CET IIA   Corrosion and Materials

Lectures 1-8: Corrosion
Michaelmas term 2017
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Outline of Corrosion Lectures

1. Corrosion and material selection
2. Thermodynamics of aqueous corrosion
3. Rates of aqueous corrosion
4. Localised corrosion mechanisms and corrosion testing
5. Corrosion protection
6. High-temperature oxidation of metals

Recommended Textbooks

The following textbooks are written at an appropriate level for this course

1. M.G. Fontana, "Corrosion Engineering" (3rd ed., 1986), McGraw-Hill
2. K.R. Trethewey and J. Chamberlain, "Corrosion for Science and Engineering" (2nd ed., 1995), Longman
3. D.A. Jones, "Principles and Prevention of Corrosion" (1995), Prentice Hall
4. E. Mattsson, "Basic Corrosion Technology for Scientists and Engineers" (2nd ed., 1996), Institute of Materials
5. P.R. Roberge, "Handbook of Corrosion Engineering" (2nd ed., 2012; or 1st ed., 2008), McGraw-Hill
6. A.C. Fisher, "Electrode Dynamics" (1996) OUP
7. Z. Ahmad, "Principles of Corrosion Engineering" (2006), Elsevier

Fontana and Tretheway have been recommended by the department for many years, and should be easy to find in college libraries.

Online course material at MSM: http://www.doitpoms.ac.uk/tlplib/aqueous_corrosion/

Further Reading and References

1. R.W. Revie "Uhlig's Corrosion Handbook" (2nd ed., 2000), Wiley.
2. "Perry's Chemical Engineers' Handbook" (7th ed., 1997), McGraw-Hill.
3. L.L. Shreir, G.T. Burstein, R.A. Jarman, Corrosion (1998), Butterworth-Heinemann

Examples Questions

Two examples papers will be distributed during this course.

Tripos questions for reference are in CET IIA Paper 1 Q 4 to 6 (2006 - 2013); Paper 3 Q 4 to 6 (2014); Paper 3 Q 4 to 5 (2015 - 2017);

1. Introduction to Corrosion

1.1 Material selection

The design phase of a project can involve optimising a choice of material, and corrosion-tolerance is an essential constraint:
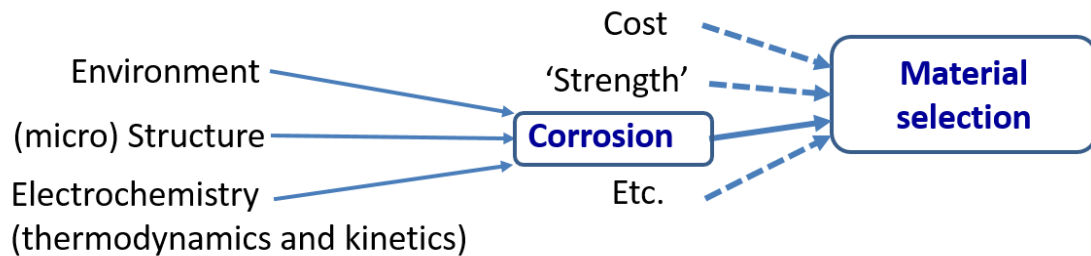
1.2 What is corrosion?

A modern definition of corrosion (from Fontana) is

> Corrosion is the deterioration of a material by chemical reaction with its environment.

Some examples of corrosion are

- o Dissolution of metal such as zinc coatings
- o Embrittlement of reinforced concrete due to tensile stress from rust
- o Many **localised corrosion** phenomena (see section 4).

Fontana's definition of corrosion is used in this course.

- ♦ Some authors restrict the definition of corrosion to metals [Ahmad p.2 A,F]. However, to solve real problems involving metals we often must consider other materials.
  - o Cement in reinforced concrete
  - o Polymer or glass coatings

Corrosion processes may be harnessed for an indirect benefit.

- o Etching circuit boards
- o Anodisation for hard coatings
- o Aesthetic improvements

Beware: different textbooks on corrosion use various different conventions for many key aspects of the subject, not just in minor details of its definition.

- ♦ X-Y axis convention for Evans diagrams (we use log-current on the x-axis)
- ♦ Positive and negative currents (we use positive values for anode currents)
- ♦ Standard pressure. Now 10^5 Pa, but used to be 101325 Pa (1 atm). Reference http://goldbook.iupac.org/S05921.html

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1.3 Why is corrosion important?

1.3.1 Corrosion leads to huge costs…

♦ Replacement (cost of new materials; downtime)

♦ Inspection and treatment

♦ Decreased process efficiency (e.g. of heat exchangers)

♦ Loss of product through leakage. (Water utilities often lose 20% of their supply through leaks).

♦ Loss of services and the need for backup.

♦ The annual cost of corrosion in the USA has often been estimated at between 3-6% of GDP.

  o Between 10-40% of these costs are thought to be avoidable [e.g. Roberge, pp 15-20].

1.3.2 Failure of structures or products…

♦ Finite lifetime. Causing vehicles/oilrigs/products to be scrapped

♦ Unexpected failures.

  o E.g. electrical components.

  o E.g. pipeline leaks and losses.

  o … which may lead to further problems: fires; loss of services…

1.3.3 Contamination…

♦ Contamination of product streams from

      o By leaching of dissolved ions

      o By leaks through perforated metal (pitting corrosion)

♦ Fouling of cooling water cooling due to corrosion of heat exchangers

  o Corrosion inhibitors / systematic design needed

1.3.4 And poisoning

♦ Leaching of Ni^{2+} from alloys

  o Ni^{2+} is a sensitising allergen, and nickel compounds can be toxic

  o Affected Euro coins

  o Justifies testing in food processing

    As stainless steel is a preferred material

♦ Dissolution of Cu^{2+} into acidic solutions

  o Cu^{2+} is toxic

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1.3.5 Disasters…

- ♦ Over 25% of accidents in the oil and gas industry are caused by corrosion
  - o Skikda explosion of natural gas compression train

    Unexpected corrosion mechanism

  - o Prudhoe Bay oil spill(s)

    Insufficient monitoring

- ♦ Guadalajara sewer explosion (1992)

  Incompatible corrosion protection methods

- ♦ Bridge collapses (E.g. Silver Bridge collapse in West Virginia 1967)

  Combination of factors. Unexpected mechanism and a design that limited monitoring.

1.3.6 Corrosion Engineering

Corrosion engineering is "the use of science and art to prevent or mitigate these problems in an economic way" [Fontana]. We can:

- ♦ Predict whether corrosion will occur…
  - o Severely, by **active corrosion**,
  - o Slowly, due to corrosion resistance or **passivity**
  - o Not at all, because a state of **immunity to corrosion** exists
- ♦ Predict the rate of corrosion
- ♦ Design systems that have sufficient corrosion resistance, so that the lifetime capital / operating costs of a process are optimised.
- ♦ Identify, measure, and treat the mechanisms of corrosion

1.4 Corrosion of metals in chemical engineering

Metals are often used in chemical engineering because their properties (strength, ductility, conductivity, etc.) are essential for many applications (structural elements, heat exchangers, etc.)
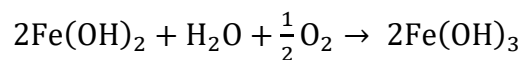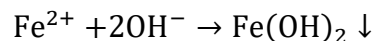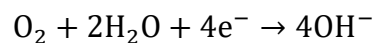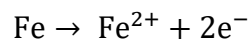
♦ There are essentially three ways in which a metal can respond to a chemical environment.

1.4.1 Active corrosion

♦ In a particular environment, some metals may undergo continuous and rapid deterioration called active corrosion.

♦ This happens if the dissolved ion is more stable that the metal phase.

♦ A simple example is the dissolution of zinc in aerated (oxygenated) solution

$$Zn \rightarrow Zn^{2+} + 2e^-$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
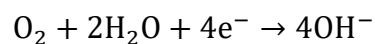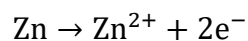
♦ Some active corrosion processes are much more complex. E.g. rust.

$$Fe \rightarrow Fe^{2+} + 2e^-$$

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

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \downarrow$$

$$2Fe(OH)_2 + H_2O + \frac{1}{2}O_2 \rightarrow 2Fe(OH)_3$$

or $$2Fe(OH)_2 + 2OH^- \rightarrow 2Fe(OH)_3 + 2e^-$$

○ The iron dissolution step is similar to the simple case of zinc dissolution, and this rate is used to quantify the speed of corrosion in this course.

♦ Actively corroding materials are often used, but methods to predict the speed of corrosion (hence lifetime, or replacement costs) are important.

1.4.2 Immunity to corrosion

♦ Thermodynamically stable metals and alloys are **immune** from corrosion.

♦ This is rare in engineering unless thermodynamic corrosion protection methods are used.

1.4.3 Passivity

♦ It is very common to select metals which are **passive** against corrosion.

♦ This means a thermodynamically stable corrosion product is solid and that the metal reacts to produce an impermeable (hydr–)oxide surface layer which prevents further corrosion.

1.5 Important metals in corrosion science

1.5.1 Zinc

Zinc is a common coating on other metals. It often dissolves actively, but slowly.

- Questions. How fast does zinc dissolve in a given environment?
- Issues. Surprisingly slow kinetics for dissolution, given the large thermodynamic driving force. Sacrificial anodes.

1.5.2 Iron alloys and carbon steel

Widely used. Active corrosion is common. Rust, which consists of hydrated iron (hydr-)oxides, is exclusive to iron alloys.

- Questions. How fast is active corrosion? How much does corrosion protection cost (often by using sacrificial anodes or cathodic protection to make the iron immune from corrosion)? How does that compare with over-specifying the metal thickness?
- Issues. Carbon steels are classified by carbon content, but often treated as pure iron in corrosion models. ('Iron' is < 0.015% carbon. Then 'steel' < 2% carbon. Then 'cast irons' < 5% carbon.)

1.5.3 Aluminium

Aluminium is passive in neutral aqueous environments because its oxide is thermodynamically stable and impermeable to water.

- Questions. Does passivation occur (depending on pH)? How does passivation occur? How does corrosion affect the material properties (e.g. does stress corrosion cracking decrease fracture toughness)?
- Passive oxide layer formation:

- Issues. Abrasion and repassivation. Acid-base chemistry. Pitting corrosion. Liquid metal embrittlement.

1.5.4 Stainless Steels

These iron alloys contain chromium which can form a passive layer. Many alloys exist, classified by composition and crystal structure. A common alloy is "Type 304", which is an 18/8 stainless steel (18% Cr, 8% Ni, max 0.08% C).

Very important in subsea oil pipelines and the process industries.

- Questions. Is an alloy passive in practice? How are problems measured?
- Issues. 'Breakdown' of stainless steel passivity is a huge topic. Many of the localised corrosion mechanisms in section 4 relate to this. (Pitting and crevice corrosion; stress corrosion cracking; welding and sensitisation due to local chromium loss.)

1.5.5 Copper alloys

Copper is immune to corrosion in some environments (not including sea water, where it dissolves slowly). Used in pipes / electronics.

♦ Questions. Calculate the boundary between active corrosion and immunity. How can copper corrosion cause problems (toxicity / bimetallic corrosion)?

♦ Issues. Copper resists biomacrofouling due to toxicity combined with slow dissolution.

1.5.6 Gold

Gold is usually immune from corrosion.

♦ Questions. Special cases when gold dissolves actively.

♦ Issues. Electroplating. Leaching of nickel from gold alloys can be mistaken for a gold allergy.

1.5.7 Titanium

Passivates by forming titanium oxide, which is generally more passive than aluminium or stainless steels.

♦ Questions. No mainstream questions (!) because only non-aqueous reducing environments really cause loss of passivity, and these are complicated and rare.

