9.6 Shipwrecks and Salvage

Peter Southwell-Keely
Two types of Chemical Reaction

- Oxidation-Reduction (Redox)

- The others
Shipwrecks and Salvage

is

Redox Chemistry
Identification and Production of Materials (core)

Shipwrecks and Salvage (option)

Industrial Chemistry (option)

Acidic Environment (core)

Chemical Monitoring and Management (core)

Biochemistry of Movement (option)

Forensic Chemistry (option)

Chemistry of Art (option)
Identification and Prod'n of Materials (org and inorg) → Shipwrecks and Salvage (inorg) → Industrial Chemistry (inorg)

Major overlaps
Shipwrecks and Salvage (*inorg*)

- Acidic Environment (*inorg*)
- Chemical Monitoring and Management (*org and inorg*)
- Forensic Chemistry (*org*)
- Biochemistry of Movement (*org*)
- Chemistry of Art (*inorg*)

Minor overlaps
Oxidation

- Loss of electrons (inorg)
- Gain of oxygen (org)
- Loss of hydrogen (org)
- Increase in oxidation number (org and inorg)

Reduction

- Gain of electrons (inorg)
- Loss of oxygen (org)
- Gain of hydrogen (org)
- Decrease in oxidation number (org and inorg)
9.6 Shipwrecks and Salvage

1.1 Identify the origins of minerals in oceans..


Analyses of the principal types of pelagic sediments (weight % oxides)

<table>
<thead>
<tr>
<th></th>
<th>Red clay</th>
<th>Calcareous ooze</th>
<th>Siliceous ooze</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>53.93</td>
<td>24.23</td>
<td>67.36</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.96</td>
<td>0.25</td>
<td>0.59</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>17.46</td>
<td>6.60</td>
<td>11.33</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>8.55</td>
<td>2.43</td>
<td>3.40</td>
</tr>
<tr>
<td>FeO</td>
<td>0.45</td>
<td>0.64</td>
<td>1.42</td>
</tr>
<tr>
<td>MnO</td>
<td>0.78</td>
<td>0.31</td>
<td>0.19</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>0.39</td>
<td>56.73</td>
<td>1.52</td>
</tr>
</tbody>
</table>
9.6 Shipwrecks and Salvage

1.2 Outline the role of electron transfer in oxidation reduction reactions cf 8.3.2.s4; 9.2.4.1; 9.2.4.3; 9.2.4.4; 9.2.4.5

Formation of sodium chloride

Oxidn: 2Na $\rightarrow$ 2Na$^+$ + 2e

Redn: Cl$_2$ + 2e $\rightarrow$ 2Cl$^-$

Overall 2Na + Cl$_2$ $\rightarrow$ 2NaCl
1.2 (cont’d)

Oxidation of methane

Oxidn: \[ \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 8\text{H}^+ + 8\text{e} \]

Redn: \[ 2(\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightarrow 2\text{H}_2\text{O}) \]

Overall: \[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]
Fermentation of glucose \((\text{CH}_2\text{O})_6\)

Oxidn: \((\text{CH}_2\text{O})_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^{-}\)

Redn: \((\text{CH}_2\text{O})_4 + 8\text{H}^+ + 8\text{e}^{-} \rightarrow 2\text{C}_2\text{H}_5\text{OH} + 2\text{H}_2\text{O}\)

Overall: \((\text{CH}_2\text{O})_6 \rightarrow 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2\)
9.6 Shipwrecks and Salvage

1.3 ...redox reactions can occur when ions are free to move in solid and liquid electrolytes cf 9.2.4.4; 9.2.4.5; 9.2.4.6; 9.2.4.7; 9.2.4.8; 9.2.4.s1; 9.2.4.s2; 9.2.4.s3; 9.2.4.s4; 9.5.3.6; 9.5.3.s2; 9.5.4.1; 9.5.4.2; 9.5.4.3; 9.5.4.s1; 9.5.4.s3
9.6 Shipwrecks and Salvage

1.4 Describe the work of Galvani, Davy and Faraday (NEW!) (www.ask.com--- Luiggi Galvani etc)
Shipwrecks and Salvage

Luigi Galvani  Humphry Davy  Michael Faraday
9.6 Shipwrecks and Salvage

2.1 Account for differences in corrosion of active and passivating metals

- On the basis of their reduction potentials, most metals except gold should oxidise in air.

- However, most metals form a thin oxide coating, which protects against further oxidation. This is *passivation*.

