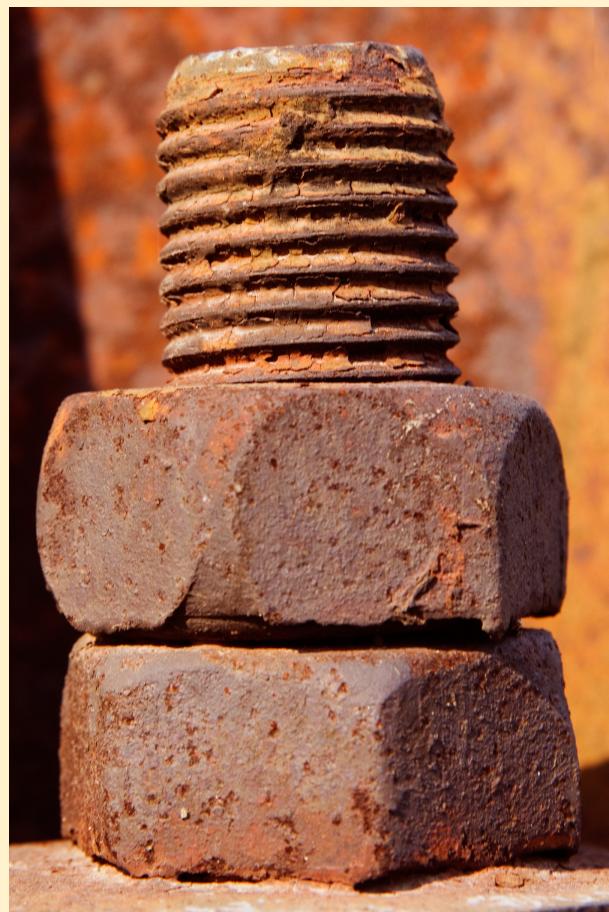


IB - Materials

2023-2024

Corrosion
Application of kinetics and thermodynamics



Lecturer: Prof Alexandre Kabla

Introduction

What is corrosion?

Corrosion is the **progressive attack** of materials, typically metals, due to **chemical reactions with their environment**.

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A common example is rust formation, occurring when iron is present alongside water and oxygen.

Why study these questions?

3



Figure 1: Social and economical impact of wear and corrosion. Left: the Silver Bridge after its collapse in 1967. Right: rusty cars out of service.

There are several reasons to consider these issues:

- **Safety**

Corrosion caused the collapse of the Silver Bridge over the Ohio River in Dec 1967, resulting in the death of 46 people. Also in Ohio, in 2002, a 10 cm hole was identified in one of the reactors lid of a nuclear plant during a routine maintenance operation. The plant was operating on the brink of a devastating accident.

- **Economic cost**

In the US alone, the annual cost of corrosion has been estimated at \$275 billion, approximately 3% of the GDP. Corrosion and wear determine the life span of many mechanical components.

- **Conservation**

Metals are limited natural resources. The estimate of the global reserves for iron was 110 years of supply in 1975, and 77 years in 1995. For copper, it was 23 years in 1975, and 16 years in 1995. Although new mining sites are discovered over time, preventing corrosion and wear might therefore help prevent or postpone shortage of these key mineral resources.

Outline

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- Fundamentals of electrochemistry
 - Metal interfaces in solution
 - Electrode potential
 - Current generation
- Metal corrosion
 - Metal degradation in aqueous environments
 - Protective methods
- Galvanic corrosion
 - Differential corrosion of connected metals in aqueous environment
 - Protective methods
- Oxide layers
 - Thermodynamics and kinetics of oxide layer formation
 - Problems and advantages of oxide layers

1 Rudiments of Electrochemistry

A metal surface takes a potential in water

In a solution, metallic ions¹ will detach from the metal surface, leaving free electrons at the interface.



If the electrons remain at the surface, an electric field develops and attracts back the ions towards the metal. This favours the inverse reaction until an **equilibrium** is reached.

Other components in the solution (ions, water², etc.) will also respond to and modify the electric field.

The development of the electric field implies that the metal (electrode) takes a **potential** with respect to the solution.

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¹Definition: An ion is an atom or molecule with a net electric charge due to the loss or gain of one or more electrons. Negatively charged ions are called anions, positively charged ions are called cations.

²Water molecules have no net charge, but the oxygen atom tends to attract the electron more than the hydrogen; the oxygen atom is slightly negatively charged, whereas the hydrogen atoms are slightly positively charged.

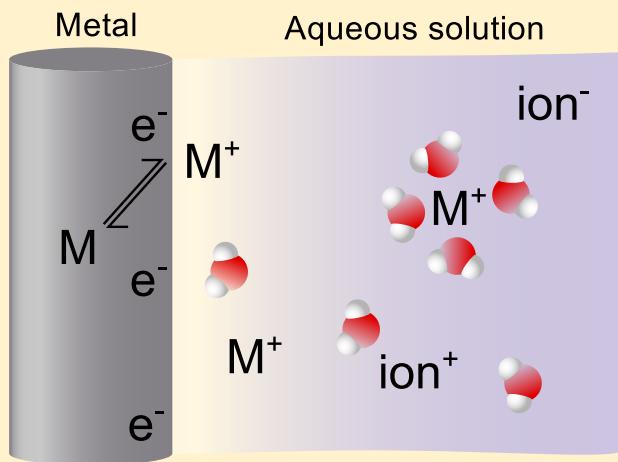


Figure 2: Microscopic origin of the surface potential of a metal. (i) Metallic ions are freed in the solution, leaving free electrons in the metal. Polar water molecules and other cations and anions also contribute to the establishment of a potential difference.

Measuring the electrode potential

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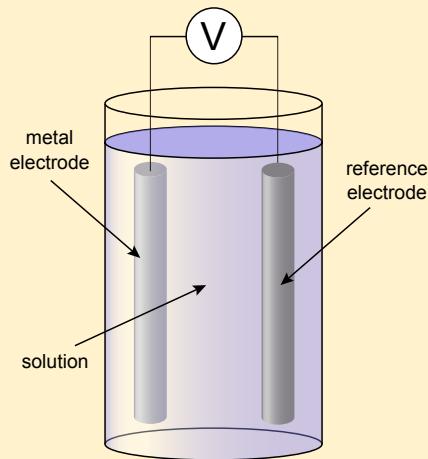


Figure 3: Measuring the potential of a metal in a solution.

- The potential will depend on the **metal** and **its environment**.
- To measure the surface potential, one needs a **reference electrode**. A reference electrode has a fixed potential with respect to the solution. There are many types of reference electrode, such as the standard hydrogen electrode, and the saturated calomel electrode. Such tools are not going to be described in these lectures.
- It is possible to classify metals if a standardised environment is used. The standard potential E^0 is defined by the potential of a metal in a solution of

its ion at a concentration of one mole per litre. The value of E^0 for common metals and their ions can be found on figure 4.