♦ Issues. Biocompatibility excellent. Chloride resistance. Some reducing environments (e.g. natural gas) cause depassivation. Titanium also reacts with chemically dry methanol and disintegrates.

2. Thermodynamics of aqueous corrosion

The purpose of thermodynamics in corrosion is to determine, for a given situation, whether a metal is thermodynamically stable and therefore <u>immune</u> from corrosion, or if is there an oxidation product with a lower free energy. It is also important to know whether the stable corrosion product is a dissolved ion which indicates <u>active corrosion</u> will occur, or if is it a solid oxide (or hydroxide) which may protect the metal and produce <u>passivity</u>.

In aqueous environments, corrosion science treats corrosion as two electrode reactions. The oxidation of a metal is an <u>anode electrode</u>. A mixture of several oxidising reactions may provide the <u>cathode</u>. A corroding electrode has an electrical <u>equilibrium potential</u> at which no net reaction occurs. The metal electrode will corrode if the mixture of oxidising species in the environment have a more oxidising equilibrium potential than the metal.

As well as oxidation of metal, which is an electron transfer process, the stability of solid, protective oxides with respect to dissolved ions are often determined by pH.

2.1 Types of corrosive environment

<u>Example question: what are some factors that speed up corrosion?</u>

Most corrosion involves oxidation $(M \rightarrow M^{n+} + ne^-)$, but it is common to distinguish between two situations

<u>2.1.1 Chemical corrosion</u>

Takes place in dry gases or non-ionic liquids

Chemical thermodynamics describes this process

♦ Oxidation of a copper in air (e.g. at 1 bara and 700 °C)

$$4Cu + O_2(g) \rightarrow 2\,Cu_2O \qquad\qquad (2.1)$$

  o $\Delta G_{\text{reaction}}$ indicates if this will occur.

<u>2.1.2 Electrochemical corrosion</u>

Occurs via electrode reactions

♦ Requires an ion-conducting solution (usually water).

♦ Electrochemical thermodynamics is used to study this process, because it supports rate-models that chemical thermodynamics does not.

♦ Electrochemical corrosion is important in the natural environment and many industrial processes.

♦ It happens under aqueous solution, and also in air above ~70% relative humidity due to the formation of surface moisture.

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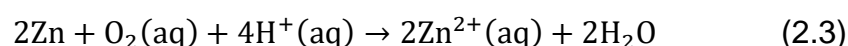## 2.2 Electrode notation: describing corrosion as electrochemistry

The dissolution of zinc in acid is a simple corrosion reaction

- There are only two phases: solid Zn and dissolved Zn^{2+}. No zinc oxides or hydroxides are stable in acid, so they are neglected.

- There are several possible chemical reactions for zinc dissolution

    Zinc-protons in any acid

$$Zn + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \qquad (2.2)$$
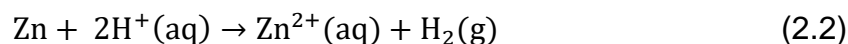
    Zinc-oxygen in aerated acid

$$2Zn + O_2(aq) + 4H^+(aq) \rightarrow 2Zn^{2+}(aq) + 2H_2O \qquad (2.3)$$

- But the zinc experiences the same <u>electrode process</u> (or 'half reaction')

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad (2.4)$$

    This is an <u>anode</u> half reaction because electrons are lost, i.e. the zinc is oxidised.

- Equation (2.2) is referred to using the following <u>electrode notation</u>

$$Zn|Zn^{2+} \qquad (2.4a)$$

    The reduced species (metal) is on the left, the oxidised species (metal ions) is on the right, and the vertical line represents a phase boundary.

- Electrode notation is used in algebra. For example, the speed of the reaction (per unit area of metal) might be described as

$$\text{rate}(Zn|Zn^{2+}) = 1 \text{ mol cm}^{-2} \text{ year} \qquad (2.5)$$

    or $\quad i(Zn|Zn^{2+}) = 6 \text{ mA cm}^{-2} \qquad (2.6)$

    where i is the current density describing this rate (see section 3).

The proton or oxygen reactions can be written separately. They are <u>cathodes</u>, because the species here are reduced and gain electrons.

- Hydrogen evolution (uses up protons in aqueous solution)

$$2H^+ + 2e^- \rightarrow H_2 \qquad (2.7)$$

    Or $\quad (H_2|H^+) \qquad$ which is the electrode notation $\qquad (2.7a)$

- Oxygen reduction (uses up dissolved oxygen molecules)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (2.8)$$

    Or $\quad (H_2O|O_2, H^+) \qquad (2.8a)$

Models of corrosion use electrochemical notation because:

- On metals, the electrode processes often takes place separately – they can be several metres apart.

- Fewer equations are needed (only one metal anode equation). The effect of several oxidising agents can be treated as a single term 'the cathode' and accounted for by a measurement using a voltmeter and a reference electrode. Electrical currents and voltages are simple to measure.

- Electrochemical equations are compatible with kinetic models which include ion transport.

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2.3 Electrochemical cell notation

Aqueous corrosion can be described as an electrochemical cell, as shown below. An electrochemical cell consists of

♦ One anode

♦ One cathode

♦ Electronic contact between the electrodes. An electrical potential difference of ΔE volts might exist between the electrode surfaces. If both electrode processes taken place on the same piece of metal, then ΔE is likely to be zero volts.

♦ Ionic contact. An ion resistance may exist, R_{ion}, but it is often neglected.

2.3.1 Diagram of an electrochemical cell
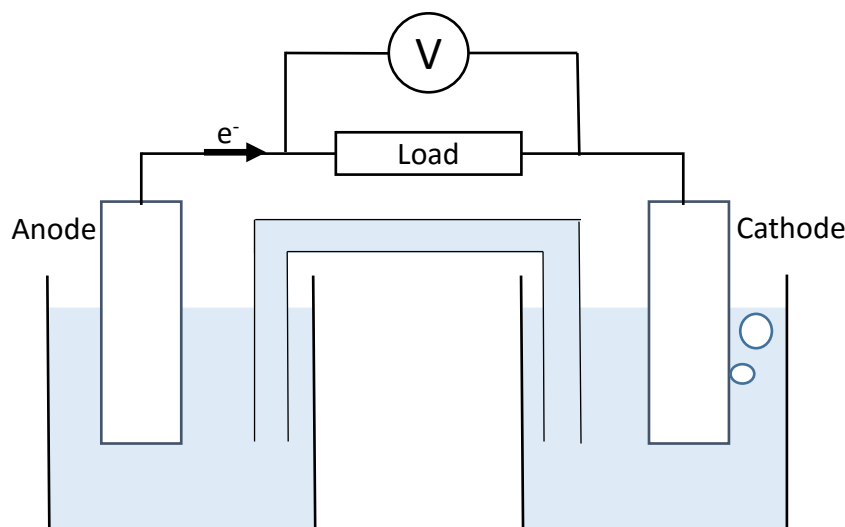
♦ Temperature must be given. E.g. 298 K.

♦ Ion activities (or concentration) must be given. E.g. $a(Zn^{2+}) = 1, \; pH = 0$

This cell can be described without a diagram by the following cell notation

$$Zn|Zn^{2+}||H^+|H_2 \qquad\qquad (2.9)$$

♦ A single electrode always has the reduced species on the left, and the oxidised species on the right. Neglect spectator ions and electrons.

$$Zn|Zn^{2+} \qquad\qquad (2.10)$$

$$H_2|H^+ \qquad\qquad (2.11)$$

♦ For the complete cell, the left hand side is the anode, and the right hand side is the cathode. At each electrode, the reagent is on the left of the single vertical line, and the product on the right. So in a complete cell the anode is written (reduced | oxidised) cathode is written (oxidised | reduced).

♦ The double vertical line in equation (2.5) is a 'salt bridge'. It represents a distance too large for rapid mixing of the electrolyte, so that different ions are involved at the anode and cathode.

2.3.2 Examples of electrochemical cell notation

♦ An electroplating cell is an example of a cell with no salt bridge. This cell would need to be driven by electrical energy supplied by the 'load'.

$$Cu|Cu^{2+}|Cu \qquad\qquad (2.12)$$

♦ A concentration cell could be used to plate copper at the cathode by using a salt bridge to separate a high and a low concentration of dissolved ions.

$$Cu|Cu^{2+}\,(0.1\ mol\ dm^{-3})||\ Cu^{2+}\,(1\ mol\ dm^{-3})|Cu \qquad (2.13)$$
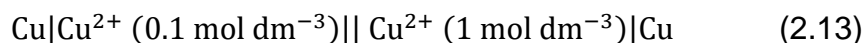
♦ A battery with zinc dissolving at the anode and silver chloride being reduced to silver at the cathode could be written as follows. A comma separates species in the same phase.

$$Zn|Zn^{2+}, Cl^-|AgCl|Ag \qquad\qquad (2.14)$$

or $\qquad Zn|ZnCl_2(aq)|AgCl|Ag \qquad\qquad (2.14a)$

♦ Sometimes it is useful to specify that the hydrogen reaction takes place on a metal surface, such as platinum. Therefore the reaction $(H_2|H^+)$ is sometimes written

$$Pt|H_2(g)|H^+ \qquad\qquad (2.15)$$

or $\qquad Pt|H_2(g)|HCl(aq) \qquad\qquad (2.15a)$

2.3.3 What is cell notation used for?

Electrochemical cell notation is used to refer to a cell in algebra.

♦ Electromotive force is the voltage supplied by a cell when it is working as a battery. Consider the following descriptions in text, and in algebra.

A cell contains hydrogen gas dissolving at the anode and silver ions (Ag^+) electroplating onto silver metal at the cathode. All species have unit activity, meaning pH=0 and $a(Ag^+) = 1$. The temperature is 25°C. It is found that the potential difference between the electrodes, ΔE, is 0.799 volts and that this is an electromotive force that supplies energy to the load.

$$\Delta E(H_2|H^+||Ag^+|Ag) = +0.799\ V \qquad\qquad (2.16)$$

At pH 0, 1 bara, with $a(Ag^+)$=1, and temperature 25°C

♦ Equation (2.16) describes a special situation used to measure the 'standard electrode potential', $E°$, of the silver electrode $(Ag|Ag^+)$. [See section 2.7.]

$$E°(Ag|Ag^+) = +0.799\ V_{SHE} \qquad\qquad (2.16a)$$

2.4 Name convention for anode and cathode

The anode is the site of an oxidation reaction, which loses electrons.

♦ A common mistake is to label one terminal of a battery as the "anode" based on its location or material.

2.5 Corrosion mainly occurs at the anode of a cell

Corrosion mainly involves loss of metal by dissolution or oxide formation, e.g.

$$Zn \rightarrow Zn^{2+} + 2e^- \tag{2.17}$$

$$Cu + H_2O \rightarrow CuO + 2H^+ + 2e^- \tag{2.18}$$

Both of these are anode processes.
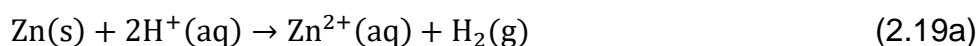
Only a few corrosion problems occur at a cathode

♦ Hydrogen embrittlement

♦ Deposition corrosion

2.6 Relating electrochemical cell voltage to the Gibbs energy of reaction

Consider the following electrochemical cell.

$$Zn(s)|Zn^{2+}(aq)|| H^+(aq)|H_2(g) \tag{2.19}$$

♦ The chemical reaction inside the cell is

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \tag{2.19a}$$

♦ The standard Gibbs energy change per mole of zinc, assuming unit ion activity, i.e. 1 molar effective concentration of all ions, is:

$$\Delta G^\circ{}_{\text{reaction}}(Zn|Zn^{2+}|\,|H^+|H_2) = -147 \text{ kJ mol}^{-1} \tag{2.20}$$

♦ And at non-standard concentrations, the Gibbs energy change is

$$\Delta G_{\text{reaction}}(Zn|Zn^{2+}|\,|H^+|H_2) = \Delta G^\circ{}_{\text{reaction}} + RT \ln(Q_r) \tag{2.21}$$

♦ Where

$$Q_r = \left(\frac{a_{(Zn^{2+})} a_{H_2}}{a_{Zn} a^2_{(H^+)}} \right) \tag{2.22}$$

Here, $a_{(Zn^{2+})}$ is the Zn^{2+} activity, $a_{(H^+)}$ is given by the pH, a_{H_2} is the partial pressure of H_2 in bar, and the activity of any pure solid or liquid phase is unity, so $a_{Zn} = 1$. Unit activity is also used for impure water.

