

An investigation into the ability of metals to protect iron from rusting

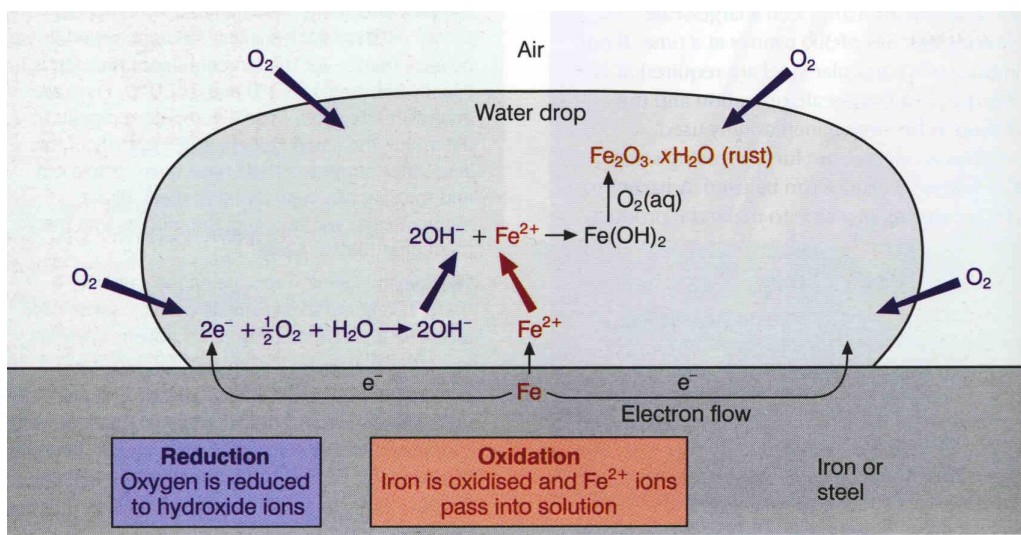
Aim

To investigate the ability of metals to act as a sacrificial protector of iron, preventing or reducing rusting.

Theory

Iron oxide is more stable than iron metal, so when given the opportunity iron will be readily oxidised. Iron reacts with oxygen and water to form a hydrated form of iron(III) oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$), known as rust, which is permeable to air and water so the metal underneath the rust layer continues to corrode¹.

This diagram shows the reactions which occur in a droplet of water on the surface of a piece of iron or steel:



Source 1

The iron atoms readily give away two electrons each, which react with oxygen and water molecules to form hydroxyl ions. These ions react with the iron ions to form iron hydroxide, which is then further oxidised and hydrated to give the iron(III) oxide.

The higher concentrations of dissolved oxygen at the edges of the drop mean that the reduction reactions happen around the edge, leaving a pit in the metal under the middle of the drop.

The rust forms away from the surface of the iron, as the iron and hydroxyl ions diffuse away.

Iron has a more negative electrode potential than oxygen + water (-0.44V compared to $+0.40\text{V}$), which explains why it gives away electrons (oxidation) instead of accepting them (reduction).

By coating the iron in a substance with a more negative electrode potential, the coating will give up electrons more readily than the iron. Therefore the coating will be oxidised and the iron will be protected.

Ferroxyl indicator is a mixture of Phenolphthalein in sodium chloride solution, and potassium hexacyanoferrate(III) . It turns from orangey-yellow to pink in the presence of hydroxyl ions, and to a blue colour in the presence of Fe^{3+} ions (the charge of the iron ions in the iron(III) oxide) ². Therefore if a piece of iron placed in the indicator rusts, a blue colour will appear. If nothing happens, there will be no colour change. If the coating is oxidised, the mixture will turn pink (as the coating's electrons will react with water and oxygen to produce hydroxyl ions, but no iron(III) ions will be produced).

The metals that will be used as a coating are magnesium, copper, zinc and lead.

Colorimeter theory

Hypothesis

Here is a table of the electrode potential values for iron and the four other metals (and hydrogen for reference):

Metal	Half-reaction	Electrode potential/V
Iron	$\text{Fe}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightarrow \text{Fe}_{(\text{s})}$	-0.44
Magnesium	$\text{Mg}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightarrow \text{Mg}_{(\text{s})}$	-2.36
Copper	$\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightarrow \text{Cu}_{(\text{s})}$	+0.34
Zinc	$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightarrow \text{Zn}_{(\text{s})}$	-0.76
Lead	$\text{Pb}^{2+}_{(\text{aq})} + 2\text{e}^{-} \rightarrow \text{Pb}_{(\text{s})}$	-0.13
Hydrogen	$2\text{H}^{+}_{(\text{aq})} + 2\text{e}^{-} \rightarrow \text{H}_{2(\text{g})}$	0.00

Source 3

As copper and lead have a higher electrode potential value than iron, they have a greater tendency to accept electrons, and therefore a lower tendency to donate electrons. I therefore predict that they will not protect the iron from rusting. On the other hand, because magnesium and zinc have a more negative electrode potential, they will donate electrons more readily than iron, so the iron will be protected.

