

What is corrosion?

What is Corrosion?

- Derived from Latin corrodere to gnaw to pieces
- Dictionary definition; to eat or wear away gradually
- Corrosion/rust/degradation
- Formation of a metal oxide
- Not just restricted to metal; glass, concrete, wood and plastics are all subject to environmental corrosion
- Electrochemical reaction

Causes

- External factors
- Water
- Acids
- Bases
- Salts
- Oils
- Solid and liquid chemicals
- Gases – acid vapours, ammonia gas, sulphur gas

Governed by energy changes

- The study of energy changes is called thermodynamics
- The system is the mass of material we are interested in.
- The environment which the system is in, is called the surroundings
- The Law: Energy can neither be created or destroyed (1st law thermodynamics)
- The Rule: All spontaneous changes occur with a release of free energy from the system to the surroundings at constant temperature and pressure. (2nd law thermodynamics)

Electrochemistry

- Electrochemistry deals with oxidation/reduction reactions.
- These reaction are associated with transfer of electrons between chemical species.
- For many reactions, we can separate the two halves of the reaction oxidation and reduction and have them take place in physically different locations.
- Then, rather than having the electrons transferred directly between the two species, we can force them to flow through an external circuit.



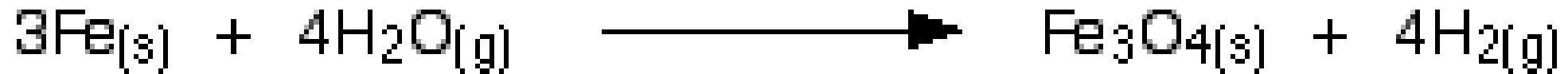
- electrical potential (voltage) is related to the free energy of the reaction
- measure the free energy as well as control the free energy by applying an external potential.

Electrode potentials and redox equilibria

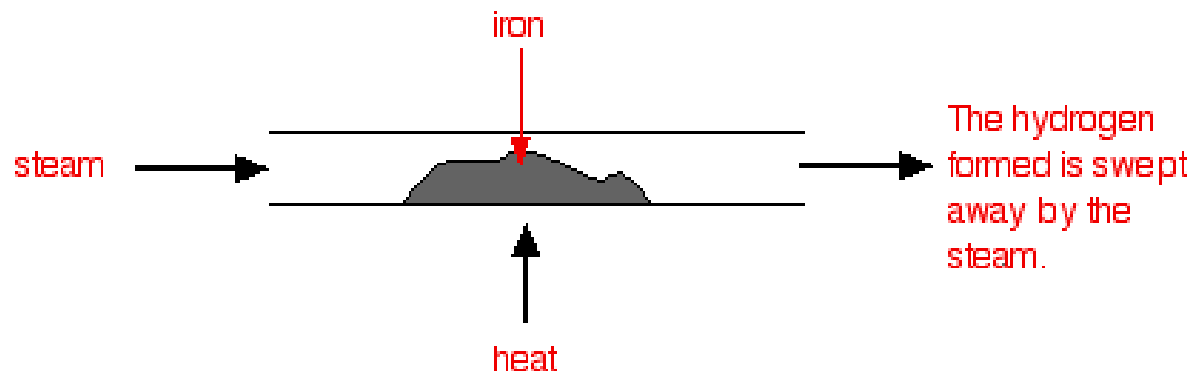
- Taken from
- <http://www.chemguide.co.uk/physical/redoxeqia/introduction.html>

Reversible reactions

- A reversible reaction is one which can be made to go in either direction depending on the conditions.
- If you pass steam over hot iron the steam reacts with the iron to produce a black, magnetic oxide of iron called tri-iron tetroxide
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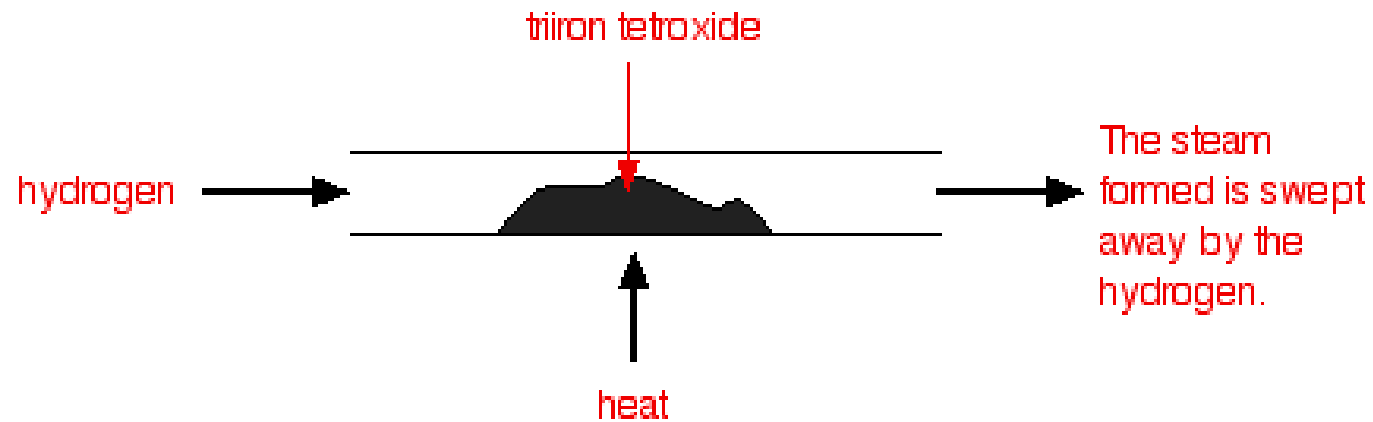
The hydrogen produced in the reaction is swept away by the stream of steam.



- Under different conditions, the products of this reaction will also react together. Hydrogen passed over hot tri-iron tetroxide reduces it to iron. Steam is also produced.



- This time the steam produced in the reaction is swept away by the stream of hydrogen.