A purely chemical process will go forwards spontaneously if $\Delta G_{\text{reaction}} < 0$ and it would be reversible if $\Delta G_{\text{reaction}} = 0$. The equation $\Delta G_{\text{reaction}} = 0$ can be used to find conditions where a chemical reaction just begins to go forwards.

In electrochemistry, a cell involves a chemical reaction, plus charge flow between the electrodes. The total Gibbs energy change of a cell therefore includes some electrical work done on the load, $\Delta W_{\text{electrical}}$

$$\Delta G_{\text{total}} = \Delta G_{\text{reaction}} + \Delta W_{\text{electrical}} \tag{2.23}$$

An electrochemical process will go forwards spontaneously if $\Delta G_{\text{total}} < 0$, and an electrochemical cell is reversible if $\Delta G_{\text{total}} = 0$. A cell can be made to operate reversibly by controlling the electromotive force that is drawn by the load.

In a reversible electrochemical cell

$$\Delta G_{\text{total}} = \Delta G_{\text{reaction}} + \Delta W_{\text{electrical}} = 0 \tag{2.24}$$

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Electrical work can be written as the charge transferred across the cell multiplied by the electromotive force experienced by the load. Assuming the cell has negligible ion resistance and is reversible, the electrical work on the load is

$$\Delta W_{\text{electrical}} = Q E_{\text{reversible cell}} \tag{2.25}$$

Where

- $Q = zF$ is the charge transferred through the cell
- $z = 2$ is the number of electrons per zinc atom in $(\text{Zn}|\text{Zn}^{2+}\|\text{H}^+|\text{H}_2)$.
- $F = 96485$ Coulombs per mole of electrons.
- $E_{\text{reversible cell}}$ is the reversible cell potential (ΔE volts) which is supplied to the electrical load by the cell acting reversibly (i.e. when $\Delta G_{\text{total}} = 0$).

Chemical thermodynamic data can therefore be converted to the voltage of a reversible electrochemical cell by the important relation

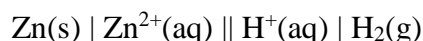$$\Delta G_{\text{reaction}} = -zF E_{\text{reversible cell}} \tag{2.26}$$

- A cell is reversible if all of the free energy change of the reaction is converted to useful electromotive force.
- This value of $E_{\text{reversible cell}}$ can be measured by a voltmeter in a cell operating reversibly.
- A high impedance voltmeter between two electrodes can find $E_{\text{reversible cell}}$. (This measurement may become difficult if a piece of metal actually hosts multiple electrode reactions on its surface. Neglect this for now.)

Purely chemical reactions proceed spontaneously if $\Delta G_{\text{reaction}} < 0$.

In electrochemistry, a corrosion reaction proceeds spontaneously if $E_{\text{reversible cell}} > 0$ which is equivalent to $\Delta G_{\text{reaction}} < 0$ and therefore $\Delta G_{\text{total}} < 0$ in the spontaneous case when zero electrical work is involved.

2.6.1 Example: converting thermodynamic data from kJ/mol to volts

What is the electromotive force (potential difference) exerted by the following zinc-acid cell when it is operated reversibly, at pH 0 with an effective dissolved Zn^{2+} concentration of 1 M?

$$\text{Zn(s)} \mid \text{Zn}^{2+}\text{(aq)} \parallel \text{H}^+\text{(aq)} \mid \text{H}_2\text{(g)}$$

Data:

$\Delta G_{\text{reaction}}(\text{Zn}|\text{Zn}^{2+}|\,|\text{H}^+|\text{H}_2) = -147 \text{ kJ mol}^{-1}$ under these conditions.

2.7 Standard electrode potential – a definition by example

The standard electrode potential of a half-reaction is the value of $E_{\text{reversible cell}}$ in a special case. For zinc, it can be defined as follows.

The standard electrode potential of the zinc electrode, $E°(\text{Zn}|\text{Zn}^{2+})$, is defined as the value of $E_{\text{reversible cell}}$ for a cell with a <u>zinc cathode</u> ($\text{Zn}|\text{Zn}^{2+}$), and a <u>hydrogen anode</u> ($\text{H}_2|\text{H}^+$), with all reagents at unit activity and the cell operating reversibly. It is usually defined at 25°C. The units are volts, and should be written V_{SHE} to make clear that the anode is a standard hydrogen electrode.

$$
\begin{aligned}
E°(\text{Zn}|\text{Zn}^{2+}) &= E_{\text{reversible cell}}(\text{H}_2|\text{H}^+||\text{Zn}^{2+}|\text{Zn}) \quad \text{[unit activities]} \quad (2.27)\\
&= -\Delta G°_{\text{reaction}}(\text{H}_2 + \text{Zn}^{2+} \rightarrow 2\text{H}^+ + \text{Zn})/zF\\
&= -(+147\ \text{kJ/mol})/(2 * 96485\ \text{C /mol})\\
&= -0.76\ \text{volts in the given conditions}\\
&= -0.76\ V_{\text{SHE}}
\end{aligned}
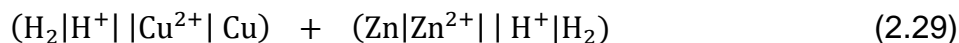$$

The reaction in this cell is zinc reduction by hydrogen.

… This reaction has negative $E°$ (and positive $\Delta G°_{\text{reaction}}$). This is consistent with zinc existing in oxidised forms in the natural world.
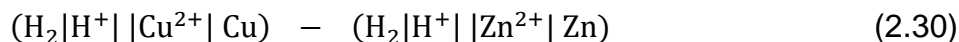

2.8 Using standard electrode potentials

The electrochemical cell

$$(\text{Zn}|\text{Zn}^{2+}|\ |\text{Cu}^{2+}|\text{Cu}) \tag{2.28}$$

Involves materially the same change in state as

$$(\text{H}_2|\text{H}^+|\ |\text{Cu}^{2+}|\ \text{Cu}) \ + \ (\text{Zn}|\text{Zn}^{2+}|\ |\ \text{H}^+|\text{H}_2) \tag{2.29}$$

Which is also the same as

$$(\text{H}_2|\text{H}^+|\ |\text{Cu}^{2+}|\ \text{Cu}) \ - \ (\text{H}_2|\text{H}^+|\ |\text{Zn}^{2+}|\ \text{Zn}) \tag{2.30}$$

So the Gibbs energy changes for (2.28) and (2.30) are the same

$$\Delta_r G(\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}) = \Delta_r G(\text{H}_2|\text{H}^+|\ |\text{Cu}^{2+}|\ \text{Cu}) - \Delta_r G(\text{H}_2|\text{H}^+|\ |\text{Zn}^{2+}|\ \text{Zn}) \tag{2.31}$$

Dividing (2.31) by $-zF$ and using ° to indicate unit activities

$$E°_{\text{reversible cell}}(\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}) = E°(\text{Cu}|\text{Cu}^{2+}) - E°(\text{Zn}|\text{Zn}^{2+}) \tag{2.32}$$

More generally, this could be done for any electrodes

$$E°_{\text{reversible cell}}(\text{anode}||\text{cathode}) = E°_{\text{cathode}} - E°_{\text{anode}} \tag{2.33}$$

<u>This makes it simple to predict if a metal will corrode</u>! If $E°_{\text{reversible cell}} > 0$ for a chosen anode and cathode, the anode will corrode (into unit activity solutions).

♦ At non-unit activities, the Gibbs energy changes $\Delta_r G$ are different from $\Delta_r G°$, but the equivalent expression to equation (2.33) is

$$E_{\text{reversible cell}} = E_{0,\text{cathode}} - E_{0,\text{anode}} \tag{2.34}$$

$E°$ values can be looked up. A correction can be added to find $E_{0,\text{anode}}$ for the metal at non-unit activity. Crucially, the effective value of $E°_{\text{cathode}}$ affecting the metal <u>can be measured with a voltmeter</u>, even if several reactions are involved.

$$E_{\text{unknown cathode}} = E_{\text{reversible cell}}(\text{H}_2|\text{H}^+ ||\ \text{unknown cathode}) \tag{2.35}$$

EJR

2.9 The IUPAC definition of standard electrode potential

The standard electrode potential, abbreviated $E°$ or $E⊖$ (with a superscript plimsoll character, pronounced "E standard" or "E nought"), is the measure of the potential of a reversible electrode at standard state, which is with solutes at an effective concentration of 1 mol dm^{-3}, and gases at a pressure of 1 bar.

[http://dx.doi.org/10.1351/goldbook.S05912]

The standard electrode potential is the value of the standard emf of a cell in which molecular hydrogen under standard pressure is oxidized to solvated protons at the left-hand electrode.

The standard electrode potential of a test electrode such as $(M|M^{z+})$ is found when:

♦ Reagents are at <u>unit activity</u>, and

♦ The cell is <u>reversible</u>

♦ Standard electrode potentials are often tabulated at 25°C.

The standard electrode potential can be measured with a high-impedance voltmeter between a test electrode and a <u>standard hydrogen electrode</u>.

♦ The standard hydrogen electrode is written $(H_2|H^+)$ at pH 0 and 1 bar H$_2$.

♦ Standard electrode potentials are therefore stated in volts (SHE) or V_{SHE}.

Then the standard electrode potential is, with unit activities:

$$E°(M|M^{z+}) = E°_{\text{reversible cell}}(H_2|H^+| | M^{z+}|M) \tag{2.36}$$

2.9.1 Practical measurement using a silver chloride electrode

In practice, $E°$ is often measured using silver chloride anodes, which are easy to fabricate and use.

$$E°(M|M^{z+}) = E°_{\text{reversible cell}}(Ag|AgCl|HCl(aq)| | M^{z+}|M) + 0.223 \text{ V} \tag{2.37}$$

Since

$$(H_2|H^+| | M^{z+}|M) = (Ag|AgCl|H^+, Cl^- | | M^{z+}|M) + (H_2|H^+, Cl^-|AgCl|Ag) \tag{2.38}$$

And at unit activities at at 25°C

$$E°(Ag|AgCl|HCl) = 0.223 \text{ V}_{SHE} \tag{2.39}$$

Which produces equation (2.37) using the same reasoning as (2.28 – 2.33).

EJR

2.10 Non-standard concentrations

Most corrosion processes involve ion activities smaller than unity.

2.10.1 Example.

Seawater has a pH ≈8. Predict whether copper dissolves in this environment, where there is 10^{-8} mol/dm^3 of H^+(aq). The copper metal is a solid phase, and has unit activity, and the dissolved copper may be at a low concentration.

The standard electrode potential of copper is

$$E°(Cu|Cu^{2+}) = +0.337 \, V_{SHE} \tag{2.40}$$

So in a corrosion cell with copper as the anode

$$E°_{reversible \, cell}(Cu|Cu^{2+} \, || \, H^+|H_2) = -0.337 \, V \tag{2.41}$$

Therefore copper would not spontaneously dissolve by reaction with protons in a solution which contained 1 mol dm^{-3} of dissolved copper ions at pH 0.