- Aluminium shows this best. Its reduction potential is -1.7V. However, Al coated with \( \text{Al}_2(\text{OH})_6 \), “passive” Al, has a reduction potential of -0.6V.
9.6 Shipwrecks and Salvage

2.2 Identify iron and steel as the main metals used in ships

2.3 Identify the composition of steel and explain how the percentage composition of steel can determine its properties (see p. 1012 Zumdahl 5th edit, 2000)
2.4 Describe the conditions under which rusting occurs and explain the process of rusting

Fe dissolves forming a pit

anode reaction:  
Fe(s) $\rightarrow$ Fe^{2+} + 2e

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

2Fe(s) + O_2 + 2H_2O $\rightarrow$ 2Fe^{2+} + 4OH^-

4Fe^{2+}(aq) + O_2(g) + (4 + 2n) H_2O(l) $\rightarrow$ 2Fe_2O_3.nH_2O(s) + 8H^+(aq)

Rust
3.1 Define the terms galvanic cell and electrolytic cell \textit{cf} 9.2.4.3; 9.2.4.4; 9.2.4.5; 9.2.4.6; 9.2.4.7

- A galvanic cell uses a spontaneous redox reaction to produce a current that can be used to do work.

- An electrolytic cell uses electrical energy to produce a chemical change that would otherwise not occur naturally.
3.2 Distinguish between and give examples of galvanic and electrolytic cells. 

**Galvanic Cell**

- **Zn electrode (anode)**
  - Oxidation: Zn(s) → Zn^{2+} + 2e^-

- **Cathode** (Cu electrode)
  - Reduction: Cu^{2+} + 2e^- → Cu(s)

- **KCl salt bridge**

- **Conducting wire**

**Electrolytic Cell**

- **Zn electrode (anode)**
  - Oxidation: Zn(s) → Zn^{2+} + 2e^-

- **Cathode** (Cu electrode)
  - Reduction: Cu^{2+} + 2e^- → Cu(s)

- **KCl salt bridge**

- **Conducting wire**

**Note:** Examples of galvanic and electrolytic cells are discussed in sections 9.2.4.4, 9.2.4.5, 9.2.4.6, and 9.2.4.7.
9.6 Shipwrecks and Salvage

3.2 Distinguish between and give examples of galvanic and electrolytic cells *cf* 9.2.4.4; 9.2.4.5; 9.2.4.6; 9.2.4.7

Electrolysis of molten sodium chloride

Oxidation: $2\text{Cl}^- \rightarrow \text{Cl}_2(g) + 2e^-$

Reduction: $\text{Na}^+ + e^- \rightarrow \text{Na}$

Diaphragm allows ions to flow but separates Cl$_2$ and Na.

Cell reaction:

$$2\text{NaCl}(l) \rightarrow 2\text{Na}(l) + \text{Cl}_2(g)$$

Addition of CaCl$_2$ to NaCl lowers the melting point enough to make the cell workable.
3.3 Describe using half-equations, what happens at the anode and cathode during electrolysis of selected aqueous solutions cf 9.2.4.6

Electrolysis of brine
possible anode reactions

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e} \quad E^0 = -1.36\text{V} \]
\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e} \quad E^0 = -1.23\text{V} \]

The most favourable reaction is the oxidation of water. In dilute solution oxygen is formed but in concentrated solution chlorine is formed and is the basis of the chlor-alkali process.
3.3 Describe using half-equations, what happens at the anode and cathode during electrolysis of selected aqueous solutions cf 9.2.4.6

**Electrolysis of brine**

possible cathode reactions

\[ \text{Na}^+ + e^{-} \rightarrow \text{Na} \quad E^0 = -2.71\text{V} \]

\[ 2\text{H}_2\text{O} + 2e^{-} \rightarrow \text{H}_2 + 2\text{OH}^- \quad E^0 = -0.83\text{V} \]

The most favourable reaction is the reduction of water to hydrogen and that is what happens both in dilute and concentrated brine. However in the mercury cell process, sodium is reduced.
3.4 Describe factors that effect an electrolysis reaction...

- magnitude of current
- time of current flow
- concentration of solutions
- overvoltage
- nature of electrode
- nature of electrolyte
3.5 Define Faraday’s first law of electrolysis (NEW!)

