Topic 4 Shipwrecks, Corrosion and Conservation	
Focus 1 The chemical composition of the ocean implies its potential role as an electrolyte.	
• **Identify the origins of the minerals in oceans as:** o **Leaching by rainwater from terrestrial environments** o **Hydrothermal vents in mid-ocean ridges**	There are many **ions** with small concentrations in the ocean. The main characteristic of the **ocean**, however, is its salt content. **Ions in the Ocean:** **Cations:** • Na^+ 0.470 mol L^{-1} • K^+ 0.010 mol L^{-1} • Mg^{2+} 0.053 mol L^{-1} • Ca^{2+} 0.010 mo, L^{-1} **Anions:** • Cl^- 0.550 mol L^{-1} • SO_4^{2-} 0.028 mol L^{-1} **Origins of the Minerals:** 1. **Leaching** from rocks and soil on land by rain and ground water results in large amounts of **dissolved ions** ending up in the **ocean**. 2. **Dissolution** of **salts** under the sea by water passing through **hydrothermal vents**. Water enters cracks in these vents and is super-heated to 350°C which increases the solubility of many ions after these are precipitated out as the water cools but may stay in **solution**.
• **Outline the role of electron transfer in oxidation-reduction reactions.**	**Oxidation-reduction** reactions are also known as either **redox reactions** or **electron transfer reactions**. **O**xidation **I**s **L**oss, **R**eduction **I**s **G**ain **OILRIG** **Electron transfer** can occur in two ways: • A transfer of **electrons** directly between **reactants** • A transfer of **electrons** from the **oxidation site** through a **conductor** to the **reduction site**. **Net Ionic Redox Reaction:** $Zn + 2H^+ \rightarrow Zn^{2+} + H_{2(g)}$ **Oxidation Half Equation:** $Zn \rightarrow Zn^{2+} + 2e^-$ **Reduction Half Equation:**

	$2H^+ + 2e^- \rightarrow H_{2(g)}$ **Redox Reaction Terms:** • A **redox reaction** is a reaction involving both a loss and gain of electrons. • A **cation** is a positive ion • An **anion** is a negative ion • An **oxidation reaction** involves a loss of electrons • A **reduction reaction** involves a gain of electrons • A **galvanic cell** is an electrochemical cell that changes chemical energy into electrical energy • An **electrolytic cell** is an electrochemical cell that changes electrical energy into chemical energy • An **electrolyte** is a liquid substance or solution through which ions can move • An **electrode** is a metal or graphite rod that transfers electrons in or out of an electrolyte • An **oxidant** is the oxidising agent • A **reductant** is the reducing agent • The **anode** is the electrode at which oxidation occurs • The **cathode** is the electrode at which reduction occurs
• **Identify that oxidation-reduction reactions can occur when ions are free to move in liquid electrolytes.**	**Redox reactions** can only occur when **ions** are free to move in solid and liquid **electrolytes**. In a **redox reaction**, **electrons** move from the **reductant** undergoing **oxidation** to the **oxidant** undergoing **reduction**. These reactions will only occur if the **ions** are free to move and an **electrochemical cell** is produced. The **circuit** must be complete and there must be no accumulation of charge. **Redox reactions** readily occur in seawater.
• **Describe the work of Galvani, Volta, Davy and Faraday in increasing understanding of electron transfer reactions.** • **Process information from secondary sources to outline and analyse the impact of the work of Galvani, Volta, Davy and Faraday in understanding**	**Luigi Galvani (1737 – 1798)** **Galvani** accidentally found that frog's legs moved when they came in contact with **two different metals**. He called this phenomenon '**animal electricity**.' • He was the first to observe the connection between two **different metals** and **electricity**. **Count Alessando Volta (1745 – 1827)** **Volta** was the first to demonstrate an **electrochemical cell**. This was the first ever battery. He called it the **voltaic pile**. • He disagreed with **Galvani** on the concept of **animal electricity** and demonstrated that it was simply the **two different metals** that were responsible for the production of **electricity**. **Humphrey Davy (1778 – 1829)**

electron transfer reactions.	**Humphrey Davy** constructed a powerful **battery** by placing **voltaic piles** in series and used this power to decompose compounds. This discovered many **new elements**. • He is the father of **electrolysis** • He discovered many **group 1** and **2** elements through **electrolytic decomposition**. **Michael Faraday (1791 – 1867)** **Faraday** followed and extended **Davy's** work. He was the first to **isolate benzene** and **liquefy chlorine**. • He developed the **laws of electrolysis**. He stated that the amount of **current** is directly **proportional** to the amount of **substance formed**. • He was the first to coin the terms: o Cation o Anion o Electrolyte o Electrode o Cathode o Anode
<u>Focus 2</u> Ships have been made of metals or alloys of metals.	
• **Account for the differences in corrosion of active and passivating metals.**	**Corrosion** is the **degradation** (or eating away) of a **metal** which causes it to lose strength and become unable to fulfil its intended purpose. When a metal **corrodes** it **oxidises** to its **cation**. Generally speaking, the **more active** a **metal**, the more likely it is to **corrode**. However, there are some **metals** that can resist **corrosion**. These are called **passivating metals**. **Passivating metals** are **metals** that readily form an **unreactive surface coating** with substances such as **oxygen**. This layer protects the metal from further **corrosion**. **Chromium** and **aluminium** are **passivating metals**. They react with the **atmosphere**, forming an **oxide film** that is **inert**, non-porous and adheres to the surface. $4Al_{(s)} + 3O_{2(g)} \rightarrow 2Al_2O_{3(s)}$ If this layer is removed or damaged, the layer quickly reforms providing **oxygen** is present. **Tendency of a Metal to Rust:**