♦ But copper actually does dissolve into seawater, to a low concentration of dissolved ions. This means, for example, that copper barrels containing nuclear waste could not safely be disposed of by dropping them to the bottom of the ocean!

2.10.2 The Nernst equation

Consider copper dissolution at 298 K in an aqueous solution of pH 0 and 1 pM dissolved copper ion concentration.

$$Cu + 2H^+ \rightarrow Cu^{2+} + H_2 \tag{2.42}$$

The Gibbs energy change, using equation (2.21), is

$$\Delta G_{reaction}(Cu|Cu^{2+}| \, |H^+|H_2) = \Delta G°_{reaction} + RT \ln(Q_r) \tag{2.43}$$
$$= +65.03 \text{ kJ mol}^{-1} + RT \ln(Q_r)$$

Where Q_r is the reaction quotient

$$Q_r = \left(\frac{a_{(Cu^{2+})}a_{(H_2)}}{a_{(Cu)}a^2_{(H^+)}} \right) \tag{2.44}$$

Hence, evaluating the Gibbs energy change

$$\Delta G_{reaction} = +65.03 \text{ kJ mol}^{-1} + RT \ln \left(\frac{10^{-12} \times 1}{1 \times (10^{-0})^2} \right) \tag{2.45}$$
$$= -3.43 \text{ kJ mol}^{-1}$$

Or equivalently

$$E_{reversible \, cell} = -\frac{\Delta G_{reaction}}{zF} - \frac{RT}{zF} \ln(Q_r) \tag{2.46}$$

$$E_{reversible \, cell} = E°_{reversible \, cell} - \frac{RT}{zF} \ln \left(\frac{a_{(Cu^{2+})}a_{(H_2)}}{a_{(Cu)}a^2_{(H^+)}} \right) \tag{2.47}$$

$$E_{reversible \, cell} = +0.0177 \, V \tag{2.48}$$

So copper would dissolve into a very dilute solution of Cu^{2+} ions at pH 0.

♦ This is part of the reason why copper dissolves in seawater.

EJR

Equation (2.46) is the Nernst equation for a complete cell reaction. If we know the properties of both electrodes in a corrosion process, then we can evaluate $E_{\text{reversible cell}}$. If $E_{\text{reversible cell}} > 0$ then the metal anode will corrode spontaneously.

However, the main reason for using electrochemical notation to study corrosion is because we only know the exact properties of the metal (the possible anode). Fortunately, the multi-reaction environment (the possible cathode) is something we can measure.

- Equation (2.47) can be expanded by separating the logarithm term

$$E_{\text{reversible cell}} = E°_{\text{reversible cell}} - \frac{RT}{zF}\ln\left(\frac{a_{(Cu^{2+})}}{a_{Cu}}\right) + \frac{RT}{zF}\ln\left(\frac{a^2_{(H^+)}}{a_{(H_2)}}\right) \qquad (2.49)$$

$$E_{\text{reversible cell}} = E°_{\text{cathode}} - E°_{\text{anode}} - \frac{RT}{zF}\ln\left(\frac{a_{(Cu^{2+})}}{a_{(Cu)}}\right) + \frac{RT}{zF}\ln\left(\frac{a^2_{(H^+)}}{a_{(H_2)}}\right) \quad (2.50)$$

- We can spot that there are separate terms for the anode and cathode, and the difference between them gives the reversible cell potential at non-standard conditions.

$$E_{0,\text{cathode}} = E°_{\text{cathode}} + \frac{RT}{zF}\ln\left(\frac{a^2_{(H^+)}}{a_{(H_2)}}\right) \qquad (2.51)$$

$$E_{0,\text{anode}} = E°_{\text{anode}} + \frac{RT}{zF}\ln\left(\frac{a_{(Cu^{2+})}}{a_{(Cu)}}\right) \qquad (2.52)$$

$$E_{\text{reversible cell}} = E_{0,\text{cathode}} - E_{0,\text{anode}} \qquad (2.53)$$

In equations (2.51-2.53), $E_{0,\text{cathode}}$ is the equilibrium potential of the cathode at a non-standard concentration. $E_{0,\text{anode}}$ is the equilibrium potential of the anode.

These equilibrium potentials obey the Nernst equation for a single electrode

$$E_{0,\text{cathode}} = E°_{\text{cathode}} + \frac{RT}{zF}\ln\left(\frac{[oxidised]}{[reduced]}\right) \qquad (2.54)$$

$$E_{0,\text{anode}} = E°_{\text{anode}} + \frac{RT}{zF}\ln\left(\frac{[oxidised]}{[reduced]}\right) \qquad (2.55)$$

The notation [*reduced*] represents the product of the concentrations (or pressures where gases are involved) of all of the species that appear on the reduced side of the electrode reaction, raised to the power of their stoichiometric coefficients. The notation [*oxidised*] represents the same for the oxidised side of the electrode reaction.

The Nernst equation is sometimes written in $\log_{10}$. This makes it easier to deal with concentration differences in terms of the number of powers of ten which are involved.

$$E_{0,\text{electrode}} = E°_{\text{electrode}} + 2.303\frac{RT}{zF}\log_{10}\left(\frac{[oxidised]}{[reduced]}\right) \qquad \textbf{\underline{(2.56)}}$$

We can compare the equilibrium potential of the metal anode, $E_{0,\text{anode}}$ [which we can calculate exactly using (2.56)] with the measured potential of the environment, $E_{0,\text{cathode}}$. Then if $E_{\text{reversible cell}} > 0$, we predict the metal corrodes.

2.11 Concentration gradient cells

<u>Example</u>

An electrochemical cell consists of a silver anode dissolving into an aqueous solution containing silver ions at 10 mM concentration, and a cathode connected by a salt bridge in which silver ions at 100 mM concentration are electroplated onto a silver block.

The temperature is 298 K.

Calculate the potential difference across the cell using the Nernst Equation, if the cell is operated reversibly.

<u>Solution</u>

Cell notation: $Ag(s) \mid Ag^+(aq, 0.01\ M) \parallel Ag^+(aq, 0.1\ M) \mid Ag(s)$

$$E_{\text{reversible cell}} = E_{0,\text{cathode}} - E_{0,\text{anode}}$$

$$E_{0,\text{cathode}} = E°_{\text{cathode}} + \frac{RT}{zF}\ln\left(\frac{[oxidised]}{[reduced]}\right) = E°(Ag|Ag^+) + \frac{RT}{zF}\ln\left(\frac{0.1}{1}\right)$$

$$E_{0,\text{anode}} = E°_{\text{anode}} + \frac{RT}{zF}\ln\left(\frac{[oxidised]}{[reduced]}\right) = E°(Ag|Ag^+) + \frac{RT}{zF}\ln\left(\frac{0.01}{1}\right)$$

$$E_{\text{reversible cell}} = E_{0,\text{cathode}} - E_{0,\text{anode}} = \frac{RT}{zF}(\ln(0.1) - \ln(0.01)) = +59\ \text{mV}$$

… Reality check: positive E_{cell} means this process is expected to go forwards spontaneously, which (since the process is the flow of silver ions from high to low concentration) is correct.

<u>... For a reaction with 1 electron per atom, the equilibrium potential of an electrode at 25°C shifts by 59 mV per decade change in concentration of the atom (or other species). This often means 59 mV per unit of pH.</u>

<u>2.11.1 Analogy between temperature and oxidation potential</u>

EJR

2.12 Predicting corrosion from thermodynamic data

A metal is expected to corrode if it is the anode in a cell where:

$$E_{\text{reversible cell}} = (E_{0,\text{cathode}} - E_{0,\text{anode}}) > 0 \qquad (2.57)$$

Where the equilibrium potentials usually need to be calculated using the Nernst equation (2.56), because usually the ion activities are not unity.

A relevant value for $E°_{\text{anode}}$ can be looked up for a metallic element in a table of standard electrode potentials. This can be used to find $E_{0,\text{anode}}$ using the Nernst equation (2.32) for the given concentration of dissolved ions.

A relevant value for the cathode usually consists of contributions from several reactions due to chemicals in the environment reacting on the metal surface. This can be measured. Tables listing measured values in common situations are called practical galvanic series.

Table 2.1. Some standard electrode potentials in aqueous solution (for unit activities)

Electrode	Standard equilibrium potential / V_{SHE}
$(Au|Au^{3+})$	+1.40
$(H_2O|O_2, H^+)$ at pH 0	+1.22
$(Pt|Pt^{2+})$	+1.19
$(Ag|Ag^+)$	+0.80
$(H_2O|O_2, H^+)$ at pH 14	+0.40
$(Cu|Cu^{2+})$	+0.34
$(H_2|H^+)$ at pH 0	0.00
$(Pb|Pb^{2+})$	-0.13
$(Fe|Fe^{2+})$	−0.44
$(Zn|Zn^{2+})$	−0.76
$(H_2|H^+)$ at pH 14	−0.83
$(Al|Al^{3+})$	−1.66
$(Mg|Mg^{2+})$	−2.36

Table 2.2. Practical galvanic series for metals in neutral soils or water [Roberge p.109]

Metal (and condition)	Potential on surface / V_{SHE}
Platinum	+0.3
Mild steel in concrete	+0.1
Copper, brass, bronze	+0.1
Mild steel (rusted)	−0.2 to +0.1
Lead	−0.2
Mild steel (shiny)	−0.5 to −0.2
Pure aluminium	−0.5
Aluminium-zinc alloy (5% Zn)	−0.75
Zinc	−0.8
Magnesium	−1.4

2.13 Practical Galvanic Series

The electrochemical series lists thermodynamic data describing individual electrode equilibrium potentials in volts (SHE).

A <u>galvanic series</u> is a table of the electrode potentials <u>measured</u> on the surface of real metals in a particular environment.

- ♦ A practical galvanic series is measured for particular conditions (e.g. "metal in neutral soils").
  - o It tabulates the potential of a metal surface which may host several reactions, involving environmental chemicals as well as the metal.
  - o Temperature, pH, and salinity may affect the potential on the metal surface, so there are different galvanic series for different environments.
- ♦ When there are many half-cell reactions on a metal surface, the galvanic potential measured on its surface is called a mixed potential:

The galvanic series tabulates the potential observed when all these electrochemical reactions occur at once. It is a weighted average of the various equilibrium potentials.

- ♦ The galvanic series is used for:
  - o Determining if the mixed electrode potential measured on a metal surface is sufficiently oxidising to cause it to corrode.

  - o Determining which of two metals may suffer increased corrosion if they are bolted together.

Galvanic potential on a metal can be very different from its equilibrium potential.

- ♦ Some metal electrodes are **kinetically slow**. The rate of reaction of $(Pb|Pb^{2+})$ is slower than reactions like $(H_2|H^+)$, and the galvanic potential will be close to the equilibrium potential of the faster reaction.
- ♦ Some materials are **strong electrocatalysts**. Rusty iron is a stronger electrocatalyst than pure iron for $(H_2|H^+)$ and $(H_2O|O_2)$.
  - o This is why rust is sometimes called 'autocatalytic'. The galvanic potential of iron becomes closer to the oxidising potentials of $(H_2|H^+)$ and $(H_2O|O_2)$ due to rust formation, and this produces a stronger cathode for corrosion.
- ♦ Some metals have **passive oxide** surfaces. Aluminium's surface chemistry is mainly affected by various reactions taking place on its Al_2O_3 surface, and not by the reaction $(Al|Al^{3+})$.