Reaction	E^0 (V vs. SHE)	
$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	+1.498	Noble
$\text{Pt}^{2+} + 2e^- \rightarrow \text{Pt}$	+1.18	
$\text{Pd}^{2+} + 2e^- \rightarrow \text{Pd}$	+0.951	↑
$\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}$	+0.851	
$\text{Ag}^+ + e^- \rightarrow \text{Au}$	+0.800	
$\text{Cu}^+ + e^- \rightarrow \text{Cu}$	+0.521	
$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+0.342	
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0.000	
$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.126	
$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$	-0.138	
$\text{Mo}^{3+} + 3e^- \rightarrow \text{Mo}$	-0.200	
$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.257	
$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$	-0.28	
$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$	-0.403	
$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.447	
$\text{Ga}^{3+} + 3e^- \rightarrow \text{Ga}$	-0.549	
$\text{Ta}^{3+} + 3e^- \rightarrow \text{Ta}$	-0.6	
$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$	-0.744	
$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.762	
$\text{Nb}^{3+} + 3e^- \rightarrow \text{Nb}$	-1.100	
$\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$	-1.185	
$\text{Zr}^{4+} + 4e^- \rightarrow \text{Ze}$	-1.45	
$\text{Hf}^{4+} + 4e^- \rightarrow \text{Hf}$	-1.55	
$\text{Ti}^{2+} + 2e^- \rightarrow \text{Ti}$	-1.630	
$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.662	
$\text{U}^{3+} + 3e^- \rightarrow \text{U}$	-1.798	
$\text{Be}^{2+} + 2e^- \rightarrow \text{Be}$	-1.847	
$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.372	
$\text{Na}^+ + e^- \rightarrow \text{Na}$	-2.71	
$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$	-2.868	
$\text{K}^+ + e^- \rightarrow \text{K}$	-2.931	↓
$\text{Li}^+ + e^- \rightarrow \text{Li}$	-3.040	Active

Figure 4: Standard potential of the main metals and their ions.

Application: the Daniell cell

Once metals are classified, it is easy to select two metal electrodes and build a simple battery. The simplest way is to assemble two half cells, each containing one metal electrode in its standard environment. The Daniell cell, invented in 1836 by the British chemist John Frederic Daniell, is based on this principle, using zinc and copper as the two metals.

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Figure 5 shows a sketch of such a cell. The difficulty here relies on the necessity to close the circuit without mixing the two solutions. For this, a salt bridge is used. It is a porous material that contains a rich ionic solution. Current can flow through the bridge thanks to ion transport instead of electron conduction.

If the circuit is open, the difference of potential measured between the two electrodes is determined by the standard potentials.

If the circuit is closed by a resistor, current will start flowing from the copper to the zinc, i.e. electrons leave the zinc electrode to go toward the copper, to compensate for the different electrode potentials. This transfer of electrons will place the electrodes out of equilibrium with respect to the solutions, leading on one side to a release of Zn^{2+} ions, freeing new electrons, and on the other to a consumption of Cu^{2+} ions, compensated for the local excess of electrons (see Figure 5). These reactions are maintained as long as the circuit is closed, or until the zinc electrode or copper ions runs out. In the present case, the progressive degradation of the zinc electrode is analogous to a corrosion process.

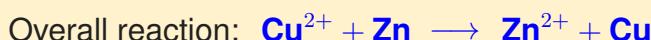
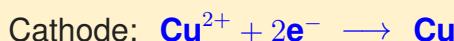
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Half cell reactions

In a cell, two different types of reactions take place simultaneously, depending on whether electrons are gained or lost.

- One compound is **oxidized**, meaning that it is **losing** electrons.
This reaction takes place at the **anode**.
- One compound is **reduced**, meaning that it is **gaining** electrons.
This reaction takes place at the **cathode**.

In the case of the Daniell Cell:



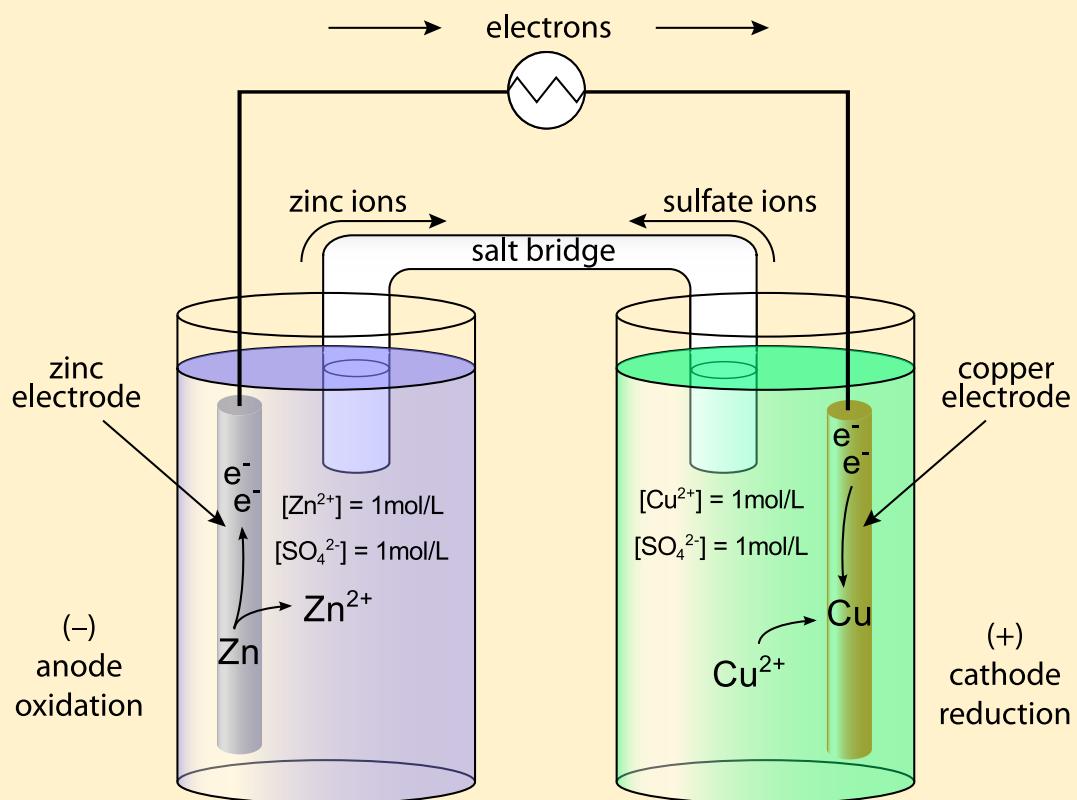


Figure 5: Sketch of a Daniell cell.

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The “lemon” cell

Although the Daniell cell predicts that the zinc is going to corrode if electrons can be transferred to copper ions. It does not tell us very much about normal environmental conditions where metallic ions are rather scarce. There is a common toy, the “lemon cell” that shows that metallic ions are not necessary to have an electron flow.

In a lemon cell (see Figure 6), a piece of zinc and a piece of copper are introduced into a lemon. A difference of potential then builds up between the two electrodes. This system is not in the standard conditions since no metallic ions are present. While the anode could still free electrons and release zinc ions, no copper ions are present to receive them. Inspection of the table of standard potential allows us nevertheless to identify other compounds that might be react when connected to zinc.

Lemon is acidic. The environment therefore contains a lot of H^+ ions that could collect the electrons on the cathode. The potential of H^+/H_2 is larger than the potential of Zn^{2+}/Zn . Hence it will spontaneously capture zinc electrons.

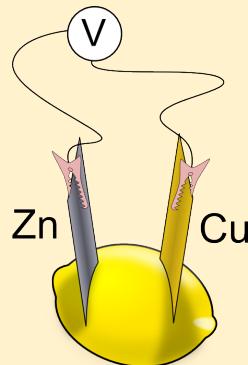
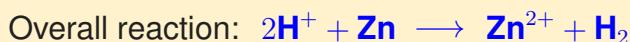
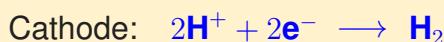


Figure 6: Sketch of a lemon battery.



