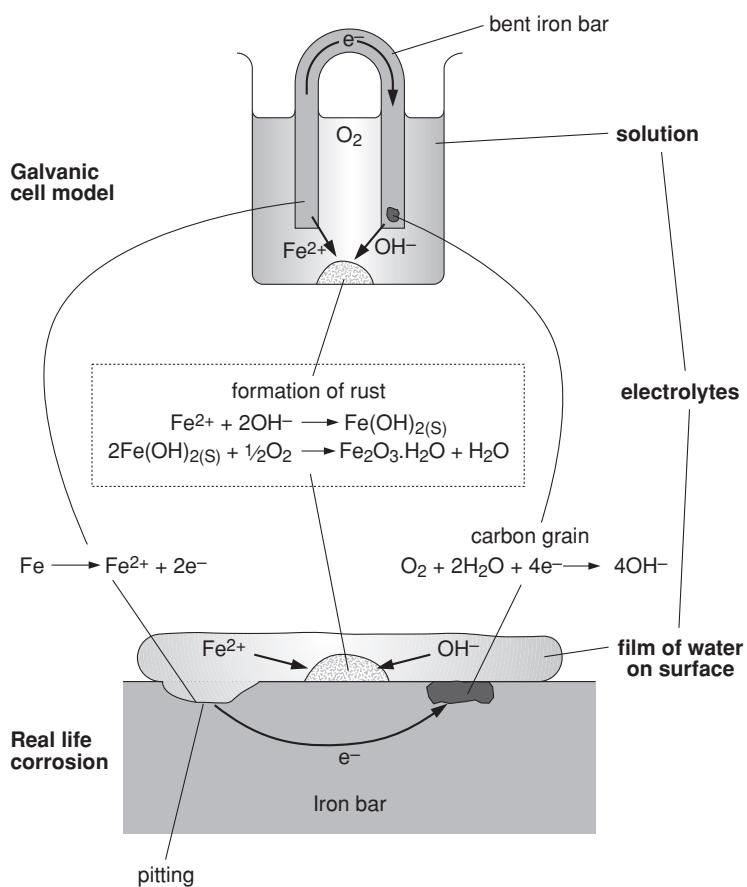
The rust can form some distance away from the pitting or erosion of iron. This is because electrons released at the pitting site can be conducted through the metal and iron(II) ions can diffuse through the surface water layer to wherever oxygen is available.

The layer of rust is porous and easily flakes off leaving a new surface of iron atoms to be rusted. This oxidation and flaking off requires about 20% of iron and steel throughout the world to be replaced each year.

As you have seen from your previous activity, salty conditions promote rusting so that ocean shipwrecks are particularly susceptible to rusting. Dissolved salt increases the conductivity of the water layer, increases the current flowing in what is effectively an electrochemical cell, and hence increases the rate of corrosion.

The diagram below illustrates that rusting involves an electrochemical cell. One end of the bent iron bar is the anode where oxidation occurs. The other end of the bar, containing a carbon grain, is the cathode where reduction occurs. The bent iron bar in between is the external circuit that conducts electrons from anode to cathode.

The solution in which the iron bar sits contains dissolved oxygen and water which are reactants at the cathode. Any dissolved salt ions will increase the conductivity of this solution and increase the current that can flow through the cell's internal circuit. If the concentration of dissolved ions is low the ion current is low. This limits the current that can flow through the iron bar and hence the amount of corrosion. The total charge carried by the electrons in the external circuit is equal to whatever total charge is carried through the internal circuit by dissolved ions.



The equations in ***bold italics*** are relevant to rusting:

oxidant	+ electron(s)	\rightleftharpoons	reductant	E^\ominus (volts)
Li^+	+ e^-	\rightleftharpoons	Li	-3.04
K^+	+ e^-	\rightleftharpoons	K	-2.94
Ba^{2+}	+ $2e^-$	\rightleftharpoons	Ba	-2.91
Ca^{2+}	+ $2e^-$	\rightleftharpoons	Ca	-2.87
Na^+	+ e^-	\rightleftharpoons	Na	-2.71
Mg^{2+}	+ $2e^-$	\rightleftharpoons	Mg	-2.36
Al^{3+}	+ $3e^-$	\rightleftharpoons	Al	-1.68
Mn^{2+}	+ $2e^-$	\rightleftharpoons	Mn	-1.18
<i>H₂O</i>	<i>+ e⁻</i>	\rightleftharpoons	<i>1/2H₂(g) + OH⁻</i>	<i>-0.83</i>
Zn^{2+}	+ $2e^-$	\rightleftharpoons	Zn	-0.76
<i>Fe²⁺</i>	<i>+ 2e⁻</i>	\rightleftharpoons	<i>Fe</i>	<i>-0.44</i>
Cd^{2+}	+ $2e^-$	\rightleftharpoons	Cd	-0.40
Ni^{2+}	+ $2e^-$	\rightleftharpoons	Ni	-0.24
Sn^{2+}	+ $2e^-$	\rightleftharpoons	Sn	-0.14
Pb^{2+}	+ $2e^-$	\rightleftharpoons	Pb	-0.13
H^+	+ e^-	\rightleftharpoons	$1/2\text{H}_2(\text{g})$	0.00
$\text{SO}_4^{2-} + 4\text{H}^+$	+ $2e^-$	\rightleftharpoons	$\text{SO}_2(\text{aq}) + 2\text{H}_2\text{O}$	0.16
Cu^{2+}	+ $2e^-$	\rightleftharpoons	Cu	0.34
<i>1/2O₂(g)+H₂O</i>	<i>+ 2e⁻</i>	\rightleftharpoons	<i>2OH⁻</i>	<i>0.40</i>
Cu^+	+ e^-	\rightleftharpoons	Cu	0.52
$1/2\text{I}_2(\text{aq})$	+ e^-	\rightleftharpoons	I ⁻	0.62
<i>Fe³⁺</i>	<i>+ e⁻</i>	\rightleftharpoons	<i>Fe²⁺</i>	<i>0.77</i>
Ag^+	+ e^-	\rightleftharpoons	Ag	0.80
$1/2\text{Br}_2(\text{aq})$	+ e^-	\rightleftharpoons	Br ⁻	1.10
<i>1/2O₂(g)+2H⁺</i>	<i>+ 2e⁻</i>	\rightleftharpoons	<i>H₂O</i>	<i>1.23</i>
$1/2\text{Cl}_2(\text{aq})$	+ e^-	\rightleftharpoons	Cl ⁻	1.40
$1/2\text{F}_2(\text{g})$	+ e^-	\rightleftharpoons	F ⁻	2.89



- 1 Write out the two half equations for the initial reactions in rusting. Place the voltage change next to each half equation then add the two half equations to give the overall redox equation for the first step and find the voltage change. The voltage change you calculate should be positive showing that the reaction occurs spontaneously.

- 2 Use the other two half equations to show how oxygen in water can oxidise iron(II) to iron(III). Does the voltage change for your overall equation show that this reaction occurs spontaneously?

- 3 Pure iron is very resistant to rusting. Explain why this is so in terms of its carbon content.

Check your answers.



Look for examples of rusting in your environment. In particular look for where the rust forms and signs of pitting in iron or steel distant from, and connected to, the location of the rust.



Assess the probable causes of the rusting examples and report your findings in Exercise 3.2.

Composition, properties and uses of a range of steels

Iron is the metal used in largest amounts. It is extremely difficult and expensive to obtain pure iron. Iron wire supplied to school laboratories and iron in nails are typically 99.5% iron and 0.5% carbon.

An enormous range of different types of iron alloys called steels has been developed with a wide range of properties and uses. Steels typically contain 0.1% to 1.5% carbon and can contain significant amounts of other elements.

The table below shows how different elements affect the properties and uses of steel.

Element	Property effects	Uses
aluminium	steel easily shaped	car body panels
chromium	corrosion resistant oxide forms on the surface	stainless steel
carbon	>3% brittle 1% wear resistant 0.2% easily shaped	cast iron static loads tools car body panels
manganese	easier to shape when hot and harder when cold	tools and dies
molybdenum	increases hardness	high speed tools
nickel	corrosion resistance	stainless steel
tungsten	abrasion resistant and high strength at high temperatures	high speed tools and fire resistant construction steel
phosphorus	reduces ductility and promotes cracking	none; manufacturers try to keep concentration below 0.01%
vanadium	wear resistance	tools; railway line switches and points

Stainless steel was made accidentally by a scientist researching alloys suitable for gun barrels. Months after his investigations he noticed some steel samples discarded as unsuitable in his scrap heap had not rusted.

These samples of nickel-chromium-iron alloy were too soft and expensive for their original large scale purpose but ideal for small scale use where rust resistance is more important than hardness eg. in cutlery.

Now you know about some of the elements and their effects on properties and uses of steels. Next you will gather information to compare the composition, properties and uses of a range of steels.



If possible use Internet search engines to find secondary sources of information. Sources of commercial information about the range of steels available worldwide is more up-to-date and readily available today on the Internet rather than in paper print form.



Tabulate information you collect in Exercise 3.3.

To complete Exercise 3.4 you must choose one type of steel and identify its composition. Then you must predict how its properties might differ from those of steel used in constructing the hull of the famous shipwreck of the *Titanic*.



Corrosion of iron and steel

In this activity you will be comparing the rate of corrosion of iron to a type of steel.

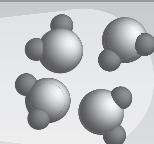
What you will need:

- iron
- an identified form of steel such as mild steel or stainless steel.
(The iron and steel should have similar areas, masses and shapes.)
Panelbeaters and welders often have mild steel offcuts.
- containers and chemicals such as salt suitable for encouraging the corrosion of the iron and the identified form of steel
- a way of comparing the rate of corrosion – this could involve quantitative measurements or qualitative observations.

What you will do:

- 1 Select equipment
- 2 Plan how you will observe and compare the rates of corrosion
- 3 Perform the investigation
- 4 Record your results
- 5 Report on this activity in Exercise 3.5.



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Active and passivating metals

A comprehensive table of standard reduction potentials can be used to predict that the activity of metals should be in the following order (from most active at the top to least active at the bottom).

- magnesium
- aluminium
- zinc
- chromium
- iron
- cadmium
- nickel
- tin
- lead
- copper

The very reactive metals towards the top of this list are said to have low reduction potentials. Their listed potentials (voltages) are low negative values. You would expect such metals to oxidise readily.

However, if you observe the two metals used in largest amounts in ship construction, aluminium and iron, you will note that much more effort goes into protecting the less active metal iron from corrosion.

In the real world, aluminium, although a stronger reducing agent than iron, reacts less readily than the iron. This is because aluminium is a passivating metal that reacts with oxygen to form an inactive and impervious coating on its surface. This film is inert, tenacious and reforms immediately if removed by abrasive action. This makes aluminium metal, despite its high activity, a useful construction metal that doesn't need painting or protective coatings.

On the other hand the oxide layer that forms more slowly on iron, rust, flakes off easily. The outer rust layer is porous allowing oxygen and water to penetrate and convert the iron layer below the surface to rust.

Aluminium is a passivating metal. However the protective oxide layer can be broken down by alkaline conditions. You should not put aluminium saucepans in dishwashers as the powder used is alkaline.

The chromium used in stainless steel and tin coating of tin cans has thin passivating layers which maintain their shiny metallic appearance.

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Suggested answers

Investigating rusting

Methane in natural gas is less dense than air so should be collected in a test tube held upside down so that the less dense gas displaces the air downwards out of the test tube.

LPG and butane gases are denser than air. The test tube should be held with mouth uppermost so that the less dense air on top of the LPG and butane gas is displaced upwards out of the test tube. The test tube should be turned over just before placing in the container of water.

- 1 Test tubes B and E where no air was in contact with the iron should show no sign of rusting. This shows that air is necessary for rust formation.
- 2 The air volume in test tube A should decrease by about 20% showing that about 20% of the air has reacted with the iron. This indicates that oxygen is the reactive gas as oxygen is about 20% of air by volume.
- 3 Tube C where no water is in contact with the iron but air is, shows no sign of rust. Tube F where water is present has rusted.
- 4 Test tubes G and H where salts are present show more rusting than the other test tubes.
- 5 Rusting of an iron ship in salt water should be greater than in freshwater because of the presence of salts.

Rusting occurs when oxygen and water are present. Fast rusting occurs in the presence of salt.

The process of rusting

1	Fe	\rightarrow	Fe^{2+}	+ 2e ⁻	0.44 V
	$1/2\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^-$	\rightarrow	2OH^-		0.40 V
<hr/>					
	Fe + $1/2\text{O}_2 + \text{H}_2\text{O}$	\rightarrow	$\text{Fe(OH)}_2(s)$		0.84 V
2	Fe^{2+}	\rightarrow	Fe^{3+}	+ e ⁻	-0.77 V
	$1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	\rightarrow	H_2O		1.23 V
<hr/>					
	$\text{Fe}^{2+} + 1/2\text{O}_2 + 2\text{H}^+$	\rightarrow	$\text{Fe}^{3+} + \text{H}_2\text{O}$		0.46 V

The positive voltage shows that this reaction will occur spontaneously.

- Pure iron does not contain grains of carbon that could act as cathodes for reduction of water. If there are no carbon grains where electrons released by oxidation of iron can reduce oxygen and water, this inhibits rusting.

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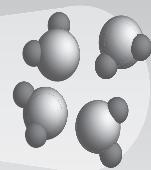


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Exercises - Part 3

Exercises 3.1 to 3.5

Name: _____

Exercise 3.1: Developments in metal use

Outline what you found out about developments in metal use in ocean-going vessels. Provide details about your sources of information. Publications should be reported as indicated below.

For books

Author. (Year of publication.) *Title*. Name of Publisher.
Relevant page numbers.

Webpages

Date downloaded. Title. Author. Date of last revision.

People

Name. Position held. Relevant experience.

Exercise 3.2: Probable causes of rusting

Report your findings of your assessment of the probable causes of rusting in an environment.

Exercise 3.3: Comparison of the composition, properties and uses of a range of steels

Tabulate the information you have gathered below.

Exercise 3.4: Predicting the properties of a steel from its percentage composition

Identify the composition of a steel by completing the table below:

Type of steel: _____

Element	C	Mn	P	S	Si	Cu	O
% by mass							

Predict how its properties might differ from those of steel used in constructing the hull of the famous shipwreck the *Titanic*. Justify your predictions using information from Part 3, *Metal and alloy corrosion*, of the module.

The *Titanic* hull plate composition is shown in the table below.