	For a metal, *M*, the lower its **standard potential** the greater its **tendency to rust**.
• **Identify iron and steel as the main metals used in ships.**	The main metal used in **ships** today is **steel**. **Ships** also have various types of **iron** used in their construction.
• **Identify the composition of steel and explain how the percentage composition of steel can determine its properties.**	**Steel** is made from **iron**. **Iron** from the blast furnace is called **pig iron** and has more than **4% carbon** as well as silicon, manganese, phosphorous and sulfur. **Pig iron** is **brittle** and of little use. **Cast iron** is made from **pig iron** by removing phosphorous and sulfur and decreasing the percentage of **carbon** to **3%**. It also contains 1% manganese and 1.1% silicon. It is **hard** and resilient but is also **brittle**. It is used in anchors and chains on ships. **Wrought iron** contains less **carbon** than **cast iron** and the percentage of silicon and manganese is also reduced. It is more **malleable** than **cast iron**. **Steel** is produced from **cast iron** by lowering its **carbon content** and adding other **elements**. **Properties of Steel:** • **Steel** is an alloy with no more than **2% carbon** • The **carbon** may form **cathodic sites** where reduction can take place. • **Mild steel** contains less than **0.2% carbon**. It is soft, malleable and readily corrodes. • **Structural steel** contains between **0.2%** and **0.5% carbon**. It is hard but malleable with high tensile strength. • **Stainless steel** is like **mild steel**. It contains less than **0.2% carbon** but also contains **5-10% nickel** and **10-20% chromium**. Generally speaking, the **higher** the **carbon content**, the **harder** the **steel** and the more likely it is to be **brittle**.
• **Describe the conditions under which rusting of iron occurs and explain the process of rusting.**	**Conditions for Rusting:** • Both **oxygen** and **water** are required. **Oxygen** will be **reduced** and a conducting film of liquid is needed to complete the circuit. • **Impurity sites** are needed to act as **cathodes** where **oxygen** can be **reduced**. Very pure **iron** corrodes slowly due to low amounts of impurities. • The **reduction process** becomes very rapid when **iron** is in contact with **less reactive metals** such as copper. This is because the **less reactive metal** provides a much

	larger site for **reduction** than the tiny carbon impurities in **steel**. • When **iron** is under stress (bends, edges, breaks), the **orderly crystal structure** is distorted. This makes it easier for the **iron** atoms to break away from the lattice to form Fe^{2+}. • When two metals are in contact, the one with the lowest **standard potential** will **corrode** (oxidise to cation) more easily than the other. **Process of Rusting:** At some spot on the **iron surface**, **iron atoms** lose **electrons** to form **cations**. $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ Sites where this **oxidation** occurs are called **anodic sites**. These **free electrons** now flow through the **iron lattice** to some other place on the surface (usually where a carbon impurity is) and **reduce oxygen** that is dissolved in the **liquid electrolyte**. $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ Sites where this **reduction** of **oxygen** occurs are called **cathodic sites**. The **Fe^{2+} ions** created during the first part of the process have since travelled through the **electrolyte solution** and they meet up with the **OH^- ions** created at the **cathode**. They then form an **insoluble iron (II) hydroxide**. $Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$ **Iron (II) hydroxide** however, is easily oxidised to **iron (III)** by **oxygen**, forming **rust**. $4Fe(OH)_2(s) + O_2(g) \rightarrow 2(Fe_2O_3.H_2O)(s) + 2H_2O(l)$
• **Identify data, select equipment, plan & perform a first-hand investigation to compare the rate of corrosion of iron and an identified form of steel.**	Experiment: Aim: To compare the rates of corrosion of stainless steel, mild steel and iron. Method: 1. Place each of the samples in a separate test tube and completely submerge with salt water. 2. Leave for one week. 3. Record observations. Conclusion: The stainless steel showed no signs of rusting but the mild steel and iron did rust. The mild steel rusted more than the iron and this is due to the

internal carbon cathodic sites that exist in mild steel.

- **Use available evidence to analyse and explain the conditions under which rusting occurs.**

Conditions for Rusting:

- Both **oxygen** and **water** are required. **Oxygen** will be **reduced** and a conducting film of liquid is needed to complete the circuit.
- **Impurity sites** are needed to act as **cathodes** where **oxygen** can be **reduced**. Very pure **iron** corrodes slowly due to low amounts of impurities.
- The **reduction process** becomes very rapid when **iron** is in contact with **less reactive metals** such as copper. This is because the **less reactive metal** provides a much larger site for **reduction** than the tiny carbon impurities in **steel**.
- When **iron** is under stress (bends, edges, breaks), the **orderly crystal structure** is distorted. This makes it easier for the **iron** atoms to break away from the lattice to form Fe^{2+}.
- When two metals are in contact, the one with the lowest **standard potential** will **corrode** (oxidise to cation) more easily than the other.

- **Gather and process secondary information to compare the composition, properties and uses of a range of steels.**

Name	Composition	Properties	Uses
Mild Steel	Less than 0.2% carbon.	Easily welded. Soft. Malleable Readily corrodes	Cars, ships.
Structural Steel	Between 0.2% & 0.5% carbon.	Hard but malleable. High tensile strength.	Buildings, railways
Stainless Steel	Like mild steel. 5-10% nickel. 10-20% chromium.	Does not corrode easily.	Ships, cutlery.