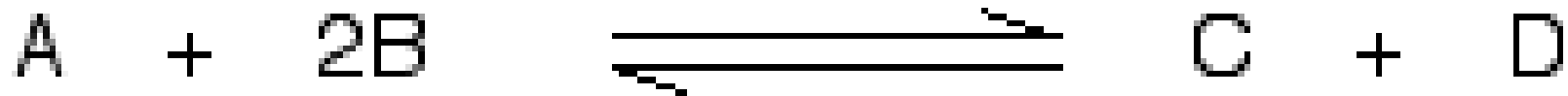


- These reactions are reversible, but under the conditions normally used, they become one-way reactions. The products aren't left in contact with each other, so the reverse reaction can't happen.
- **Reversible reactions happening in a closed system**
- A ***closed system*** is one in which no substances are either added to the system or lost from it. Energy can, however, be transferred in or out at will.

- In the example we've been looking at, you would have to imagine iron being heated in steam in a closed container. Heat is being added to the system, but none of the substances in the reaction can escape. The system is closed.
- As the triiron tetroxide and hydrogen start to be formed, they will also react again to give the original iron and steam. So, if you analysed the mixture after a while, what would you find?
- You would find that you had established what is known as a ***dynamic equilibrium***.

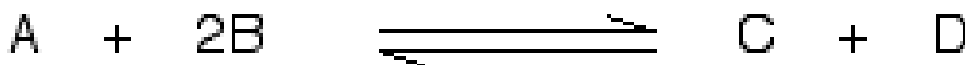
Le Chatelier's Principle

- If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change.
- Suppose you have an equilibrium established between four substances A, B, C and D.



What would happen if you changed the conditions by increasing the concentration of A?

- According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the concentration of A decreases again - by reacting it with B and turning it into C + D. The position of equilibrium moves to the right.

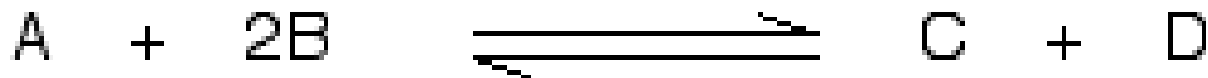


The position of equilibrium moves to the right if you increase the concentration of A.

This is a useful way of converting the maximum possible amount of B into C and D. You might use it if, for example, B was a relatively expensive material whereas A was cheap and plentiful.

What would happen if you changed the conditions by decreasing the concentration of A?

- According to Le Chatelier, the position of equilibrium will move so that the concentration of A increases again. That means that more C and D will react to replace the A that has been removed. The position of equilibrium moves to the left.

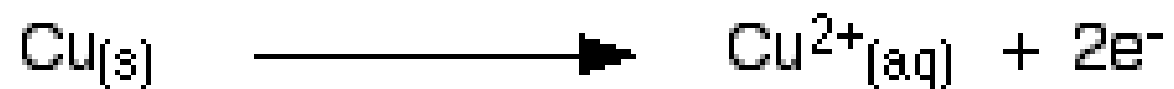
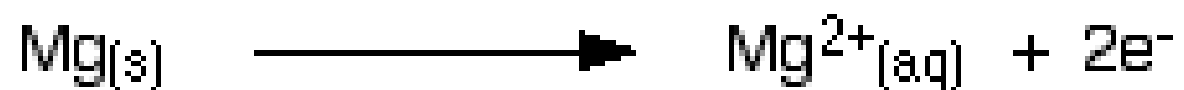


The position of equilibrium moves to the left if you decrease the concentration of A.

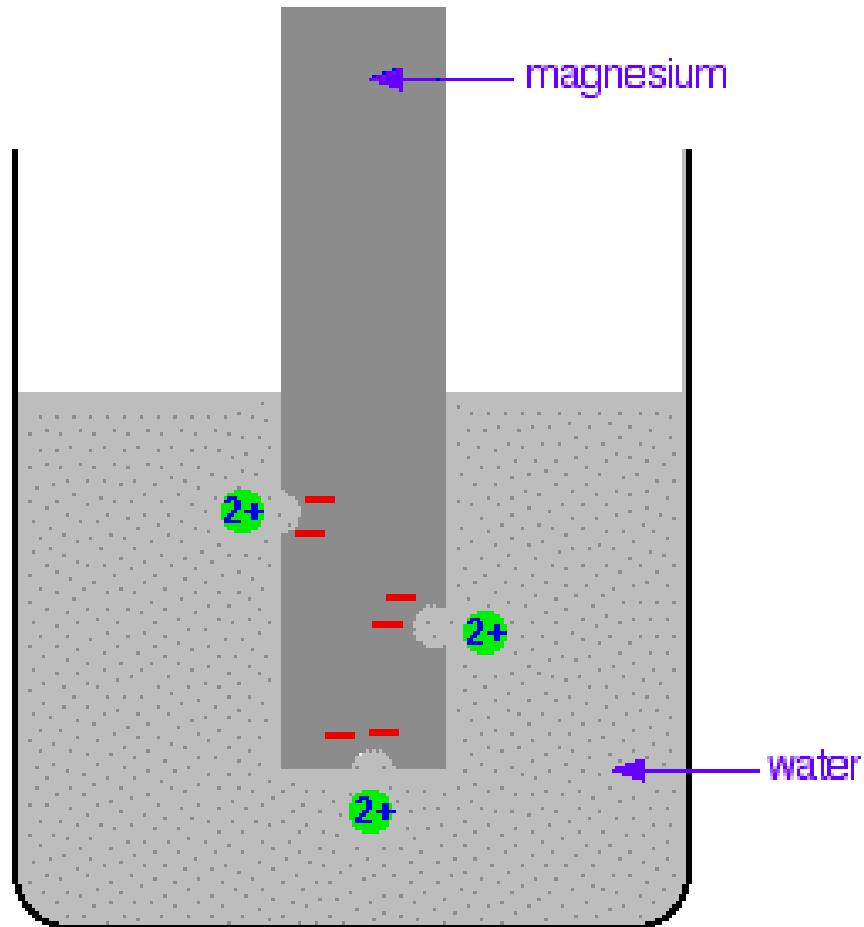
- This is essentially what happens if you remove one of the products of the reaction as soon as it is formed. If, for example, you removed C as soon as it was formed, the position of equilibrium would move to the right to replace it. If you kept on removing it, the equilibrium position would keep on moving rightwards - turning this into a one-way reaction.
- This isn't in any way an *explanation* of why the position of equilibrium moves in the ways described. All Le Chatelier's Principle gives you is a quick way of working out what happens.