Based on the standard electrode potential of H^+/H_2 and Zn^{2+}/Zn , we expect to read a voltage of the order of **0.75V**, which is roughly what we get.

This is the electro-chemical potential that would corrode zinc in an acidic environment.

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A piece of Zn in an acidic solution

In the previous experiment, the copper does not play an important role; it just redistributes the electrons to the hydrogen ions, but is not directly involved in the chemical reactions. But the zinc strip could also deliver these electrons to the environment; if we place a piece of zinc in a lemon (Figure 7), it would be eroded in the same way, although it would be slower, and without any opportunity to do something useful with these electrons. This is what corrosion is about.

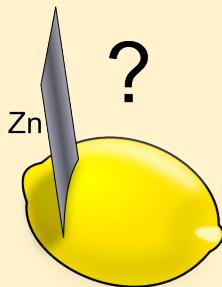
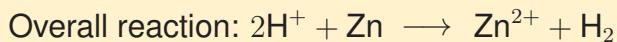
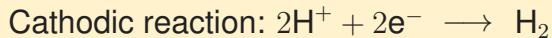


Figure 7: A piece of zinc in a lemon would also corrode.



These examples help us get a basic understanding of what drives corrosion. It is essentially a differential affinity for electrons of two different compounds that are electrically connected. The lower the electrode potential, the more likely the metal will degrade (oxidise) by giving away electrons. Iron or zinc therefore appear easy to oxidise, although it depends on the environment. On the contrary, gold and platinum are very stable. They are called noble metals. We will now use that knowledge to study cases that are more specific to real life corrosion problems.

Summary

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- A metal placed in an environment that can accept metal ions, such as water, takes at the equilibrium an electric potential with respect to this environment.
- The value of the electric potential depends on the metal and the chemical composition of the environment.
- Metals can be classified based on their electric potential in a standardised environment, consisting of a 1M solution of the corresponding metal ion in pure water, at standard temperature and pressure.
- The electro-potentials may drive a useful electric current but also lead to the consumption of the metal.

2 Corrosion of metals in water

2.1 Reactive metals in water

Iron and steel corrosion

We consider first the case of iron or steel in an aqueous environment. As in the case of the zinc, in acidic conditions it could react with hydrogen ions. We all know however that rust also appears in neutral water. Depending on the chemical environments, there are in fact different types of reaction that can take place.

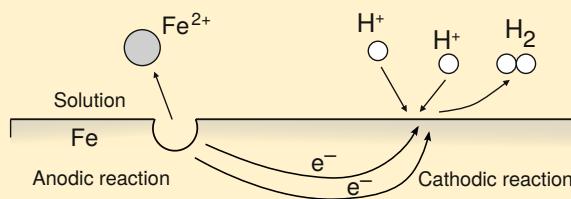


Figure 8: Reactions involved in iron corrosion in acidic environments.

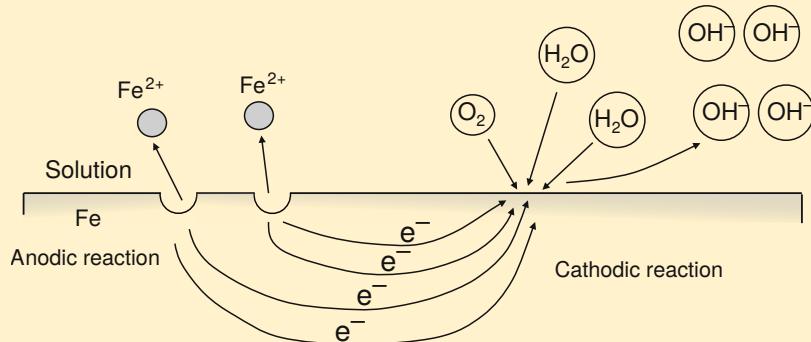
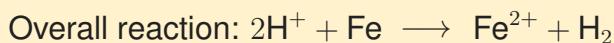
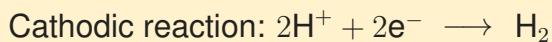


Figure 9: Reactions involved in iron corrosion in neutral environments with oxygen.

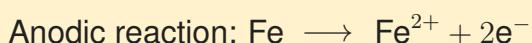
Iron in acidic environment



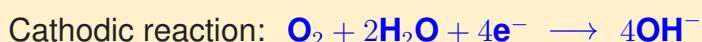
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Iron in a neutral environment with oxygen



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Rust

Iron corrosion in the presence of water and oxygen results in the formation of a solid oxide called rust. Iron ions and hydroxide ions (OH^-) first form together a ferrous hydroxide precipitate that often deposits on the metal (see Figure 10a). The precipitate then reacts with water to form a hydrated ferric oxide (see Figure 10b). This oxide unfortunately adheres very poorly to the metal surface and tends to form flakes that further expose the metallic surface to corrosion.

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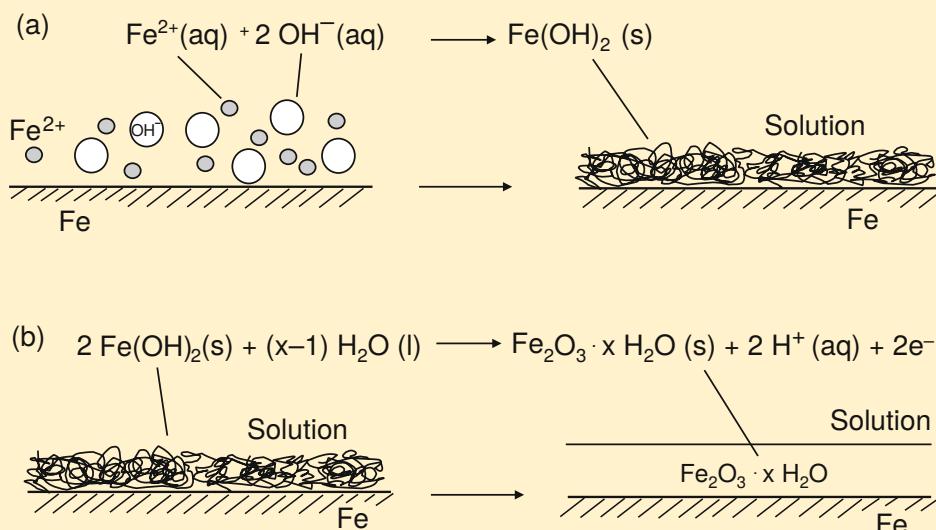


Figure 10: Steps involved in rust formation: (a) formation of a ferrous hydroxide precipitate, and (b) formation of the hydrated ferric hydroxide on the metal surface. Adapted from McCafferty, E., *Introduction to Corrosion Science*, Springer, 2010.

Other metals

In principle, the lower the standard potential, the more the metal will corrode. Noble metals will not corrode, whereas iron, zinc or aluminium would be expected to corrode very rapidly. In fact, many are rather stable in normal conditions due to the formation of a protective oxide layer (discussed later in the course). Aluminium is nowadays commonly used as the hull material of small boats despite its very low potential ($E^0 = -1.66V$).