Element	C	Mn	P	S	Si	Cu	O
% by mass	0.21	0.47	0.05	0.07	0.02	0.02	0.01

Exercise 3.5: Report on comparing the rate of corrosion of iron and a steel

Source of iron: _____ Type of steel: _____

1 Labelled diagram of equipment.

2 Description of how you compared the rates.

3 Conclusion.



Shipwrecks, corrosion and conservation

Part 4: Protection from the marine environment

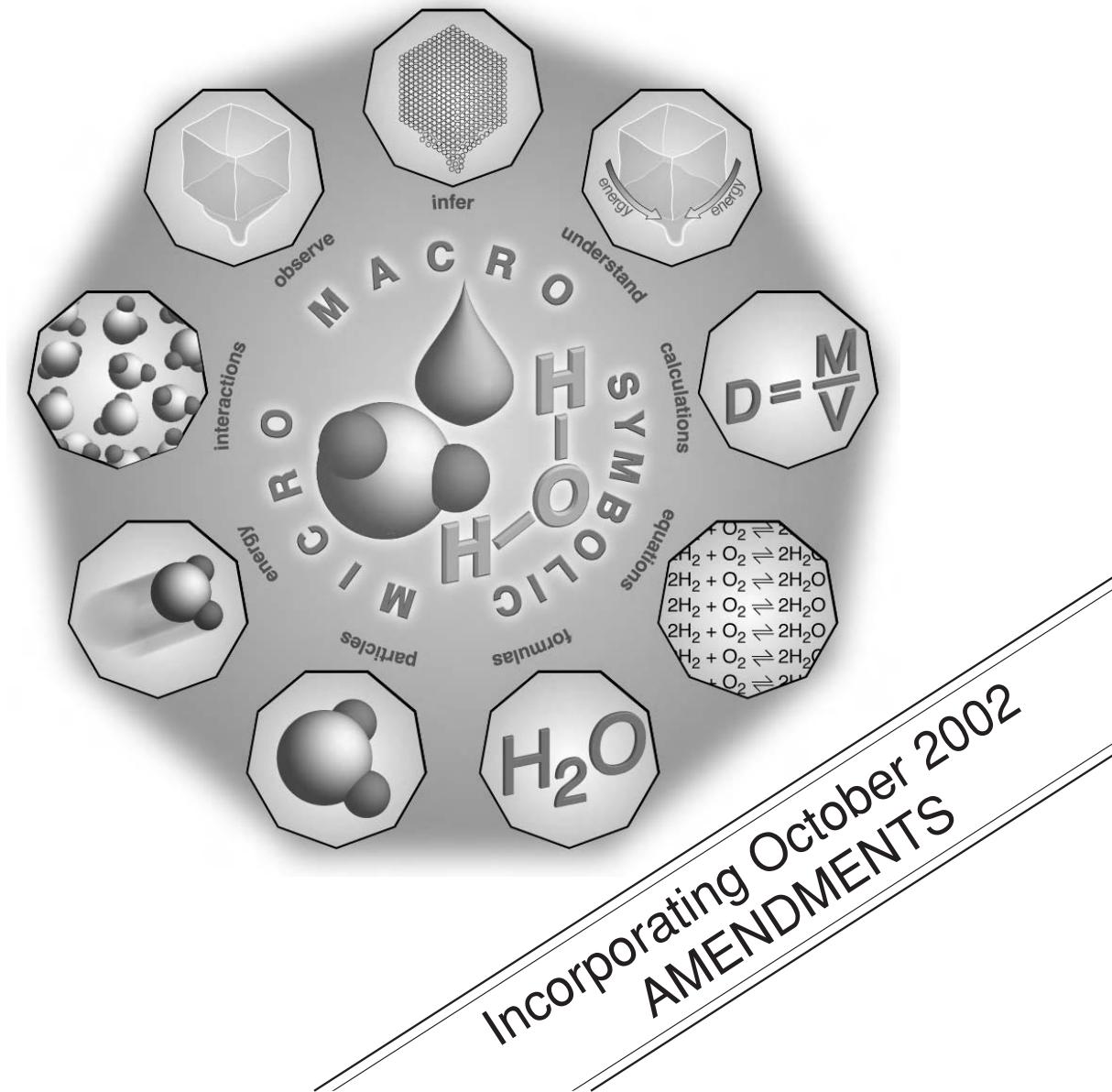
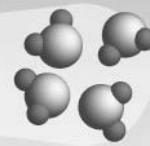


Table of standard potentials and half equations

oxidant	+ electron(s)	\rightleftharpoons	reductant	E^\ominus (volts)
Li^+	+ e ⁻	\rightleftharpoons	Li	-3.04
K^+	+ e ⁻	\rightleftharpoons	K	-2.94
Ca^{2+}	+ 2e ⁻	\rightleftharpoons	Ca	-2.87
Na^+	+ e ⁻	\rightleftharpoons	Na	-2.71
Mg^{2+}	+ 2e ⁻	\rightleftharpoons	Mg	-2.36
Al^{3+}	+ 3e ⁻	\rightleftharpoons	Al	-1.68
H_2O	+ e ⁻	\rightleftharpoons	1/2H ₂ (g) + OH ⁻	-0.83
Zn^{2+}	+ 2e ⁻	\rightleftharpoons	Zn	-0.76
Fe^{2+}	+ 2e ⁻	\rightleftharpoons	Fe	-0.44
Cd^{2+}	+ 2e ⁻	\rightleftharpoons	Cd	-0.40
Ni^{2+}	+ 2e ⁻	\rightleftharpoons	Ni	-0.24
Sn^{2+}	+ 2e ⁻	\rightleftharpoons	Sn	-0.14
Pb^{2+}	+ 2e ⁻	\rightleftharpoons	Pb	-0.13
H ⁺	+ e ⁻	\rightleftharpoons	1/2H ₂ (g)	0.00
Cu^{2+}	+ 2e ⁻	\rightleftharpoons	Cu	0.34
1/2O ₂ (g)+H ₂ O	+ 2e ⁻	\rightleftharpoons	2OH ⁻	0.40
Cu^+	+ e ⁻	\rightleftharpoons	Cu	0.52
1/2I ₂ (aq)	+ e ⁻	\rightleftharpoons	I ⁻	0.62
Fe^{3+}	+ e ⁻	\rightleftharpoons	Fe ²⁺	0.77
Ag^+	+ e ⁻	\rightleftharpoons	Ag	0.80
1/2Br ₂ (aq)	+ e ⁻	\rightleftharpoons	Br ⁻	1.10
1/2O ₂ (g)+2H ⁺	+ 2e ⁻	\rightleftharpoons	H ₂ O	1.23
1/2Cl ₂ (aq)	+ e ⁻	\rightleftharpoons	Cl ⁻	1.40
1/2F ₂ (g)	+ e ⁻	\rightleftharpoons	F ⁻	2.89

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Introduction

The main material used for building ocean-going vessels is steel, an alloy of iron typically containing 0.1–1.5% carbon. Steel is relatively hard, easily worked to produce different shapes and structures, mechanically strong and sections can be riveted or welded together. Adjustments in the percentage of carbon and addition of other elements has produced a wide range of steels with different properties.

Steel is an alloy of iron, carbon and other elements. The iron metal in steel corrodes quickly in marine environments. Protecting metal parts is a major task during production and for the working lifetime of marine vessels and equipment.

In Part 4 you will be given opportunities to learn to:

- identify the ways in which a metal hull may be protected including:
 - corrosion resistant metals
 - development of surface alloys
 - new paints
- predict the metal which corrodes when two metals form an electrochemical cell using a list of standard potentials
- outline the process of cathodic protection, describing examples of its use in both marine and wet terrestrial environments
- describe the process of cathodic protection in selected examples in terms of the oxidation/reduction chemistry involved.

In Part 4 you will be given opportunities to:

- identify data, choose equipment, plan and perform a first-hand investigation to compare the corrosion rate, in a suitable electrolyte, of a variety of metals, including named modern alloys to identify those best suited for use in marine vessels
- plan and perform a first-hand investigation to compare the effectiveness of different protections used to coat a metal such as iron and prevent corrosion

- gather and process information to identify applications of cathodic protection, and use available evidence to identify the reasons for their use and the chemistry involved.

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Availability of metals for ocean-going vessel construction



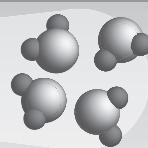
In the Preliminary module *Metals* you investigated the **chronology** of metal use by humans. The incomplete table below sets out a chronology of the approximate first use of metals in the construction of ocean-going vessels.

Use the alphabetic list of metals and alloys below to complete this table.

aluminium, brass, bronze, copper, iron, lead, phosphor bronze,
stainless steel, steel, titanium

Approximate years Before Present (BP)	Metal/alloy	Use
4000	_____ metal	nails, spikes
3000	_____ alloy	nails, spikes
2500	_____ metal	nails, spikes
1000	_____ metal	sheeting to protect wood
500	_____ alloy	deck fittings
150	_____ alloy	hulls
100	_____ alloy	propellers
50	_____ metal	small boat hulls
30	_____ alloy	wires on ocean racers
20	_____ metal	submarine hulls

Check your answers.

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Corrosion

Comparing corrosion rates

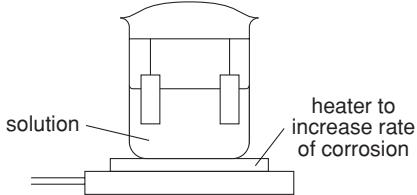
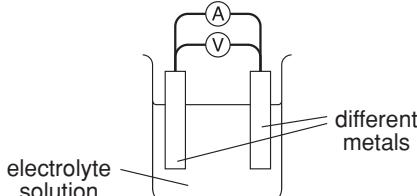
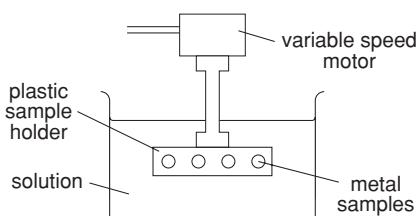


In this activity you will be comparing corrosion rates of metals and modern alloys suited for marine vessels. This activity requires you to choose the most appropriate equipment and chemicals to undertake the investigation.

Remember that air, water and salt are significant factors in causing corrosion of metals. Use at least three different metals/alloys from the list for the table on the previous page. Wherever possible have the different metals/alloys in the same form such as wire, sheet, nails of similar dimensions. The electrolyte should have a similar composition to and a salt concentration at least as great as sea water.

Quantitative measurement of corrosion rate is more difficult than qualitative observations. However it can be achieved by measuring the mass of samples before and after corrosion. Accuracy (closeness of measurements to true values) is important in quantitative work.

The diagrams on the next page illustrate some of the techniques that are used in laboratories for quantitative measurements.

general corrosion		<ul style="list-style-type: none"> samples weighed before and after samples can be hung half in air and half in solution
galvanic corrosion		<ul style="list-style-type: none"> corrosion current measured by ammeter corrosion potential measured by voltmeter
liquid movement corrosion		<ul style="list-style-type: none"> effect of velocity on the corrosion rate of different metal samples is measured by weight loss

Qualitative descriptions of the extent of corrosion such as changes in the appearance of exposed surfaces are easier to make. Where possible, these should be supplemented with estimates of the size of the change.

Fair procedure, reliable (trustworthy and repeatable) and valid (leading to effective and worthwhile) results and conclusions should be aims of all your practical activities.

Start the activity as soon as possible as this activity could take a week before you observe significant changes.

Plan, perform and report on your investigation in Exercise 4.1. Use the space below for your planning.



Predicting corrosion

Theoretical predictions

The E^\ominus values in the table of reduction potentials are for one molar solutions, gases at atmospheric pressure and a temperature of 25°C. If conditions are different from any of these conditions then predictions made, based upon these conditions, may not be fulfilled. Nevertheless comparison of reduction potentials should be the first step in predicting corrosion caused by formation of a galvanic cell – **galvanic corrosion**. The further apart the potentials of two metals are, the greater the possibility of a galvanic corrosion cell forming between them.



Predict which metal will be the anode and which will be the cathode in the following metal couples. Assume there is electrically conducting contact between the two metals and both metals are in contact with an electrolyte solution so that a galvanic cell is formed.

- 1 zinc and iron
- 2 copper and zinc
- 3 iron and magnesium
- 4 copper and iron
- 5 iron and tin.

Check your answers.

Practical testing

Other factors which can affect the extent of reaction include impurities in the metal, build up of gas layers on the surface of an electrode, distance between the anode and cathode members of a two metal couple and even cathode/anode area ratios. For example, a small piece of zinc in contact with a large piece of aluminium corrodes. The passivating layer on the surface of the aluminium changes the reduction potential from -1.68 V to about -0.6 V so that the zinc is now the more active metal of the couple. A large piece of zinc in contact with a small piece of aluminium does not corrode significantly.

At normal temperatures zinc is more active than iron. So, iron is often coated with zinc (galvanised) to protect the iron. However when zinc-coated iron hot water systems were made in the 1940s it was found that they rapidly corroded. At 60°C and higher temperatures the iron was found to be more active than zinc.

Empirical testing of metal couples in marine environments is carried out to check on predictions made using tables of reduction potentials.



The table of standard potentials predicts aluminium should corrode before zinc. This is not the case. Explain why by comparing their oxide coatings.

Check your answer.

For shipwrecks in a marine environment water composition, marine growth, the composition of the seabed, depth of burial and extent of water movement can also be important.

A galvanic series based on measurements of metals and alloys in sea water is listed below:

magnesium
zinc
zinc-coated (galvanised) steel or iron
aluminium
cadmium
aluminium rivet alloy
mild (low carbon) steel
50% lead/50% tin solder
stainless steel type 316
lead
tin
nickel
brasses
copper
bronzes
titanium
carbon (graphite)

The further apart two materials are on this list the more likely galvanic corrosion will occur if they are connected.



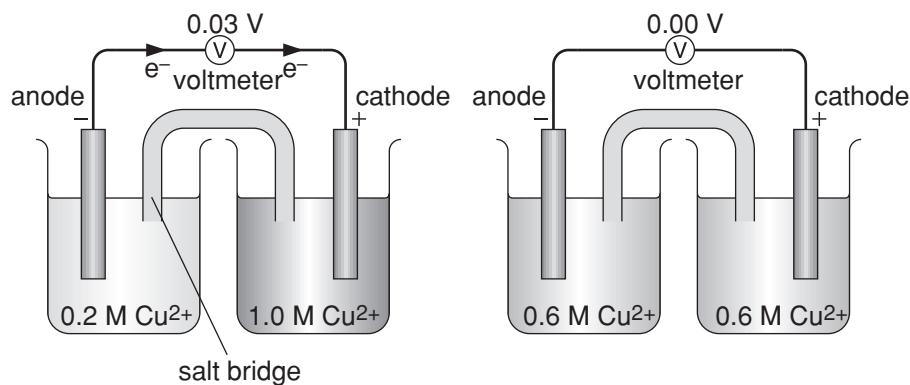
- 1 Explain why the carbon content of steel can affect its rate of corrosion.

- 2 Give one example where practical testing in sea water produces a result different from that predicted using a list of standard potentials.

Check your answers.

Corrosion can also occur on the one metal if conditions are different at different locations.

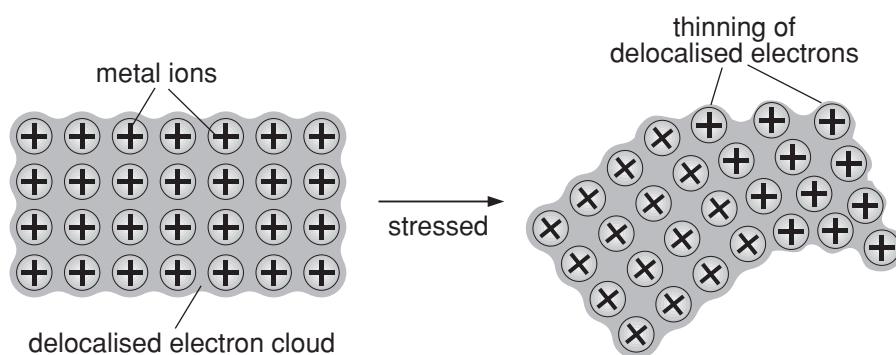
- If a piece of metal has different oxygen concentrations at different locations **differential aeration** is said to occur. Differential aeration can cause a galvanic cell to exist between these two locations. This is important in corrosion of metal supports of wharves where the top of the support is in air, other parts are in the tidal zone and lower parts could be in sea water or acidic bottom soil. Surprisingly it is the section of iron that has least exposure to oxygen that corrodes (becomes **anodic**). The iron which is most exposed to oxygen acts as a cathode (become **cathodic**) and is protected from corrosion!
- Different concentrations of the same ion at different locations can produce a galvanic cell. The diagram below shows how this can be demonstrated in a school laboratory.



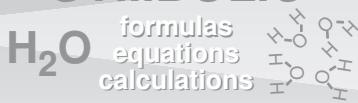
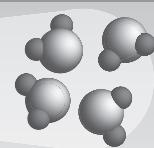
The lower concentration (0.20 M concentration of copper ions) causes the equilibrium $\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu(s)}$ to shift position to the left. Thus in the 0.20 M half cell oxidation occurs. Copper metal in the 1.0 M solution becomes a cathode and copper deposits on its surface until the copper ion concentration in each half cell becomes the same.

- If one part of a section of iron becomes covered with iron oxide it becomes cathodic while the uncorroded steel becomes anodic and then corrodes.
- Similarly significantly different temperatures between two locations can lead to the formation of a galvanic cell in the walls of metal furnaces. Temperature differences are not normally significant in marine environments.

Physical stress can distort and fracture the structure of metals. This can increase exposure of metal atoms to corroding chemicals and increase corrosion.



The thinner ‘glue’ of delocalised electrons makes it easier for a cation to break away from the stressed metal structure leaving electrons behind. This is equivalent to oxidation or corrosion of the metal.