- **The differing reactivities of metals**
- When metals react, they give away electrons and form positive ions. This particular topic sets about comparing the ease with which a metal does this to form hydrated ions in solution - for example, $\text{Mg}^{2+}_{(\text{aq})}$ or $\text{Cu}^{2+}_{(\text{aq})}$.

- We might want to compare the ease with which these two changes take place:

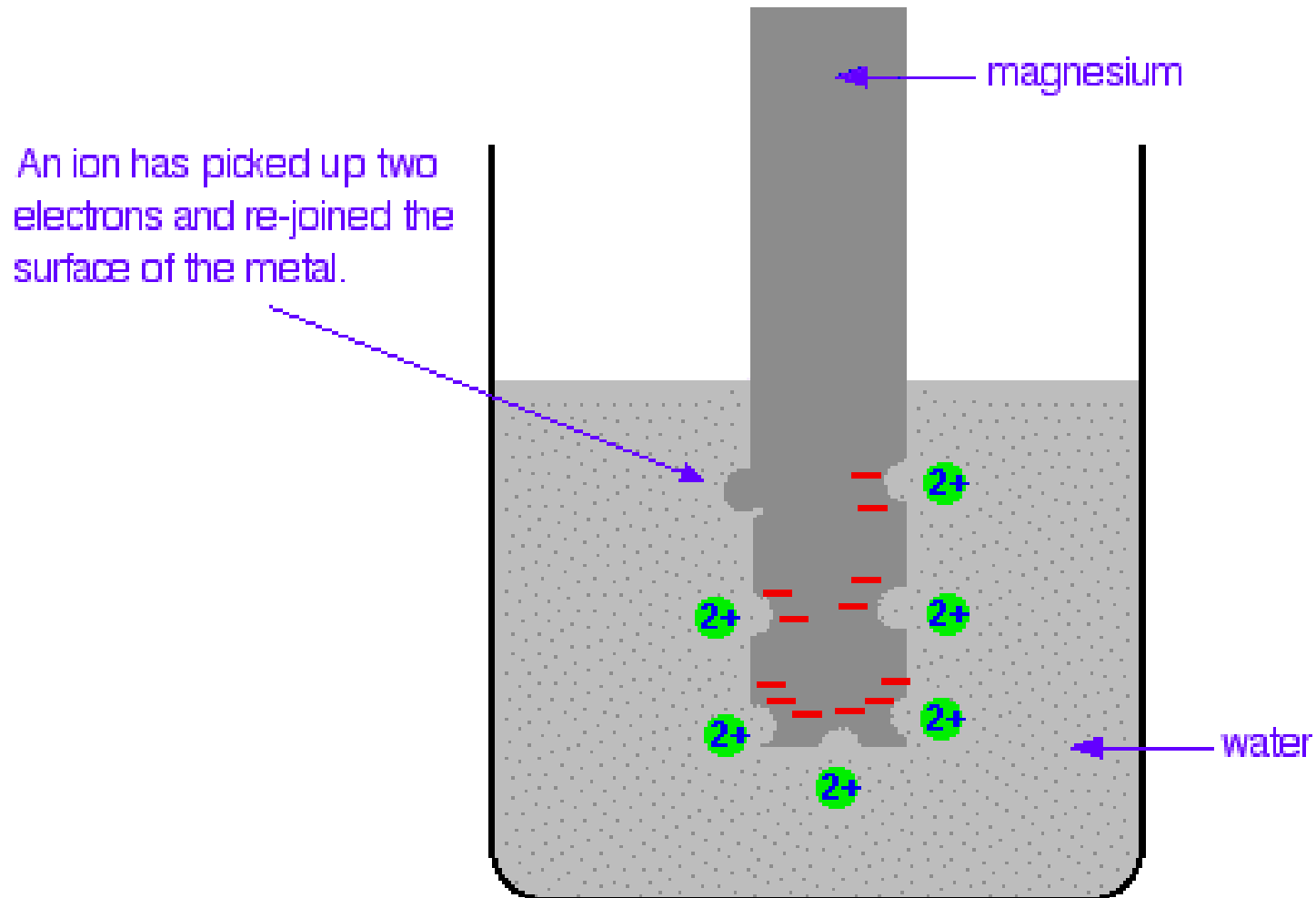


- magnesium is more reactive than copper.
- The first reaction happens much more readily than the second one.
- express this with some numbers
- Suppose you have a piece of magnesium in a beaker of water. There will be some tendency for the magnesium atoms to shed electrons and go into solution as magnesium ions. The electrons will be left behind on the magnesium.



