Experiment 6a

CORROSION OF METALS

In this experiment, the students are divided into groups of five and each group researches 5 methods of protection against corrosion and then protects two nails by each method; two nails are kept untreated as controls. One of the nails, both unprotected and protected is bent with pliers or hammered. The 12 nails are then placed in agar gel, which has been made to incorporate potassium hexacyanoferrate(III) and phenolphthalein indicator. The sections of the nails where corrosion is taking place turn blue within an hour.

Equipment

- 12 iron nails per student group of 5
- 6 petri dishes and 2 pairs of pliers, and/or a hammer

Reagents for two 10-cm petri dishes

- potassium hexacyanoferrate(III), K₃[Fe(CN)₆] (33 g)
- phenolphthalein indicator (2 mL)
- potassium nitrate, KNO₃ (5 g)
- agar (1 g)

Procedure

- Issue twelve nails per group and request that they protect the nails from corrosion by five different methods. Set up two nails using each method and leave two nails unprotected.
- Simple possibilities are: galvanising; tin plating; cathodic protection; paint of various types; anti-rust compounds; grease.
- Hammer or bend one of the nails in each pair.

Preparation of the agar gel - recipe for two petri dishes

- Prepare a 0.1 M potassium hexacyanoferrate(III) solution by dissolving 33 g in 1 L of distilled water.
- Prepare the agar gel by making a mixture of 50 mL of distilled water, 5 g of potassium nitrate, 1 g of agar, 10 mL of 0.1 M potassium hexacyanoferrate(III) and 10 drops of phenolphthalein indicator.
- Place this mixture on a steam bath until the agar dissolves (usually about 20 minutes).
- Place some agar gel in 6 petri dishes.
- In each petri dish place two nails that have been protected against corrosion by the same method, one of which has been bent with the pliers.

Results

The unprotected nails and bent nails will show regions of blue and pink coloration. Iron is oxidised to Fe²⁺, which then reacts with potassium hexacyanoferrate(III) ion to give the dark blue precipitate known as Turnbull’s blue. These blue regions appear around the head and tip of the nail that has not been bent and also around the bend in the bent nails. Oxidation occurs at these areas because the strained metal is more anodic (more active) than the body of the nail.

The unprotected and protected bent and unbent nails react to various degrees, blue and black areas indicate where corrosion is taking place. Magenta areas indicate the location of the cathode.

\[ \text{Fe}^{2+}(aq) + [\text{Fe(CN)}_6]^{3-}(aq) + \text{K}^+(aq) + \text{H}_2\text{O}(l) \rightarrow \text{KFe[Fe(CN)}_6]\cdot\text{H}_2\text{O(s)} \]
The electrons released by corrosion of the nails migrate along the nail where they are used to reduce dissolved oxygen in the gel to OH\(^-\)(aq). The increased concentration of OH\(^-\)(aq) causes the phenolphthalein to turn magenta.

At the anode corrosion takes place:

\[
\text{Fe(s)} \rightarrow \text{Fe}^{2+}(\text{aq}) + 2e^- 
\]

The Fe\(^{2+}\)(aq) reacts with K\(_3\)[Fe(CN)\(_6\)] to produce the blue colour.

At the cathode the following reaction takes place:

\[
\text{O}_2(\text{aq}) + 2\text{H}_2\text{O}(l) + 4e^- \rightarrow 4\text{OH}^- (\text{aq}) 
\]

The OH\(^-\)(aq) turns the phenolphthalein magenta.

The overall redox reaction is:

\[
\begin{align*}
\text{Fe(s)} & \rightarrow \text{Fe}^{2+}(\text{aq}) + 2e^- \\
\text{O}_2(\text{aq}) + 2\text{H}_2\text{O}(l) + 4e^- & \rightarrow 4\text{OH}^- (\text{aq}) \\
2\text{Fe(s)} + \text{O}_2(\text{aq}) + 2\text{H}_2\text{O}(l) & \rightarrow 2\text{Fe}^{2+}(\text{aq}) + 4\text{OH}^- (\text{aq})
\end{align*}
\]

\[
E'_{\text{OX}} = +0.41 \text{ V} \\
E'^* = +0.40 \text{ V} \\
E'_{\text{cell}} = +0.81 \text{ V}
\]