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Protection from corrosion

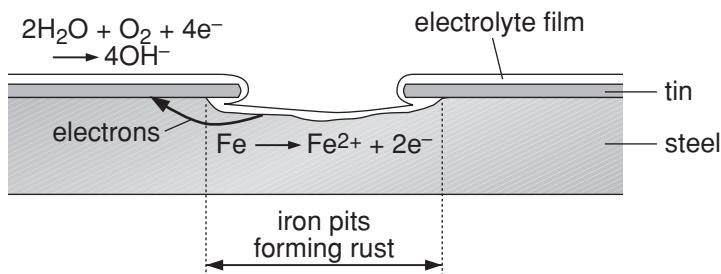
Metal coatings to protect steel

Tin plating – a physical barrier



Tin cans are made from steel with a very thin coating of tin on both surfaces.

- Using the table of reduction potentials, predict what would happen if the surface of the tin was scratched through, exposing the steel.



- Explain why aluminium cans but not tin cans are a long term litter problem.

Check your answers.

Galvanising with zinc – a chemical barrier

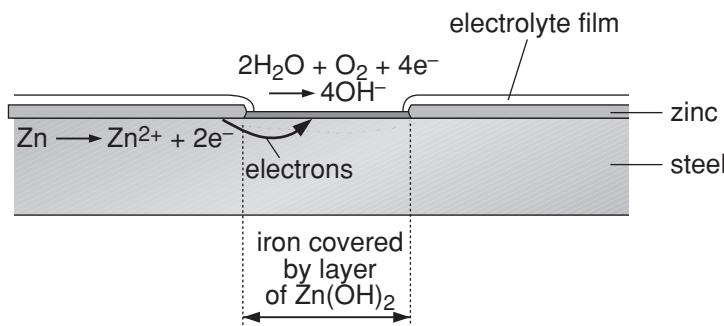
Galvanising is covering a metal with a zinc layer by dipping the metal into molten zinc. Galvanised iron, steel coated with zinc, is one of the most common roofing materials used throughout the world.

Metallic zinc becomes covered with a layer of dull white zinc hydroxide/oxide/carbonate that protects it from further corrosion.

When the surface of zinc is scratched through, exposing the steel, a galvanic cell is formed involving zinc and iron when moisture is present:



The zinc ions and hydroxide ions form zinc hydroxide $\text{Zn}(\text{OH})_2$ which loses water to form a protective coating of zinc oxide over exposed steel. ZnCO_3 can also form by reaction of ZnO with CO_2 .



Corrosion of zinc galvanised steel.

In coastal areas subject to salt spray a coating of zinc only 0.06 mm thick can provide about 10 years protection to iron. Greater protection is provided by using a coating of zinc and aluminium in a product called zincalume steel.

Metal hull protection

Ways in which the metal hull of ocean-going vessels may be protected have included:

- lead and copper sheeting over timber
- coal tar, asphalt and other petroleum based coatings
- varnishes made from plant resins and oils.

More recent hull protection methods are:

- using corrosion resistant metals and alloys
- development of surface alloys where the outer exposed surface is changed to become corrosion resistant e.g. a cheap carbon steel surface can be bombarded with chromium and nickel ions in a plasma ('ion gas') to form an outer surface of stainless steel
- new paints which can provide protection by:
 - preventing metal contact with electrolytes or oxygen or water
 - containing more active metals such as zinc which corrode first
 - release **biocides** such as copper or tin which inhibit marine organism growth (but cause environmental concerns especially in areas where boats are harboured and biocides like tributyl tin are applied).

Rustmaster Pro® paint is a water based polymer paint that forms a polymer layer that electrolytes, oxygen and water cannot penetrate. Chemicals in this paint also form a protective layer of the mineral pyroaurite between the polymer and the steel. This prevents movement of ions just as removing the salt bridge stops chemical reaction in a galvanic cell.



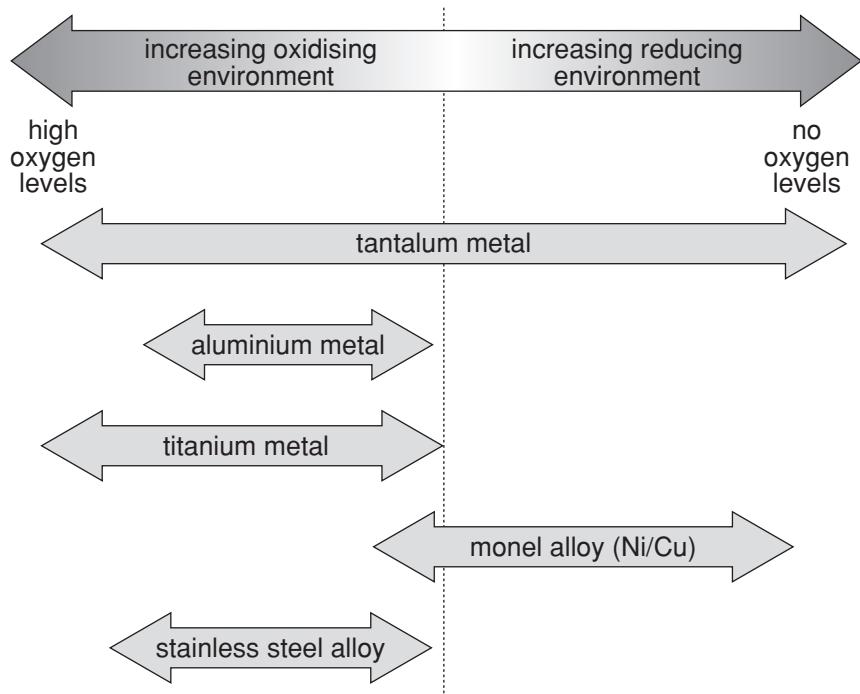
Two of the world's leading companies in the building of light weight aluminium hulls are Austal in Fremantle, Western Australia, and Incat in Hobart, Tasmania.

Use an Internet search engine to find out what these companies do to produce corrosion resistant hulls.

Passivating metal and alloys

Aluminium, titanium and stainless steels have durable oxide layers on their surface. The oxide layer does not conduct electricity so the metal cannot form a galvanic cell with other metals and therefore resists corrosion.

If placed in a low oxygen environment (reducing conditions in sea water or sediment that contains hardly any oxygen) the oxide layer can be removed or damaged and corrosion occurs. Alkaline conditions can dissolve the protective oxide layer.



Effect of oxidising and reducing environments on different metals and alloys.



Explain why aluminium, titanium and stainless steel cannot be, but tantalum metal and monel alloy can be, used in reducing environments.

Check your answer.

Investigating the effectiveness of coatings on iron to prevent corrosion



This activity requires you to plan and perform a first-hand investigation. Choose the most appropriate equipment and chemicals you have access to.

Remember that air, water and salt are significant in causing corrosion of metals. Use a metal such as iron that is available with and without a coating. You may be able to find a piece of iron that is partly coated and immerse the coated and non-coated sections in the same electrolyte. The electrolyte should have a similar composition to, and a salt concentration at least as great as, sea water.

Coatings could be:

- water based paint
- oil based paint
- rust preventing paint.

Qualitative descriptions of the extent of corrosion such as changes in exposed surface appearance are easy to make but, where possible, should be supplemented with estimates of the size of the change.

Fair procedure, reliable (trustworthy and repeatable) and valid (leading to effective and worthwhile) results and conclusions should be aims of all your practical activities.

Start the activity as soon as possible. This activity could take a week before you observe significant changes.



Report on your investigation in Exercise 4.2.

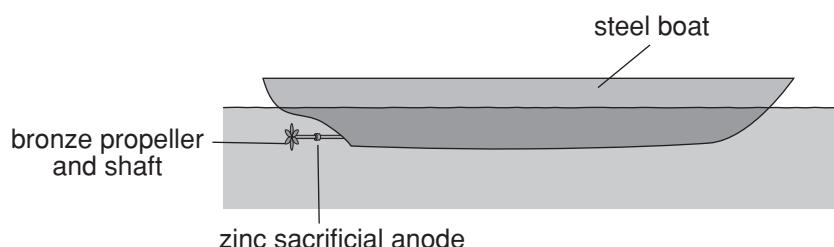
Cathodic protection

Cathodic protection is the supply of electrons to a metal to prevent it oxidising to metal ions. Instead of the metal behaving as an anode and undergoing oxidation the metal becomes a cathode. The metal is protected by becoming a cathode.

There are two types of cathodic protection – sacrificial anode and impressed current.

Sacrificial anode

Attachment of a **sacrificial anode** that oxidises thus supplying electrons to the metal being protected (the cathode metal). The supplied electrons prevent loss of cathodic metal atoms as positive ions.

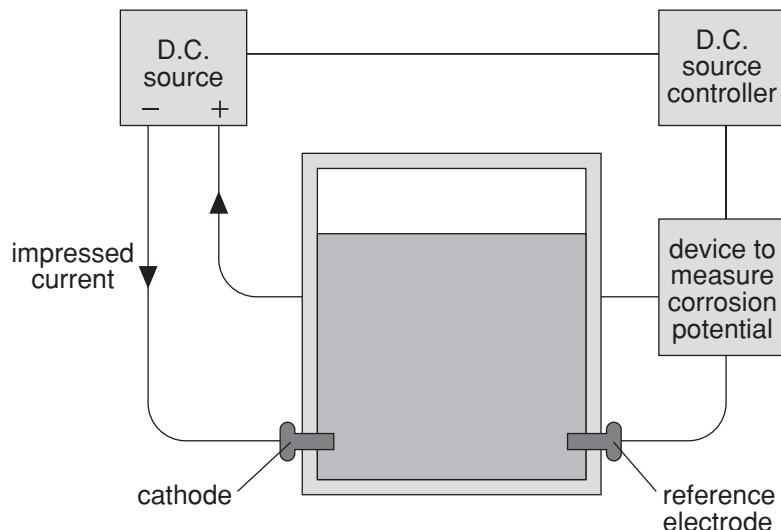


Hot water systems usually contain a magnesium rod sacrificial anode while zinc sacrificial anodes are attached to many outboard boat motors. Titanium and niobium sacrificial anodes are used on some large ocean-going vessels.

Regular checks may be needed to see if these sacrificial anodes need replacing. The ions released by the anodes usually have negligible environmental impact.

Impressed current

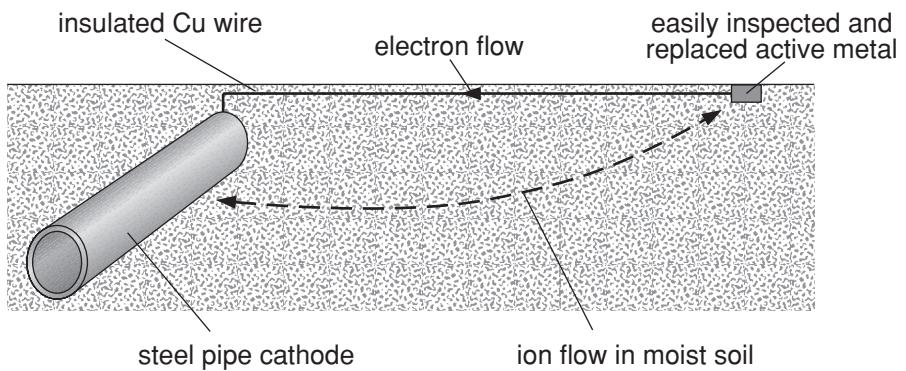
Supplying an **impressed current** by connecting the metal being protected to the negative terminal of a low voltage DC electrical energy source.



Impressed current systems are used for large hulls, steel wharves and metal pipelines especially in waterlogged sediments. The anode material used is inert (eg. platinum) to prevent its consumption.



Use this diagram showing how steel pipe can be protected in wet terrestrial environments to answer the questions.



- 1 Is this method of cathodic protection use of a sacrificial anode or use of impressed current? Justify your answer.

- 2 Identify a suitable active metal. Explain why this metal needs to be inspected and, if necessary, replaced.

- 3 Explain why this method is ineffective in dry terrestrial environments

Check your answers.



- 1 A steel hot water tank contains a long magnesium rod as sacrificial anode.
- Write an oxidation half equation for the magnesium anode.
-
- Write a reduction half equation for iron(II) ions that have formed somewhere on the iron (steel) tank as the first stage in corrosion.
-
- Combine the oxidation and reduction half equations to obtain a full equation to show how corrosion of the iron is prevented.
-

- 2 Most cars have a negatively grounded battery. The negative terminal of the car battery is connected by a thick conductor to the metal body. When the ignition is turned on, electrons can flow from the negative terminal, through the metal body to the starter motor and then to the positive terminal of the battery. (The electric current flowing through the metal car body is large but at too low a voltage to enter a person's body.)
- a) Why does the electron flow from the battery through the car body go back to the battery instead of flowing to the earth?

- b) Electrons flow in an external circuit from the negative terminal to the positive terminal through the metal car body. While this is happening what charged particles are flowing in the internal circuit inside the battery?
- c) Justify how negative grounding rather than positive grounding (positive terminal of battery connected to the metal car body) may reduce corrosion of the metal car body.

Check your answers.



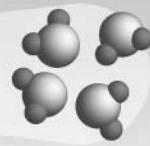
Gather and process information on at least two applications of cathodic protection. Include at least one example involving a sacrificial anode and another involving impressed current.

Identify the reasons for their use and the chemistry involved.



Report your findings in Exercise 4.3.

Complete Exercise 4.4.

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Suggested answers

Availability of metals for ocean-going vessel construction

Approximate years Before Present (BP)	Metal/alloy	Use
4000	copper metal	nails, spikes
3000	bronze alloy	nails, spikes
2500	iron metal	nails, spikes
1000	lead metal	sheeting to protect wood
500	brass alloy	deck fittings
150	steel alloy	hulls
100	phosphor bronze alloy	propellers
50	aluminium metal	small boat hulls
30	stainless steel alloy	wires on ocean racers
20	titanium metal	submarine hulls

Theoretical predictions

- 1 zinc anode, iron cathode
- 2 zinc anode, copper cathode
- 3 magnesium anode, iron cathode
- 4 iron anode, copper cathode
- 5 iron anode, tin cathode

Practical testing

The stable aluminium oxide surface layer protects underlying reactive aluminium from corrosive chemicals. The zinc oxide layer that forms on the surface of zinc is not as stable and corrosive chemicals can reach the underlying zinc.

- 1 Carbon grains can act as inert cathodes for the reduction of water and oxygen to hydroxide ions. This reduction requires electrons which come from the oxidation of iron atoms to iron(II) ions.
- 2 Using a list of standard potentials, nickel and tin are predicted to be more active than lead. This is not the case in sea water.

Tin plating – a physical barrier

- 1 Iron has a lower reduction potential ($\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe} - 0.44 \text{ V}$) than tin ($\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn} - 0.14 \text{ V}$). Thus iron is more easily oxidised than tin and the steel will rust away. The iron actually oxidises more rapidly when it is in contact with the tin than when it is uncoated.
- 2 Although aluminium has a lower reduction potential ($\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al} - 1.68 \text{ V}$) than the iron ($\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe} - 0.44 \text{ V}$) which is exposed when a tin can is opened, the iron in the tin can corrodes faster. The stable oxide (passivating) layer on the surface of the aluminium prevents aluminium from corroding.

Passivating metal and alloys

Aluminium, titanium and stainless steel are all protected by inert, tenacious, oxide layers. In a reducing environment reducing agents can react with the oxide layer in redox reactions removing this protective layer. The exposed underlying metal can be corroded by other chemicals.

Cathodic protection

- 1 This method is the use of a sacrificial anode. An active metal rather than a DC source is connected to the steel pipe.
- 2 Magnesium or zinc would be suitable metals. They are not so reactive that they would react with water in the environment. They are more reactive than steel and so should oxidise before the iron in the steel.
- 3 Ions could not flow through dry soil. There is no complete galvanic cell and so galvanic corrosion stops.

- 1 a) $Mg_{(s)} \rightarrow Mg^{2+} + 2e^-$
 b) $Fe^{2+} + 2e^- \rightarrow Fe_{(s)}$
 c) $Mg_{(s)} + Fe^{2+} \rightarrow Mg^{2+} + Fe_{(s)}$
- 2 a) The four rubber tyres prevent electron flow to earth. The low voltage (12 V) of the electrical system is not high enough to force current through a person's body to the earth when they touch the car and the earth simultaneously.
 b) Anions and cations flow in the electrolyte solution of the battery.
 c) Negative grounding supplies electrons directly to the metal car body. These electrons could reduce any newly formed iron ions back to the iron atoms. This would reduce corrosion of the car body. If positive grounding is used the electron flow is not directed to the car body where it could reduce metal ions back to metal atoms.