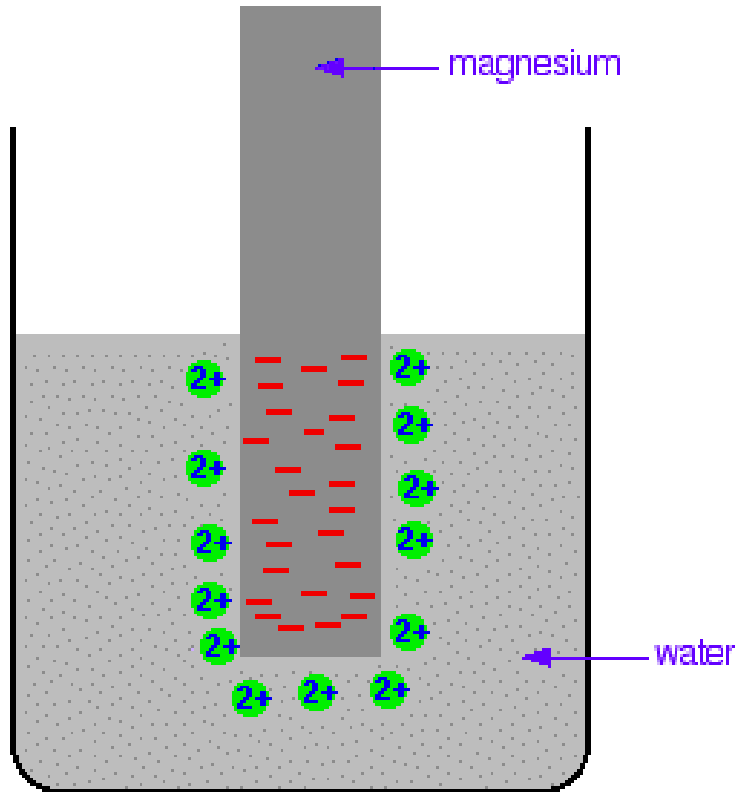
In a very short time, there will be a build-up of electrons on the magnesium, and it will be surrounded in the solution by a layer of positive ions. These will tend to stay close because they are attracted to the negative charge on the piece of metal.

Some of them will be attracted enough that they will reclaim their electrons and stick back on to the piece of metal.

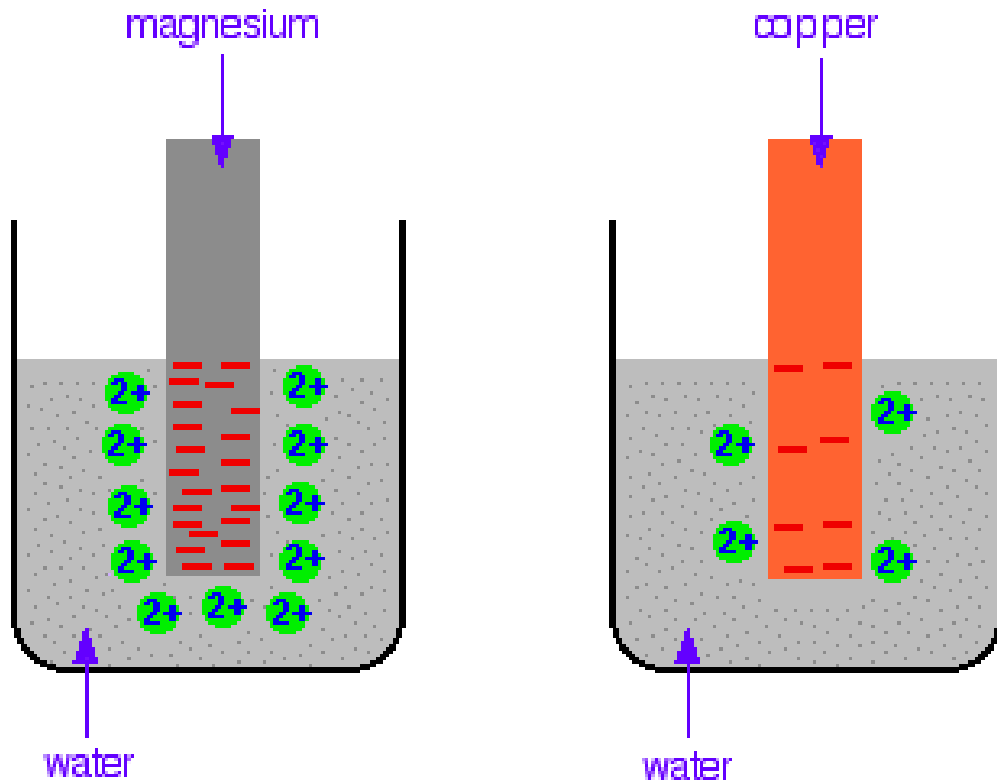


A dynamic equilibrium will be established when the rate at which ions are leaving the surface is exactly equal to the rate at which they are joining it again. At that point there will be a constant negative charge on the magnesium, and a constant number of magnesium ions present in the solution around it.

A snapshot of a dynamic equilibrium. Ions are continually leaving and rejoining the surface.



How would this be different if you used a piece of copper instead of a piece of magnesium?



Copper is less reactive and so forms its ions less readily. Any ions which do break away are more likely to reclaim their electrons and stick back on to the metal again. You will still reach an equilibrium position, but there will be less charge on the metal, and fewer ions in solution.

If we write the two reactions as equilibria, then what we are doing is comparing the two positions of equilibrium.



The position of the magnesium equilibrium lies further to the left than that of the copper equilibrium.



By convention, all these equilibria are written with the electrons on the left-hand side of the equation.