<u>Focus 3</u>

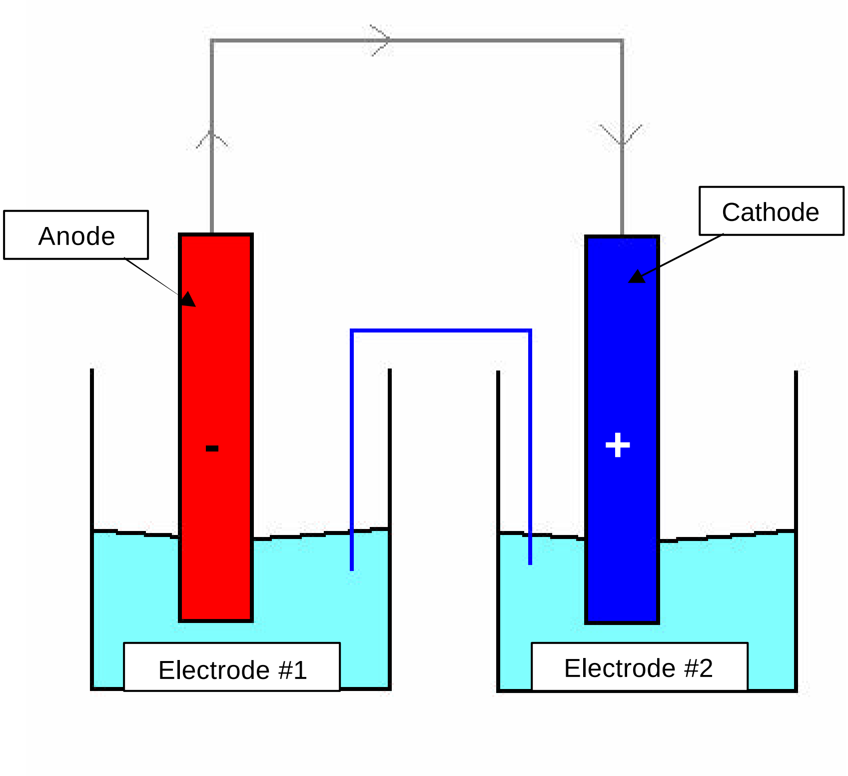
Electrolytic cells involve oxidation-reduction reactions.

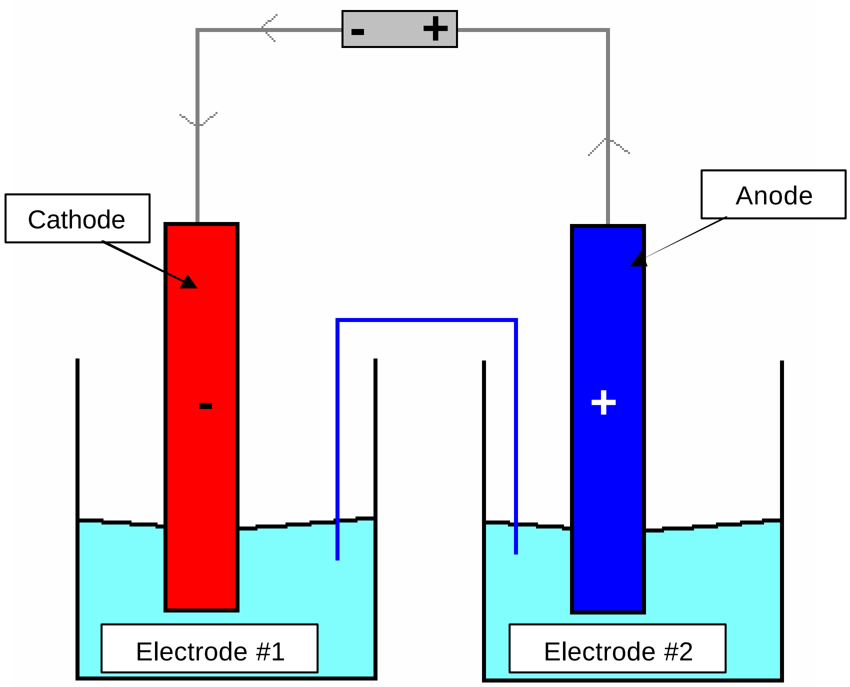
- **Describe, using half-equations, what happens at the anode and cathode during electrolysis of selected aqueous solutions.**

In an **electrolysis reaction**, a **transfer of electrons** takes place.

Electrolytic cells carry out the reverse reaction to a **galvanic cell**. They convert **electrical energy** into **chemical potential energy**.