2.14 Corrosion and pH

pH affect aqueous corrosion for several reasons.

♦ pH affects the ion conductivity of solutions. Ion mobility is needed for electrochemical corrosion, and can be rate-limiting.

♦ pH determines the oxidising potential exerted by protons dissolved in water. From equations 2.3 and 2.10, at 298 K.

$$E_{0,\text{cathode}} = E°_{\text{cathode}} + \frac{RT}{zF} \ln \left(\frac{a^2_{(H^+)}}{a_{(H_2)}} \right) \tag{2.58}$$

Example

Effect of pH on reactions in copper corrosion at 298 K, and unit activity of dissolved copper.

Corrosion reaction	Notation	Equilibrium potential / V_{SHE}
(A) Hydrogen evolution	$(H_2|H^+)$	$E_0 = 0.00 - 0.059 \, \text{pH}$
(B) Oxygen reduction	$(H_2O|O_2, H^+)$	$E_0 = 1.228 - 0.059 \, \text{pH}$
(C) Copper dissolution	$(Cu|Cu^{2+})$	$E_0 = +0.337$
(D) Copper oxide formation	$Cu + H_2O = CuO + 2H^+ + 2 \, e^-$	$E_0 = 0.570 - 0.059 \, \text{pH}$
(E) Copper oxide dissolution	$Cu^{2+} + H_2O = CuO + 2H^+$	E_0 is not determined for a pure acid-base reaction $\log_{10}\left(a(Cu^{2+})\right) = 7.9 - 2 \, \text{pH}$

2.15 Mapping out corrosion products on pH-potential diagrams

The pH-potential diagram, also called a Pourbaix diagram, maps out the thermodynamically stable phase of a metal in aqueous solution as a function of the oxidation potential and pH of the environment.

<u>Example:</u> Construct the pH-potential diagram for copper in aqueous solution, from pH 0 to 10 and oxidation potential -1.5 V_{SHE} to + 1.5 V_{SHE}.
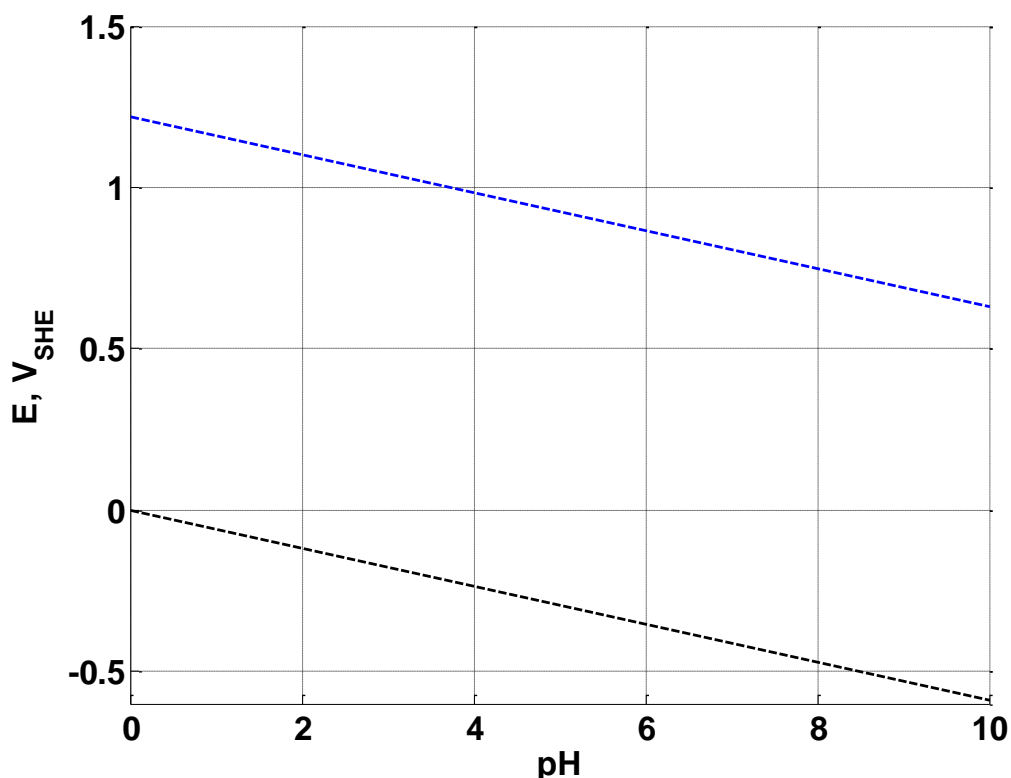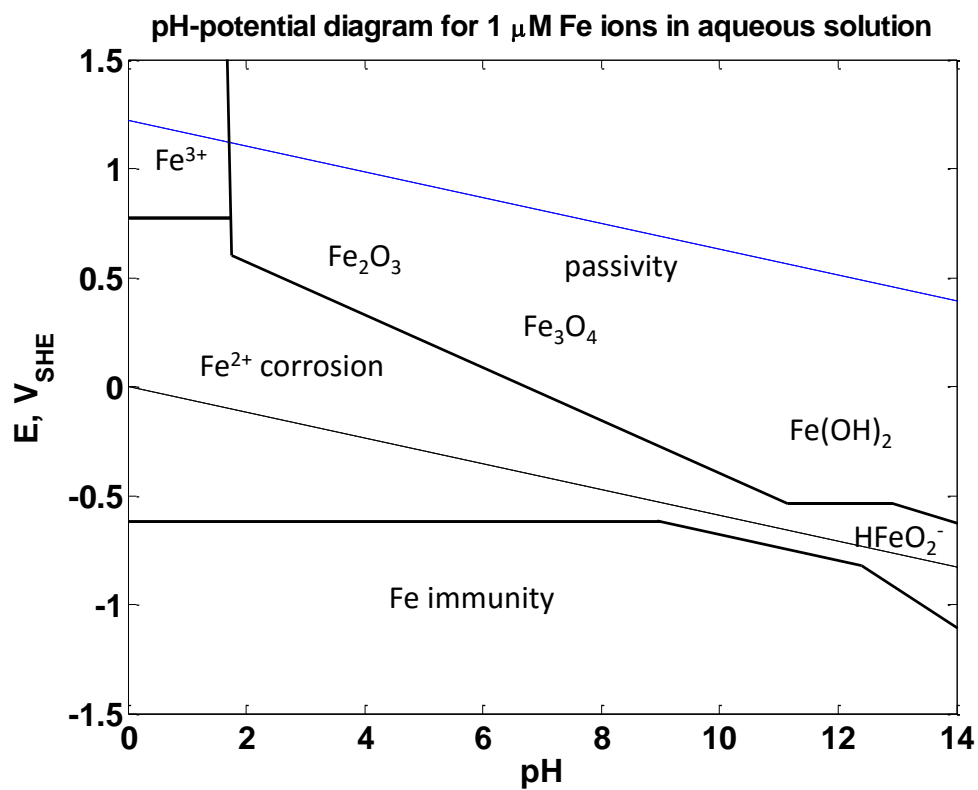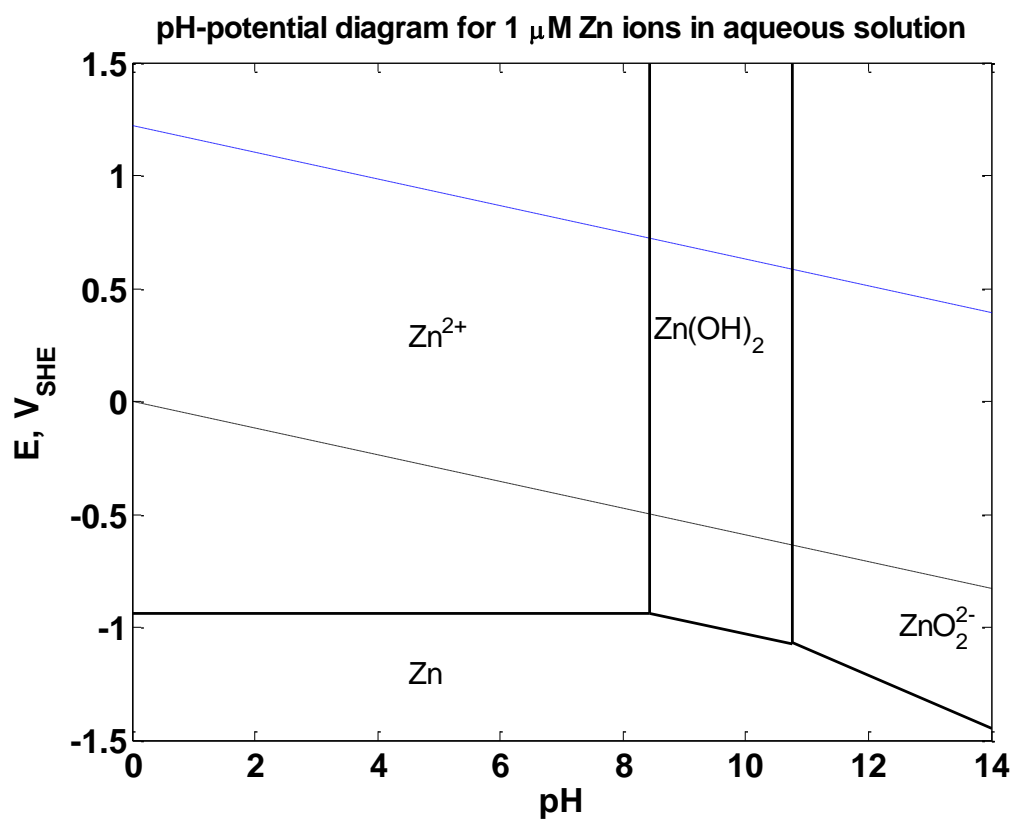

Instructions:

♦ pH on x-axis, oxidation potential on y-axis.

♦ Dashed lines showing oxidising agents (half-reactions A, B, above)

♦ Label common environments (e.g. de-aerated neutral water).

♦ Draw the horizontal line of the $Cu \,|\, Cu^{2+}$ equilibrium.

♦ Draw the vertical line showing the $Cu^{2+} \,|\, CuO$ equilibrium.

♦ Draw the diagonal line showing $Cu \,|\, CuO$ equilibrium.

♦ Label the stable phases.

♦ Note this diagram was simplified by neglecting:

  ○ CuO_2^{2-} which is stable at pH > 12.

  ○ A small region of Cu_2O stability between the hydroxide and metal.

  ○ All of the chloride complexes which can appear in salt water.

EJR

2.16 Simplified Pourbaix (pH-potential) diagrams for zinc and iron

pH-potential diagram for 1 μM Zn ions in aqueous solution

pH-potential diagram for 1 μM Fe ions in aqueous solution

Reference: Marcel Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solution." Pergamon (1974).

2.17 The purpose and limitations of pH-potential diagrams

Purpose

♦ Data on a small number of equilibria can predict stable phases at any possible value of { pH , E }.

♦ Can measure pH and oxidation potential, then refer to Pourbaix diagrams to find a suitable, passive metal.

♦ Represents redox and acid-base interactions visually

   o Redox: electron transfer, y-axis, so pure redox equilibria are separated by horizontal lines of constant oxidation potential

   o Acid-base: proton transfer is only affected by pH, so pure acid-base reactions (between ions and oxides at the same metal oxidation state) are separated by vertical lines of constant pH

   o Mixed (metal | metal oxide) reactions combine redox and acid base, and are separated by diagonal lines.

Limitations

♦ Does not predict kinetics. Driving force in volts can be measured on the diagrams, but this is just one input to kinetic models

♦ Simple versions neglect chloride and other complexing ions – would have to add a third axis, or multiple diagrams, to show the effect of different chloride concentration.