“The extent to which an electrochemical reaction occurs is in direct proportion to the number of moles of electrons transferred.”

\[
q = I \times t
\]

charge (coulombs) \hspace{1cm} current (amps) \hspace{1cm} time (sec)

1 mole of electrons = 96,500 coulombs (1 faraday)
9.6 Shipwrecks and Salvage

4.1 Identify ways in which a metal hull may be protected including corrosion resistant metals, development of **surface alloys**, new paints.

- Instead of forming a metal alloy such as stainless steel, which has the same composition throughout, a cheaper carbon steel is treated by ion bombardment to produce a thin layer of stainless steel, or other desirable alloy on the surface.

In this process a “plasma” or “ion gas” of the alloying ions is formed at high temperatures and directed onto the surface of the metal.
9.6 Shipwrecks and Salvage

4.1 Identify ways in which a metal hull may be protected including corrosion resistant metals, development of surface alloys, new paints.

- Rustmaster paint is a water-based polymer that prevents corrosion in two ways:

  - Firstly, the polymer layer forms a barrier impenetrable to both oxygen and water vapour.

  - Secondly, the chemicals in the coating react with the steel surface to form a complex mineral inter-layer called *pyroaurite* between the metal and the polymer coating.
4.1 Identify ways in which a metal hull may be protected including corrosion resistant metals, development of surface alloys, new paints.

- *Pyroaurite* has the form \([M_{1-x}Z_x(OH)_2]^{x+}\) where M is a 2+ ion (Mg\(^{2+}\), Fe\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\) or Ni\(^{2+}\)), Z is a 3+ ion (Al\(^{3+}\), Fe\(^{3+}\), Mn\(^{3+}\), Co\(^{3+}\), or Ni\(^{3+}\)) and x is a number between 0 and 1. The anions in *pyroaurite* are typically CO\(_3^{2-}\), Cl\(^-\) and/or SO\(_4^{2-}\).

The *pyroaurite* layer grows into the neighbouring polymer layer preventing the movement of ions between the anodic and cathodic areas on the surface of the steel.
9.6 Shipwrecks and Salvage

4.2 Predict the metal that corrodes when two metals form an electrochemical cell using a list of standard potentials (*in old syllabus*)
4.3 outline the process of cathodic protection, describing examples of its use in both marine and wet terrestrial environments (*in old syllabus*)

- Cathodic protection is used to protect steel in buried fuel tanks, pipelines and ships.

- A metal such as magnesium is connected by a wire to the tank or pipeline creating an electrochemical cell in which the moist soil is the electrolyte. As magnesium is the more active metal, it becomes the anode and is preferentially oxidised, donating electrons to the steel and maintaining it in the reduced state. Thus steel is the cathode in this system.
4.3 outline the process of cathodic protection, describing examples of its use in both marine and wet terrestrial environments (*in old syllabus*)

- Thus in cathodic protection, the metal being protected is made the inert cathode of an electrochemical cell.

- The hulls of ships are protected in the same way by using bars of titanium steel (as anodes) connected by wire to the hull.
4.4 Describe the process of cathodic protection in terms of the oxidation reduction chemistry involved (*in old syllabus*)

- **anode:** $\text{Mg} \rightarrow \text{Mg}^{2+} + 2e$
- **cathode:** $\text{O}_2 + 2\text{H}_2\text{O} + 4e \rightarrow 4\text{OH}^-$
- **overall:** $2\text{Mg} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Mg}^{2+} + 4\text{OH}^-$
9.6 Shipwrecks and Salvage

5.1 Outline the effect of temp. and pressure on the solubility of gases and salts (NEW!) (gases/temp SI Data Book, 4th ed., p.141; Conserv’n of Marine Archeological Objects, C. Pearson, p.5)

Oxygen solubility in sea water (ml/l)

<table>
<thead>
<tr>
<th>Salinity Temp</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>36</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.22</td>
<td>9.54</td>
<td>8.91</td>
<td>7.99</td>
</tr>
<tr>
<td>5</td>
<td>8.93</td>
<td>8.36</td>
<td>7.83</td>
<td>7.04</td>
</tr>
<tr>
<td>10</td>
<td>7.89</td>
<td>7.41</td>
<td>6.95</td>
<td>6.28</td>
</tr>
<tr>
<td>15</td>
<td>7.05</td>
<td>6.63</td>
<td>6.24</td>
<td>5.65</td>
</tr>
<tr>
<td>20</td>
<td>6.35</td>
<td>5.99</td>
<td>5.64</td>
<td>5.14</td>
</tr>
<tr>
<td>25</td>
<td>5.77</td>
<td>5.45</td>
<td>5.15</td>
<td>4.70</td>
</tr>
<tr>
<td>30</td>
<td>5.28</td>
<td>4.99</td>
<td>4.73</td>
<td>4.33</td>
</tr>
<tr>
<td>35</td>
<td>4.85</td>
<td>4.60</td>
<td>4.36</td>
<td>4.01</td>
</tr>
</tbody>
</table>
9.6 Shipwrecks and Salvage

5.2 Identify that gases are normally dissolved in the oceans and compare their concentrations in the oceans to their concentrations in the atmosphere (NEW!).