- **OX**idation occurs at the **AN**ode (**AN OX**)
- **RED**uction occurs at the **CAT**hode (**RED CAT**)

	For an **electrolytic cell** to operate, it requires an input voltage that is greater than the **standard potential** of the cell. In an **electrolytic cell**, the electrode to which the electrons flow, the **cathode**, is negative. **Galvanic Cell:**  This is now the exact same cell but with a power supply added. **Electrolytic:**

	 **Example:** The electrolysis of $CuSO_4$. Copper metal is produced at the **cathode**: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ And O_2 forms at the **anode**. In this **electrolysis reaction**, sulfate ions migrate to the **anode** but are too stable to be oxidised so water is oxidised instead. $2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$ Doubling the first equation and adding it to the second we get: $2Cu^{2+}(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 4H^+(aq)$
• **Describe factors that affect an electrolysis reaction** o **Effect of concentration** o **Nature of electrolyte** o **Nature of electrodes**	**Factors that affect the rate of electrolysis:** • The **greater the conductance**, the **greater the voltage** and hence the **greater the rate of electrolysis**. **Factors Affecting the Conductance** • The **higher the concentration of ions**, the greater the **conductance**. The greater the conductance, the greater the current and hence, the greater the rate of electrolysis. • The **greater the surface area** of the electrodes, the greater the **conductance**. • The **shorter the distance** between the electrodes, the

greater the **conductance**.

- Changing the anode to a new substance that has a lower standard potential will decrease the voltage required for electrolysis to occur.
- Changing the anode to an inert one will mean that the anion in the electrolyte will be oxidised.
- Using an electrolyte that contains anions with a lower standard potential than the anode will cause the anion to be oxidised instead of the anode itself.
- Using an electrolyte that contains cations with a higher standard potential than the cathode will cause the cation to be reduced instead of the cathode itself.

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

Experiment:

Aim:

To identify factors that affect the rate of electrolysis.

Method:

1. Set up 6 beakers each with two strips of copper connected to a battery pack by alligator clips.
2. Before attaching copper strips, cleaned and weighed them.
3. Connected up the copper wires and set up six different tests:

Test #	Electrode Length (cm)	Electrode Separation (cm)	Electrolyte Conc. (mol/L)	Voltage (V)
1	2	2	1.0	2
2	2	2	1.0	4
3	2	2	1.0	6
4	5	2	1.0	2
5	2	5	1.0	2
6	2	2	0.1	2

4. Turned on the power packs and allowed to run for 30 minutes ensuring all tests were undertaking electrolysis for the same duration.

Results:

Test #	Mass of Anode (g)			Mass of Cathode (g)		
	Initial	Final	Change	Initial	Final	Change
1	4.00	3.87	-0.13	3.21	3.34	0.13
2	5.08	4.93	-0.15	5.61	5.77	0.16
3	5.07	4.87	-0.20	5.00	5.21	0.21
4	16.41	16.22	-0.19	17.52	17.71	0.19
5	3.08	3.02	-0.06	2.89	2.94	0.05
6	5.11	5.10	-0.01	3.59	3.61	0.02

Conclusion:

- The greater the voltage, the greater the rate of electrolysis.
- The greater the distance of separation, the lesser the rate of electrolysis.
- The larger the surface area of the electrodes, the greater

	the rate of electrolysis. • The greater the concentration of the electrolyte, the greater the rate of electrolysis.
<u>Focus 4</u> Iron & steel corrode quickly in a marine environment and must be protected.	
• **Identify the ways in which a metal hull may be protected including:** o **Corrosion resistant metals** o **Development of surface alloys** o **New paints**	**Corrosion Resistant Metals:** **Corrosion resistant** metals can be used, such as **stainless steel**, but this generally does not occur on large projects such as ships as it is **too expensive**. **Surface Alloys:** With **surface alloys**, the **steel** surface is alloyed with **chromium** and **nickel**. The **ions** of these metals bombard the surface and are embedded as atoms. The ions are in the form of **plasma**. Once a **surface alloy** has been created, it is very similar to **stainless steel**. **New Paints:** Nowadays, there are **polymer based paints** available that contain additives that form a very insoluble substance with the steel called **pyroaurite**. The additives contain **cations** that are mixed **hydroxides** such as: • $M_2Z(OH)_6^+$ • $M_3Z(OH)_8^+$ • $M_4Z(OH)_{10}^+$ Where M is a **2+ ion** (eg: Mg, Zn, Fe, Co, Ni) and Z is a **3+ ion** (eg: Al, Mn, Fe). The **iron ions** come from the **steel** and the accompanying **anions** are generally Cl^-, SO_4^{2-} or CO_3^{2-}. This **ionic layer** extends into the **polymer layer** and prevents a migration of ions on the steel surface, hence preventing **corrosion**.
• **Predict the metal which corrodes when two metals form an electrochemical cell using a list of standard potentials.**	When **two metals** come in contact, the one with the **lowest standard potential** will **corrode** (oxidise to cation) more easily than the other. This metal will hence become the **anode**.
• **Outline the process of cathodic protection, describing examples of its use in both marine and**	**Cathodic protection** is a method of protecting a metal from **corrosion** by making it the **cathode** of a **galvanic cell**. There are three types of **cathodic protection**: **galvanising**, **sacrificial anodes** and **applied voltages**. **Galvanising:**