♦ Lines refer to equilibria at particular solution concentrations. Need to adjust line position for different concentrations. Lines are often drawn for equilibrium with 1 M or 1 micromolar activities, with the latter used to determine stability against corrosion in most environments.

♦ Identifies when solid oxidation products are stable, but does not give information on whether they are impermeable (protective) and thus lead to passivity.

3. Kinetics of aqueous corrosion

Thermodynamics can determine whether aqueous corrosion will occur, and its driving force. To predict the rate, a kinetic model is needed.

The rate of an electrochemical reaction is expressed as an electronic <u>current density</u> which is related to the molar rate by <u>Faraday's law</u>.

In models of electrochemical kinetics, a zero rate of corrosion for an electrode such as ($Cu|Cu^{2+}$) means there is dynamic equilibrium with an equal rate of oxidation and reduction. When the environment of a metal exerts an oxidising action, the electrode potential is <u>polarised</u> away from the equilibrium potential, and the oxidation of the metal proceeds faster than reduction. This leads to a net positive rate of corrosion. The rate of corrosion is predicted by two factors: the baseline rate of the dynamic equilibrium reactions, called the <u>exchange current density</u>, and by the way this baseline rate is increased by polarisation.

3.1 Measuring rates of corrosion

Methods of measuring corrosion depend on its rate and mechanism.

Measurement	Units	Applications
Weight change	As mm/year loss of thickness (speed)	Most metals
	% weight change	Rare. Need standard test objects.
Permeation	Volume flux per unit pressure	Special gases (hydrogen blistering).
Penetration	mm	Depth of corrosion pits
	mm	Depletion of alloy component
Tensile properties	Pa m$^{0.5}$ (sometimes)	Change in fracture toughness due to embrittlement
Appearance	'Surface texture'	Counting number of pits
	'Colour'	E.g. copper alloys
Effect on environment		Toxicity / contamination
Current density	A/m^2	Electrochemical corrosion

3.1.1 Current density

Electronic current density, i, (measured in mA/cm^2 or A/m^2), is used to quantify reaction rate in aqueous corrosion.

♦ Current is easy to measure.

♦ Current density is related to molar corrosion rate by Faraday's law.

♦ It is easily converted to mm/year.

3.2 Relation of current density to speed of corrosion

In a cell, the corrosion rate at the anode $(M \rightarrow M^{z+} + ze^-)$ is proportional to the electronic current, I.

♦ One mole of metal M reacting gives out z moles of electrons.

♦ The total charge that passes through the cell when N moles of metal M react is Q.

$$Q = zFN \tag{3.1}$$

♦ The current flowing through an electrochemical cell in which the metal M is oxidised at a rate of $\mathrm{d}N/\mathrm{d}t$ moles per unit time is given by Faraday's law:

$$I = zF(\mathrm{d}N/\mathrm{d}t) \tag{3.2}$$

or $\quad i = \left(\frac{zF}{A}\right)(\mathrm{d}N/\mathrm{d}t) \tag{3.3}$

♦ Where the <u>current density</u>, i, given the electrode area A, is

$$i = I/A \tag{3.4}$$

An anodic current density is positive and can be written i_a, and a cathodic current density is negative, and can be written as i_c. Sometimes, the absolute values $|i_a|$ and $|i_c|$ may be written for clarity. The following equation uses $|i_a|$ and $|i_c|$ to describe copper behaviour near a dynamic equilibrium:

$$i_{net}(Cu|Cu^{2+}) = i_a + i_c = |i_a| - |i_c| \tag{3.5}$$
$$= |i(Cu \rightarrow Cu^{2+} + 2e^-)| - |i(Cu^{2+} + 2e^- \rightarrow Cu)|$$

<u>3.2.1 Example</u>

Calculate the net current density equivalent to the steady-rate dissolution of 1 mm/year of steel. Assume the reaction is $Fe = Fe^{2+} + 2e^-$.

Data:

Density of iron = 7874 kg/m^3

Atomic mass of iron = 55.85

3.3 Polarisation (sometimes called 'overpotential')

In a real environment, there are many electrochemical reactions taking place on the surface of a metal object.

♦ The metal surface has an <u>electrochemical potential</u>, E.

♦ E may be called E_{mixed} if the potential is caused by a mixture of chemical species, or E_{applied} if the potential is applied by external electronics.

♦ E may be different from the equilibrium potential, E_0, of an individual electrode reaction. Suppose a piece of copper in water has an electrode potential $E \neq E_0(\text{Cu|Cu}^{2+})$. Then the electrode is said to be <u>polarised</u> with respect to (Cu|Cu^{2+}). The <u>polarisation</u>, η, is measured in volts.

$$\eta = E - E_0 \tag{3.6}$$

Or $\qquad \eta(\text{Cu|Cu}^{2+}) = E - E_0(\text{Cu|Cu}^{2+}) \qquad$ which specifies the reaction

The polarisation of an electrode is the driving force for corrosion. Compare equation (3.6) with thermodynamics (sections 2.2 – 2.12).

Recall that a two-electrode process proceeds if

$$E_{\text{reversible cell}} = (E_{0,\text{cathode}} - E_{0,\text{anode}}) > 0 \tag{2.57}$$

Corrosion of copper, (Cu|Cu^{2+}), in a complex environment proceeds if

$$E_{\text{reversible cell}}(\text{Cu|Cu}^{2+}||\ '\text{environment}') > 0 \tag{3.7a}$$

Or $\qquad\qquad E - E_0(\text{Cu|Cu}^{2+}) > 0 \tag{3.7b}$
Or just $\qquad\qquad \eta(\text{Cu|Cu}^{2+}) > 0 \tag{3.7c}$

♦ $\eta(\text{M|M}^+) > 0$ means the local environment will make (M|M⁺) an anode and so the metal will be oxidised.

♦ $\eta(\text{M|M}^+) < 0$ means the local environment will not corrode (M|M⁺). In this case:

$$E_{\text{reversible cell}}(\text{Cu|Cu}^{2+}||\ '\text{environment}') = \eta(\text{Cu|Cu}^{2+}) < 0$$

There is a driving force for the reverse process in the cell – electroplating.

♦ η = 0 indicates there is zero driving force for corrosion or electroplating.

Electrochemical kinetics assumes that <u>a zero net rate of corrosion, when $\eta = 0$, involves a dynamic equilibrium</u>, with equal rates of dissolution and plating.

$$\text{Oxidised species} + z\text{e}^- \leftrightarrow \text{Reduced species}$$
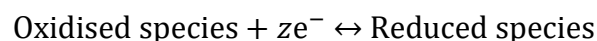
For example, a (Cu|Cu^{2+}) electrode with $\eta(\text{Cu|Cu}^{2+}) = 0$ V might experience:

$$i_{\text{net}}(\text{Cu|Cu}^{2+}) = |i_a(\text{Cu|Cu}^{2+})| - |i_c(\text{Cu|Cu}^{2+})| = i_0 - i_0 = 0 \tag{3.8}$$

Where i_0 is property called the <u>exchange current density</u> of the electrode.

EJR

3.4 Exchange current density

Exchange current densities, i_0, can be found from experimental data.

Exchange current densities depend on the surface chemistry.

♦ E.g. in electrolysis of water, the hydrogen electrode $(H_2|H^+)$ involves several steps: (1) electron transfer, (2) H atom diffusion, and (3) desorption of H_2 molecules. The rates of these steps depend on electrocatalysis, so different values of i_0 exist for the same reaction on different metals.

Table 3.2. Exchange current densities for $2H^+ + 2e^- = H_2$ [Bockris, Textbook of electrochemistry, 1951].

Metal	$i_0(H_2|H^+)$
Platinum	1×10^{-3} A/cm²
Nickel	4×10^{-6} A/cm²
Iron	2×10^{-6} A/cm²
Zinc	1×10^{-8} A/cm²
Lead	2×10^{-13} A/cm²

Polarisation and exchange current density are the two key concepts needed to relate corrosion rate to thermodynamic driving force.

3.4.1 Diagram of factors which may limit electrochemical reaction rate
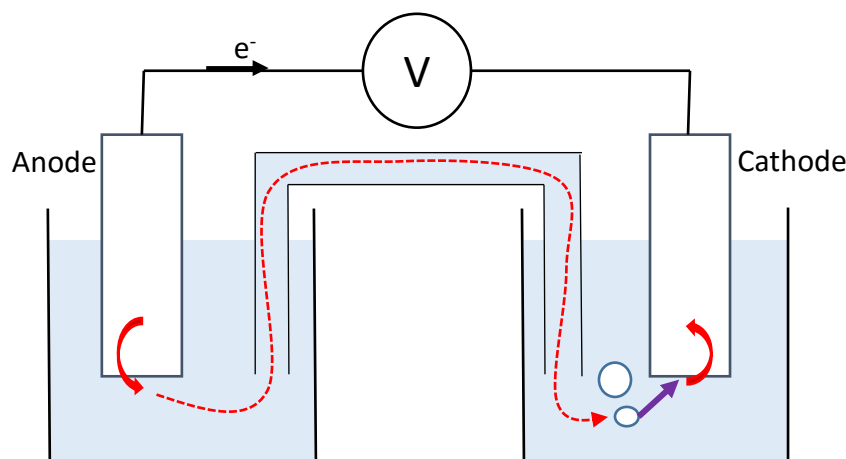
In this model, consider:

$$\left(\frac{-\Delta_r G}{zF}\right) = E_{cell} + |\eta_{anode}| + |\eta_{cathode}| + |\eta_{ion\ resistance}| + |\eta_{diffusion}| \quad (3.9)$$

3.5 The Tafel equation: a model for the current density of an electrode when the only significant limiting factor is activation

The Tafel equation is used to estimate the current density of an electrode reaction such as $(Cu|Cu^{2+})$, assuming:

♦ The reaction is slow, so there are negligible energy losses due to mass transport, which means $\eta_{\text{diffusion}} = \eta_{\text{ion resistance}} = 0$

♦ The surface of the metal is at a potential, E

$$\eta_{\text{anode}}(Cu|Cu^{2+}) = E - E_0(Cu|Cu^{2+}) \tag{3.10}$$

The following 'distance model' is used in electrochemistry. The Gibbs energy of an electrode is plotted as a metal atom is moved a distance Δx into the solution, where the atom eventually becomes a fully dissolved ion.
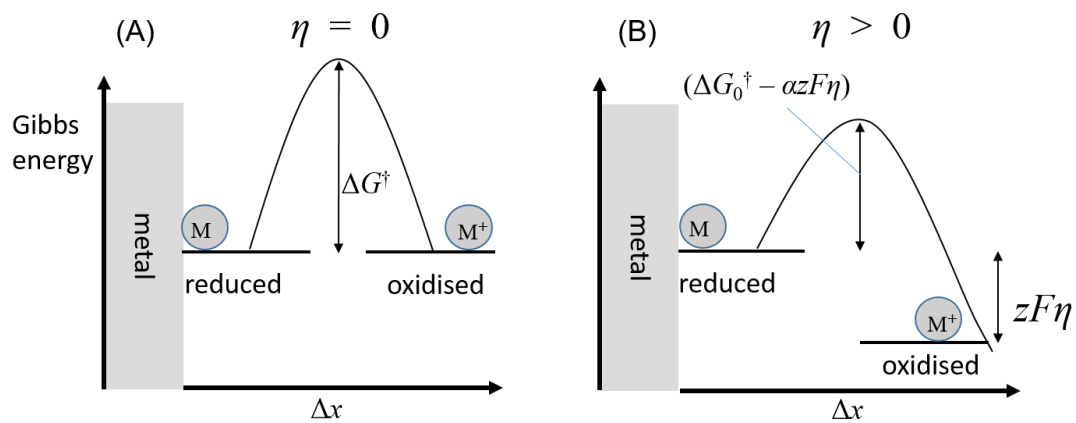
The net rate of the $(Cu|Cu^{2+})$ reaction is obtained by adding up simultaneous forward and reverse reactions. The forward and reverse reactions are both described as Arrhenius-limited with attempt rates A and activation energies ΔG^*.