<table>
<thead>
<tr>
<th></th>
<th>% Concn in air (0°C)</th>
<th>% Concn in water (0°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>21</td>
<td>0.0015</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>78</td>
<td>0.0023</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.04</td>
<td>0.014</td>
</tr>
</tbody>
</table>
9.6 Shipwrecks and Salvage

5.3 Compare and explain the solubility of selected gases at increasing depths in the oceans (NEW!). (c.f C. Pearson)
9.6 Shipwrecks and Salvage

5.4 Predict the effect of low temperatures at great depths on the rate of corrosion of a metal (NEW!).
9.6 Shipwrecks and Salvage

6.1 Explain that shipwrecks at great depths are not corroded by electrochemical reactions but by anaerobic bacteria (NEW!).

At great depths oxygen depletion occurs

- due to pollution or high microbiological activity

- when the object is buried beneath the seabed and oxygen diffusion from the overlying water is restricted

- when the artefact becomes covered by marine growth
6.1 Explain that shipwrecks at great depths are not corroded by electrochemical reactions but by anaerobic bacteria (NEW!).

I believe this statement is incorrect because it implies that electrochemical reactions do not occur. What actually happens is that the cathode reaction changes from

\[
O_2 + 2H_2O + 4e \rightarrow 4OH^- \\
\text{to} \\
2H^+ + 2e \rightarrow H_2
\]
The reaction \( 2H^+ + 2e \rightarrow H_2 \)
is usually slow on most metals in the seawater pH range.

Sulfate-reducing bacteria speed up this reaction as they produce sulfide ions which react with metal ions to form sulfides, such as FeS, and elemental sulfur on which the hydrogen evolution reaction can occur more rapidly than on the metal surface.

The sulfate-reducing bacteria may also increase the corrosion rate by forming acids which lower the pH.
6.2 Describe the bacteria as sulfur-reducing species whose wastes produce acidic environments around deep wrecks (NEW!).

\[ 4H_2 + SO_4^{2-} + 2H^+ \rightarrow H_2S + 4H_2O \]
Production of H$_2$S by Sulfate-reducing bacteria

$$\text{SO}_4^{2-} \xrightarrow{\text{ATP}} \text{Adenylyl Sulfate} \xrightarrow{\text{PPI}} \text{cyt c}_3 \text{ (red)} \xrightarrow{2\text{H}^+} \text{Hydrogenase} \xrightarrow{\text{H}_2} \text{cyt c}_3 \text{ (oxid)} \xrightarrow{\text{HSO}_3^-} \text{H}_2 \text{S} \xrightarrow{\text{Hydrogenase}} 2\text{H}^+$$
Bacteria of the species *Thiobacillus* are able to oxidise sulfide, elemental sulfur, thiosulfate and sulfite to sulfate. These are the types of organisms which deplete the oxygen on the ocean floor and make it anaerobic.

\[
\begin{align*}
S^{2-} & \rightarrow S^0 \\
S-\text{SO}_3^{2-} & \rightarrow \text{SO}_3^{2-} \\
\text{SO}_3^{2-} & \rightarrow \text{SO}_4^{2-} \\
\text{H}_2\text{O} \text{ sulfite oxidase} & \rightarrow 2\text{H}^+ 
\end{align*}
\]
6.3 Explain that acidic environments accelerate corrosion in non-passivating metals cf 8.3.2.1; 8.3.2.2; 8.3.2.3; 8.3.2.4; 8.3.2.s3; 8.3.2.s4; 9.2.4.l.

- Formation of ferrous ions is promoted by an increase in the \([H^+]\) (i.e. lowering of pH). The presence of CO\(_2\) in rain water causes Fe to rust much more rapidly than if it were absent.