wet terrestrial environments. • **Describe the process of cathodic protection in selected examples in terms of the oxidation/reduction chemistry involved.** • **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.**	**Galvanising** is where **iron** is coated with **zinc**. This has a special advantage in that the surface is **self-repairing** if scratched. The **zinc** and **iron** create a **galvanic cell** where the zinc is the **anode** and the iron is the **cathode**. Any iron that is **oxidised** is then displaced by Zn^{2+} ions. Also occurring is: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ The Zn^{2+} and OH^- combine forming $Zn(OH)_2$ that covers the scratch and protects the steel again. The two reduction half equations are: $Fe^{2+} + 2e^- \rightarrow Fe(s)$ E = -0.45V $Zn^{2+} + 2e^- \rightarrow Zn(s)$ E = -0.76V As the **zinc** has the **lower standard potential**, it becomes the **anode** and is **oxidised**, displacing any Fe^{2+} formed. $Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+} + Fe(s)$ Some of the $Zn(OH)_2$ formed is converted to $ZnCO_3$ and these reform the impervious layer. **Sacrificial Anodes:** **Sacrificial anodes** are blocks of **magnesium** or **zinc** attached to the hull if a ship, buried tank or pipeline, that **corrodes** preferentially. The **zinc** or **magnesium** block, and the potential sites for **corrosion** must be connected by a **moderately conducting medium**. These mediums act as the **salt bridge**. As the **sacrificial anodes** are only able to protect steel within a particular distance (many metres), large ships must have many attached. **Zinc** and **magnesium** are usually used because their rate of **corrosion** is slow but can still provide enough current to protect the **steel**. **Applied Voltage:** **Inert electrodes** insulated from the hull are placed below the water level and a **voltage applied**. The **voltage** forces **electrons** into potentially active sites on the **steel**. This prevents **oxidation** in the same way as the use of **sacrificial anodes**. **Reasons for Cathodic Protection:** • **Cathodic protection** is done to protect ships and other

	marine vehicles from **corrosion**.
• **Identify data, gather and process information from secondary sources to trace historical developments in the choice of materials used in the construction of ocean going vessels with a focus on the metals used.**	**Early vessels** were made from organic materials that float, for example **timber**. **Metals** started to make their way into ship construction in the use of **keels**, **anchors** and **cannons**. These items were normally made from **wrought iron** or **bronze**. **Lead sheeting** was introduced in the 17th century and this was nailed onto the timber hulls. The purpose of this was to stop marine life attacking the **timber hull**. **Copper sheeting** was the next metal used, and it replaced **lead sheeting** because it was toxic to marine life, meaning no organisms would grow on it. **Brass sheeting** replaced **copper sheeting** because it was **cheaper** and more **corrosion resistant**. Around the 1600's, more and more ships were using **iron** for materials. In 1818, the first **all iron ship**, 'The Vulcan' was launched. Around 1900, **steel** was becoming the preferred material for ships as it was **stronger** and **lighter**. However, the ships had to be washed and dry-docked because of the threat of **corrosion**. Nowadays, various additives such as **chromium**, **zinc** and **nickel** are added to make the **steel** more resistant to **corrosion**.
• **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.**	<u>Experiment:</u> <u>Aim:</u> To identify, from a variety of metals, which materials would be more suitable to use in ship construction based on their resistance to corrosion. <u>Method:</u> 1. Set up five test tubes each with the same amount of salt water at the same concentration. 2. Placed a sample of each of the metals in a separate test tube. 3. Allowed to corrode for a week and observed results. <u>Conclusion:</u> The order of corrosion from most corrosion to least corrosion was: • Mild Steel • Aluminium • Copper • Brass • Stainless Steel From this information, stainless steel would be the most

	suitable material but other factors such as cost need to be considered.
• **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.**	Experiment: Aim: To compare the effectiveness of different protective coatings in preventing corrosion. Method: 1. Cleaned 12 iron nails and 3 galvanised nails 2. Covered three nails with grease. 3. Covered three nails with 'Kill Rust.' 4. Covered three nails with enamel paint 5. Left three nails as a control. 6. Did not cover the galvanised nails with anything. 7. Leave each of the tests in a separate agar plate for a week. Results: • The best protection was the galvanised nails. They showed no signs of rust at all. • The next best was the 'Kill Rust,' which only had small amounts of rust. • The enamel paint covered nails only corroded slightly more than the 'Kill Rust' nails. • The grease was the next best, with the nails only rusting where the grease was thin. • The control nails corroded strongly.
Focus 5 **When a ship sinks, the rate of decay and corrosion may be dependant on the final depth of the wreck.**	
• **Outline the effect of:** o **Temperature** o **Pressure** **On the solubility of gases and salts.**	**Gases:** • **Solubility** of a **gas increases** as **pressure** of that gas in contact with the solution **increases**. • **Solubility** of **gases decreases** as **temperature increases**. **Salts:** • Generally, the **solubility** of **salts increase** with **increased temperature** but there are some exceptions. • The **solubility** of **salts** is mostly **unaffected** by **pressure**.
• **Identify that gases are normally dissolved in the oceans and compare their concentrations in the oceans to their concentrations in**	There are many **gases** that a normally found **dissolved** in the **ocean**. These include **nitrogen**, **oxygen** and **carbon dioxide**.

Gas	% Volume in Air	% Volume in the Ocean
Nitrogen	78.1%	0.8 – 1.5%
Oxygen	20.9%	0 – 0.9%

the atmosphere.

Carbon Dioxide	0.03%	4.5 – 5.4%

- **Carbon dioxide** levels are high due to the reactions that occur with water to produce more soluble ions.
- **Oxygen** levels vary with the presence of photosynthetic organisms and consumers.

- **Compare and explain the solubility of selected gases at increasing depths in the oceans.**

Since the **solubility** of **gases increase** with **increasing pressure** and **decreasing temperature**, the **solubility** of most **gases increase** with **ocean depth**.

This is because the **temperature** of the ocean **decreases** with **depth**, **increasing solubility**. Also, the **pressure increases** with **depth** and this also **increases solubility**.