$$i_{\text{for}} = i(Cu \rightarrow Cu^{2+} + 2e^-) = A_{\text{for}}\, e^{-\left(\frac{\Delta G^*_{\text{for}}}{RT}\right)} \tag{3.11}$$

$$i_{\text{rev}} = i(Cu^{2+} + 2e^- \rightarrow Cu) = A_{\text{rev}}\, e^{-\left(\frac{\Delta G^*_{\text{rev}}}{RT}\right)} \tag{3.12}$$

(A) When the polarisation is zero, the forward and reverse activation energies are the same $(\Delta G^\dagger)$, and the net reaction rate is zero (from equation 3.7). Therefore we can identify:

$$i_{\text{for}} = i_{\text{rev}} = A_{\text{for}}\, e^{-\left(\frac{\Delta G^\dagger}{RT}\right)} = A_{\text{rev}}\, e^{-\left(\frac{\Delta G^\dagger}{RT}\right)} = i_0 \tag{3.13}$$

(B) When there is some polarisation, $\eta > 0$, the forward activation energy is decreased, and the reverse activation energy is increased, to the values given in the figure. (Often, $\alpha=0.5$.) The reaction rates becomes:

$$i_{\text{net}} = i_{\text{for}} - i_{\text{rev}} = A_{\text{for}}\, e^{-\left(\frac{\Delta G^\dagger - \alpha z F\eta}{RT}\right)} - A_{\text{rev}}e^{-\left(\frac{\Delta G^\dagger + (1-\alpha)z F\eta}{RT}\right)} \tag{3.14}$$

Which simplifies to the Butler-Volmer equation (Databook p.33):

$$i_{\text{net}}(Cu|Cu^{2+}) = i_0\left[\exp\left(+\frac{\alpha z F\eta}{RT}\right) - \exp\left(-\frac{(1-\alpha)z F\eta}{RT}\right)\right] \tag{3.15}$$

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<u>3.5.1 Figure showing the exact kinetic behaviour of an electrode, according to the Butler-Volmer model</u> (with α=0.5, i_0=1 μA/cm^2, 298 K, z=1).
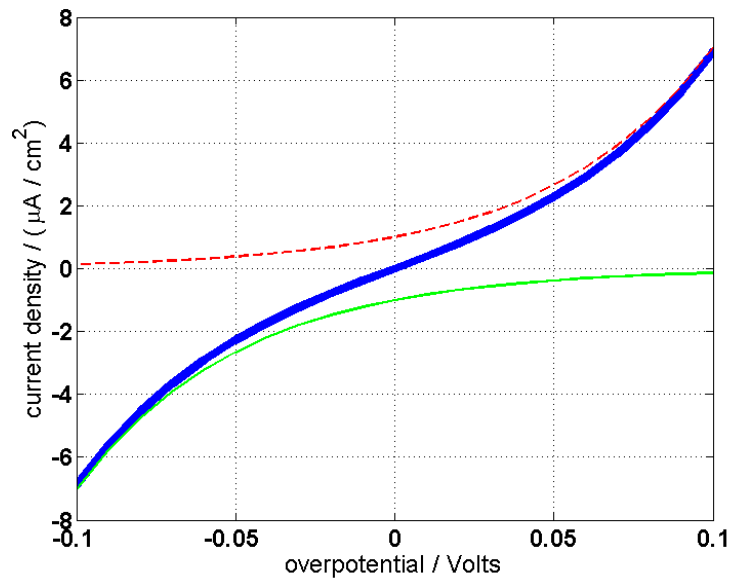
3.5.2 The Tafel equation (Databook p.33)

The Tafel equation is a simplified case of (3.15).

The Tafel equation is an approximation which considers only the forward or reverse reaction. From Figure (3.5.1), it is a good approximation if the polarisation is at least 50 mV, which is often a valid approximation in corrosion.

<u>Corrosion (anodic polarisation)</u>

Only the first term is significant if η > +50 mV, since $|i_a| \gg |i_c|$

$$i \approx i_{\text{for}} = i_0 \exp\left(\frac{\alpha zF\eta}{RT}\right) = i_0 \times 10^{\eta/\beta_a} \qquad (3.16)$$

So $\qquad i = i_0 \times 10^{\eta/\beta_a}$ **(3.17a)**

Or $\qquad \eta = \beta_a \log_{10}(i/i_0)$ **<u>(3.17b)</u>**

Where $\qquad \beta_a = 2.303\frac{RT}{\alpha zF}$ (3.18)

Equation (3.17) is the **<u>Tafel equation</u>** for an anode, and β_a is the Tafel slope.

<u>Reduction reaction (cathodic polarisation)</u>

Only the second term is significant if $\eta < -50$ mV, since $|i_a| \ll |i_c|$

$$i \approx -|i_c| = -i_0 \times 10^{\eta/\beta_c} \quad \text{with } \eta \text{ and } \beta_c \text{ negative} \qquad (3.19)$$

So $\qquad i = -i_0 \times 10^{\eta/\beta_c}$ **(3.20a)**

$\qquad\qquad \eta = \beta_c \log_{10}(|i|/i_0)$ **<u>(3.20b)</u>**

Where $\qquad \beta_c = -2.303\frac{RT}{(1-\alpha)zF}$ (3.21)

Equation (3.20) is the Tafel equation for a cathode.

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3.5.3 Notes on using the Tafel equation

Sometimes, the cathodic Tafel slope β_c and the cathodic polarisation η_c might both be treated as absolute values instead of being considered negative.

Near equilibrium

For small polarisations, $|\eta| < 50\,\text{mV}$, both terms in the Butler-Volmer equation are significant. In simple reactions, $\alpha = 0.5$, in which case

$$i = 2\,i_0 \sinh\left(\frac{zF\eta}{2RT}\right) \tag{3.22}$$

or $\qquad i \approx \frac{i_0 zF\eta}{RT} \qquad$ for small values of η. $\qquad$ (3.23)

Hence linear behaviour is expected for low polarisations, meaning the <u>Tafel equation is not obeyed at low polarisations</u>.

♦ We are normally interested only in the behaviour when the polarisation is moderately large (i.e. the Tafel equation region).

3.6 Corrosion of a two-electrode system with no mass transport limitation (and unit activities).

Example problem

Determine the corrosion current density of an iron object dissolving in deaerated acid at pH 0 containing $1\,M$ Fe^{2+}. Assume the anode reaction is $Fe \rightarrow Fe^{2+} + 2e^-$, and the only cathode reaction is $2H^+ + 2e^- \rightarrow H_2$, and that there is no mass transport limitation.

Note there is just one metal surface, so $|i_a| = |i_c| = i_{corr}$ at the solution

Data:

$E_0(H_2|H^+)\ \ = 0.00\ V_{SHE}$ (same as $E°$ since activity $= 1$)

$i_0(H_2|H^+)\ \ = 10^{-3}\ mA/cm^2$ on iron

$\beta_c(H_2|H^+)\ \ = -0.118\ V/decade$

$E_0(Fe|Fe^{2+}) = -0.44\ V_{SHE}$ (same as $E°$ since activity $= 1$)

$i_0(Fe|Fe^{2+})\ = 10^{-5}\ mA/cm^2$

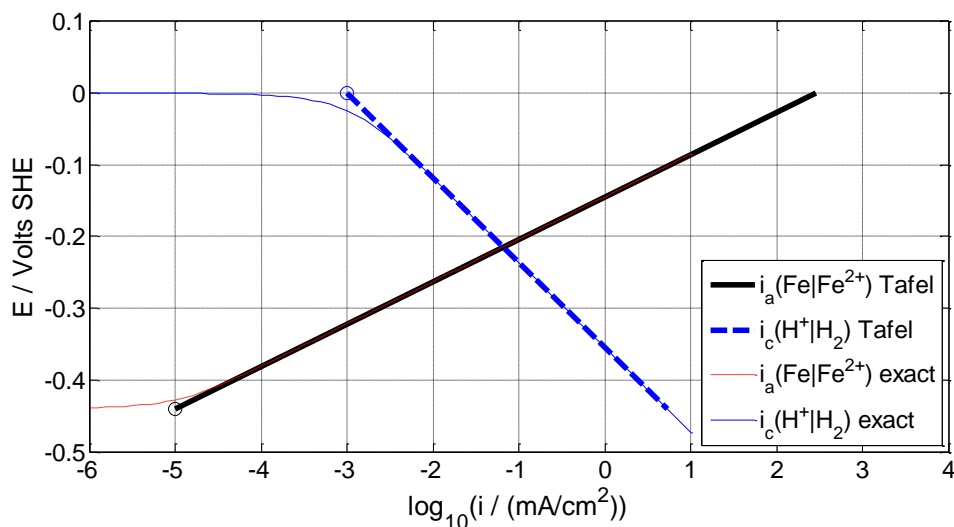$\beta_a(Fe|Fe^{2+})\ = +0.059\ V/decade$

Figure. An <u>Evans diagram</u> is a plot of potential against log of current density. Here, the corrosion rate of a two-electrode system is found by the Tafel equation and the Butler-Volmer model, neglecting mass transport limitation.

3.7 Diffusion-limited corrosion rate

In the iron-acid example above, the chemical reaction was the rate-determining step. However, diffusion of species to or from the electrode surface may be rate-limiting.

- ♦ This is particularly important for corrosion caused by a dilute oxidising agent, such as dissolved oxygen.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (H_2O|O_2, H^+) \text{ cathode} \qquad (3.24)$$

$$E_0 = +1.22 \text{ V}_{\text{SHE}}, \quad i_0 = 10^{-5} \frac{\text{mA}}{\text{cm}^2}, \quad \beta_c = -0.1 \text{ V/decade} \qquad (3.25)$$

To model diffusion-limited corrosion, a linear diffusion boundary layer is assumed to exist.

- ♦ The molar flux of oxygen is $\frac{1}{A}\left(\frac{dN}{dt}\right) = k_g(c_b - c_i)$, where k_g is a mass transfer coefficient.

- ♦ Alternatively, by Fick's law, $\frac{1}{A}\left(\frac{dN}{dt}\right) = -D\frac{dc}{dx}$ \qquad (3.26)

- ♦ The current density is related to this rate of diffusion by Faraday's law

$$|i| = zFk_g(c_b - c_i) \quad \text{or} \quad |i| = zFD\,(c_b - c_i)/x \qquad (3.27)$$

- ♦ So the maximum current density of corrosion on this surface is

$$i_L = zFk_gc_b \qquad \text{or} \qquad i_L = zFD\,(c_b)/x \qquad (3.28)$$

- ♦ Crucially, the surface concentration of oxygen can be related to current density. Using the versions of (3.27) and (3.28) involving k_g

$$c_i = c_b - \frac{|i|}{zFk_g} = c_b - \frac{|i|c_b}{zFk_gc_b} = c_b\left(1 - \frac{|i|}{i_L}\right) \qquad (3.29)$$

- ♦ The depleted surface concentration of oxygen affects the equilibrium potential of the $(H_2O|O_2, H^+)$ cathode according to the Nernst equation.

$$\begin{aligned} E_0(H_2O|O_2, H^+) \quad &= E^0 + 2.3\frac{RT}{zF}\log_{10}\left(\frac{a_{\text{Oxidised}}}{a_{\text{Reduced}}}\right) \qquad (3.30) \\[2mm] &= E^0 + 2.3\frac{RT}{zF}\log_{10}(c_i) \\[2mm] &= E^0 + 2.3\frac{RT}{zF}\log_{10}(c_b) + 2.3\frac{RT}{zF}\log_{10}\left(1 - \frac{|i|}{i_L}\right) \\[2mm] &= \lim_{i\to0}(E_0) + 2.3\frac{RT}{zF}\log_{10}\left(1 - \frac{|i|}{i_L}\right) \end{aligned}$$

- ♦ So diffusion limitation can be modelled by a voltage loss

$$|\eta_{\text{diffusion}}| = 2.3\frac{RT}{zF}\log_{10}\left(1 - \frac{|i|}{i_L}\right) \qquad (3.31)$$

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Diffusion-limitation can be added to the existing corrosion model.