- \[ \text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e} \rightarrow 2\text{H}_2\text{O(l)} \quad 1.23\text{V} \]
- \[ \text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)} + 4\text{e} \rightarrow 4\text{OH}^- \quad 0.41\text{V} \]
9.6 Shipwrecks and Salvage

7.1 Explain that artefacts from long submerged wrecks will be saturated with dissolved chlorides and sulfates

<table>
<thead>
<tr>
<th>Ion</th>
<th>Amount in water (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>19.35</td>
</tr>
<tr>
<td>Na⁺</td>
<td>10.76</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>2.71</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.29</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.41</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.39</td>
</tr>
</tbody>
</table>
9.6 Shipwrecks and Salvage
7.1 (cont’d)

Composition of concretions (*Batavia* wreck)

<table>
<thead>
<tr>
<th></th>
<th>Iron concretion (wt %) Inner red zone (4 cm below seaward surface)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (total)</td>
<td>53.2</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>47</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.22</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.07</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.12</td>
</tr>
<tr>
<td>S (total)</td>
<td>2.2</td>
</tr>
<tr>
<td>P</td>
<td>0.18</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>6.35</td>
</tr>
</tbody>
</table>
9.6 Shipwrecks and Salvage

7.2 Describe the processes that occur when a saturated solution evaporates and relate this to the potential damage to drying artefacts.
9.6 Shipwrecks and Salvage

7.3 Identify the use of electrolysis as a means of removing salt

The two most significant problems in marine metal conservation are:

1. Retention and stabilisation of corrosion products
2. Removal of chlorides

• After the removal of an iron object from water, the presence of chlorides can bring about the same amount of corrosion in a few days as takes months or years under water.
7.3 (cont’d)

- The corrosion product on partially corroded cast iron contains FeO(OH), iron chlorides, SiO$_2$, Fe$_3$C and graphite.

- On drying in air the iron chlorides decompose to Fe$_2$O$_3$, FeCl$_3$, HCl and FeO(OH) generating ideal conditions for rapid corrosion.

- The principal aim of all marine iron treatment is to remove chlorides from corrosion products which is achieved by
  1. Washing
  2. Heat treatment
9.6 Shipwrecks and Salvage

7.3 (cont’d)

Washing

\[ \text{Fe(OH)}\text{Cl(s)} + X^-(\text{wash water}) \rightarrow \text{Fe(OH)}X(s) + \text{Cl}^- (\text{wash water}) \]

(where \( X = \text{OH}^-, \text{HCO}_3^-, \text{CO}_3^{2-} \))

The most effective means of increasing Cl\(^-\) diffusion within the corrosion products is to increase their porosity by converting the iron compounds to a denser state. Reduction of iron compounds increases their density.
9.6 Shipwrecks and Salvage

7.3 (cont’d)

*Washing (cont’d)*

Reduction of the iron compounds can be achieved by

1. Electrolysis
2. Alkaline sulfite
3. Hydrogen furnace

\[ 3\text{FeO(OH)} + \text{H}^+ + \text{e} \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} \]
7.3 (cont’d)

Heat treatment
in air at 400°C

\[ 4\text{FeOCl} + \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 2\text{Cl}_2 \]

\[ 3\text{FeOCl} \rightarrow \text{Fe}_2\text{O}_3 + \text{FeCl}_3 \]

\[ 4\text{FeCl}_2 + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{Cl}_2 \]
9.6 Shipwrecks and Salvage

7.3 (cont’d)

*Heat treatment*

in H₂/N₂ at 100 - 300°C

\[
10\text{FeOCl} + 3\text{H}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + 4\text{FeCl}_2 + 2\text{HCl} + 2\text{H}_2\text{O}
\]

\[
\text{FeCl}_3\cdot\text{H}_2\text{O} \rightarrow \text{FeOCl} + 2\text{HCl}
\]

\[
\text{FeCl}_2 + \text{H}_2 \rightarrow \text{Fe} + 2\text{HCl}
\]

\[
\text{Fe}_3\text{O}_4 + 3\text{H}_2 \rightarrow 3\text{Fe} + 4\text{H}_2\text{O}
\]
7.4 Identify the use of electrolysis as a means of cleaning and stabilising strong metal artefacts (NEW!).