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Uniform versus localised corrosion

Corrosion, although a progressive process, is dangerous because it can lead to catastrophic failures. This is particularly the case if corrosion takes place unevenly on the surface (see Figure 11). Localised corrosion occurs when sites of the material promote the anodic reaction. This could be due to:

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- defects in a protective coating (paint, natural oxide layer, etc). This leads to **pitting**.
- electrolyte present in **crevices**. The lack of oxygen favours the anodic reaction.
- cracks. Corrosion can directly promote **crack growth**.

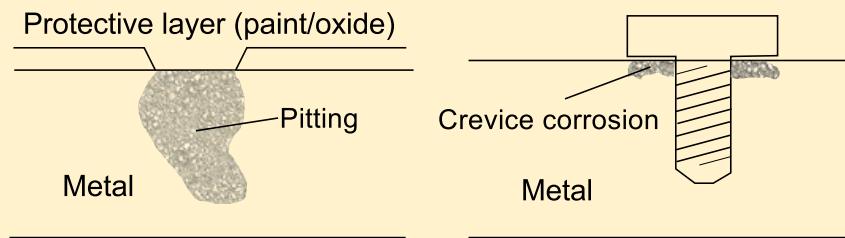


Figure 11: Pitting (left) occurs under defects in a metal's coating. Crevice corrosion (right) is often observed in the small gap under screws and other crevices that favours anodic reactions.

Conditions required for aqueous corrosion

To prevent corrosion one can act on the various ingredients required for it to happen:

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- **an anodic reaction,**
- **a cathodic reaction,**
- **a conductive path** between the anodic and cathodic sites,
- a solution containing ions in order to transport charges. It is called **an electrolyte**.

Possible solutions might therefore involve:

- displacing the anodic reaction (see next section)
- controlling the environment so that cathodic reaction is avoided
- insulating the path between the anodic and cathodic sites (oxide/coating)
- avoiding water accumulation and salty environments (avoid crevices)

Example - the Forth Rail Bridge in Scotland

"Painting the Forth Bridge" is a colloquial expression for a never ending task. This work has been nearly continuous since the construction of the steel structure in 1890 (see Figure 12). Painting it is not just aesthetic, but necessary for the corrosion protection of the structure.

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Figure 12: The Forth Rail Bridge (source: Wikimedia).

Between 2002 and 2011, the massive job has been undertaken of removing the old paint layers, repairing the steel structure, and coating it with a triple layer of new glass flake epoxy paint, similar to that used in the offshore oil industry. This is expected to last 25 years.

2.2 Galvanic corrosion/protection

The issue of galvanic corrosion is well illustrated by the lemon battery experiment we introduced earlier. If two metals of different electro-potential are connected in an electrolyte, the metal with the lower potential will be oxidised (i.e. become an anode), but the metal with the higher potential can collect these electrons and provide a much increased area for the cathodic reaction (see Figure 13). The resulting rate of corrosion of the more reactive metal will as a result be very significantly increased.

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This is in practice an important issue as contacts between different metals are very common:

- copper piping connected to steel tanks,
- nickel or aluminium alloy hull connected to steel rivets in boats

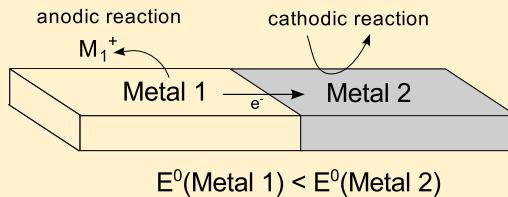


Figure 13: Principle of galvanic corrosion.

- zinc/steel/aluminium screws and flashing used with copper sheets for roofing
- electronic connectors made of different metals (e.g. tin plated against gold plate)



Figure 14: Example of galvanic corrosion in a domestic context. Many houses have old steel or cast iron pipes combined with newer copper pipes. This results in excessive corrosion. A good plumber should avoid such situations.

Galvanic compatibility

The best way to avoid galvanic corrosion is to avoid joining metals of very different electro-potentials in the relevant environment. Figure 15 shows for instance, the ranking of various metals and alloys in seawater, one of the harshest environments. Based on the data, here are a few conclusions we can draw:

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- Could we combine mild steel and cast iron? Answer: **yes**
- Tin, copper and brass? Answer: **yes**
- Mild steel and stainless steel? Answer: **no**
- Zinc with copper? Answer: **no**

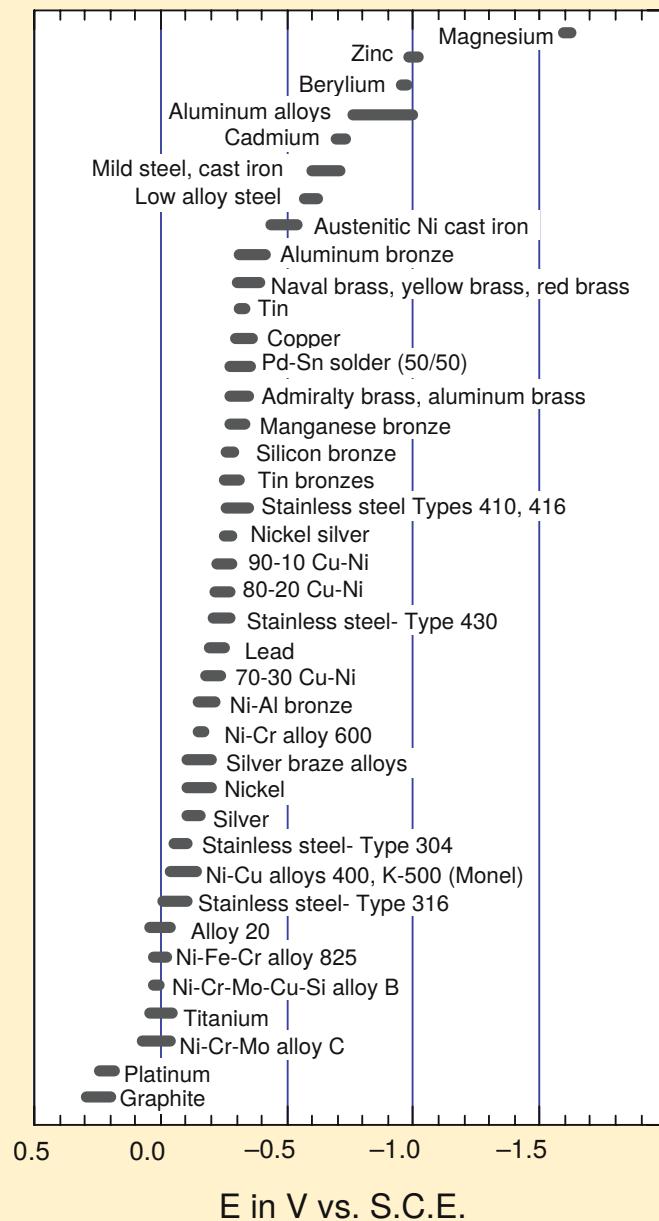


Figure 15: Galvanic series in seawater. Potentials are expressed in Volt, measured against a Saturated Calomel Electrode (SCE). Source: F.L. LaQue, *Marine Corrosion*, John Wiley, 1975.

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Case study: Statue of Liberty

The Statue of Liberty, designed by the sculptor Bartholdi and built by the engineer Eiffel in 1886, consists of a copper skin attached to a steel structure (or more exactly wrought iron, which contains a lower carbon content). The problem of galvanic corrosion was well known by Eiffel. He took the precaution of binding the steel armature to the skin using copper saddles and rivets (see Figure 16). The armature was then insulated from the copper using natural resins and asbestos. Although it was fine at the time, it had to be replaced after about 100 years. A massive renovation work started in the 1980s. Stainless steel has now replaced the iron-based armature, and PTFE was used to insulate the two metals. The choice of PTFE is also due to the fact that it allows the skin to slide with respect to the armature and better accommodate variations in temperature and wind conditions.