Sometimes you will see advertisements for impressed current or cathodic protection systems for car bodies. Unfortunately they don't appear to work. Sea water and moisture in soil provide a path for a complete electrical circuit when cathodic protection systems are used on boats or underground structures. On a car body there is not always an electrically conducting path connecting the site of possible corrosion back to the positive terminal of the battery. Thus there is often no complete electrical circuit and electrons cannot flow out of the negative battery terminal to the site of possible corrosion.

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Exercises – Part 4

Exercises 4.1 to 4.3

Name: _____

Exercise 4.1: Comparing corrosion rates

Labelled diagram of equipment and chemicals used**Table of results****Conclusions**

Exercise 4.2: Investigating the effectiveness of coatings on iron to prevent corrosion

Labelled diagram of equipment and chemicals used

Table of results

Conclusions

List of features that make your investigation reliable

Exercise 4.3: Cathodic protection

Application		
Sacrificial anode OR impressed current		
Where used		
Reasons for use		
Diagram of use		
Electrolyte		
Oxidation equation		
Reduction equation		

Exercise 4.4: Marine protection

- 1 Explain why paints used on boats should be electrical non-conductors.

- 2 Explain why grease used for lubrication on boats should not contain graphite.



Shipwrecks, corrosion and conservation

Part 5: Rate of corrosion and depth

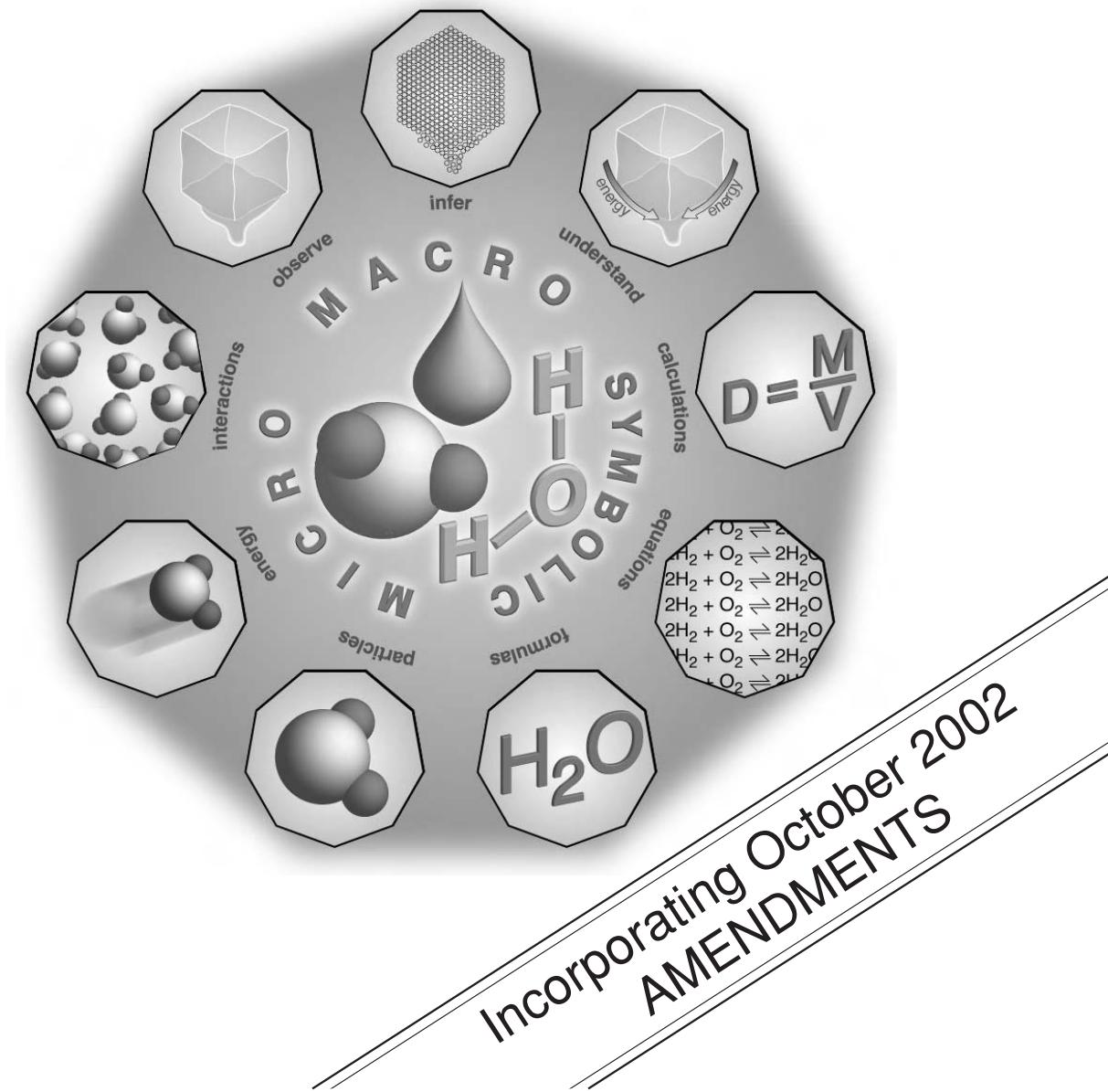
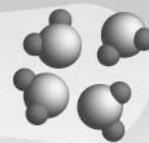


Table of standard potentials and half equations

oxidant	+ electron(s)	\rightleftharpoons	reductant	E^\ominus (volts)
Li^+	+ e ⁻	\rightleftharpoons	Li	-3.04
K^+	+ e ⁻	\rightleftharpoons	K	-2.94
Ca^{2+}	+ 2e ⁻	\rightleftharpoons	Ca	-2.87
Na^+	+ e ⁻	\rightleftharpoons	Na	-2.71
Mg^{2+}	+ 2e ⁻	\rightleftharpoons	Mg	-2.36
Al^{3+}	+ 3e ⁻	\rightleftharpoons	Al	-1.68
150 H_2O	+ e ⁻	\rightleftharpoons	1/2H ₂ (g) + OH ⁻	-0.83
Zn^{2+}	+ 2e ⁻	\rightleftharpoons	Zn	-0.76
Fe^{2+}	+ 2e ⁻	\rightleftharpoons	Fe	-0.44
Cd^{2+}	+ 2e ⁻	\rightleftharpoons	Cd	-0.40
Ni^{2+}	+ 2e ⁻	\rightleftharpoons	Ni	-0.24
Sn^{2+}	+ 2e ⁻	\rightleftharpoons	Sn	-0.14
Pb^{2+}	+ 2e ⁻	\rightleftharpoons	Pb	-0.13
H ⁺	+ e ⁻	\rightleftharpoons	1/2H ₂ (g)	0.00
Cu^{2+}	+ 2e ⁻	\rightleftharpoons	Cu	0.34
1/2O ₂ (g)+H ₂ O	+ 2e ⁻	\rightleftharpoons	2OH ⁻	0.40
Cu^+	+ e ⁻	\rightleftharpoons	Cu	0.52
1/2I ₂ (aq)	+ e ⁻	\rightleftharpoons	I ⁻	0.62
Fe^{3+}	+ e ⁻	\rightleftharpoons	Fe ²⁺	0.77
Ag^+	+ e ⁻	\rightleftharpoons	Ag	0.80
1/2Br ₂ (aq)	+ e ⁻	\rightleftharpoons	Br ⁻	1.10
1/2O ₂ (g)+2H ⁺	+ 2e ⁻	\rightleftharpoons	H ₂ O	1.23
1/2Cl ₂ (aq)	+ e ⁻	\rightleftharpoons	Cl ⁻	1.40
1/2F ₂ (g)	+ e ⁻	\rightleftharpoons	F ⁻	2.89

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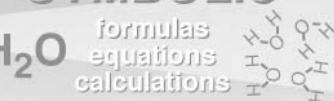
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Introduction

Metal is normally the main material used in ship construction. However, a ship and its fittings contain a range of materials such as metal, plastic, glass, ceramics, wood, leather and cloth. Up to this point you have concentrated on corrosion of metals. In these last two parts you will look more broadly at corrosion. **Corrosion** will be regarded as deterioration of any material or its properties because of chemical reaction with its environment.

After a ship has sunk the rate of decay of organic matter and the rate of corrosion of metals will depend on the final depth of the wreck. The final depth of the wreck can determine the temperature, pressure of dissolved gases and concentration of dissolved salts – all factors that can influence rates of reaction and equilibria positions.

Predictions of slow corrosion at great depths were not fulfilled when the nearly four kilometre deep wreck of the *Titanic* was discovered in 1985 and explored.

In Part 5 you will be given opportunities to learn to:

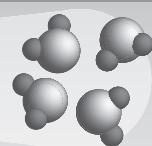
- outline the effect of:
 - temperature
 - pressure
 - on the solubility of gases and salts
- identify that gases are normally dissolved in the oceans and compare their concentrations in the oceans to their concentrations in the atmosphere
- compare and explain the solubility of selected gases at increasing depths in the oceans
- predict the effect of low temperatures at great depths on the rate of corrosion of a metal
- explain that ship wrecks at great depths are corroded by electrochemical reactions and by anaerobic bacteria
- describe the action of sulfate reducing bacteria around deep wrecks

- explain that acidic environments accelerate corrosion in non-passivating metals.

In Part 5 you will be given opportunities to:

- perform a first-hand investigation to compare and describe the rate of corrosion of materials in different:
 - oxygen concentrations
 - temperatures
 - salt concentrations
- use available evidence to predict the rate of corrosion of a metal wreck at great depths in the oceans and give reasons for the prediction made
- perform a first-hand investigation to compare and describe the rate of corrosion of metals in different acidic and neutral solutions.

Extracts from *Chemistry Stage 6 Syllabus* © Board of Studies NSW, November 2002. The most up-to-date version can be found on the Board's web site at http://www.boardofstudies.nsw.edu.au/syllabus_hsc/index.html

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Rate of corrosion



In this activity you will compare and describe the rate of corrosion of metals (using at least two different metals) in different conditions.

The conditions that will vary are:

- temperature
- oxygen concentration
- salt concentration
- pH (acid, neutral and basic conditions).

Temperature affects the dissolved oxygen levels in water. You will need to be careful to obtain valid (trustworthy) results that distinguish between the effects of oxygen and temperature. Change one variable such as oxygen concentration, while trying to keep all other variables constant.

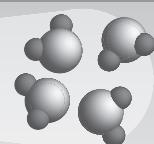
Some possible approaches are outlined following.

- Raise the oxygen concentration in water by using an aquarium air pump. Air bubbling continuously through the water will raise the dissolved oxygen concentration.
- Use a container completely filled with recently boiled but cooled water. Boiling should remove most dissolved gas while filling a sealed container that excludes air prevents more gas dissolving.
- Keep the water temperature at a raised or lowered temperature for days or even weeks by placing a solution somewhere warm and an identical solution somewhere cold. The top of a refrigerator above the condenser coils is a warm location whilst inside is cool. Note that evaporation of water will increase the concentration of salt.
- Use at least two metals that you have used for previous investigations of rates of corrosion. You will already have an idea how long it takes before you can observe or measure corrosion.
- If you cannot obtain sea water use a solution of table salt, NaCl, as this is the most common salt in sea water.

- Vinegar (pH about 3), table salt solution (pH about 7) and washing soda solution (pH about 11) should be suitable for investigating the effect of pH on rate of corrosion.



Plan, perform and report on your first-hand investigation in Exercise 5.1.

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Effect of temperature and pressure

Effect on the solubility of gases



What happens to the solubility of carbon dioxide gas in a soft drink when you remove the lid?

- 1 List your observations.

- 2 Explain your observations using the particle theory.

Check your answers.

Removing the lid lowers the pressure and dissolved gas particles are released. The greater the pressure of gas above a liquid the more particles there are colliding with the surface and the greater the solubility.



What happens to the dissolved air in water when a small container of water is placed in a warm location?

- 1 List your observations.

- 2 Explain your observations using the particle theory.

Check your answers.

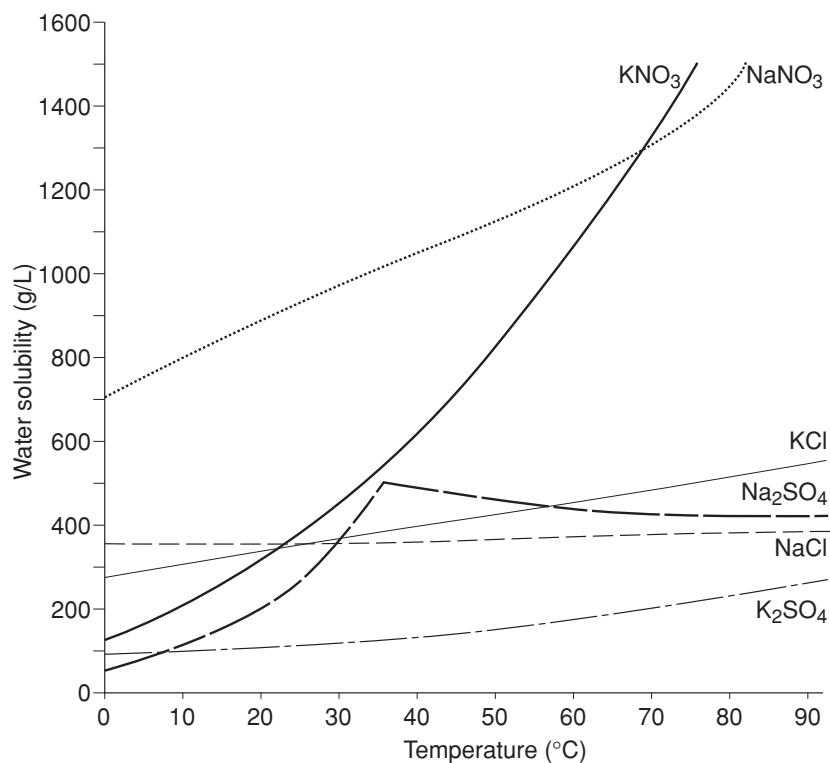
Raising the temperature lowers the solubility of gases in water. This is why fish may not obtain sufficient oxygen to stay alive when water is thermally polluted or overheated.

Effect on the solubility of salts

The application of pressure does not normally affect the solubility of salts but temperature change can have a significant effect.



The graph below shows the solubilities of a number of salts at different temperatures. Make a general statement about the solubility of salts and temperature. Comment specifically about the solubility of sodium chloride, the main salt in sea water, and temperature.



Check your answer.

Salt ion	Formula	Ion conc. in sea water (g L ⁻¹)	Salt solubilities in water (g L ⁻¹)
chloride	Cl ⁻	1.90	
sodium	Na ⁺	1.06	NaCl 360
sulfate	SO ₄ ²⁻	0.26	
magnesium	Mg ²⁺	0.13	MgSO ₄ 36 MgCl ₂ 55
calcium	Ca ²⁺	0.04	CaSO ₄ 0.2 CaCO ₃ 0.001
potassium	K ⁺	0.04	KCl 36
hydrogen carbonate	HCO ₃ ⁻	0.01	
bromide	Br ⁻	0.01	NaBr 95

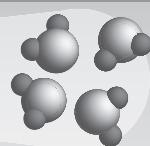
When sea water evaporates salts will precipitate in a particular order.
The order depends on salt solubility and the relative amounts of ions.
The order is normally CaCO₃, CaSO₄, NaCl, MgSO₄, MgCl₂, NaBr, KCl.

The solubility of calcium carbonate, CaCO₃, a major constituent of marine organism shells, is of interest. CaCO₃ is actually more soluble in cold water than warm water! There is a depth below which CaCO₃ remains of dead organisms do not accumulate because the deep water is cold enough to dissolve all carbonate. This depth is called the carbonate compensation depth (CCD). Below the CCD (about 5 km near the equator and 3 km near the poles) only silicate remains of dead organisms accumulate on the ocean floor.



Account for the difference in CCD between the Equator and the poles.

Check your answer.

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Gas concentrations

Many different units are used to measure gas concentrations in the ocean and atmosphere. It is important that you compare measurements given in the same units for the different gases, and understand why variations occur for some gases but not others.

