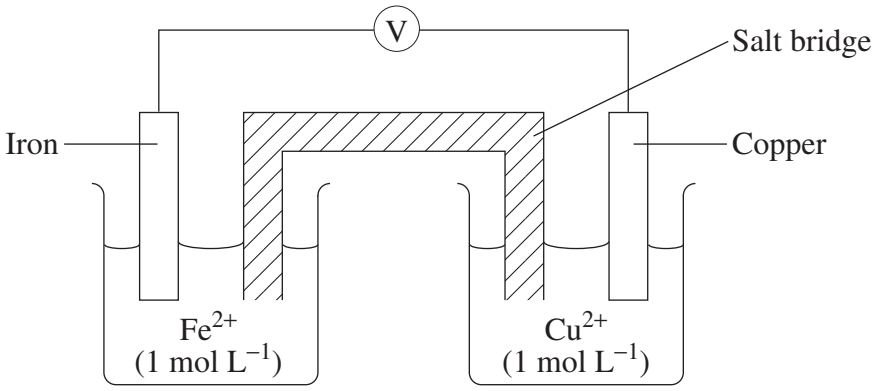
Marks

Question 29 — Shipwrecks and Salvage (25 marks)

(a) (i) Name the type of electrochemical cell that produces a spontaneous reaction. **1**

(ii) Calculate the voltage required to operate the cell shown in the diagram as an electrolytic cell, showing relevant half-equations in your working. **3**



(b) Describe how the work of early scientists increased our understanding of electron transfer reactions. **4**

(c) (i) Name ONE method for removing salt from an artefact recovered from a wreck. **1**

(ii) Explain, using an example, chemical procedures used to clean and preserve artefacts from wrecks. **4**

(d) During your practical work you performed a first-hand investigation to compare and describe the rate of corrosion of materials in different acidic and neutral solutions.

(i) Outline the procedure used. **2**

(ii) It is hypothesised that acidic environments accelerate the corrosion of shipwrecks. **4**

Explain how data obtained from the procedure in part (d) (i) does or does not support this hypothesis.

(e) Analyse the effect of ocean depth on corrosion of metallic objects. **6**

(29)

a) i) A Galvanic Cell produces a spontaneous reaction.

ii) $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ $\quad E^\circ = -0.44\ V$

↓ reduction at the cathode (negative electrode)

$Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2e^-$ $\quad +0.34\ V$

↓ oxidation at the anode (positive electrode)

total cell EMF = -0.78 V

∴ a voltage in excess of 0.78 V is required for electrolysis.

b) Galvani, Davy and Faraday collectively revolutionised our understanding of electron transfer reactions. Galvani's work centered around the effects of electricity on muscular motion. He mistakenly thought he had discovered that animals posess some sort of "electric fluid" in their muscles. The phenomena he had discovered, however, was the generation of an electric current when two metals came into contact with a moist environment. He paved the path for further

investigation.

Davy's work drew on earlier theories proposed by Carlisle. ~~He~~ Davy invented electrolysis, successfully electrolysing water using Voltaic piles in 1800. He proved the relation between the reactivity of the electrolyte and the overall voltage ~~generated by~~ (current) of the cell. He proved that electrolysis was possible only if the ~~reactivity of the~~ electrolyte was capable of oxidising one of the metals. He successfully isolated pure metals including sodium and potassium using electrolysis.

Faraday's work centered around quantitative analysis of electron transfer reactions, and his First Principles of Electromagnetism formed the basis of power generation today, with all Generators based on his theories. He proved that static, magnetic and voltaic energy were identical. He proved in his First Law of Electrolysis that the mass of product formed during an electrolytic reaction

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is directly related to the amount of current passing through the cell. ie $Q = It$

These three pioneers of early scientific discovery have had an incremental role in developing our understanding of $\bar{e}$ transfer reactions.

c) i) Electrolysis.

(or ~~leaching~~ ...)

ii) Leaching in deionised pure water or dilute NaOH(aq) removes salts as well as chlorides and sulfates. Electrolytic reduction then removes chlorides from insoluble $Fe(OH)Cl$ in iron objects, for example:

$$Fe(OH)Cl(s) + 2\bar{e} \longrightarrow Fe(s) + OH^-(aq) + Cl^-(aq)$$

The NaOH electrolyte is replaced so as to avoid a build up of Cl^- ions.

If the object is encrusted eg. silver coins encrusted with limestone or $CaCO_3$ deposits, leaching in a dilute acid solution and a pneumatic chisel (using air pressure) can remove encrustations.