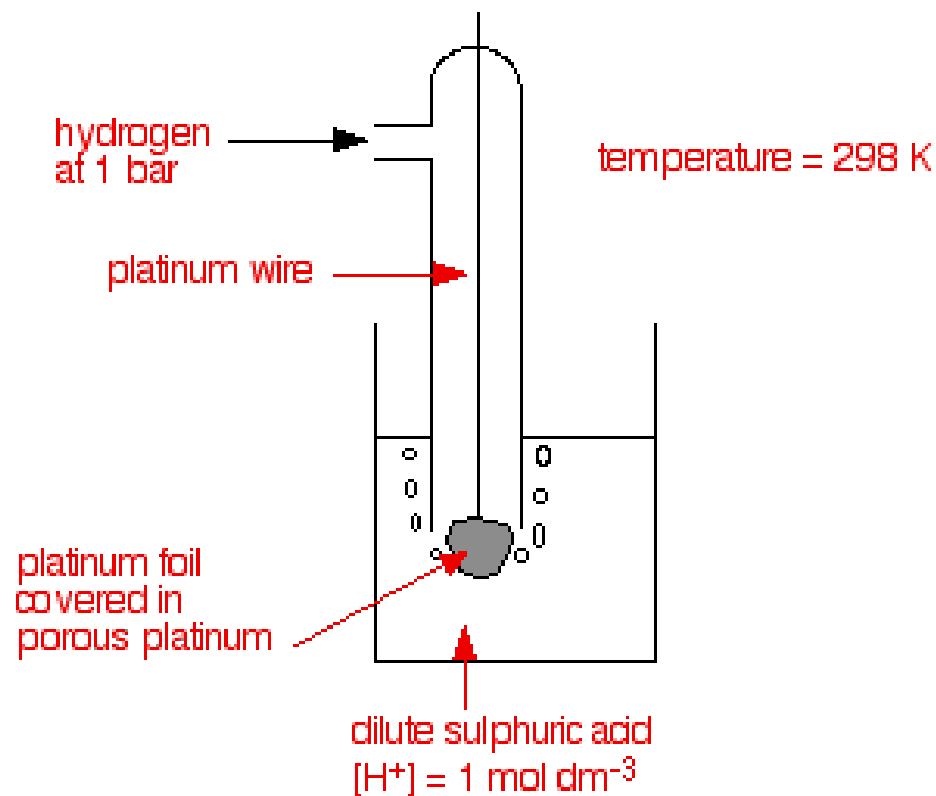
Let's attach some numbers to these differing positions of equilibrium

- In the magnesium case, there is a lot of difference between the negativeness of the metal and the positiveness of the solution around it. In the copper case, the difference is much less.
- This potential difference could be recorded as a voltage - the bigger the difference between the positiveness and the negativeness, the bigger the voltage.

How do you measure the voltage?

- Impossible!
- But we can measure the relative difference
- the magnesium equilibrium lies further to the left than the copper one.
- magnesium sheds electrons and forms ions more readily than copper does.
- we don't need to be able to measure the absolute voltage between the metal and the solution.
- It is enough to compare the voltage with a standardised system called a ***reference electrode***.
- The system used is called a standard hydrogen electrode.

Measuring standard electrode potentials (standard redox potentials)



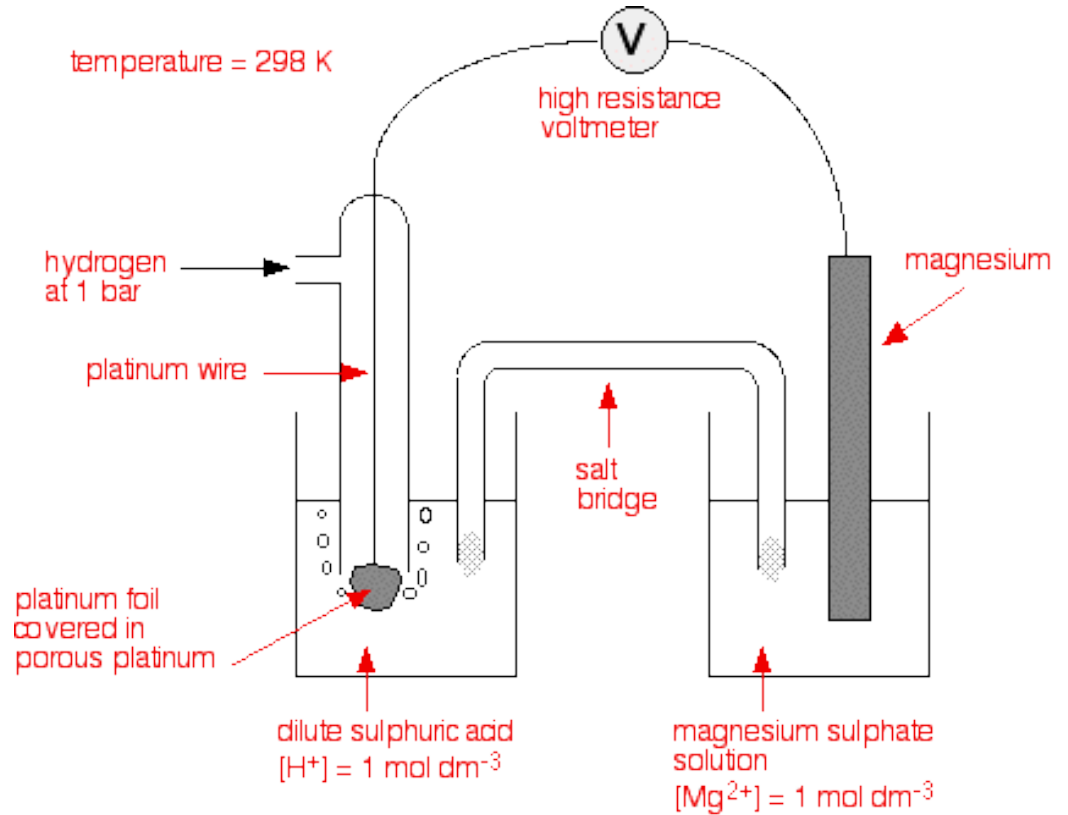
As the hydrogen gas flows over the porous platinum, an equilibrium is set up between hydrogen molecules and hydrogen ions in solution. The reaction is catalysed by the platinum.



This is the equilibrium that we are going to compare all the others with the reference equilibrium or standard hydrogen electrode.

Using the standard hydrogen electrode

- The standard hydrogen electrode is attached to the electrode system you are investigating - for example, a piece of magnesium in a solution containing magnesium ions.