Surface air and surface sea water

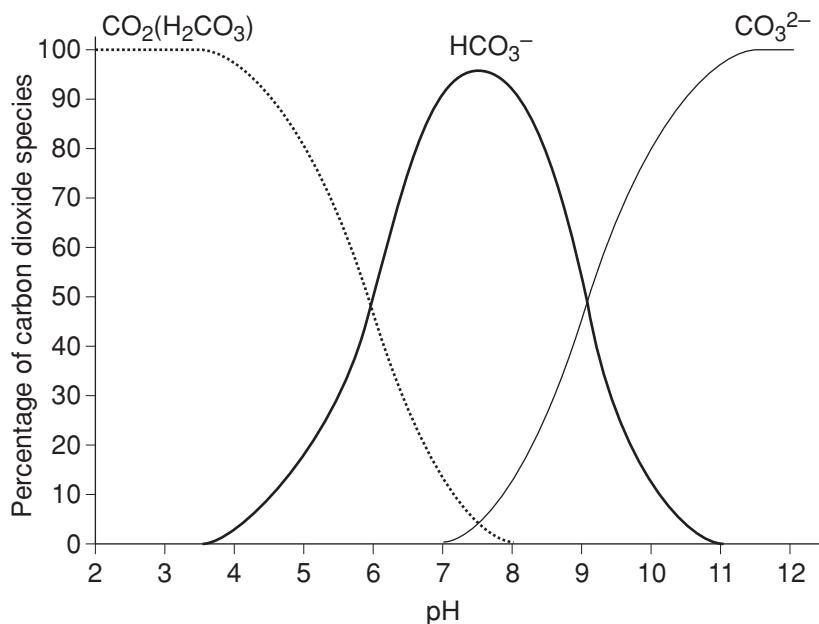
Gas	Air % (v/v)	Surface sea water % (v/v)
N ₂	78	0.8 – 1.5
O ₂	21	0 – 0.9
CO ₂	0.03	4.5 – 5.4

- 1 Account for the great variation in oxygen in surface sea water.



- 2 Explain why the CO₂ level is so high in surface sea water.

- 3 Dissolved carbon dioxide is principally in the form of dissolved gas molecules $\text{CO}_2(\text{g})$, hydrogen carbonate ions HCO_3^- or carbonate ions. Use the diagram below to estimate the percentages of these different forms in sea water with a pH of 7.5.



Carbon dioxide species in sea water as a function of pH.

Check your answers.

The average balance for inorganic carbon in a sea water sample is 88% as hydrogen carbonate ion, 11% as carbonate ion and 1% as carbon dioxide (carbonic acid). The amount of carbon stored as HCO_3^- , CO_3^{2-} and $\text{CO}_2(\text{H}_2\text{CO}_3)$ in the oceans is enormous – it is 3.5 times the carbon in fossil fuel deposits and 50 times the carbon in atmospheric CO_2 !

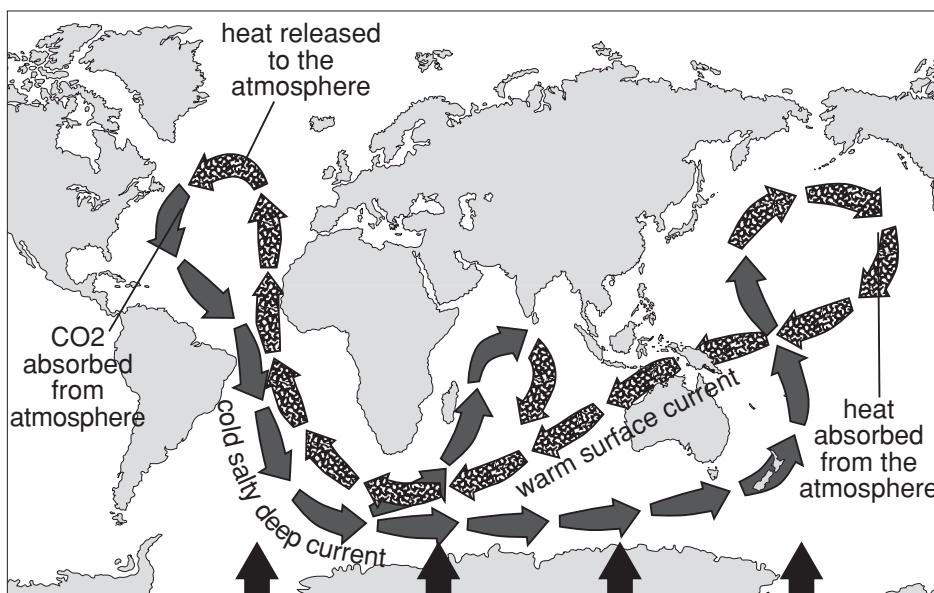
Gas concentrations and ocean depth

The data in the previous table shows significant variation in gas concentrations in surface sea water.

At greater depths there is less variation unless there is a water current present containing very different concentrations of dissolved gas.

In the last ten years major movements of ocean water have been discovered that are believed to have a significant impact on atmospheric climate and gas concentrations.

Up to a third of the carbon dioxide released into the atmosphere each year may be absorbed in the North Atlantic Ocean and carried by what has been called the great ocean conveyor belt into the Indian and Pacific Oceans. The water in this ‘conveyor belt’ is very salty because it starts near Greenland where ice containing hardly any salt freezes out of sea water. Because it transfers heat and salt it is also called the thermohaline circulation.



Thermohaline circulation of ocean water

The Antarctic continent has an eastward circular movement, known as the Antarctic circumpolar current, surrounding it. This circumpolar current ensures mixing of the waters of the three most important oceans.

Cold dense sea water containing large amounts of dissolved gas moves from the edge of Antarctica to the Equator at great depths. This is represented in the diagram by the four thick arrows pointing upwards.

The concentrations of chemically inert gases such as nitrogen and argon increase steadily with depth as the temperature of the water decreases. Sea water is generally saturated with nitrogen and argon.

Much more variation occurs in the concentrations of the biologically and chemically active gases oxygen and carbon dioxide.

Photosynthesis by plants, $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$, is important in the top 100 m where light can penetrate.

Significant respiration ($\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$) occurs in the top 1000 m where most animals are found. As the remains of dead organisms sink towards the ocean floor bacterial decay consumes oxygen. This is replaced by oxygen passing upwards from the deep, well-oxygenated waters of the great conveyor belt.

Solubility of O_2 and CO_2 at different depths



Examine the graphs on the next page for a deep part of the Pacific Ocean:
Then explain the following phenomena.

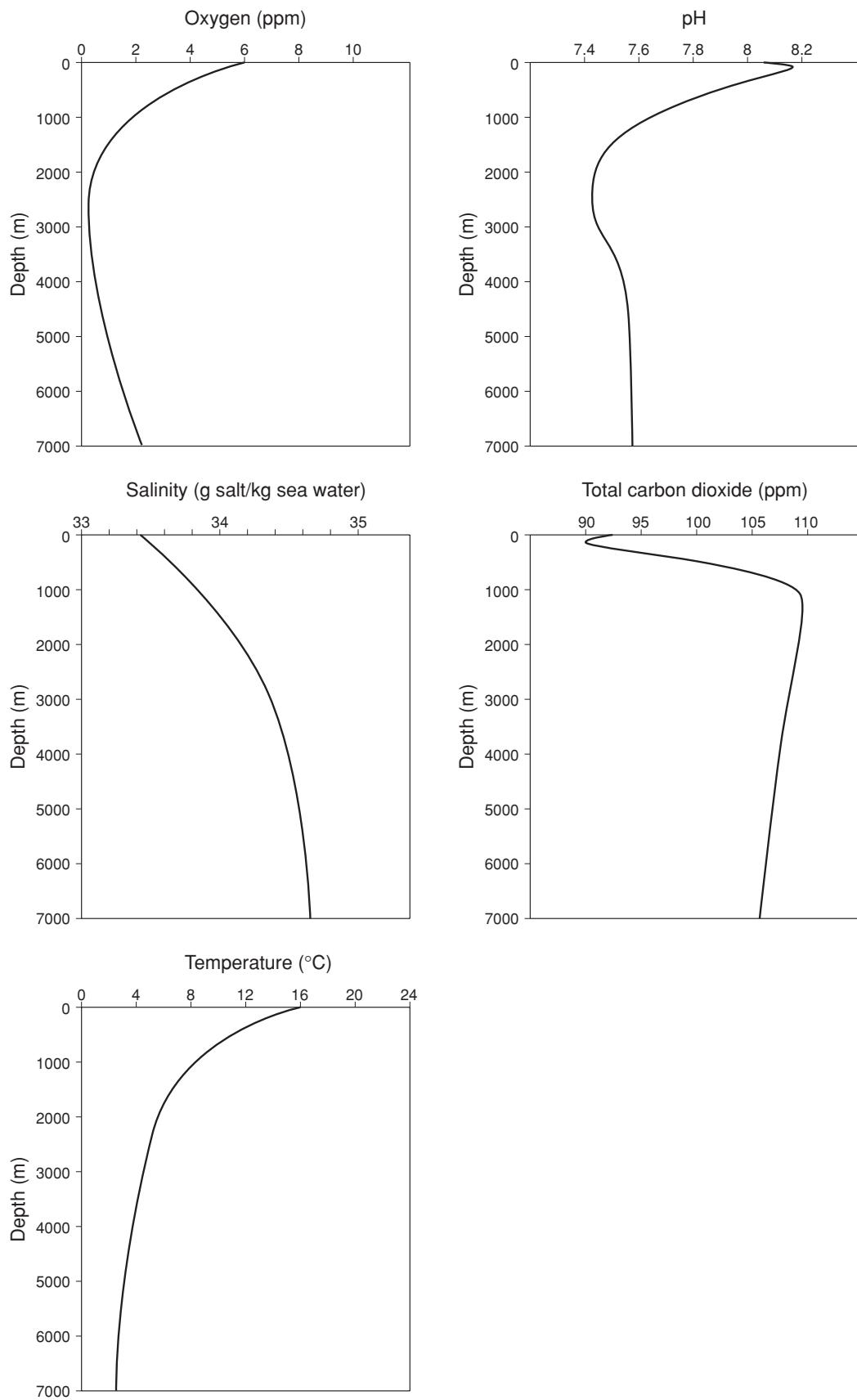
- 1 Oxygen level is at a maximum at the water surface.

- 2 Carbon dioxide level decreases for the first 100 m then increases.

- 3 Oxygen levels increase after a minimum between 2 000 m and 4 000 m

- 4 Oxygen graph is for dissolved O_2 but carbon dioxide graph refers to total carbon dioxide instead of just carbon dioxide.

Check your answers.



Rate of metal corrosion

The rate of corrosion of iron varies enormously with conditions. A rough figure is 0.1 mm of thickness per year in moist air and about ten times this rate in sea water. In some locations such as dry desert regions corrosion rates are close to zero. The environmental factors that are most important are listed below.

- Oxygen concentration. The higher the oxygen concentration, the greater the rate of oxidation.
- Salinity, that is, salt concentration. The higher the salinity, the greater the conductivity and the greater the rate of galvanic corrosion.
- Temperature. The lower the temperature, the slower the rate of reaction.
- pH. The more acidic the pH, the greater the rate of corrosion for most metals.



Use the evidence in the graphs given for the previous exercise to predict the depth for:

- a maximum rate of corrosion of a metal wreck. _____
- b minimum rate of corrosion of a metal wreck. _____

Give reasons for the predictions made.

Check your answers.

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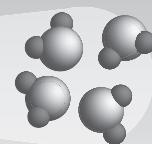
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The *Titanic*

Background

The most publicised shipwreck of the twentieth century was the wreck of the *Titanic*. It was the largest ship ever built when launched in 1912.

The supposedly ‘unsinkable’ *Titanic* sank in cold waters of the North Atlantic Ocean in April 1912 after hitting an iceberg on its first journey. Over 1500 lives were lost.

The hull was made of steel coated with a lead-based paint. Most metal fittings on the ship were bronze (Cu-Sn) or brass (Cu-Zn). Kitchen utensils would have included copper or silver plate. Engine parts were cast iron protected by oil and grease.

This mixture of metals ended up at a depth of nearly 4 km where the water temperature was about 4°C and the pressure was close to the equivalent of 400 atmospheres. The depth at which the *Titanic* lies is very close to the average depth of the Earth’s oceans. The mixture of metals comprising the *Titanic* shipwreck is surrounded by sea water, an electrolyte.

In the 1980s an extensive search was launched for the remains which were predicted to have undergone little corrosion at a depth of nearly 4 km. In 1985 part of the wreck was found and photographed. A second expedition in 1986 explored the whole wreck. In 1987 an investor-financed group gathered objects from the wreck site and began restoration of these objects. In the 1990s these restored objects began to be displayed in museums around the world.

No human remains or bones could be found on site. However pairs of leather shoes were found, positioned as though the feet had been completely removed without undoing the shoes.



Is it ethical to remove objects from the *Titanic* site where so many people died? Is this the same as looting a cemetery or is it archeological exploration of a legitimate site? Discuss this with at least one other person.

Predictions



Using the data presented in the graphs showing how factors (oxygen, pH, salinity, total carbon dioxide, temperature) change with ocean depth, evaluate why it was predicted that the *Titanic* shipwreck would show little corrosion.

Check your answer.

In 1976 a novel called *Raise the Titanic* was published and later made into a film. In the novel the complete hull in good condition was sealed and filled with air to raise it to the surface. The next section shows you why not many people read this novel or watch the film these days.

Observations

The *Titanic* wreck consisted of two sections surrounded by debris. The water temperature was around 4°C, the temperature at which water has maximum density. There was very little oxygen (only about 0.2 ppm) and a complete absence of light.

Much of the wreckage was covered with rust flows, rust flakes and stalactite-like structures called rusticles. Black iron(II) sulfide, FeS, covered other areas. The rusticles are mostly iron(II) oxide and iron(II) hydroxide with a dark red outer surface and an orange inner surface. They contained bacteria, mostly of the sulfate reducing type which thrive in anaerobic conditions.

Corrosion was much more extensive than predicted. Hardly any wooden objects could be found. Any metal in direct contact with wood had corroded rapidly. Bronze objects appeared least corroded.

Leather shoes were found in pairs.

Explanations

Bacterial action:

Bacterial action as well as electrochemical reactions were important. Bacteria are essential for the formation of rusticles and rust flows which can grow as much as 10 cm every year.

Bacteria form thin layers called **biofilms** or slime layers on metal surfaces. The physical presence of the bacteria and their **metabolism** produces chemical changes. Changes in dissolved oxygen concentration, pH and concentration of organic and inorganic species at different locations on a metal surface can set up electrochemical cells. This leads to **microbiologically influenced corrosion** which is now recognised by engineers as significantly reducing the useful lifetime of equipment.

Low oxygen environment in which:

- anaerobic **sulfate reducing bacteria** (SRB) which change sulfate ions SO_4^{2-} to hydrogen sulfide H_2S thrive as long as they have a suitable source of organic material as food
- the cathode reaction in galvanic corrosion cells changes from a reaction requiring oxygen $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ to a reaction that does not require oxygen $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

Sulfate reducing bacteria form a slime layer between the water and any iron surface. (You can feel a bacterial slime layer when you don't clean your teeth for a day or two! Unless you eat teeth cleaning foods such as celery or apples you can develop a micro-environment in your mouth that encourages bacterial slime growth on your teeth.) The slime layer around SRB creates a micro-environment more acidic than the surrounding sea water.



Sulfate reducing bacteria change sulfate ions SO_4^{2-} to elemental sulfur S, hydrogen sulfide H_2S and sulfide ions S^{2-} . Determine the oxidation states of sulfur in these four species. Justify the use of the term *reducing* to describe the bacteria.

Check your answer.

The SRB use organic material such as human remains, food, wood and fabric from the *Titanic* as well as organic material from the bodies of dead organisms dropping to the ocean floor.

Most living things carry out redox reactions between organic material and oxygen to release energy for living. SRB, having evolved in an environment without oxygen, carry out redox reactions between organic material and sulfate ions to release energy for living.



- 1 Examine a periodic table and evaluate sulfur as an alternative oxidant to oxygen.

- 2 Overall reduction of sulfate ions by the bacteria can be represented as



Use Le Chatelier's principle to explain why this reaction is favoured by acid conditions.

Check your answers.