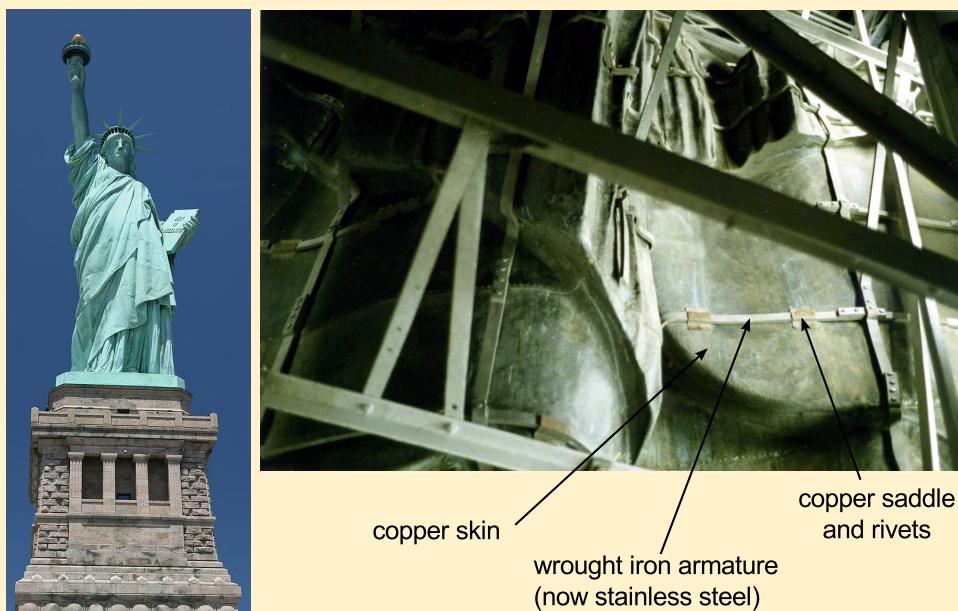


Figure 16: Statue of liberty and its internal structure. Source (right image): <http://mathtourist.blogspot.co.uk/2010/07/liberty-revealed.html>

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Galvanic protection

Galvanic corrosion has also a beneficial side to it. Because it concentrates the corrosion on the more reactive metal (lowest potential), it protects as a result the nobler metal where cathodic reactions take place. We can use this principle to protect metals from corrosion.

Galvanisation is the process of coating zinc on other metals or alloys such as steel or iron (see Figure 17). As long as zinc is present, it will be preferentially corroded, providing as a result protection to the steel structure.

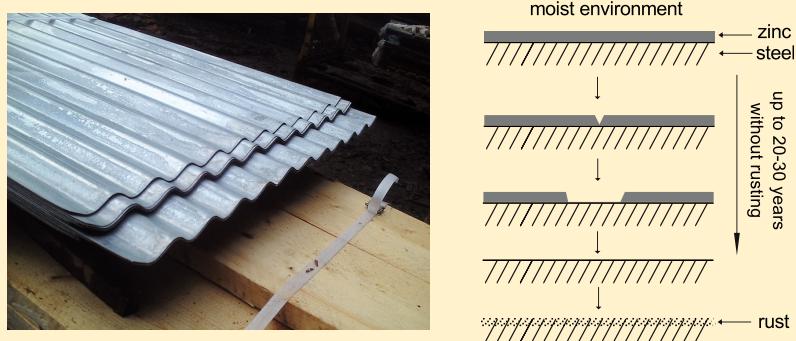


Figure 17: Left: Corrugated steel roofing sheets made of galvanised steel. Right: the main steps in the life-time of a galvanised metal sheet.

Sacrificial anodes

Coating the whole surface provides the best protection, but it is not required in many applications. The metal to be protected just needs to be electrically connected with the more reactive metal, and both need to be in the same electrolyte. When the lifetime of the structure needs to be longer than the lifetime of the coating, it is preferred to have a separate anode that can be replaced as often as required. This is called a sacrificial anode.

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It is common to use blocks of zinc to protect ships in water (see Figure 18). Zinc is a good material to protect iron and steel, but also aluminium in seawater as can be seen on the galvanic series in seawater (Figure 15). In fact, in sea water, aluminium is also protected by anodes made of alloys of zinc and magnesium.

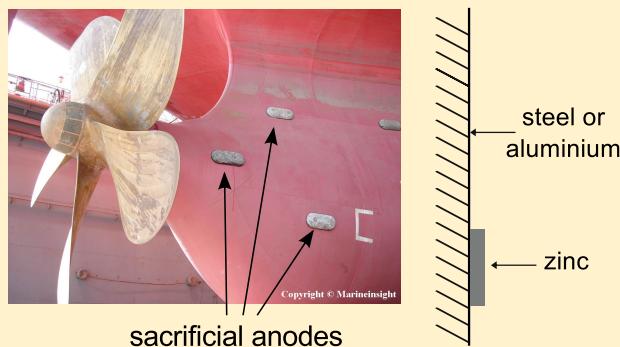


Figure 18: Sacrificial zinc anodes protecting the hull of a ship. Source (photo): <http://www.marineinsight.com>

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Impressed current protection

For very large structures, sacrificial anodes are costly and might fail to deliver the necessary current to protect the cathode. The source of current can then be provided by an external generator connected to an anode. This would be buried in an on-shore application. Either a stable anode, where the environment surrounding the anode is oxidised, or a consumable anode (e.g. scrap iron which would corrode away) can be used. Major applications are pipeline and offshore platform protection (see Figure 19).