The artefact can then be electrolytically restored

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in many cases, including iron objects and silver which has reacted with sulfide. He made the cathode as follows:

$$Ag_2S_{(s)} + 2e^- \rightleftharpoons 2Ag_{(s)} + S^{2-}_{(aq)}$$

In the case of wooden artefacts, preservation includes injecting inert materials to fill corroded cavities to prevent shrinking and distortion. Microcrystalline waxes and protective polymer coatings can prevent further corrosion in salvaged artefacts, stored in low oxidising conditions.

d) i) One variable is changed at a time, ie. a range of materials including bronze, iron, steel, leather, duralium, zinc, wood etc are done in separate repetitions of the following procedure (using mild steel as an example).

The only variable of the experiment is the pH of solution, which should rage from zero to 8 (slightly more alkaline than neutral). This

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can be measured using a pH meter with a glass electrode connected to a data logger. Exposure to light, oxygen supply, temperature, etc should be kept constant. Each piece of mild steel is placed in a separate, standard-sized test tube ~~of iron~~ with equal volumes of solutions with known pH. The metals are identical in terms of shape, size, surface area and points of stress to ensure uniform, accurate results, and are of equal mass initially. The setup is left for three weeks and changes are observed visually after this period. Comparison can be further enhanced by re-weighing the samples when they are dry to determine mass loss of $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + e^-$, but ~~much of this~~ some will be present as rust ($Fe_2O_3 \cdot xH_2O$), therefore not all mass lost is directly proportional to corrosion.

ii) The results from the above experiment directly support the hypothesis in that solutions of low pH displayed greater rates of corrosion than

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the more neutral fothtubes.

This is partly due to the direct anaerobic action of H^+ ions on the iron in the steel.

$$Fe(s) + 2H^+(aq) \rightleftharpoons Fe^{2+}(aq) + H_2(g)$$

Acidic conditions also accelerate aerobic corrosion of iron in the 'usual' aerobic manner.

At the anode iron is oxidised

$$Fe(s) \rightleftharpoons Fe^{2+}(aq) + 2e^-$$

At the cathode oxygen ~~water~~ is reduced

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-(aq)$$

The hydroxide ions formed are removed from solution by the H_3O^+ in acidic solutions, thus favouring the oxidation of iron by providing a path for the released electrons.

(ie. $OH^-_{(aq)} + H_3O^+_{(aq)} \rightleftharpoons 2H_2O(l)$)

By demonstrating this practically (ie. the metal samples are visually corroded more in low pHs (0, 1, 2, 3) than in the neutral range) our experiment supports the hypothesis that acidic environments accelerate the corrosion of shipwrecks. The shipwreck material is made the anodic component of a 'galvanic cell' in which the acidic sea water acts as the electrolyte.

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e) Theoretically the solubility of gases such as O_2, N_2 and CO_2 is favoured by high pressures and low temperatures, as occur at great ocean depths. However there is little mixing with atmospheric gases (as occurs at surface depths) and hence very low concentrations of these gases diffuse down to great depths. O_2 is removed by the respiration of marine organisms, and is unable to be replaced photosynthetically due to the inability of sunlight to penetrate to the bottom of the ocean.

Hence scientists once believed that the virtual absence of oxygen and the low temperatures at ~~depth~~ as depth increased (reducing kinetic energy, reducing the rate of corrosion) the rate of corrosion would decrease.

It has always been known that at surface depths and ~~at~~ for shipwrecks or metallic objects exposed at low tide - that the plentiful supply of oxygen, warm temperatures increasing the rate of reaction, and exposure to the

electrolytic seawater (with high ion concentration to facilitate the movement of ions) corrosion of metallic objects is exacerbated.

Scientists were surprised to find, however, that at great depths corrosion is far from prevented. The activity of sulfur-reducing bacterial species like the Desulfovibrio family affect the following:

$$SO_4^{2-}(aq) + 5H_2O(l) + 8e^- \rightleftharpoons HS^-(aq) + 9OH^-(aq)$$

This provides a path for electrons released in the oxidation of iron, facilitating

$$Fe(s) \rightleftharpoons Fe^{2+}(aq) + 2e^-$$

Also, large concentrations of bacteria colonies surrounding shipwrecks produce slightly acidic environments by their normal metabolic processes. H^+ ions can directly reduce iron and some other metallic objects eg. $Fe(s) + 2H^+(aq) \rightleftharpoons Fe^{2+}(aq) + H_2(g)$

Thus corrosion of metallic objects can occur at all ocean depths, but by different aerobic or anaerobic processes depending on available oxygen at the depths. (eg. the differential aeration principle can exacerbate corrosion at surface depths).