Slightly acidic environment:

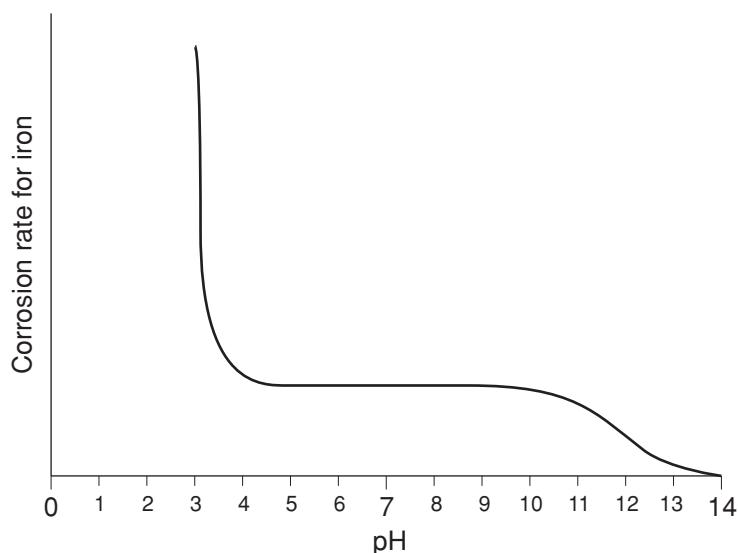
The sulfate reducing reaction $\text{SO}_4^{2-} + 5\text{H}_2\text{O} + 8\text{e}^- \rightarrow \text{HS}^- + 9\text{OH}^-$ is favoured by acid conditions. However ocean water normally has a pH of about 8 while SRB operate best in a slightly acid environment.

A number of factors contributed to creating a slightly acid environment for the SRB on the *Titanic*:

- The higher solubility of carbon dioxide with increasing depth (a pressure of about 400 atm and a temperature close to 4°C at the *Titanic* site) increases the hydrogen ion concentration.
- Any iron(II) ions produced in corrosion reactions can hydrolyse (react with water) precipitating insoluble iron(II) hydroxide and producing hydrogen ions: $\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+$
- Iron(II) ions can also react with hydrogen sulfide (produced by SRB) precipitating insoluble black iron(II) sulfide and producing hydrogen ions: $\text{Fe}^{2+} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+$
- The hydrogen sulfide released by SRB is a weak acid producing hydrogen ions and sulfide ions: $\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$
- Anaerobic SRB were found on the inside of rusticles while oxygen dependent aerobic bacteria were on the outside. Both these bacteria may release acid waste which could explain measurements near the *Titanic* wreck of micro-environments with pH as low as 4.2.

Plenty of iron:

Acidic environments accelerate corrosion in **non-passivating metals** such as iron, the main metal in the *Titanic*.



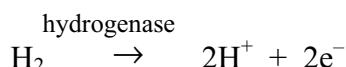
Non-passivating metals are metals which do not have protective oxide layers – all metals except aluminium, chromium, titanium, tin and zinc.

Hydrogen ions in acidic environments react with iron producing hydrogen: $\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2$

Hydrogen gas as well as organic substances can provide electrons to reduce sulfate ions.

Hydrogenase:

SRB contain hydrogenase enzymes which produce hydrogen ions (able to react with iron) and electrons (able to reduce sulfate ions in the sea water). These electrons originally came from oxidation of iron.



Have you ever walked through black stinking mud and smelt rotten egg gas, hydrogen sulfide H_2S ? If you have, you have been in close contact with SRB – sulfate reducing bacteria.

SRB may be one of the oldest forms of life on Earth. They deposited large amounts of iron pyrites FeS_2 in rocks as old as 3 400 million years. SRB are widespread in marine and terrestrial aquatic environments that are deficient in oxygen.

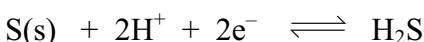
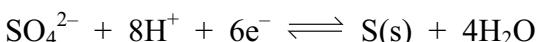
Hydrothermal vents on the ocean floor where SO_2 and H_2S gases are released forming sulfate ions and hydrogen ions are the type of environment where SRB flourish.

Hydrogen sulfide:

Hydrogen sulfide released by SRB can react with just about every metal except gold.



The metal ions produced by the oxidation of metals combine with the sulfide ions to form insoluble sulfides such as FeS . Explain how this precipitation could affect the following two reaction steps:



Check your answer.

Elemental sulfur S is formed by the partial reduction of sulfate ions. Particles of this sulfur provide a surface on which hydrogen gas evolution occurs faster than on metals. SRB near these sulfur particles use the enzyme hydrogenase that changes the hydrogen gas to hydrogen ions: $\text{H}_2 \rightleftharpoons 2\text{H}^+ + 2\text{e}^-$. The hydrogen ions increase the rate of iron corrosion. The electrons are available to reduce sulfate ions.

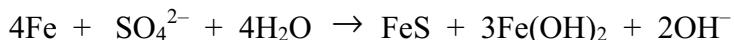
Electrochemical reactions and anaerobic bacteria:

You probably realise now that many electrochemical reactions are promoted by the presence of bacteria. One microbiologist has predicted that, within a century, bacterial action will have converted the *Titanic* to nothing more than a huge iron ore deposit!

Summary of SRB action:

SRB use the high oxidation state of sulfur (+6) in sulfate ions present in sea water to oxidise iron atoms to iron(II) ions. The reactions are favoured by slightly acid conditions leading to the formation of iron(II) sulfide and iron(II) hydroxide.

Since iron provides the electrons that reduce the protons to hydrogen, and hydrogen provides the electrons for the reduction of sulfate, an equation representing the overall change brought about by SRB is:



Explain why corrosion of iron in the *Titanic* produced iron(II) compounds whereas corrosion of iron normally forms iron(III) compounds.

Check your answer.

The lack of wood:

Many of the *Titanic*'s wooden objects unprotected by paint had been eaten by shipworms. Shipworms and land termites have gut bacteria to convert wood (cellulose) and nitrogen compounds to protein. (This similarity is why shipworms have been called 'termites of the sea'). Other wooden objects appear to have been decayed by aerobic bacteria that consume oxygen thus creating an anaerobic environment that suits SRB.

Little corrosion of bronze:

Bronze is resistant to sea water corrosion. The high copper content is toxic to most marine organisms.

Pairs of leather shoes:

The pairs of leather shoes were probably intact because of chemical treatments such as tannic acids that had been used in the tanning of the leather. No human remains were found inside shoes because of bacterial decay and solution of phosphate and carbonate salts from bones.



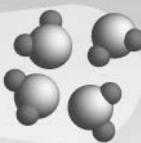
Should you believe everything you read on the world wide web?

Check out the site

<http://antoine.frostburg.edu/chem/senese/101/redox/faq/titanic.shtml>



Complete Exercise 5.2.

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Suggested answers

Effect on the solubility of gases

- 1 A hissing sound is heard when lid is removed. This sound is immediately followed by bubbles of gas being released from the solution.
- 2 The high pressure achieved by many CO₂ molecules hitting the surface of the liquid is lost when the lid is removed. By Le Chatelier's principle, lowering the CO₂ gas pressure causes CO₂ molecules to shift from solution to the gas phase in the equilibrium. CO₂(aq) ⇌ CO₂(g). CO₂ is lost from solution.
- 1 Small bubbles appear in the liquid as the solution temperature increases.
- 2 As the temperature rises the dissolved gas molecules move faster. More have sufficient kinetic energy to overcome attraction of the water molecules and escape from solution forming gas bubbles.

Effect on the solubility of salts

Most salts increase in solubility as the temperature rises. The change in solubility with temperature is different for different salts. Unusually, the solubility of sodium chloride hardly changes with temperature.

It is only possible for water to be cold enough to dissolve CaCO₃ at a depth below 5 km near the Equator. A depth of 3 km is cold enough near the poles.

Gas concentrations in the ocean and atmosphere

- 1 Low oxygen concentrations could be in water containing decaying organic matter. High oxygen concentration could be in water with extensive photosynthesis by algae.

- 2 CO₂ from the air reacts chemically with water to form hydrogen carbonate and carbonate ions. These ions are more soluble in polar water molecules than non-polar CO₂ molecules could be.
- 3 3% dissolved CO₂ gas or H₂CO₃, 94% HCO₃⁻, 3% CO₃²⁻

Solubility of O₂ and CO₂ at different depths

- 1 Wind and wave turbulence increases contact between air and water and oxygen solubility. Photosynthesis by algae at surface raises oxygen concentration.
- 2 Photosynthetic algae have sufficient light available in the top 100 m to absorb carbon dioxide by carrying out photosynthesis.
- 3 Dense cold water currents from cold regions carry much oxygen to low depths and this oxygen diffuses upwards.
- 4 All dissolved oxygen is in the form of dissolved O₂ molecules. Total carbon dioxide consists of dissolved gas (H₂CO₃), HCO₃⁻ and CO₃²⁻.

Rate of metal corrosion

- a Maximum rate of corrosion would probably be at shallow depths of a few hundred metres where oxygen levels and temperature are highest. Salinity levels and pH levels do not change very much with depth.
- b Minimum rate of corrosion would be between 2 to 4 km depth where oxygen levels are at a minimum and temperature is 5 to 3°C.

Predictions

The *Titanic* was in the region of lowest oxygen level and a temperature of 4°C. Low oxygen levels and little heat energy slow the rate of corrosion.



Explanations

Knowing that the oxidation state of oxygen is always -2 and hydrogen is +1 the oxidation states of sulfur are:

+6 in SO₄²⁻, 0 in S, -2 in H₂S, -2 in S²⁻

The changes from sulfate, oxidation state +6, to S, H₂S or S²⁻ all involve reducing the oxidation state of sulfur. Thus the term, sulfate reducing describes what the bacteria do to sulfate ions.

- 1 Sulfur is directly under oxygen in Group 16. These two elements have similar chemical properties. In an environment free of oxygen sulfur can be an alternative oxidant. The high oxidation state of sulfur, +6, in SO_4^{2-} will be a better oxidant, able to attract more electrons, than lower oxidation states such as in elemental sulfur, 0.
- 2 In the equilibrium $\text{SO}_4^{2-} + 5\text{H}_2\text{O} + 8\text{e}^- \rightleftharpoons \text{HS}^- + 9\text{OH}^-$ the hydrogen ions neutralise the hydroxide ions. A lower concentration of hydroxide ions causes the equilibrium position to move to the right.

Metal ions such as Fe^{2+} combine with sulfide ions S^{2-} forming insoluble sulfides such as FeS . This reduces the concentration of S^{2-} and, by Le Chatelier's Principle, leads to more ionisation of hydrogen sulfide molecules. $\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$. In turn $\text{S(s)} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{S}$ shifts position to the right causing $\text{SO}_4^{2-} + 8\text{H}^+ + 6\text{e}^- \rightleftharpoons \text{S(s)} + 4\text{H}_2\text{O}$ to shift position to the right. The two equilibria shifting position to the right result in more reduction of sulfate ions.

Corrosion of iron in the *Titanic* forms iron(II) compounds because there was no O_2 available to oxidise iron(II) to iron(III). Remember that the rusting of iron normally involves two steps, formation of iron(II) hydroxide followed by oxidation with oxygen to rust.

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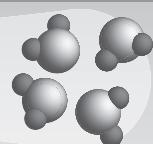
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Exercise - Part 5

Exercises 5.1 to 5.2

Name: _____

Exercise 5.1: Rate of corrosion in different conditions

Metals used:

Labelled diagrams of equipment and chemicals used:

Table of results:

Conclusions:

Exercise 5.2: Evaluating ways in which accuracy and reliability could be improved in investigations

Have you ever noticed that paper clips often rust on the underside where they are in contact with paper but not on the upper side most in contact with air? A student who observed this came up with three hypotheses:

- Chemicals such as acids in the paper were accelerating corrosion.
- Differential aeration corrosion cells were set up because there was little oxygen in contact with the underside but a lot in contact with the upper side.
- Cellulose in the paper attracted and held water in contact with the underside of the paper clip.

To try to decide between these hypotheses she set up three investigations:

- The student compared paper clips in contact with ordinary paper and acid-free paper.
- The student compared paper clips in contact with paper but with one in the air and the other in a vacuum bag (of the type used to store food) from which air had been withdrawn by a pump.
- The student compared paper clips in contact with paper in two sealed bags, one of which contained silica gel to absorb water.

Select one of these three investigations and evaluate ways in which accuracy and reliability could be improved. Make sure you distinguish between accuracy (freedom of measurement from error) and reliability (trustworthiness of information and data) in your answer.



Shipwrecks, corrosion and conservation

Part 6: Shipwreck conservation and restoration

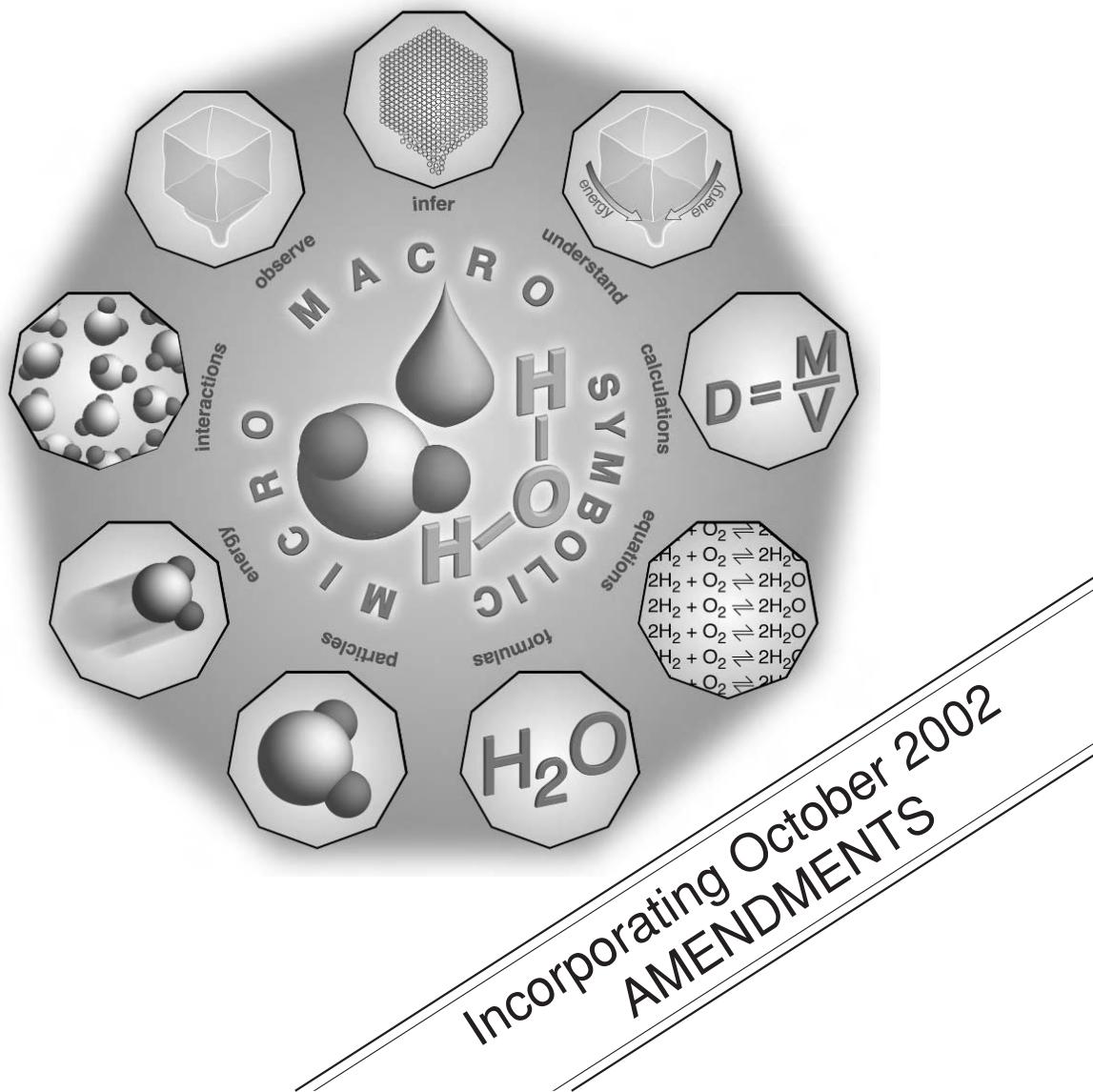


Table of standard potentials and half equations

oxidant	+ electron(s)	\rightleftharpoons	reductant	E^\ominus (volts)
Li^+	+ e^-	\rightleftharpoons	Li	-3.04
K^+	+ e^-	\rightleftharpoons	K	-2.94
Ca^{2+}	+ $2e^-$	\rightleftharpoons	Ca	-2.87
Na^+	+ e^-	\rightleftharpoons	Na	-2.71
Mg^{2+}	+ $2e^-$	\rightleftharpoons	Mg	-2.36
Al^{3+}	+ $3e^-$	\rightleftharpoons	Al	-1.68
H_2O	+ e^-	\rightleftharpoons	$1/2\text{H}_2(\text{g}) + \text{OH}^-$	-0.83
Zn^{2+}	+ $2e^-$	\rightleftharpoons	Zn	-0.76
Fe^{2+}	+ $2e^-$	\rightleftharpoons	Fe	-0.44
Cd^{2+}	+ $2e^-$	\rightleftharpoons	Cd	-0.40
Ni^{2+}	+ $2e^-$	\rightleftharpoons	Ni	-0.24
Sn^{2+}	+ $2e^-$	\rightleftharpoons	Sn	-0.14
Pb^{2+}	+ $2e^-$	\rightleftharpoons	Pb	-0.13
H^+	+ e^-	\rightleftharpoons	$1/2\text{H}_2(\text{g})$	0.00
Cu^{2+}	+ $2e^-$	\rightleftharpoons	Cu	0.34
$1/2\text{O}_2(\text{g}) + \text{H}_2\text{O}$	+ $2e^-$	\rightleftharpoons	2OH^-	0.40
Cu^+	+ e^-	\rightleftharpoons	Cu	0.52
$1/2\text{I}_2(\text{aq})$	+ e^-	\rightleftharpoons	I^-	0.62
Fe^{3+}	+ e^-	\rightleftharpoons	Fe^{2+}	0.77
Ag^+	+ e^-	\rightleftharpoons	Ag	0.80
$1/2\text{Br}_2(\text{aq})$	+ e^-	\rightleftharpoons	Br^-	1.10
$1/2\text{O}_2(\text{g}) + 2\text{H}^+$	+ $2e^-$	\rightleftharpoons	H_2O	1.23
$1/2\text{Cl}_2(\text{aq})$	+ e^-	\rightleftharpoons	Cl^-	1.40
$1/2\text{F}_2(\text{g})$	+ e^-	\rightleftharpoons	F^-	2.89