A nail that has been protected successfully shows no blue or black region, indicating that no corrosion of the iron nail has taken place. An example is a nail protected with magnesium wire, in this case the magnesium is oxidised in preference to the iron. The electrons released in the oxidation of the magnesium are again used to reduce oxygen to hydroxide, which turns the phenolphthalein magenta.

\[
\begin{align*}
\text{Mg(s)} & \rightarrow \text{Mg}^{2+}(\text{aq}) + 2e^- \\
\text{O}_2(\text{aq}) + 2\text{H}_2\text{O}(l) + 4e^- & \rightarrow 4\text{OH}^- (\text{aq}) \\
2\text{Mg(s)} + \text{O}_2(\text{aq}) + 2\text{H}_2\text{O} & \rightarrow 2\text{Mg}^{2+}(\text{aq}) + 4\text{OH}^- (\text{aq})
\end{align*}
\]

\[
E'_{\text{OX}} = +2.36 \text{ V} \\
E'^* = +0.40 \text{ V} \\
E'_{\text{cell}} = +2.76 \text{ V}
\]
Experiment 6b

CORROSION OF METALS

Aim: To investigate the effect of:
(i) Air
(ii) Stress
(iii) Contact with dissimilar metals
(iv) Treatment with rust inhibitors
      on the corrosion of metals, particularly steel.
(v) Acids

THEORY

Corrosion of metals in an electrolyte solution is an electro–chemical phenomenon, that is, a transfer of electrons is involved between different parts of the corroding system. Thus parts of the corroding system are anodic (electron rich) and other parts are cathodic (electron poor). At the anodic areas corrosion of the metal occurs:

$$M \rightarrow M^+ + e$$

At the cathodic regions there is no attack on the metal and the reaction, depending on the pH of the solution, may be either :

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$
or

$$2H^+ + 2e \rightarrow H_2$$

Note that parts of the metal which have been stressed are more likely to be corroded.

Question. Why?

Corrosion products, (for example, surface oxide layers), can sometimes inhibit further corrosion.

Question. Why?

Since corrosion occurs because of the reaction between oxygen in the air and the metal (even though the reaction sites may be different), the easiest way to prevent corrosion is to place an oxygen–inert layer in between the metal and the air (e.g. with paint or some other chemical treatment). In addition to chemical barriers, an electrical charge may be supplied to the metal to prevent corrosion.
Question. Why would an electrical charge prevent corrosion? What charge would be needed (+ or −)?

Question. In car electrical systems, the chassis is often connected to one terminal. Electrical circuits are then completed by attaching a lead to the chassis. Which terminal is attached to the chassis? (Have a look at your car!) Why this terminal?

The mechanism of the first stage in the rusting of iron is similar to that of an electrochemical cell:

\[
\text{Fe(s)} \rightarrow \text{Fe}^{2+} \text{(aq)} + 2e^- + \frac{1}{2} \text{O}_2 \text{(g)} + \text{2H}_2\text{O(l)} + 4e^- \rightarrow 4\text{OH}^- \text{(aq)}
\]

Diagrammatic representation of electrochemical processes in the corrosion of iron in aerated sodium chloride solution.

The anodic and cathodic areas in iron may be revealed by using Ferroxyl indicator. This consists of an agar jelly containing sodium chloride, phenolphthalein (an acid–base indicator) and potassium ferricyanide.

Regions where the iron corrodes will appear deep blue due to the formation of the complex potassium ferrous ferricyanide, "Prussian blue" (potassium hexacyanoferrate(III))

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-\quad \text{Fe}^{2+} + \text{Fe(CN)}_6^{3-} \rightarrow \text{Fe[Fe(CN)}_6]^-\quad \text{(blue)}
\]

Phenolphthalein turns from colourless to pink in the cathodic regions where hydroxyl ions are produced:

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-
\]

Similar indicator systems can be used to study the corrosion of other metals.
EXPERIMENTAL

EFFECT OF HISTORY AND STRESS ON CORROSION.

→ Take two 25 mm nails and clean one of them by wiping with a filter paper wet with acetone. Pour a 0.5 cm of the liquid ferroxyl jelly into a beaker. Allow the jelly to set slightly, then press the nails into the jelly lightly and cover completely with more liquid indicator. Make sure the nails are well separated. If you are using a small beaker, you may have to allow one nail per beaker.
→ Record in your notebooks the colours developed over the next few hours.
→ Explain your observations.
→ Repeat the above experiment with a length of steel wire which has been bent sharply (until nearly broken).
→ Record and explain your observations.