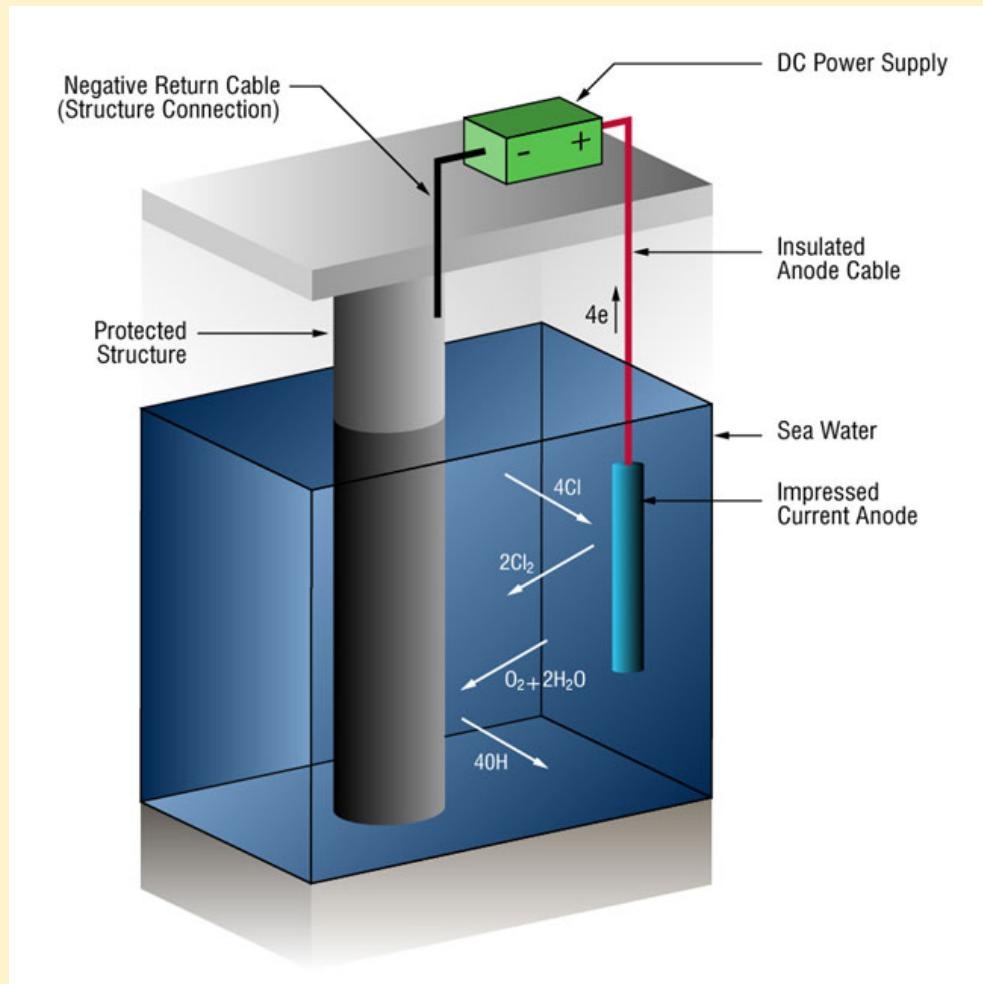


Figure 19: Protection on an offshore platform using impressed currents. Source: <http://www.cathodicprotection101.com/>

Summary

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- In water, metals with a negative electropotential get corroded. This requires either the presence of oxygen or an acidic environment.
- Corrosion requires:
 - an anodic reaction (consuming the metal and producing electrons),
 - a cathodic reaction (consuming these electrons),
 - a conductive path to transfer the electrons from the site of the anodic reaction to the site of the cathodic reaction,
 - an electrolyte to transfer the charges in the liquid and close the circuit.
- Galvanic corrosion happens when a metal with lower electropotential is electrically connected to another, more noble metal, and gets preferentially corroded.
- Galvanic corrosion should be considered when selecting materials to be joined together. Tables of the galvanic series in a range of chemical environments may be used to inform design decisions.
- Conversely, galvanic corrosion can be used to develop sacrificial anodes as a protective method.

3 Oxide layers

We have mentioned already that some metals form an oxide on their surface. The formation of such oxide layers is an oxidation process where the anodic and cathodic reactions are coupled and take place at the same location. Moreover, this does not rely on water and can occur under dry/high temperature conditions. These reactions will be considered in this section.

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3.1 Formation of the oxide layers

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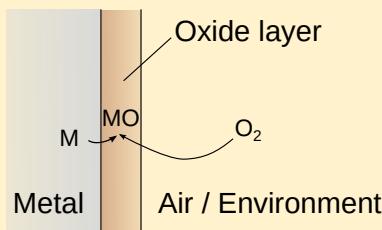
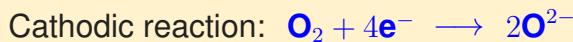
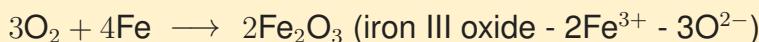
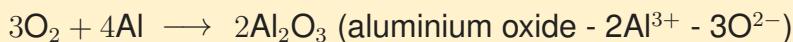


Figure 20: Sketch of the formation of an oxide layer, assuming the metal is oxidised by giving away two electrons ($M \rightarrow M^{2+} + 2 e^-$).

For metal oxidised by releasing 2 electrons:



Actual examples:

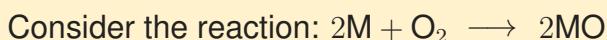


Thermodynamic considerations

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In the case of aqueous solutions, we could use the electrode potential to predict if a reaction could happen or not; the energy associated with the displacement of electrons from a low potential anode to a high potential cathode corresponds to the energy freed by the chemical reaction. For oxide layers, it is difficult to quantify electric potentials as half cells cannot be built. One prefers in this case to directly characterise the reaction in terms of an energetic quantity, called the standard Gibbs free energy of reaction, ΔG^0 . It represents the difference of free energy

between the products (oxide) and reactants (metal and oxygen) at a particular temperature and pressure, per mole.



To know if a reaction can take place or not, we calculate:

$$\Delta G^0(P, T) = \text{Energy(2 moles of MO)} - \text{Energy(1 mole of O}_2 + 2 \text{ moles of M)}$$

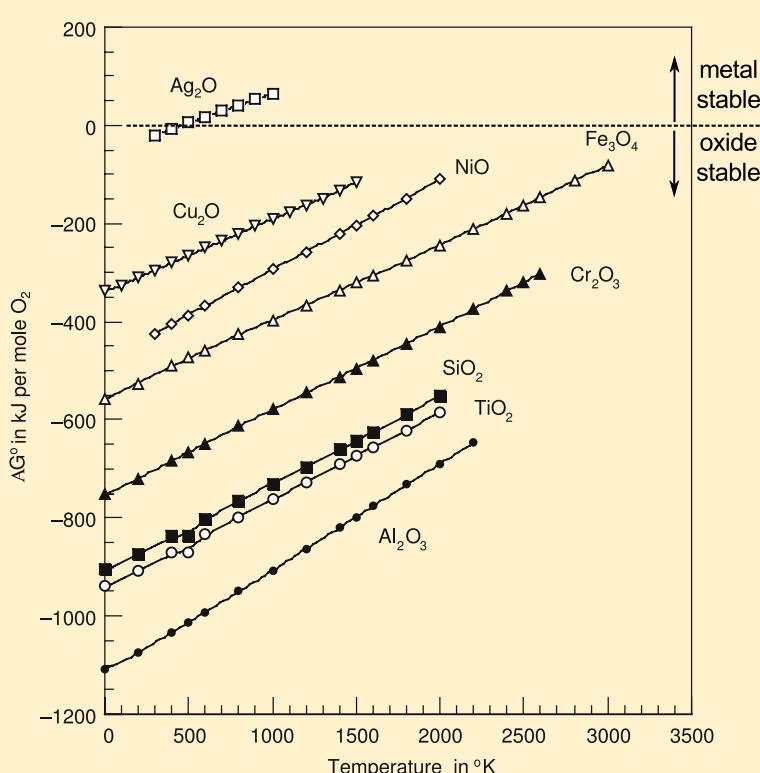
Like the standard potentials, it depends on the temperature, but also on the pressure.

- if $\Delta G^0(P, T) > 0$, the reaction will **not spontaneously happen**.

The **metal surface** is stable (it has in this case the **lowest** energy).

- if $\Delta G^0(P, T) < 0$, the reaction will **spontaneously happen**.

The **oxide layer** is stable.



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Figure 21: Free energy of formation of a few metal oxides as a function of temperature (also called Ellingham diagrams)

As can be seen on figure 21:

- At room temperature, silver is **essentially stable** in oxygen,
- Copper, iron and aluminium are **not stable**.