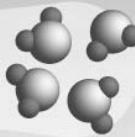
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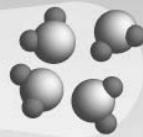
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Introduction

Objects salvaged from shipwrecks may have important historical value. However, if not treated carefully, by a conservation expert with an understanding of the behaviour of chemicals, it would have been better to leave the objects on the ocean floor. Museums sometimes attach zinc sacrificial anodes to certain metallic submerged objects to conserve them until ready for recovery. Any wreck site and underwater environment should be recorded and object locations mapped before any removal.

The underwater environment is usually stable. Shipwrecks and **artifacts** are in chemical equilibrium with surrounding sea water. When the object is removed to the atmosphere, deterioration can increase rapidly as the chemicals in the object change to reach equilibrium in a different environment.

Monitoring and managing the deteriorations of an object in the atmospheric environment should be the responsibility of a chemically trained conservation expert. If not cleaned, stabilised and preserved by conservators with expertise, much damage can be done. Wooden objects can shrink and crack as they dry out, iron cannonballs can crumble to pieces within hours, while the surface layers of glass and ceramics can flake off. Once stabilized, objects of value can undergo restoration.

Studying ancient shipwrecks in a range of depths and conditions has increased understanding of long term deterioration rates of different materials. This is useful for monitoring and management of modern underwater constructions such as wharf supports and oil rigs.

Iron can be pictured as a lattice of iron cations surrounded by a sea of electrons. When the iron is stressed, for example by bending, the surrounding electron cloud becomes thinner. This makes it easier for iron particles to break away from the lattice as free cations and thus corrode. The stresses set up in metal parts when a ship is wrecked or sinks provide points where corrosion will preferentially occur.

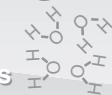
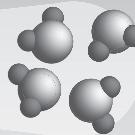
In Part 6 you will be given opportunities to learn to:

- explain that artefacts from long submerged wrecks will be saturated with dissolved chlorides and sulfates
- describe the processes that occur when a saturated solution evaporates and relate this to the potential damage to drying artefacts
- identify the use of electrolysis as a means of removing salt
- identify the use of electrolysis as a means of cleaning and stabilising iron, copper and lead artefacts
- discuss the range of chemical procedures which can be used to clean, preserve and stabilise artefacts from wrecks and, where possible, provide an example of the use of each procedure.

In Part 6 you will be given opportunities to:

- perform investigations and gather information from secondary sources to compare conservation and restoration techniques applied in two Australian maritime archaeological projects.

Extracts from Chemistry Stage 6 Syllabus © Board of Studies NSW, November 2002. The most up-to-date version can be found on the Board's web site at
http://www.boardofstudies.nsw.edu.au/syllabus_hsc/index.html

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Artefacts from shipwrecks

An artefact is any object made by humans. Artefacts salvaged from shipwrecks are rarely in original condition because:

- most metals have corroded to some extent
- porous objects made of wood, leather or textile contain dissolved chloride and sulfate salts
- objects which have been recovered at depths less than 3 to 5 km under sea water are often covered with calcium carbonate deposits.

The extent of change to the artefact whilst under water depends on many factors such as depth, oxygen level, pH, ocean currents, the type of marine organisms present and length of time the object has been under water. A shipwreck contains many galvanic corrosion cells.

Dramatic deterioration in the condition of an artefact can occur as soon as it is exposed to air or starts to dry out. As salt water soaked artefacts dry out, the solution becomes saturated with salts normally in the order CaCO_3 , CaSO_4 , NaCl , MgSO_4 , MgCl_2 , NaBr , KCl . Salt crystals of different shapes and sizes form inside the artefact and their growth can destroy the structure of the artefact.



Investigate the effect of crystal growth on artefacts by placing some small pieces of fruit or salad in a freezer overnight. As the water in the plant cells freeze forming ice crystals damage will occur to the plant structure. Compare the structure of unfrozen and frozen samples.



Were all fruit pieces and salad plants damaged to the same extent?

Check your answer.

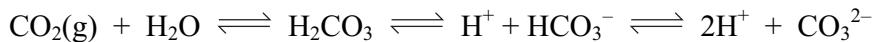
The growth of salt crystals as sea water soaked artefacts dry out can cause similar damage to that caused by growth of ice crystals. The slower the rate of evaporation of sea water the larger the crystals that form and the greater the damage to artefacts.

Restoration of artefacts

As well as being soaked with chlorides and sulfates many artefacts are covered with deposits. These deposits are called **encrustations** or **concretions**. These calcareous deposits are mostly of precipitated CaCO_3 and some $\text{Mg}(\text{OH})_2$ but can include sand, marine life and corrosion products. Typically their thickness ranges from a few millimetres in cold polar waters to 30-40 mm in warm tropical waters.



An important half reaction in corrosion is $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$. Explain how this reaction affects the equilibrium involving CO_2 and hence the precipitation of CaCO_3 as calcareous deposits.



Check your answer.

Concretion can surround an object which is then completely corroded away leaving a perfect mould. If an artefact contains two different metals the growth of an encrustation can separate the different metals and stop galvanic corrosion between the two metals.

A recommended procedure for treating artefacts brought to the surface, to restore them as close as possible to their original state, is listed below:

- 1 Wash with sea water to remove silt which is usually acidic.
- 2 Leave the artefact in sea water, pack in expanded plastic foam or plastic packaging bubbles and transport to a laboratory.
- 3 Identify the materials making up the artefact. This could be done by visual examination, X-ray imaging, testing for magnetism, chemical identification of corrosion products or even analysis of a small sample taken from the artefact.

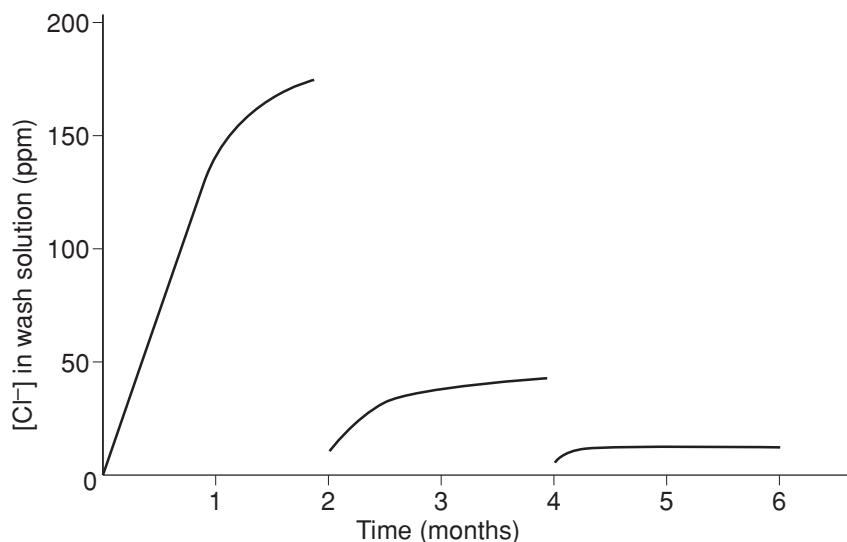
Non-destructive tests such as X-rays are preferred and should be completed before any destructive testing such as chemical analysis (of a small sample) occurs.

- 4 Wash in a mixture of fresh water and sea water followed by a wash of fresh water.
- 5 If robust enough, brush to remove attached concretions. Extra care is needed if there are different materials inside a concretion.
- 6 Store artefacts in water containing chemicals to remove or inhibit fungi and bacteria.
- 7 Salts can be removed by soaking in water over many weeks.

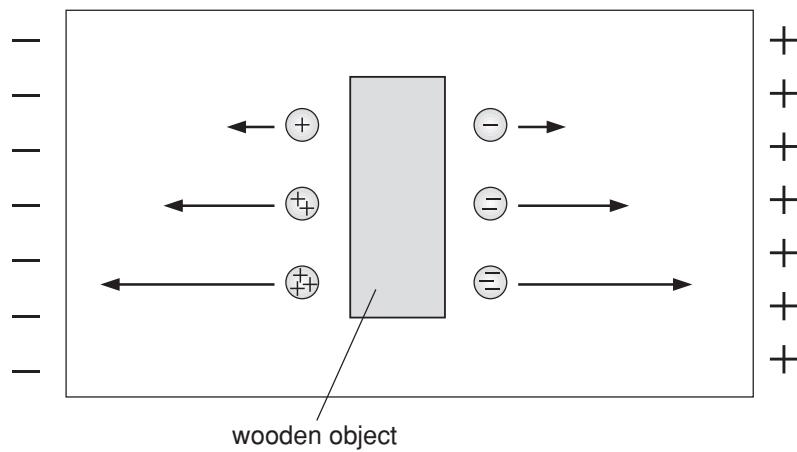


The graph below shows chloride ion concentration in wash solutions used to remove salt from an artefact.

- 1 How many different wash solutions were used? _____
- 2 Assess the value of leaving the artefact in wash solutions for six months.



Organic materials, such as wood, and ceramic materials, such as pottery, can be cleaned by **electrophoresis**. The artefact is placed between a positive electrode and a negative electrode which attract any charged particles out of the artefact to the electrode surfaces.



Electrophoresis withdrawing charge particles out of organic material.

Particularly valuable or highly corrosion-susceptible artefacts should undergo chemical treatment within minutes of reaching the atmosphere where the oxygen levels are so high. If the necessary laboratory facilities are not available to provide immediate restoration the artefacts should be left in the shipwreck until suitable treatment facilities are ready.

Concretions of CaCO_3 can be dissolved by soaking in 1 M HCl(aq) . If the release of carbon dioxide bubbles could damage the artefact's surface a milder acetic acid/sodium acetate buffer solution can be used.

Restoration of iron artefacts

Washing

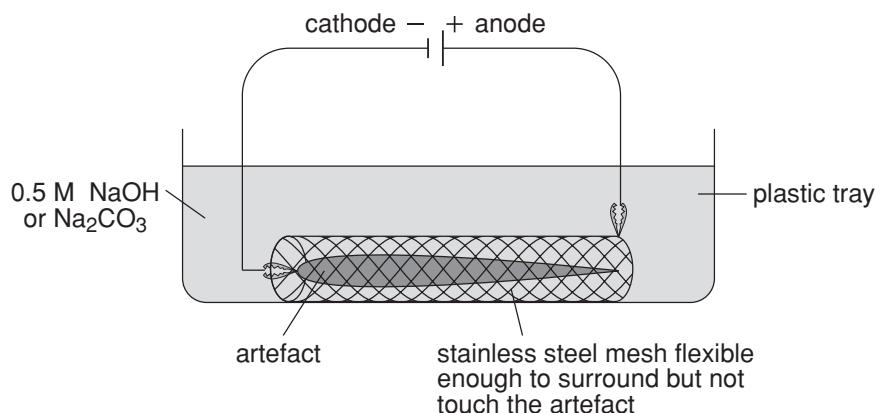
It can be difficult to remove salt from artefacts made of iron, the most common metal in shipwrecks, by just washing.

More effective methods for iron than washing are:

- soaking in dilute sodium hydroxide which forms protective oxide layers and converts FeCl_2 to Fe(OH)_2 releasing chloride ions
- electrolytically cleaning in an alkaline electrolyte.

Electrolysis

More extensive electrolysis stabilises the iron structure as well as removing salt. The iron artefact is made the cathode and placed in an alkaline solution (about 0.5 M NaOH or Na_2CO_3) containing a stainless steel anode. A small electric current attracts negative chloride ions out of the artefact to the anode.



If a high enough potential (voltage) is applied water is reduced at the artefact cathode.

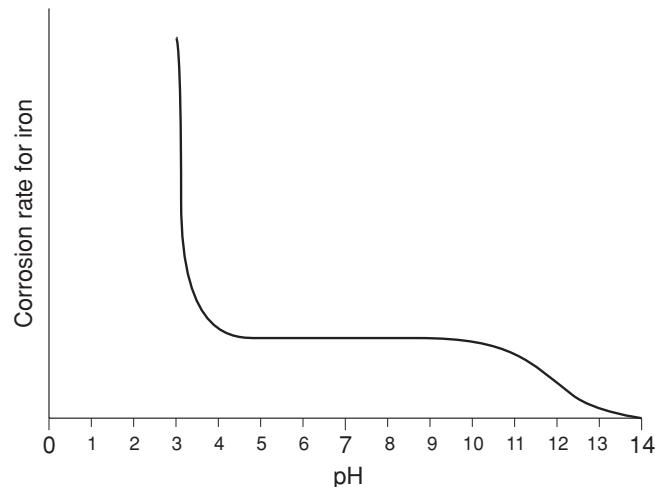
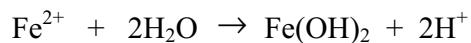
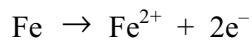
$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$$

The hydrogen bubbles produced at the surface loosen corrosion products and calcareous deposits. This is called electrolytic cleaning.

Corrosion of iron is reduced by including dithionite ions, $\text{S}_2\text{O}_4^{2-}$, in the alkaline solution. Dithionite is a reducing agent that inhibits further oxidation of iron.

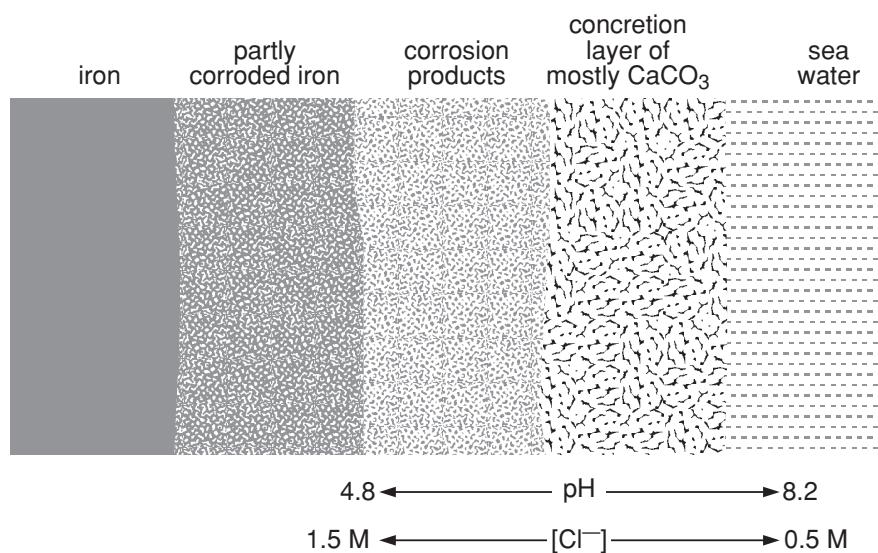
Why alkaline conditions are best

If iron oxidises to iron(II) ions which hydrolyse in water, the pH of the water could drop to 4 which makes the iron surface more susceptible to corrosion.