EFFECT OF AIR ON CORROSION.

→ Take a piece of Satinex (mild steel) plate and clean its surface. Place this sample in indicator jelly using the method described above.
→ Record your observations with time and explain.

Question. Which areas of the steel are anodic and which are cathodic? Draw a picture and mark these areas accordingly.

Question. In the above experiment (or, indeed, in any of these experiments) does corrosion appear more intense on the topside or underside of the piece of metal? Why might this be so?

→ Test your above explanation by standing a 40 mm nail upright in 20 cm of jelly in a test tube.
→ Record your observations.

Question. Do the results confirm your explanation?

→ Now put a 2 cm drop of jelly onto some Satinex.
→ Record and explain your observations, paying close attention to the time development of the colours.

Question. What does the term differential aeration mean, and how does it apply to the above two experiments?
EFFECT OF CONTACT WITH DISSIMILAR METALS ON CORROSION.

Repeat the ferroxyl jelly experiment with 25 cm nails having several turns of the following wire around their middle sections so that the metals touch and the ends of the wire are at right angles to the nail:

(i) Zinc
(ii) Tin
(iii) Copper

→ For each of the above nails, record and explain your observations.

Question. What is the white precipitate which forms around the zinc wire?

Question. From your observations, which metals are "electron rich" and which are "electron poor" in relation to steel? Do these terms mean anything when applied to metals which are not in contact?

Question. Do any of the above experiments suggest a way of preventing corrosion of steel? Which one?

CORROSION OF MILD STEEL IN SALT SOLUTION.

→ Select four equally rusty pieces of Satinex and totally immerse one piece in each of the following solutions in the baths provided in the fumehood for 15 minutes:

(i) Concentrated phosphoric acid
(ii) 10% potassium chromate.
(iii) 10% sodium silicate.

→ Wash each sample thoroughly in distilled water and half immerse them, together with the untreated sample, in a 2 – 5% solution of ammonium nitrate in individual 100 mL beakers.

→ Compare the results after standing for 1 – 2 hours. You should note any discolouration of the ammonium nitrate solution, and compare the fragility of the iron oxide layers of (i) and (ii) with that of the control. One way to do this is to place the pieces of wet metal on a sheet of paper and compare the amount of oxide layer shed.

Question. Are sodium silicate and potassium chromate used as rust inhibitors? Give examples.
CORROSION OF MILD STEEL IN ACID MEDIA.

(Carry out this experiment in the fume hood)
→ Clean six pieces of Satinex.
→ Half immerse one sample in each of the following acids:
  (a) Concentrated sulfuric, approximately 18 mol L\(^{-1}\)
  (b) 1 mol L\(^{-1}\) sulfuric
  (c) Concentrated nitric, approximately 15 mol L\(^{-1}\)
  (d) 2 mol L\(^{-1}\) nitric
  (e) Concentrated hydrochloric, approximately 10 mol L\(^{-1}\)
  (f) 2 mol L\(^{-1}\) hydrochloric.

NOTE: Take great care when handling concentrated acids.
→ Record your initial observations and subsequent observations over a period of 1 – 1 1/2 hours.
→ Completely immerse a clean piece of Satinex mild steel in concentrated nitric acid for 5 minutes.
→ Carefully pour off the acid without disturbing the sample and replace with 2 mol L\(^{-1}\) nitric acid.
→ Compare the results with that obtained above.
→ Rub one portion of the surface with a glass rod while it is still immersed and explain your result.

CORROSION OF ALUMINIUM.

Aluminium is normally covered with a thin tightly bound layer of oxide which protects the metal from further corrosion.

NOTE: Aluminium, small pieces and foil, are provided.

→ Immerse a small piece of aluminium in fresh samples of each of the acids (a) to (f) used above.