However, as this experiment will most likely be under non-standard conditions (1atm pressure, 298K), these electrode potential values may vary. The ferroxyl indicator is a solution of ions, which increase the conductivity of the solution compared to distilled water. Also, the ferroxyl indicator is hot when made up, which will increase the temperature of the reaction.

Equipment

Quantity	Equipment	Other details
30	Iron nails	0.3g each
6 pieces each	Magnesium sheet	0.1g each 1cm x 1cm squares
	Copper sheet	
	Zinc sheet	
	Lead sheet	
36	Test tubes	
6	Test tube racks	
1	5cm ³ graduated pipette	For ferroxyl indicator, graduated every 0.1cm ³
1	Wheel pipette filler	
108cm ³ , plus extra to wash pipette	Fresh ferroxyl indicator Concentration	WITHOUT GELATINE PLEASE; YOU SAID IT IS NOT NECESSARY SO WHY WASTE AN ANIMAL'S LIFE?!
2	Colorimeters	Make and model
36	Clean plastic cuvettes	To fit colorimeter
36	Bulb pipettes	To transfer mixture from test tubes to cuvette
	Fine grade sandpaper	To clean metals
1	Balance	Reading to 0.01g
1	100cm ³ beaker	To hold the ferroxyl indicator
6	Stopwatches	To 0.01 seconds

Method

1. Fit the graduated pipette to the pipette filler and submerge the end of the pipette into the beaker of ferroxyl indicator. Turn the wheel to draw up the solution until the pipette is approximately 1/3 full. Remove the filler, and quickly cover the end with your thumb. Tilt the pipette up and down, rotating it to rinse it. Run the contents out by removing your thumb.
2. Fit the pipette filler to the end again, and draw up the solution until the meniscus is above the 2cm³ mark. Remove the filler and cover the end with your thumb. If the meniscus has dropped below the 2cm³ mark, let the solution run out and begin this step again. If it is still above the 2cm³ mark, release the pressure with your thumb so that the solution runs out slowly. Keep releasing the pressure until the bottom of the meniscus is on the 2cm³ mark, then press down to form a vacuum and hold that volume of solution in the pipette. Transfer the pipette to the first test tube, and release the pressure until the bottom of the meniscus reaches the 5cm³ mark.
3. Repeat step 2 to transfer 3cm³ ferroxyl indicator into each of the 36 test tubes. Start a stopwatch.
4. Label 6 test tubes with "Indicator only". These will be the negative controls.

5. Use the sandpaper to clean the nails and metal sheets. Place 6 of the nails in 6 test tubes of ferroxyl indicator, and start a stopwatch. Label these 6 test tubes with "Iron only"; these will be the positive controls.
6. Use pliers to fold a piece of sanded magnesium sheet around one of the sanded nails. It should be tight enough that it does not fall off, but should not completely cover the iron. Repeat for the other 5 pieces of magnesium, and place each in a test tube. Start a stopwatch. Label these 6 test tubes with "Fe + Mg".
7. Repeat with the 6 pieces of each of the other metals, and label the test tubes with "Fe + Cu", "Fe + Zn" and "Fe + Pb" as appropriate. Start a stopwatch for each set of 6 test tubes.
8. Set up the colorimeter **MORE DETAIL**
9. Use the bulb pipette to transfer some of the ferroxyl indicator into a plastic cuvette, to a depth of less than 1cm from the top.. Ensure the cuvette is only held on the frosted sides, as the light is shone through the clear sides and fingerprints could leave a smudge, which will absorb light and therefore create an error in the readings.
10. Place the cuvette in the colorimeter with the blue/green filter, the side with the arrow facing the light source. Close the lid and take a reading for the blue/green absorbance. Repeat in the colorimeter with the red filter and record both readings.
11. Repeat steps 9 and 10 for each of the solutions at 10, 20, 30, 40, 50 and 60 minutes, shaking the test tube first to unify any color change. Use a different test tube each time.