- Silver reacts very readily with very low concentrations of Hydrogen sulfide to form the very insoluble silver sulfide

\[
2\text{Ag}(s) + \text{H}_2\text{S}(aq) \rightarrow \text{Ag}_2\text{S}(s) + \text{H}_2(g)
\]
9.6 Shipwrecks and Salvage

7.4 (cont’d)

The reaction

\[ 2\text{Ag}(s) + \text{H}_2\text{S(aq)} \rightarrow \text{Ag}_2\text{S(s)} + \text{H}_2(g) \]

seems improbable until one examines the reduction potentials

\[
\begin{align*}
\text{O}_2(g) + 4\text{H}^+ + 4\text{e} & \rightarrow 2\text{H}_2\text{O(l)} & 1.23\text{V} \\
\text{Ag}^+ + \text{e} & \rightarrow \text{Ag} & 0.80\text{V} \\
\text{AgCl} + \text{e} & \rightarrow \text{Ag} + \text{Cl}^- & 0.22\text{V} \\
2\text{H}^+ + 2\text{e} & \rightarrow \text{H}_2 & 0.00\text{V} \\
\text{Ag}_2\text{S} + 2\text{H}^+ + 2\text{e} & \rightarrow 2\text{Ag} + \text{H}_2\text{S} & -0.037\text{V} \\
\text{Ag}_2\text{S} + 2\text{e} & \rightarrow 2\text{Ag} + \text{S}^{2-} & -0.705\text{V}
\end{align*}
\]
7.4 Identify the use of electrolysis as a means of cleaning and stabilising strong metal artefacts (NEW!).

\[
\begin{align*}
\text{Ag}_2\text{S} + 2\text{e}^- & \rightarrow 2\text{Ag} + \text{S}^{2-} \\
2\text{H}_2\text{O} + 2\text{e}^- & \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^- 
\end{align*}
\]
7.5 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 (NEW!). (Chem. in Brit. 1995, 5-7. Nat. Maritime Museum --> PORT database)

- Some bronze objects (cannons) can be simply washed with clean water to remove corrosive salts from sea water.

- Smaller artifacts of bronze, copper brass, lead, pewter and gold are preserved either by electrolysis or hydrogen reduction as described below for iron.
7.5 (cont’d)

• The patina on bronzes consists of a range of compounds of which malachite $\text{CuCO}_3\cdot\text{Cu(OH)}_2$ and azurite $\text{Cu(OH)}_2\cdot2\text{CuCO}_3$ are common constituents.

• “Bronze disease” occurs when deep seated $\text{CuCl}$ reacts with moisture to form e.g. $\text{Cu}_2(\text{OH})_3\text{Cl}$ which the breaks through and blisters the patina and causes gradual disintegration of the bronze.
9.6 Shipwrecks and Salvage

7.5 (cont’d)

- Usual treatment of “bronze disease” involves
  1. Removal of any surface concretions (carbonates). This is often done with citric acid.
  
  2. Hydrolysis of CuCl and Cu$_2$(OH)$_3$Cl with a solution of sodium carbonate/sodium bicarbonate to remove the chloride.

  3. Impregnation with benzotriazole.
7.5 (cont’d)

• As an alternative to the alkaline wash, electrolysis can be used to liberate the chlorides.

\[
\text{CuCl} + e^{-} \rightarrow \text{Cu} + \text{Cl}^{-}
\]

\[
\text{Cu(OH)₃Cl} + 4e^{-} \rightarrow \text{Cu} + 3\text{OH}^{-} + \text{Cl}^{-}
\]

• A recent treatment for bronze disease is to dust the surface with zinc which stabilises the site and prevents further decay. (Zn reduces Cu\(^{2+}\) back to metal (?))
9.6 Shipwrecks and Salvage

7.5 (cont’d)

- For iron objects, as much oxidation as possible is removed by heating the object in a reducing atmosphere of hydrogen. The hydrogen is derived by cracking liquid ammonia.

\[
\begin{align*}
2\text{NH}_3(l) & \rightarrow \text{N}_2(g) + 3\text{H}_2(g) \quad (\text{Mary Rose}) \\
\text{Fe}_2\text{O}_3 + 3\text{H}_2 & \rightarrow 2\text{Fe} + 3\text{H}_2\text{O} \quad (800^\circ \text{C}) \\
\text{FeCl}_2 + \text{H}_2 & \rightarrow \text{Fe} + 2\text{HCl} \quad (800^\circ \text{C}) \\
\text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2 & \rightarrow 2\text{Fe} + 3\text{H}_2\text{SO}_4 \quad (800^\circ \text{C})
\end{align*}
\]
7.5 (cont’d)

- Wooden objects, such as the hull of the Mary Rose, are stabilised by spraying with successive lots of polyethylene glycol (PEG) of gradually increasing molecular weight.