The following table compares the **saturation concentration** of oxygen and carbon dioxide at different temperatures.

Gas	Oxygen	Carbon Dioxide
Saturation at 0 °C	70 mg/L	3360 mg/L
Saturation at 20°C	40 mg/L	1720 mg/L

- **Predict the effect of low temperatures at great depths on the rate of corrosion of a metal.**

Based on the information contained above, a **metal** should **corrode** very slowly in the ocean depths due to a **low temperature** down there.

- **Perform a first-hand investigation to compare and describe the rate of corrosion of materials in different:**
  - **Oxygen concentrations**
  - **Temperatures**
  - **Salt Concentrations**

<u>Experiment:</u>

<u>Aim:</u>

To compare the effect that oxygen concentrations, temperature and salt concentration have on the corrosion of metals.

<u>Method:</u>

1. Set up three test tubes each with a cleaned iron nail.
2. Filled one with water and oil, completely covering the nail. Partially filled another with water so part of the nail was in the air, and completely filled the final test tube with water so the nail is covered.
3. Allowed these three to sit for a week.
4. Set up four more test tubes each containing a cleaned iron nail.
5. Filled them one by one with distilled water, 0.01 mol/L salt water, 0.1 mol/L salt water and 1.0 mol/L salt water respectfully.
6. Allowed to sit for a week.
7. Set up three more test tubes each containing a clean iron nail.
8. Filled them all with the same volume of salt water that was of the same concentration.
9. Placed one in the fridge, another in an oven and left the third at room temperature.
10. Allowed them to sit for a week.

	11. Collected all 10 test tubes and recorded results. Results: For the first three test tubes, the order of most corrosion to least corrosion was: • Partially covered iron nail • Fully covered iron nail • Water covered nail with oil For the set of four test tubes, the order of most corrosion to least corrosion was: • 1.0 mol/L salt water • 0.1 mol/L salt water • 0.01 mol/L salt water • Distilled water control For the final set of three test tubes, the order from most corrosion to least corrosion was: • Warm temperature • Room temperature • Cold temperature Conclusion: From these results, we are able to conclude that: • Oxygen is required for corrosion. The more oxygen, the greater the rate of corrosion. • The higher the salt concentration of a particular electrolyte, the greater the rate of corrosion. • The warmer the temperature, the greater the rate of corrosion.
• **Use available evidence to predict the rate of corrosion of a metal wreck at great depths in the oceans and give reasons for the predictions made.**	Many scientists believed that **corrosion** would take place slowly at **ocean depths**. They concluded that from the following set of arguments for, and against **corrosion**. **For Corrosion:** • Sea water is a good electrolyte • Steel and iron are prone to corrosion • There are less active metals present **Against Corrosion:** • Sea water has a basic pH (8) • The temperature at those depths is extremely low. • There is low amounts of oxygen • There are more active metals present.
Focus 6 **Predictions of slow corrosion at great depths were apparently incorrect.**	
• **Explain the ship wrecks at great depths are corroded by**	Many scientists believed that **corrosion** would occur slowly at great depths due to the extremely **low temperatures**. When the *Titanic* was discovered, it changed the way scientists thought about **corrosion**.

For Corrosion	Against Corrosion
• Sea water is a good electrolyte • Steel and iron are prone to corrosion • There are less active metals present	• Sea water has a basic pH (8) • The temperature at those depths is extremely low. • There is low amounts of oxygen • There are more active metals present.

electrochemical reactions and by anaerobic bacteria. • **Describe the action of sulfate reducing bacteria around deep wrecks.**	Much of the **corrosion** that occurs at great depths is caused by **bacterial corrosion**. There are some forms of **anaerobic bacteria** that obtain their energy by reducing **sulfate** to **sulfide**. $SO_4^{2-}(aq) + 5H_2O(l) + 8e^- \rightarrow HS^-(aq) + 9OH^-(aq)$ Chemically, this reaction is very slow, but can be brought about more rapidly by bacteria of the **desulfovibrio** family. The **oxidation** half reaction is the normal **oxidation** of **iron**. $4Fe(s) \rightarrow 4Fe^{2+}(aq) + 8e^-$ If we add these two equations we get the overall equation to be: $4Fe(s) + SO_4^{2-}(aq) + 5H_2O(l) \rightarrow 4Fe^{2+}(aq) + HS^-(aq) + 9OH^-(aq)$ The **Fe^{2+}** formed reacts with HS^- and OH^- to form the insoluble **FeS** and **$Fe(OH)_2$**. $4Fe^{2+}(aq) + HS^-(aq) + 7OH^-(aq) \rightarrow FeS(s) + 3Fe(OH)_2(s) + H_2O(l)$ By equating these last two formulas we get the formula for the overall process. $4Fe(s) + SO_4^-(aq) + 4H_2O(l) \rightarrow FeS(s) + 3Fe(OH)_2(s) + 2OH^-(aq)$ Black **iron(II) sulfide** forms on the steel along with **iron(II) hydroxide**, which, in the absence of **oxygen** is not converted to **iron(III)** as in normal **corrosion**. This **corrosion** by **bacterial reduction** of **sulfate** accounts for much of the **corrosion** on deeply submerged shipwrecks. It forms as fingers of reddish-brown growth called **rusticles** that hang from the steel structure.
• **Explain that acidic environments accelerate corrosion in non-passivating metals.**	**Corrosion** is accelerated in **acidic environments**. The reason for this can be established by examining the half reaction of normal **galvanic corrosion**. $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ When **acidic conditions** are introduced, the **electrode potential** of the cell rises from 0.4V to 0.99V for a pH of 4. When working with **acidic conditions**, the half reaction is written in terms of **H^+** instead of using OH^-. In **acidic conditions**, the half reaction becomes: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Whilst these two reactions may look different, they are essentially still the **reduction** of **oxygen** to **water**.