Concretions

Iron inside a concretion is surrounded by soluble iron(II) chloride FeCl_2 and insoluble iron(II) hydroxychloride Fe(OH)Cl . The chloride ion concentration is about three times that of the sea water outside the concretion.

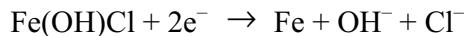
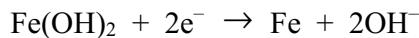


Electrolysis converts iron(II), but not iron(III) ions, back to iron atoms.

Electrolysis removes chloride ions by attraction to the anode as well as converting many iron(II) oxides and hydroxides back to iron.

Coral encrusted cannon from James Cook's ship *Endeavour* were conserved by treatment that included about eight weeks of electrolysis.

Possible cathode reactions are:



Give relevant balanced equations for the anode reactions where:

- a water is the electrolyte

-
- b a solution of NaOH is the electrolyte.
-

Check your answers.

Modern developments in restoration of iron

Modern developments heat the artefact to 120°C to remove water.

The artefact is then kept at 400°C in a stream of hydrogen for two days to reduce iron oxides to iron, then slowly cooled. At 100°C inert nitrogen gas replaces the hydrogen gas.



Give a word equation for the reaction of hydrogen with iron oxide.

Check your answer.

Next, electrolysis of the artefact in sodium hydroxide solution removes chloride ions. Negative chloride ions are attracted out of the corrosion layers towards the positive anode. At the anode, provided the voltage between cathode and anode is high enough, the chloride ions can be oxidised releasing chlorine gas.

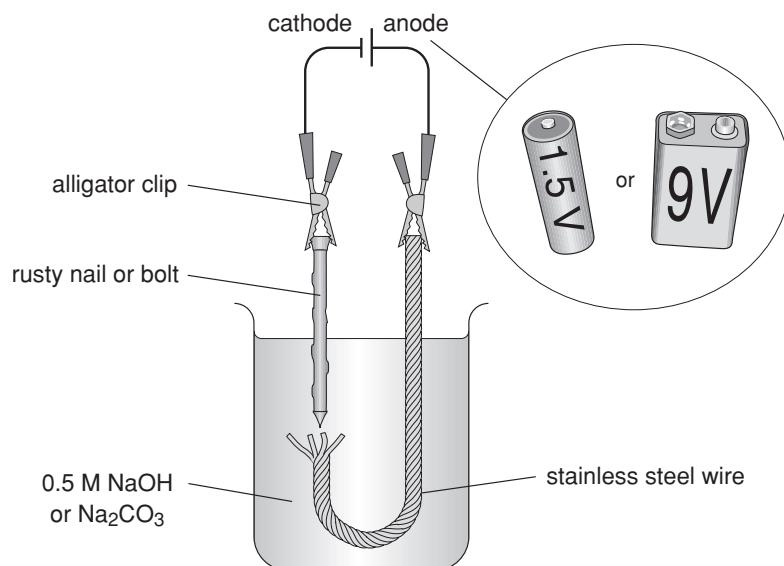


Give a half equation for the oxidation of chloride ions to chlorine gas.

Check your answer.

After drying a microcrystalline wax coat is applied to give a lustre to the iron surface and protect it from further corrosion.

A simple way of using electrolysis on iron

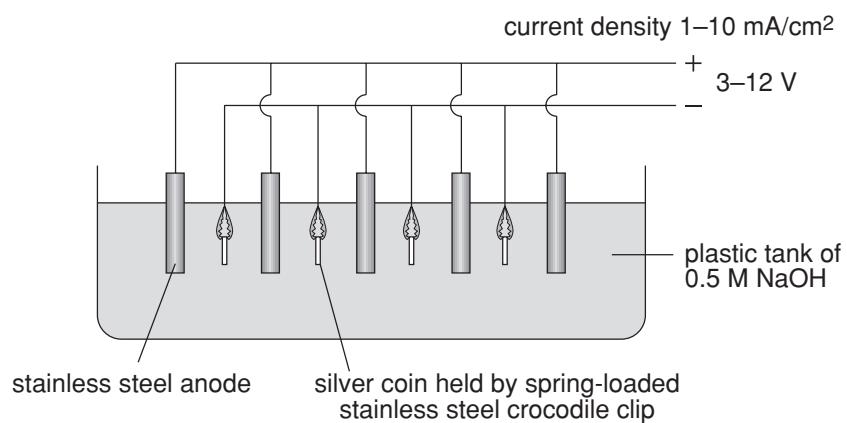


Restoration of silver and its alloys

Some silver alloys are found in surprisingly good condition. Silver has a very low activity and so other, more active metals in the alloy, present in small amounts, react first and provide electrons to protect the silver.

Have you ever eaten an egg with a silver plated spoon or noticed discolouration of silver jewellery? The silver surface darkens with deposits of silver sulfide compounds formed from reaction with sulfur compounds in the egg or sweat.

Here is a simple way of restoring the silver ions in the dark compounds back to silver atoms:



Restoration of copper and its alloys

Copper and its alloys bronze and brass are usually free of, or lightly covered with, marine growth. Released copper ions act as a **biocide**.

In a marine environment the most common surface layers are copper(I) chloride and copper(I) sulfide. Oxidation of these layers on exposure to air would produce acid which further degrades the artefact.

If the surface layers are thin and their loss is not critical the artefact could be placed in 5 to 10% citric acid. The thin surface layers of copper(I) chloride CuCl, copper hydroxychloride Cu(OH)Cl and copper(I) sulfide Cu₂S will dissolve.

Thicker layers may need oxidation to copper(II) followed by electrolysis to form Cu atoms.



Copper(II) chloride on a copper coin surface can be reduced to copper metal and chloride ions by electrolysis in water.

- 1 Draw a labelled diagram showing how you would carry out this process.

 - 2 Give equations for the anode and cathode reactions.
-
-

Check your answers.

Further corrosion of restored copper can be stopped by coating it with a transparent acrylic lacquer.

Restoration of lead

Lead has been used on ships for cannonballs, weights and protective sheeting. Lead corrodes less in sea water than most other metals.

When exposed to air, the coatings that form in marine environments (lead oxide, lead carbonate, lead chloride or lead sulfate), provide a protective layer preventing further oxidation.

Anaerobic marine environments can turn lead objects to black lead sulfide. Lead objects attached to wood are particularly affected as the decaying wood provides nourishment for sulfate reducing bacteria.

The condition of salvaged pewter, an alloy of lead and tin, depends on the amount of lead. Normally the higher the lead content, the better the condition of the artefact. This is because of formation of a protective layer of water insoluble lead sulfate.

If a lead artefact is lightly corroded washing in 10% hydrochloric acid to remove PbCO_3 , PbO , PbS and CaCO_3 encrustation may be adequate.

Soaking in a 5% EDTA (ethylenediaminetetra-acetic acid) solution can remove all lead compounds from the surface.

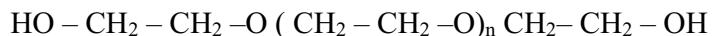
If the surface detail of a lead object is important, electrolysis in which the metal ions are reduced back to metal atoms is preferred. Equipment used is the same as for electrolytic reduction of iron artefacts – artefact as the cathode, stainless steel anode and an electrolyte of 0.5 M NaOH or Na₂CO₃.

Because lead hydroxide is soluble in alkaline solutions the current should be turned on before the lead artefact is immersed. Also great care should be taken that current flow is not stopped while the artefact is immersed in an alkaline solution. If no current is flowing lead oxide and lead hydroxide layers will dissolve in the alkaline solution; the lead ions in these layers are lost and not restored as lead atoms.

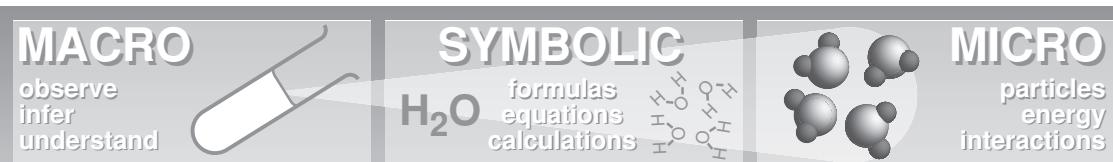
Restoration of wood

Conservation of wood involves stabilising the size and shape and providing durability.

The main method developed in the last fifty years is to bulk the wooden remains with a polymer called polyethylene glycol (PEG). Polyethylene oxide would be a better name for this polymer with the structure:



PEG is a synthetic wax completely soluble in water in all proportions. Increasing concentrations have been used in treatment of the famous 17th century Swedish ship *Wasa*, various Viking longboats and the *Batavia*, the second oldest shipwreck so far found in Australian waters.



Australian maritime archaeological projects

Conservation is the act of saving or preserving to prevent further deterioration. When an important shipwreck is discovered in Australia conservation is practically always used to preserve recovered artefacts. The artefacts may then be displayed in their conserved but incompletely restored state. Sometimes the shipwreck is conserved **in situ** (at the site) by measures such as adding sacrificial anodes or discouraging human activity near the site.

Full restoration involves restoring the artefact as close as possible to its original condition. This is a more difficult technique.

Australia, an island continent, has many shipwrecks. Historically important and unusual shipwrecks can become maritime archaeological projects for museums.

The list below shows some important Australian shipwreck archaeological projects:

Year	Ship /shipwreck / artefact	State
1622	Tryall	WA
1629	Batavia	WA
1770	Endeavour	Q
1790	Sirius	NSW
1791	Pandora	Q
1841	James Mathews	WA
1867	Zanoni	SA
1872	Xantho	WA
1875	Cambridgeshire	Tas

The oldest shipwreck discovered in Australia to date is the 1622 *Tryall* off Onslow in Western Australia. Three anchors and a cannon were recovered and conserved. Unfortunately an explosion carried out on the site by a diver seeking artefacts destroyed most of the shipwreck.

The Western Australian maritime museum has a display of part of the conserved hull of the *Batavia*. Many artefacts including stoneware ceramics and a bronze astrolabe have also been conserved. The bronze astrolabe was naturally preserved from being imbedded in concretions.

Captain Cook's ship *Endeavour* was temporarily stranded on a coral reef near present day Cooktown in Queensland in 1770. (The final shipwreck of *Endeavour* may lie near Rhode Island in the USA.) Cannons and other heavy objects were thrown overboard to help refloat the ship. In 1969, Cook's records of the 1770 location and modern magnetometers were used to detect the cannons covered by coral. One of the conserved cannons is now on display at the National Maritime Museum, Darling Harbour, Sydney.

The *Sirius* sank off Norfolk Island in 1790 two years after arriving at Sydney with the First Fleet. Sacrificial anodes have been attached to the wreck to conserve as yet unrecovered parts.

In 1841 the *James Matthews*, previously a slaveship, was wrecked off Western Australia. This was a copper sheathed wooden vessel and although in shallow water was protected by seagrasses which trapped sediment that covered the shipwreck. Activity at a nearby cement works jetty needs controlling to minimise disturbance to protective seagrasses.

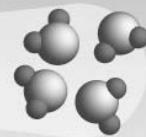
One of the most intact shipwrecks in Australian waters is the 1867 *Zanoni* in South Australia. Ships are sometimes sunk to provide places where fish will gather for recreational fishing. The *Zanoni* was being damaged by anchors from small fishing boats attracted to the site. In 1984 a barge was sunk about 2 km away to provide an alternative fishing site and a 550 m protection zone was provided around the *Zanoni* site.

The steam engine of the 1872 wreck *Xantho* has been recovered, over a tonne of concretion removed, and restoration carried out.

The iron hulled sailing ship the *Cambridgeshire* has been a source of artefacts for the Flinders Island Museum, Tasmania.



Go to <http://www.lmpc.edu.au/science> then *Chemistry*, then *Shipwrecks, corrosion and conservation* for more information about these Australian shipwreck sites, their exploration, conservation and restoration of artefacts.

MACROobserve
infer
understand**SYMBOLIC** H_2O formulas
equations
calculations**MICRO**particles
energy
interactions

Suggested answers

Artefacts from shipwrecks

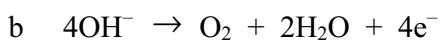
You should have found variations in resistance to freezing. For example carrots are much more resistant to changes in structure than lettuce.

Chemical procedures

The hydroxide ions produced will react with the hydrogen ions causing CO_2 equilibrium positions to shift to the right. This increases concentration of carbonate ions and precipitation of $CaCO_3$.

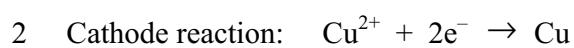
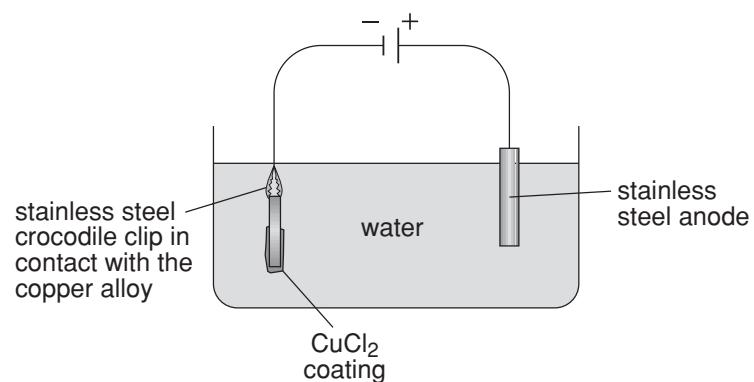
- 1 Three
- 2 Just over four months appears to be adequate washing time.
After this time there was no further indication of chloride ions entering the wash solution.

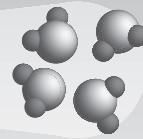
Restoration of iron artefacts



Restoration of copper and its alloys

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Exercises – Part 6

Exercises 6.1

Name: _____

Exercise 6.1: Comparing conservation and restoration techniques in Australian projects



After you have gone to <http://www.lmpc.edu.au/science> then *Chemistry*, then *Shipwrecks, corrosion and conservation* for more information about Australian shipwreck sites and conservation, answer the questions below.

- 1 Most maritime archaeological projects lead to conservation rather than restoration of the shipwreck or artefacts. Explain the difference between conservation and restoration and why restoration is less common than conservation.

- 2 Compare conservation techniques applied *in situ* at actual shipwreck sites with conservation techniques applied in laboratories.

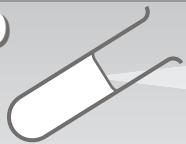
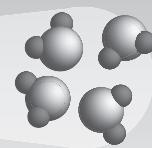
- 3 Compare conservation of the timber hull of the *Batavia* using PEG with conservation of the timber stocks of the *Endeavour* cannons.

- 4 Final treatment for the iron cannon of the *Endeavour* involves immersion in microcrystalline wax. Justify the use of this reversible treatment.

- 5 Suggest two materials suitable as sacrificial anodes for iron on shipwrecks.

- 6 Explain why the technique of using sacrificial anodes on shipwrecks is also called cathodic pretreatment.

- 7 Electrolysis in alkaline solutions can be used to restore iron, copper and lead artefacts. Explain why the current must be on before a lead, but not before an iron or copper, artefact is immersed in alkaline solution.

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Student evaluation of the module

Name: _____ Location: _____

We need your input! Can you please complete this short evaluation to provide us with information about this module. This information will help us to improve the design of these materials for future publications.

- 1 Did you find the information in the module clear and easy to understand?

2 What did you most like learning about? Why?

- 3 Which sort of learning activity did you enjoy the most? Why?
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- 4 Did you complete the module within 30 hours? (Please indicate the approximate length of time spent on the module.)
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- 5 Do you have access to the appropriate resources? eg a computer, the Internet, scientific equipment, chemicals, people that can provide information and help with understanding science.
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