Cells and half cells

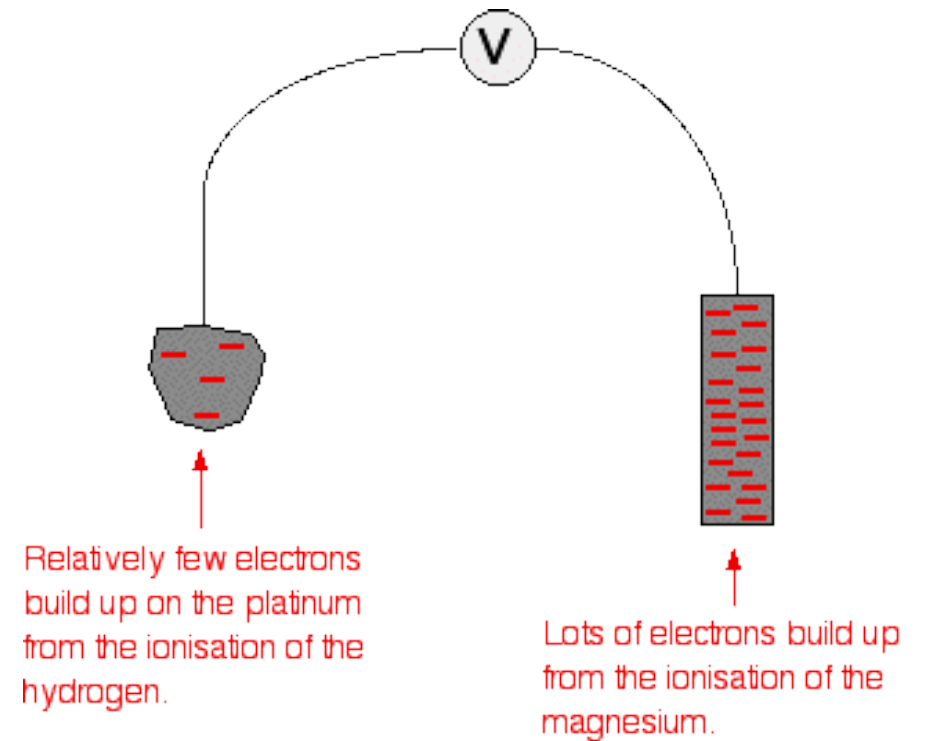
- The whole of this set-up is described as a cell. It is a simple system which generates a voltage. Each of the two beakers and their contents are described as half cells.
- ***The salt bridge***
- The salt bridge is included to complete the electrical circuit but without introducing any more bits of metal into the system. It is just a glass tube filled with an electrolyte like potassium nitrate solution. The ends are "stoppered" by bits of cotton wool. This stops too much mixing of the contents of the salt bridge with the contents of the two beakers.
- The electrolyte in the salt bridge is chosen so that it doesn't react with the contents of either beaker.

What happens?

- These two equilibria are set up on the two electrodes (the magnesium and the porous platinum):



- Magnesium has a much greater tendency to form its ions than hydrogen does. The position of the magnesium equilibrium will be well to the left of that of the hydrogen equilibrium.
- That means that there will be a much greater build-up of electrons on the piece of magnesium than on the platinum.



- There is a major difference between the charge on the two electrodes - a potential difference which can be measured with a voltmeter. The voltage measured would be 2.37 volts and the voltmeter would show the magnesium as the negative electrode and the hydrogen electrode as being positive.
- This sometimes confuses people! Obviously, the platinum in the hydrogen electrode isn't positive in real terms - there is a slight excess of electrons built up on it. But voltmeters don't deal in absolute terms - they simply measure a difference.

- The magnesium has the greater amount of negativeness - the voltmeter records that as negative. The platinum of the hydrogen electrode isn't as negative - it is *relatively* more positive. The voltmeter records it as positive.
- Throughout the whole of this redox potential work, you have to think in relative terms. For example, $+0.4$ is relatively more negative than $+1.2$. Or, another example, -0.3 is relatively more positive than -0.9 .

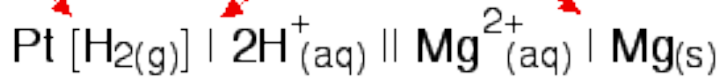
The voltmeter

- voltmeter is described as having a "high resistance". Ideally, it wants to have an infinitely high resistance.
- This is to avoid any flow of current through the circuit. If there was a low resistance in the circuit, electrons would flow from where there are a lot of them (around the magnesium, for example) to where there are less (on the hydrogen electrode).
- If any current flows, the voltage measured drops. In order to make proper comparisons, it is important to measure the maximum possible voltage in any situation. This is called the ***electromotive force*** or ***emf***.
- The emf of a cell measured under standard conditions is given the symbol E°_{cell} . (E standard)

Drawing a full diagram to represent a cell takes too long. Instead, the cell in which a magnesium electrode is coupled to a hydrogen electrode is represented like this:

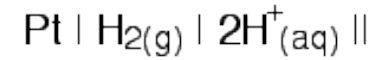
Square brackets show the hydrogen flowing over the platinum.

Single vertical lines show a boundary between two phases - for example, between the magnesium ions and the solid metal.



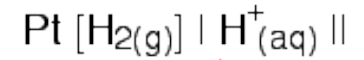
Double vertical lines show the salt bridge. This is sometimes shown by a single (or double) *broken* vertical line (or lines).

OR



Square brackets replaced by a vertical line showing the boundary between the platinum and the hydrogen.

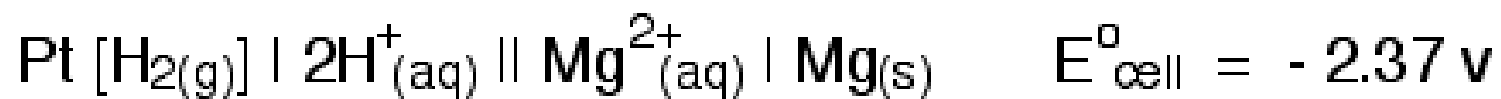
or



One hydrogen ion shown rather than the 2 from the equation.