Normally the ocean has an **alkaline pH**, but around shipwrecks **bacteria** are present in large amounts. These bacteria produce **hydrogen ions** during their metabolism and this can give the ocean surrounding a shipwreck an **acidic pH**, which increases the rate of **corrosion**.

- **Perform a first-hand investigation to compare and describe the rate of corrosion of metals in different acidic and neutral solutions.**

Experiment:

Aim:

To compare the rate of corrosion in different solutions.

Method:

1. Set up three test tubes each with a cleaned iron nail that has been weighed.
2. Fill one test tube with distilled water, one with an acid and one with a base, ensuring that each test tube was filled with the same amount of solution.
3. Left to sit for a week.
4. Recorded qualitative data on the rusting of each of the three nails.
5. Re-weighed each of the three nails

Results:

Solution	pH	Starting Mass (g)	Final Mass (g)	Rust?
Control	7	0.21	0.19	Medium
Acid	4	0.19	0.15	Lots
Base	11	0.19	0.19	None

The most corrosion occurred in the acidic conditions.

Focus 7

Salvage, conservation and restoration of objects from wrecks requires careful planning and understanding of the behaviour of chemicals.

- **Explain that artefacts from long submerged wrecks will be saturated with dissolved chlorides and sulfates.**

Apart from being valuable in their own right, **artefacts** from shipwrecks can provide insight into the technology and way of life in past eras.

Often, however, these artefacts are in poor condition.

- **Metals** can be seriously **corroded**.
- **Artefacts** are often encrusted with **calcium carbonate** and coral, etc. These are known as **concretions** or **encrustations**.
- Porous objects, particularly those of organic origin, are often impregnated with dissolved **chlorides** and **sulfates**.

- **Describe the**

When **artefacts** are first pulled from the **ocean,** they are washed clean of silt. Once this has been completed, the

processes that occur when a saturated solution evaporates and relate this to the potential damage to drying artefacts.	**artefacts** must be dried out. Great care must be taken when drying out artefacts recovered from the sea. As they have absorbed sea water, they are filled with **dissolved salts**. When they begin to dry out, the **evaporation** of water will leave **saturated solutions** and then the **crystallisation** of **salts**. Once these particles have become solid, they pose a threat to the **artefact** as they can cause pressure in the structure, leading to **weakening**, **cracking** and **deformation** of the objects. Therefore, before an **artefact** can be dried out it must be **desalinated** first. **Desalination:** To **desalinate artefacts** they are soaked in fresh water or dilute **NaOH**. The solutions are regularly changed which encourages further **diffusion of salts** until almost all of the **soluble salts** are removed. There are, however, significant amounts of chlorides present in the form of **insoluble hydroxy chlorides** (eg: Fe(OH)Cl or Cu(OH)Cl).
• **Identify the use of electrolysis as a means of removing salt.**	As mentioned above, there are some **insoluble hydroxy chlorides** left over from the **desalination** process. These salts are able to be removed by **electrolysis**. The problem with these **chlorides** is that they can form **hydrochloric acid** and restart the **corrosion** process. $Cu(OH)Cl(s) + H_2O(l) \rightarrow Cu(OH)_2(s) + HCl(aq)$ $Fe(OH)Cl(s) + H_2O(l) \rightarrow Fe(OH)_2(s) + HCl(aq)$ The second reaction is also accompanied by the **oxidation** of Fe^{2+} to Fe^{3+} leading to the overall reaction: $4Fe(OH)Cl(s) + 6H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s) + 4HCl(aq)$ To remove the remaining **chlorides**, **electrolysis** is used. The metal object is made the cathode and a stainless steel **anode** is used. These **electrodes** are immersed in a solution of 0.5 mol/L NaOH. At the cathode: $Fe(OH)_2(s) + 2e^- \rightarrow Fe(s) + 2OH^-(aq)$ & $Fe(OH)Cl(s) + 2e^- \rightarrow Fe(s) + OH^-(aq) + Cl^-(aq)$ These reactions free **Cl^-** and **OH^-** from the solid and they migrate towards the **anode**. While they don't react they are at least moved out of the iron and into solution. Depending on the size of the object this process can take many weeks.