Question. If aluminium has a protective oxide layer why does it react with some acids and not with others? Which acids?
→ Compare the behaviour of aluminium with that of steel.
→ Abrade the surface of some aluminium foil with emery and immediately rub the bare patch with cotton wool wet with mercuric chloride solution.
→ Observe the surface very closely and explain the results.
→ Abrade the surface of a small piece of aluminium with emery in the presence of copper sulphate solution.
→ Observe and explain the results.
Experiment 6c
CORROSION OF METALS

Date: ______________________

Name: ______________________ Working with: ______________________

Aim: To determine the effect on the corrosion of an iron nail when it
• is bent
• is closely touching zinc metal
• is closely touching copper metal

Background:
Several equations describe the rusting of iron:

Oxidation of iron  \[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]

Reduction of oxygen and water  \[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]

Start of rust deposition:  \[ \text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2(s) \]

Second stage rust deposition  \[ 2\text{Fe(OH)}_2(s) + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O} + \text{H}_2\text{O} \]

The oxidation and reduction are essential first steps for the rusting of iron.
In this practical, we test for the formation of these two essential products (Fe²⁺ and OH⁻) using hexacyanoferrate III ions (in K₃Fe(CN)₆) and phenolphthalein indicator respectively.
These indicators, together with ordinary oxygenated tap water, are added to a jelly and the iron nails are set in the jelly.

Procedure:
You need
4 iron nails
3 petri dishes with lids
one strip of zinc metal
one strip of copper metal
tube of hot agar jelly (don’t get this till you need it - it will solidify)
some indicator solutions - potassium hexacyanoferrate III and phenolphthalein

Make some initial tests to see a positive reaction:

Test Results

<table>
<thead>
<tr>
<th></th>
<th>K₃Fe(CN)₆</th>
<th>K₃Fe(CN)₆ and Fe²⁺</th>
<th>NaOH</th>
<th>NaOH and phenolphthalein</th>
</tr>
</thead>
<tbody>
<tr>
<td>colour</td>
<td></td>
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</tbody>
</table>

Label the sides of your dishes with pen
Prepare your nails as in the diagrams
Add the indicators to the hot agar jelly.
Pour the hot agar with indicators over the nails in the dishes. Allow the jelly to set.
Make drawings and observations of your nails and agar jelly after \( \frac{1}{2} \) an hour and after several days.
Results - Draw, colour and describe
After half an hour

Bent and normal nail

After .... days

copper strip around nail

Zinc strip around nail
Write-up and Discussion questions:

1. What colour is the agar alone? ..........................
2. What colour is the agar with the two indicators? ..........................
3. What colour indicates the site of oxidation? ..........................
4. What colour indicates the site of reduction? ..........................
5. What other colour(s) were produced? ........................... Explain the colour(s)
6. Why was jelly added to the dishes since it did not react at all? ..........................
7. Describe and explain the effect on the corrosion of an iron nail when it
   • is bent
   • is closely touching zinc metal
   • is closely touching copper metal
Nails in jelly - teacher’s pages

<table>
<thead>
<tr>
<th>Test Results</th>
<th>$K_3[Fe(CN)]_6$</th>
<th>$K_3[Fe(CN)]_6$ and $Fe^{2+}$</th>
<th>NaOH</th>
<th>NaOH and phenolphthalein</th>
</tr>
</thead>
<tbody>
<tr>
<td>colour</td>
<td>yellow</td>
<td>navy blue</td>
<td>clear</td>
<td>pink</td>
</tr>
</tbody>
</table>

Results - Draw, colour and describe

After half an hour

Bent and normal nail

Copper strip around nail

After .7. days

White

Zinc strip around nail
Nails in jelly - teacher’s pages cont’d

Write-up and Discussion questions:

1. What colour is the agar alone? pale brown - clear
2. What colour is the agar with the two indicators? yellow
3. What colour indicates the site of oxidation? navy blue \((\text{Fe}^{2+})\)
4. What colour indicates the site of reduction? pink \((\text{OH}^-)\)
5. What other colour(s) were produced? rust + white. Explain the colour(s)
   - Rust - the natural red-brown colour of the hydrated iron III oxide. White is ZnO, ZnCO₃.
6. Why was jelly added to the dishes since it did not react at all? Jelly was added to keep the products of corrosion at the site where they were formed.
7. Describe and explain the effect on the corrosion of an iron nail when it
   - is bent
   - is closely touching zinc metal
   - is closely touching copper metal

- Bent nail seems to accelerate corrosion. Bending creates a corner with more surface area for rusting to occur. Also, fine cracks expose more carbon impurities for additional oxidation sites (anode).
- Zinc prevents rusting. The zinc is oxidised in preference. It is the sacrificial anode. Zn oxidises and forms white ZnO and ZnO₂ with the CO₂ dissolved in the water.
- Cu accelerates the rusting of iron. It becomes the cathode making the Fe the anode. Oxidation (of iron) occurs at the anode. Cu provides ample sites for the reduction of Cu²⁺ in water half equation to occur.