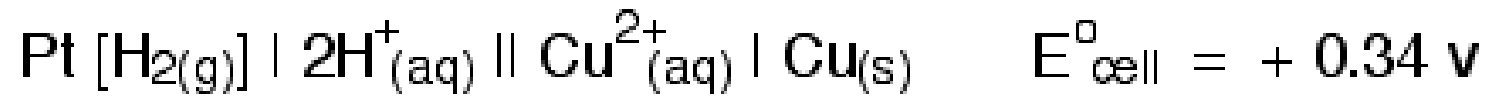
Attaching a sign to the cell voltage

- The convention is that you ***show the sign of the right-hand electrode*** (as you have drawn it) when you quote the E°_{cell} value. For example:



Shows that the magnesium (the right-hand electrode) is the negative one.

In the copper case:



Shows that the copper (the right-hand electrode) is the positive one.

Defining standard electrode potential (standard redox potential)

- The values that we have just quoted for the two cells are actually the standard electrode potentials of the $\text{Mg}^{2+} / \text{Mg}$ and $\text{Cu}^{2+} / \text{Cu}$ systems.
- The emf measured when a metal / metal ion electrode is coupled to a hydrogen electrode under standard conditions is known as the standard electrode potential of that metal / metal ion combination.
- By convention, the hydrogen electrode is always written as the left-hand electrode of the cell. That means that the sign of the voltage quoted always gives you the sign of the metal electrode.
- Standard electrode potential is given the symbol E° .

Summarizing what standard electrode potentials tell you

- Remember that the standard electrode potential of a metal / metal ion combination is the emf measured when that metal / metal ion electrode is coupled to a hydrogen electrode under standard conditions.
- What you are doing is comparing the position of the metal / metal ion equilibrium with the equilibrium involving hydrogen.
- Here are a few typical standard electrode potentials:

EMF series

OXIDISING AGENTS (Oxidants)	Redox table - list of reduction potentials measured under standard conditions (25°C, 1 atmosphere pressure, 1 mol/L solution)	REDUCING AGENTS (Reductants)
Weakest oxidising agents	$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li(s)} \quad -3.04 \text{ V}$ $\text{K}^+ + \text{e}^- \rightleftharpoons \text{K(s)} \quad -2.92 \text{ V}$ $\text{Ba}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ba(s)} \quad -2.90 \text{ V}$ $\text{Ca}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ca(s)} \quad -2.87 \text{ V}$ $\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na(s)} \quad -2.71 \text{ V}$ $\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg(s)} \quad -2.36 \text{ V}$ $\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al(s)} \quad -1.66 \text{ V}$	Strongest reducing agents
Strength of oxidising agents increases down table	$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn(s)} \quad -0.76 \text{ V}$ $\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe(s)} \quad -0.41 \text{ V}$ $\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn(s)} \quad -0.14 \text{ V}$ $\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb(s)} \quad -0.13 \text{ V}$ $\text{Fe}^{3+} + 3\text{e}^- \rightleftharpoons \text{Fe(s)} \quad -0.02 \text{ V}$ $\text{H}^+ + \text{e}^- \rightleftharpoons 1/2\text{H}_2(\text{g}) \quad 0.00 \text{ V}$	Strength of reducing agents decreases down table
Strongest oxidising agents	$\text{SO}_4^{2-} + 2\text{e}^- + 4\text{H}^+ \rightleftharpoons \text{SO}_2(\text{g}) + 2\text{H}_2\text{O} \quad 0.21 \text{ V}$ $\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu(s)} \quad 0.34 \text{ V}$ $1/2\text{I}_2(\text{s}) + \text{e}^- \rightleftharpoons \text{I}^- \quad 0.54 \text{ V}$ $1/2\text{I}_2(\text{aq}) + \text{e}^- \rightleftharpoons \text{I}^- \quad 0.62 \text{ V}$ $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+} \quad 0.77 \text{ V}$ $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag(s)} \quad 0.80 \text{ V}$ $1/2\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O} \quad 1.23 \text{ V}$ $1/2\text{Cl}_2(\text{g}) + \text{e}^- \rightleftharpoons \text{Cl}^- \quad 1.36 \text{ V}$ $\text{MnO}_4^- + 5\text{e}^- + 8\text{H}^+ \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad 1.51 \text{ V}$ <u>$1/2 \text{F}_2(\text{g}) + \text{e}^- \rightleftharpoons \text{F}^- \quad 2.87 \text{ V}$</u>	Weakest reducing agents
	The higher the reduction potential, (e.g. F_2), the more easily the substance is reduced (and thus the greater its oxidising power).	

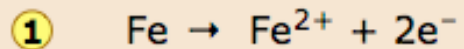
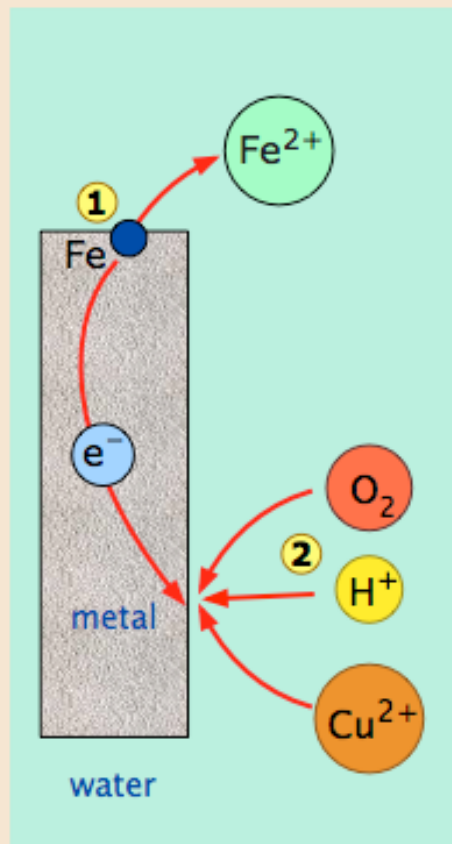
- E° values give you a way of comparing the positions of equilibrium when these elements lose electrons to form ions in solution.
- The more negative the E° value, the further the equilibrium lies to the left - the more readily the element loses electrons and forms ions.
- The more positive (or less negative) the E° value, the further the equilibrium lies to the right - the less readily the element loses electrons and forms ions.