Rates of oxidation

If one measures the rates of oxidation, it appears however that there is no correlation between the value of the rate and how negative the free energy variation is. The table below shows for instance that, although aluminium is one of the most unstable metals, its oxide only forms very slowly. On the contrary, copper and iron relatively rapidly form their oxide.

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Material	Time (hours) for oxidizing 0.1mm deep at 0.7 T_M	$\Delta G^0(0.7 T_M)$ per mole O_2	Melting point T_M (K)
Gold	infinite	> 0	1336
Silver	very long	> 0	1234
Silicon	2×10^6	-700 kJ	1687
Chromium	1600	-500 kJ	2180
Nickel	600	-260 kJ	1726
Copper	25	-200 kJ	1356
Iron	24	-400 kJ	1811

This anomaly is in fact a common feature of physical chemistry. Even if the thermodynamics tell us that a reaction is favourable from an energetic point of view, its rate is controlled at the microscopic level and depends on the details of the molecular processes. As we will see now, to interpret these differences, we have to understand how easily the oxygen and metal can meet to form the oxide.

Kinetics of the oxide formation

The rate of oxidation is often estimated from the mass variation of the metal per unit surface area. There are three main types of evolution that can be observed:

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- Linear loss: when the oxide does not stay at the surface or is **volatile**.
- parabolic gain: when the oxide **adheres to** the metal and provides a barrier to the **diffusion** of reactants. The thicker the oxide, the slower it grows. Figure 22 shows experimental data obtained for such oxide.

Although the oxide formation is less favourable from an energetic point of view at higher temperatures (ΔG^0 is less negative), the rate of oxide formation sharply increases with temperature (see Figure 22). This is because diffusion through the oxide layer is greatly enhanced at higher temperature.

- Linear gain: when the oxide stays on the metal surface but cracks/peels off and allows oxygen to reach freely the metallic surface for further oxidation.

3.2 Silicon oxide in electronics

Metal-oxide-semiconductor field-effect transistor (MOSFET)

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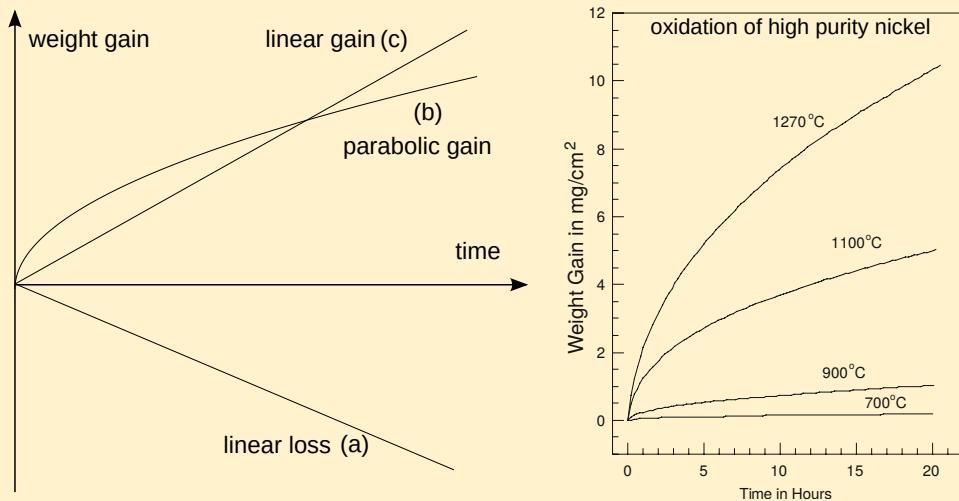


Figure 22: Left: Sketch of the three main types of oxide formation kinetics. Right: experimental data on nickel in oxygen. Source: Caplan, Graham and Cohen, J. Electrochem. Soc. 119:1205 (1972).

MOSFETs are the most common transistors in digital electronics, including in memory and microprocessors.

The presence of an oxide layer between the gate and the channel means that there is essentially no (DC) current flowing through the gate.

This reduces power consumption compared with traditional transistors.

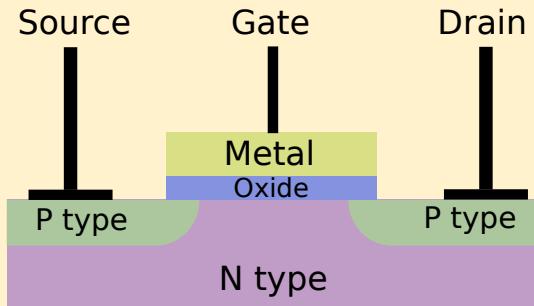


Figure 23: Sketch of a MOSFET.

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Silicon oxide formation - Deal-Grove model

Because of its importance in electronic applications, the kinetics of silicon oxide formation has been thoroughly studied, and accurate models have been developed. In this section, a simplified version of the Deal-Grove model (1965) is presented as an example of quantitative analysis of oxide growth dynamics.

In this model, the following assumptions are made:

- Si reacts with a gas component, for instance O_2 (or H_2O in moist environment),
- the oxide is formed at the oxide-silicon interface,
- there is an infinite supply of gas at constant concentration at the gas-oxide interface,
- the gas diffuses through the oxide layer.

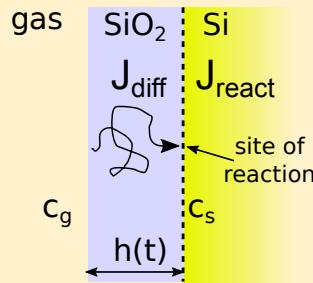


Figure 24: Supporting sketch for the Deal-Grove model.

During the growth of the oxide, the diffusive flux of gas J_{diff} must balance the rate of reaction J_{react} :

$$J_{\text{diff}} = J_{\text{react}} \quad (1)$$

where J_{react} is the number of oxide moles produced per unit time and area.

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- c_g is the (constant) gas concentration at the gas-oxide interface,
- $c_s(t)$ is the gas concentration at the oxide-silicon interface,
- D_{ox} if the coefficient of diffusion of the gas in the oxide,
- $h(t)$ is the thickness of the oxide layer.

$$J_{\text{diff}} = D_{\text{ox}} \frac{c_g - c_s}{h} \quad (2)$$

$$J_{\text{react}} = k c_s \quad (3)$$

where k is a rate constant.

But we can also link J_{react} and the geometry.

If we consider a small area A on the silicon surface, the number of moles of oxide produced per unit time is

$$dN = J_{\text{react}} Adt$$

The volume Adh of dN moles of oxide is:

$$Adh = \frac{M}{\rho} dN$$

where M is the molar mass of the oxide, and ρ its density.