	The reaction at the **anode** is the normal **oxidation** of water to oxygen. $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ Or more appropriately for the alkaline conditions. $4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-$
• **Identify the use of electrolysis as a means of cleaning and stabilising iron, copper and lead artefacts.**	**Iron** **Iron objects** are restored using mechanical and chemical removal of **concretions** and **electrolyte removal** of **chlorides**. The **electrolysis** also restores iron oxide back to iron. In recent times, **reductive heating** and **electrolytic removal** of residual **chlorides** has been employed. • Object heated to 120°C to remove water. • It is then heated to 400°C in a stream of hydrogen for several days to reduce iron oxide to iron. • As it cools to approximately 100°C, the H_2 is replaced with N_2. • It is then placed in NaOH to prevent corrosion and electrolysed to remove Cl^-. • It is then washed, dried and coated in wax for long term stabilisation. **Copper & Copper Alloys** Marine organisms don't readily grow on **copper** based artefacts due to the toxicity of the **copper ions**. They do, however, form surface layers of **copper(I) chlorides** and **copper(II) hydroxy chlorides**. These are removed by **chemical stripping**. The artefact is soaked in a solution of **5-10% citric acid** with **1-2% thiourea** (a corrosion inhibitor). This process strips the surface back to bare metal. **Residual Cl^-** is removed through **electrolysis** but **Na_2CO_3** solution is used as zinc and tin dissolve in NaOH. It is then coated with a clear lacquer. **Lead** As with copper, **lead's toxicity** prevents marine growth. Any **CO_3^{2-} concretions** that do form are removed with dilute HCl. The objects are then soaked with **EDTA** which removes the insoluble lead compounds due to the strong bonds formed with Pb^{2+} ions. The solution is **buffered** to a pH of 10-11. Leaching with H_2O or **electrolysis** is used to remove Cl^- ions. As lead also reacts with NaOH, **Na_2CO_3** is once again used as the **electrolyte**. It is then finally coated with a clear lacquer.
• **Discuss the range**	**Removing Crusty Deposits**

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.	The more readily available food supply provided by materials in ship wrecks leads to increased populations of bacteria and other organisms. Higher **concentrations of CO_2** are produced as a result of the metabolism of these **organisms**. This extra CO_2 leads to the precipitation of **$CaCO_3$**. $CO_2(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + HCO_3^-(aq)$ $HCO_3^-(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + CO_3^{2-}(aq)$ The equilibrium of both these reactions is pushed to the right by increased **concentration of CO_2**. $Ca^{2+}(aq) + CO_3^{2-}(aq) \leftrightarrow CaCO_3(s)$ As a result of this, many **artefacts** recovered from wrecks are covered with **crusty deposits of $CaCO_3$**. There are two ways of removing these **concretions/encrustations**. • **Physical Removal** – the concretions are hit with a hammer to chip it away. • **Chemical Removal** – the artefact is treated with acid. $CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$ o Typically, 1 mol/L HCl is used although if the artefact is very fragile, a weak acid is used instead such as acetic acid. The weak acid reduces the vigour of CO_2 evolution. **Restoring Silver Artefacts** **Silver artefacts** such as coins or cutlery are often covered with **silver sulfide**. **Desulfouibrio bacteria** reduce sulfate to sulfide which forms HS^-, which is in equilibrium with H_2S. H_2S reacts with silver. $HS^-(aq) + H_2O(l) \leftrightarrow H_2S(aq) + OH^-(aq)$ $2Ag(s) + H_2S(aq) \leftrightarrow Ag_2S(s) + H_2(g)$ The black sulfide layer protects the metal from further **corrosion** and the object gradually becomes covered with **carbonate concretions**. These concretions are removed using acid. **Electrolysis** is used to remove the Ag_2S by reversing the formation process. The following equation occurs at the **cathode**. $Ag_2S(s) + 2e^- \rightarrow Ag(s) + S^{2-}(aq)$

	The **electrolyte** used in the above reaction is **NaOH** and the **anode** is inert (platinum or stainless steel) where water is **oxidised**. $2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$ Or in alkaline conditions: $4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-$ For long term stabilisation, objects are covered with a clear **lacquer**. **Wooden Objects** Long submerged **wooden objects** are very fragile as the **cellulose** has been removed by **bacteria**. The objects must be kept wet and away from light to avoid warping, splitting and the crystallisation of salts. The restoration involves: • The cleaning of silt, mud and other debris. This is done by the gentle washing of the object in cold water for a long time. • The sea water is replaced by an inert was or oil. **Polyethyleneglycol** (PEG) is widely used, which is soluble in water and alcohol. $-(CH_2 - CH_2 - O)_n -$ Objects are soaked in a solution of **PEG** of gradually increasing concentrations until virtually all the water is replaced. **PEG** fills cavities and stabilises the wood by restoring some of its strength. Finally the object is air dried and coated with a **PEG** of higher **melting point**.
• **Perform investigations and gather information from secondary sources to compare conservation and restoration techniques applied in two Australian maritime archaeological projects.**	**Maritime archaeology** is the examination, interpretation and conservation of marine materials. Two Australian projects are the restoration of iron cannons from **Captain Cook's *Endeavour*** and the Dutch trading ship, the ***Batavia***. **Captain Cook's Cannons:** In 1770, Captain Cook's ship, the ***Endeavour***, hit a reef of the Queensland coast and had to throw its cannons overboard to lighten the vessel. These cannons were discovered in 1969 and were: • Cleaned by chipping of the coral (**calcium carbonate concretions**) that had become stuck to them. • Restored by **electrolysis** to remove **chlorides** and reduce **oxides**. • Preserved by coating with **wax**.

	The *Batavia*: The ***Batavia*** was a seventeenth century trading ship which was built in 1628. It was wrecked off the Western Australian coast in 1629 and discovered in 1963. On board the ship, silverware, ceramics and coins were discovered. • Extensive **desalination** and **electrolysis** was used to restore and stabilise the coins. The timber hull was raised in sections, but was badly decayed by **micro-organisms** feeding on the **cellulose**. • The timbers were treated in batches, washed free of sediments, and then **desalinated**. The timbers were then restored by **impregnation** with **PEG**.