Electrochemical corrosion of iron

- Corrosion often begins at a location
- **(1)** where the metal is under stress (at a bend or weld)
- or is isolated from the air (where two pieces of metal are joined or under a loosely-adhering paint film.)
- The metal ions dissolve in the moisture film and the electrons migrate to another location **(2)** where they are taken up by a ***depolarizer***.
- Oxygen is the most common depolarizer; the resulting hydroxide ions react with the Fe^{2+} to form the mixture of hydrous iron oxides known as ***rust***.

Electrochemical corrosion of iron

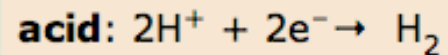
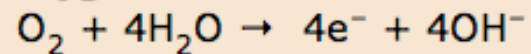
Corrosion is a two-step process



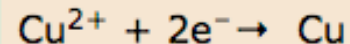
Fe atom at metal surface dissolves into moisture film, leaving negative charge in metal.

② Corrosion continues as a *depolarizer* removes electrons from metal.
Common depolarizers are:

oxygen:



cation of more-noble metal:



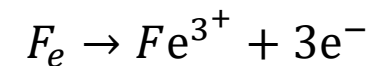
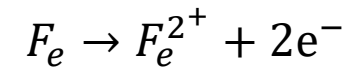
Stephen Lower

Corrosion reaction for iron

Iron has two valencies: 2 or 3

Valency

Valency is the combining power of an element. Elements in the same group of the periodic table have the same valency. The valency of an element is related to how many electrons are in the outer shell.



Dissimilar metal corrosion/ bimetallic or galvanic

- Dissimilar metal corrosion results from the coupling of two different metals. It is also called bimetallic corrosion or galvanic corrosion.
- Sacrificial anode cathodic protection is the constructive use of the galvanic corrosion.

Origin of the word galvanic

- Professor Luigi Galvani discovered the physiological action of electricity and demonstrated the existence of natural electric current in animal tissue.
- Volta, a professor of experimental physics in the University of Pavia, was among the first scientists who repeated and verified Galvani's experiments.
- At first, he embraced animal electricity. Galvani believed that the animal electricity came from the muscle in its pelvis.
- Volta, in opposition, reasoned that the animal electricity was a physical phenomenon caused by rubbing frog skin.
- Volta, essentially, objected to Galvani's conclusions about "animal electric fluid", but the two scientists disagreed respectfully and Volta coined the term "Galvanism" for a direct current of electricity produced by chemical action.
- http://ethw.org/Luigi_Galvani

Galvanic Series

[illegible]

Galvanic Corrosion Risk

Anodic (Corrodes)	Cathodic															
	Magnesium & Alloys	Zinc & Alloys	Aluminum & Alloys	Cadmium	Steel (Carbon)	Cast Iron	Stainless Steels	Lead, Tin & Alloys	Nickel	Brasses, Nickel-Silvers	Copper	Bronzes, Cupro-Nickels	Nickel Copper Alloys	Nickel-Chrome Alloys	Titanium	Silver
Magnesium & Alloys																
Zinc & Alloys																
Aluminum & Alloys																
Cadmium																
Steel (Carbon)																
Cast Iron																
Stainless Steels																
Lead, Tin & Alloys																
Nickel																
Brasses, Nickel-Silvers																
Copper																
Bronzes, Cupro-Nickels																
Nickel Copper Alloys																
Nickel-Chrome Alloys																
Titanium																
Silver																
Graphite																
Gold																
Platinum																

The table can be used as a quick guide to select compatible metals. Where two materials meet in a green region the corrosion potential can be thought of negligible, meaning, a good combination. Materials that meet in the red zone however should be avoided or used with caution.

Temperature effect

- The order of galvanic series may reverse under certain circumstances
- For example Zn and Fe at elevated temperatures in potable water systems

Area Effect

- In two dissimilar metals, more active metal becomes anode of the couple in wet corrosion cell
- More noble becomes cathode
- Corrosion rate of the more active metal will be accelerated
- More noble metal corrosion retarded BUT
- Cathode may still corrode
- Greater cathode to anode area ratio will result in a greater accelerating factor in the rate of galvanic corrosion

The ElectroMotive Force (EMF) series compared to Galvanic Series

- EMF is an orderly listing of standard half-cell electrode potentials
- Galvanic series is an orderly list of corrosion potentials for various pure metals and alloys

Difference between EMF series and Galvanic Series

EMF	Galvanic
Absolute	Relative
Quantitative	Qualitative
Pure metals only	Metals and alloys
Half cell potential	Corrosion potential
Standard conditions	Any specified conditions
Based on thermodynamic analysis	Based on thermodynamic analysis
Used for theoretical calculations	Used for practical applications

- Good engineers don't need to remember every formula; they just need to know where they can find them

Cathodic Protection

- The reduction or prevention of corrosion by making metallic structure as cathode in the electrolytic cell
- No anodic area on the metal so no corrosion
- 2 methods
- Sacrificial anodic protection (galvanic protection)
- Impressed current cathodic protection

Anodic Protection

- Controls the corrosion of a metal surface by making it the anode of an electrochemical cell and controlling the electrode potential in a zone where the metal is passive
- Decreases the rate of hydrogen evolution
- Potentiostat is an electronic device that maintains a metal at a constant potential
- Shifts corrosion potential to passive which stops corrosion
- Potential range depends on the environment

Anodic Protection

- Applications
- Applicable in extremely corrosive environments
- Low current requirement
- Acid coolers in dilute sulphuric acid plants
- Storage tanks for sulphuric tanks
- Chromium in contact with hydrofluoric acid

Cathodic Protection	Anodic Protection
Applicable to all metals	Applicable only to those metals that show active passive behaviour
Used where there is no source of power by employing sacrificial anodes	More aggressive corrodents can be handled
Lower installation costs	Operating costs are lower although installation costs are higher
Standard and well established method	Feasibility can be predicted in laboratory and the design is easier