We therefore get:

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$$Adh = \frac{M}{\rho} J_{\text{react}} Adt \implies J_{\text{react}} = \frac{\rho}{M} \frac{dh}{dt} \quad (4)$$

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Combining equations 1, 2 and 3, we get:

$$\begin{aligned} D_{\text{ox}} \frac{c_g - c_s}{h} &= kc_s \implies kc_s = \frac{c_g}{\frac{h}{D_{\text{ox}}} + \frac{1}{k}} \\ \text{combining now with equ 4, } \frac{\rho}{M} \frac{dh}{dt} &= \frac{c_g}{\frac{h}{D_{\text{ox}}} + \frac{1}{k}} \\ \left(\frac{h}{D_{\text{ox}}} + \frac{1}{k} \right) \frac{d(h/D_{\text{ox}})}{dt} D_{\text{ox}} &= \frac{Mc_g}{\rho} \\ \frac{1}{2} \left(\frac{h}{D_{\text{ox}}} + \frac{1}{k} \right)^2 &= \frac{Mc_g}{\rho D_{\text{ox}}} t + K \end{aligned}$$

Since $h = 0$ at $t = 0$, we get $K = \frac{1}{2k^2}$

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$$h(t) = D_{\text{ox}} \left(\sqrt{\frac{2Mc_g}{\rho D_{\text{ox}}} t + \frac{1}{k^2}} - \frac{1}{k} \right) \quad (5)$$

We can make this dimensionless to better understand the form of the solution and analyse data:

$$\frac{kh(t)}{D_{ox}} = \left(\sqrt{\frac{2Mc_gk^2}{\rho D_{ox}}t + 1} - 1 \right) \quad (6)$$

With $\tilde{h} = \frac{kh(t)}{D_{ox}}$ and $\tilde{t} = \frac{2Mc_gk^2}{\rho D_{ox}}t$, we get:

$$\tilde{h} = \left(\sqrt{\tilde{t} + 1} - 1 \right) \quad (7)$$

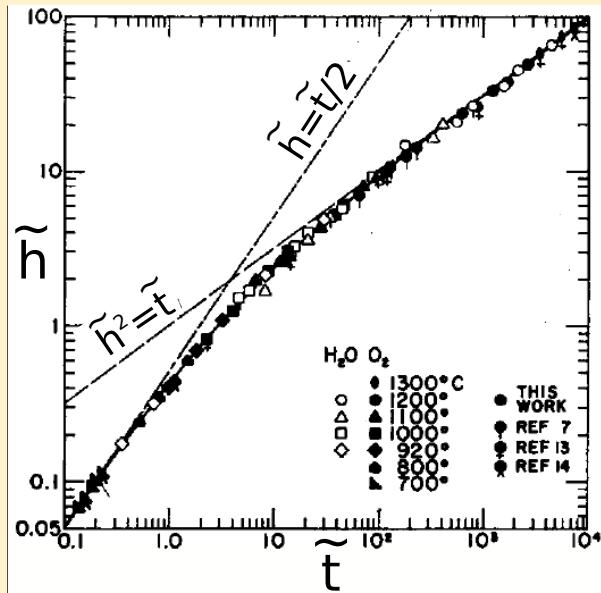


Figure 25: Adapted from B. Deal and A. Grove 1965. "General Relationship for the Thermal Oxidation of Silicon". Journal of Applied Physics 36 (12): 3770-3778.

This equation has two limit behaviours:

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$\tilde{t} \ll 1$ Reaction rate limited: h grows linearly,

$\tilde{t} \gg 1$ Diffusion limited: $h^2 \propto t$, i.e. parabolic profile.

The agreement between the model and experimental data (see Fig 25) is excellent, which supports the model assumptions, and demonstrates that the kinetics of silicon oxide formation is indeed limited by diffusion at large time-scales, although a reaction-limited transient is observed at short time-scales.

3.3 Other examples

Problems and benefits of metal oxide layers

Cons:

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- Loss of raw material → reduces **lifetime**, in particular for high temperature applications.
- Oxides have **poor mechanical properties (brittle)**.
- Heterogeneities in the oxide layer can initiate **fatigue cracks**.

Pros:

- Protect from **corrosion**. Ex: Al_2O_3 or CuO_2 at ambient temperature.
- Provide **thermal insulation**.
- Reduce the **coefficient of friction**.
- Might look good too...

Worked example: Turbine blades of a jet engine

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- Turbine blades (Figure 26) experience high temperatures ($\approx 950^\circ\text{C}$) and high stresses that both favour corrosion and mechanical failure.
- A good candidate material for turbine blades is nickel, because of creep properties.
- The cost per rotor is about £50,000, and it is expected to last at least 5000h.
- At this temperature, it forms a nickel oxide with a parabolic growth profile, at a rate of 0.1mm in 600h.

Calculation of the material lost before replacement: We know that $\delta m/\sqrt{t}$ is constant. Hence, during 5000h, the material would lose a thickness equal to $0.1\sqrt{5000/600}=0.3\text{mm}$, which is not acceptable for such a small component.

Solution: It is critically important to use alloys which have better oxide layers (lower oxidation rates), along with better creep and thermal properties. Coatings with aluminide and ceramics are common to further improve corrosion resistance and provide a thermal barrier.



Figure 26: Turbine blade attacked by hot corrosion. Its length is of the order of 10cm, with a thickness of a few millimetres. Source: www.lifepredictiontech.com

Oxide layers and passivation

Some metals, such as copper and aluminium, spontaneously form protective oxide layers, called a **passivation** layer. For other metals, such as iron, there are particular environmental conditions where a protective oxide layer would form and act as a protective layer against corrosion. Steel possesses, in an alkaline environment, a micron-thick protective oxide layer of **magnetite** Fe_3O_4 instead of rust.

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Hot bluing protects iron or steel by placing the metal in a hot alkaline solution followed by an oil coating. This is a standard technique for protecting guns.

Concrete provides a naturally alkaline environment that preserves the steel reinforcement bars.

Stainless steel

As in the case of the turbine blades, alloying steel is also an excellent way to improve its corrosion resistance. Stainless steel is a steel alloy that contains more than 10% chromium by mass, up to 25% for resisting harsh environments.

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The large proportion of chromium ensures that a layer of **chromium oxide** (Cr_2O_3) will form spontaneously at the surface, protecting as a result the iron content. These are **self-healing** materials; if the coating is damaged, a new protective oxide layer is instantly reformed.

Summary

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Figure 27: Left: example of hot bluing finish. Middle: reinforced concrete walls. Right: Stainless steel cooking tools are very common.

- Oxide layers form directly at the surface if the oxide formation is thermodynamically favourable.
- The rate of oxide formation is most important in practice, and is not directly related to the thermodynamic driving force in this context.
- Oxide layers may be:
 - protective, staying at the surface of the metal, and grow slowly (parabolic profile), or
 - be porous or volatile, formed with a fixed rate over time and causing sustained damage.
- The parabolic rate of oxide formation (mass gain $\propto \sqrt{t}$) reflects the fact that the reaction rate is limited by diffusive transport.

Conclusion

We have covered some of the key problems and solutions associated with corrosion. The study of corrosion is multi-disciplinary, and combines material sciences, chemistry and physics, all required to understand these issues and develop protective methods. As seen in the next part of the IB Materials course, the distinction between thermodynamics and kinetics also illuminates many aspects of materials engineering and manufacturing.

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Intended Learning Outcomes

The intended learning outcomes of this section are:

- Explain qualitatively why metals develop a potential difference with respect to a solution in which they are placed, and why this potential depends on the metal and the solution.
- Use the standard electrode potential to determine the chemical stability of metals with respect to oxidation.
- Write chemical reactions associated with the corrosion of iron in acidic and in oxygen rich environments.
- Explain the process of galvanic reaction and how it enables to protect materials in some circumstances.
- Use the standard Gibbs free energy of reaction to determine if metals would spontaneously form oxide layers or not.
- Describe the different mechanisms responsible for the kinetics of oxide formation.
- Model diffusive and reactive processes in relatively simple cases, such as silicon oxides, in order to predict the evolution of the oxide thickness over time.

You can test yourself against these to make sure you have covered the relevant content, and return to your notes if necessary. The week 4 quiz and examples paper questions may now be fully attempted and will also cover most of these learning outcomes.