Example problem

Determine the corrosion current density of a copper object dissolving in aerated acid at pH 0 containing dissolved Cu^{2+} and O_2 both at unit activity (this is unrealistically high for oxygen). Assume the anode reaction is $Cu \rightarrow Cu^{2+}+2e^-$, and the only cathode reaction is $O_2+4H^++4e^- \rightarrow 2H_2O$, and that there is diffusion limitation of oxygen.

Note there is just one metal surface, so $|i_a| = |i_c| = i_{corr}$ at steady state

Data:

$E_0(Cu|Cu^{2+}) = +0.34\ V_{SHE}$	$E_0(H_2O|O_2, H^+) = +1.22\ V_{SHE}$
$i_0(Cu|Cu^{2+}) = 10^{-5}\ mA/cm^2$	$i_0(H_2O|O_2, H^+) = 10^{-5}\ mA/cm^2$
$\beta_a(Cu|Cu^{2+}) = +0.059\ V/decade$	$\beta_c(H_2O|O_2, H^+) = -0.059\ V/decade$
$i_L = 2\ mA/cm^2$ for oxygen	

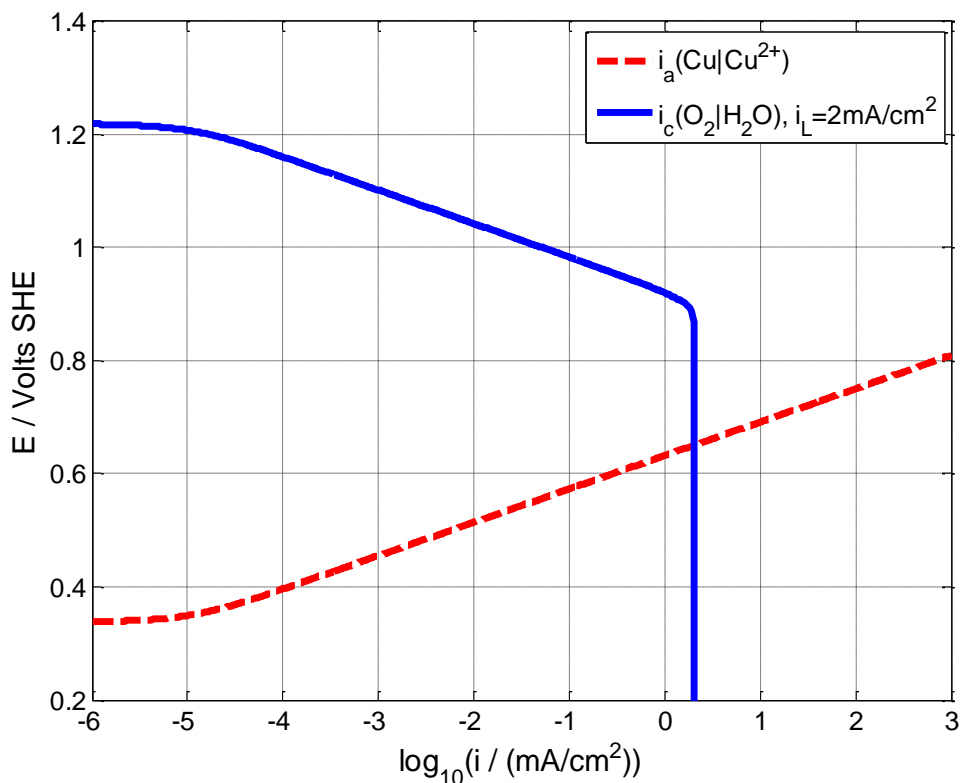The solution to this problem is the intersection of the current-potential curves of the anode and cathode

$$\eta_{anode} = E - E_0(Cu|Cu^{2+}) \tag{3.32}$$

$$\beta_a \log_{10}\left(\frac{i_a}{i_0}\right) = E - E_0(Cu|Cu^{2+}) \tag{3.32a}$$

$$\eta_{cathode} + \eta_{diffusion} = E - E_0(H_2O|O_2, H^+) \tag{3.33}$$

$$\beta_c \log_{10}\left(\frac{|i_c|}{i_0}\right) + 2.3\frac{RT}{zF}\log_{10}\left(1 - \frac{|i_c|}{i_L}\right) = E - E_0(H_2O|O_2, H^+) \tag{3.33a}$$

This can be plotted

♦ Concentration polarisation at the anode (caused by slow desorption of metal ions), is rarely important.

- ♦ The diffusion-limited current density i_L, depends on several factors.
  - ○ Diffusivity of oxygen in water (affected by temperature)
  - ○ Dissolved oxygen concentration in the bulk
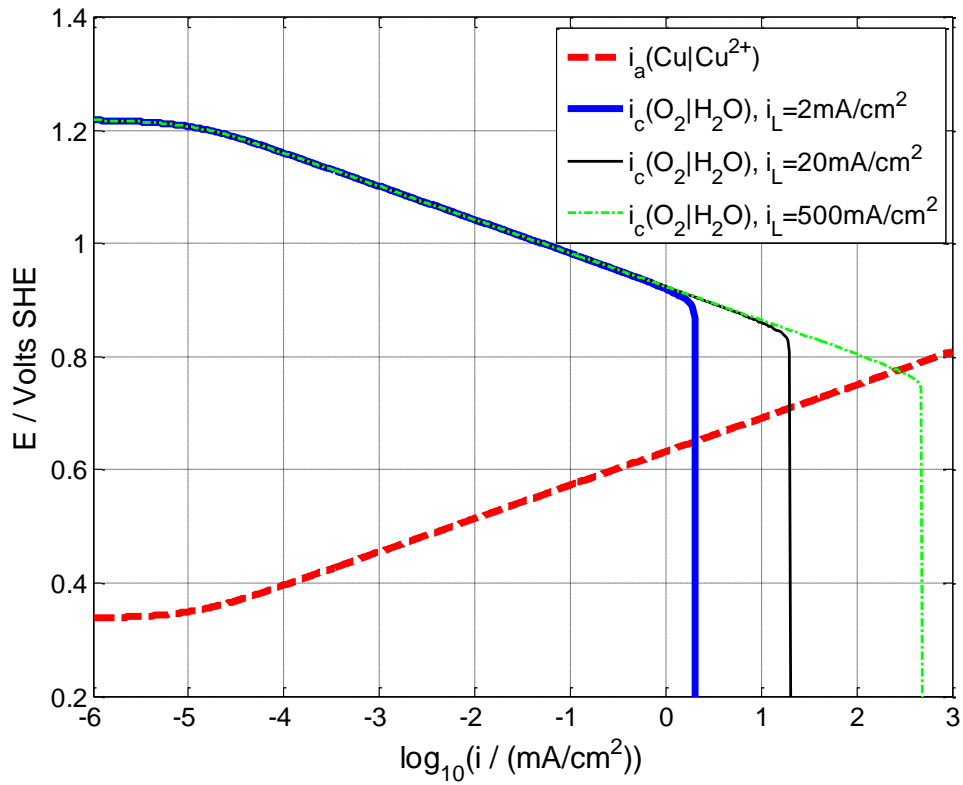 - ○ Reynolds number (affects boundary layer thickness)

Figure 3.6. Effect of increasing i_L on the diffusion-limited corrosion rate

3.8 Ion conductivity limited corrosion rate (non examinable)

The final limiting factor in aqueous corrosion is resistance to ion flow.

Consider a model of spontaneous corrosion of copper $(Cu|Cu^{2+}||O_2,H^+|H_2O)$ where

♦ The anode and cathode are activation limited

♦ Diffusion limitation is not significant $(i_L = 500 \text{ mA/cm}^2)$

♦ There is significant resistance to ion flow between the electrodes

$$\frac{-\Delta_r G}{zF} - E_{cell} = |\eta_{anode}| + |\eta_{cathode}| + |\eta_{oxygen\ diffusion}| + |\eta_{ion\ resistance}|$$

(3.34)

For illustrative purposes, it is possible to write, for an electrolyte of resistivity ρ and a characteristic length scale l.
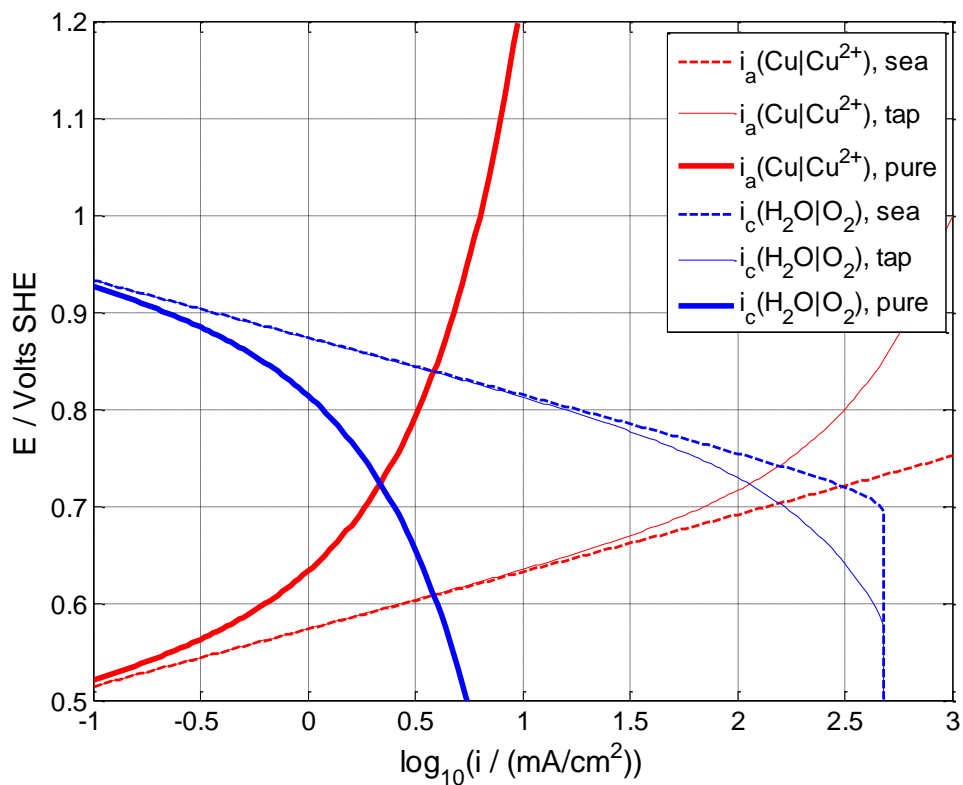
$$\eta_{ion\ resistance} = i\rho l \quad\quad (3.35)$$

It is also possible to construct a model so that

$$\eta_{anode} + 0.5\,\eta_{ion\ resistance} = E - E_0(Cu|Cu^{2+}) \quad\quad (3.36)$$

$$\eta_{cathode} + \eta_{diffusion} - 0.5\,\eta_{ion\ resistance} = E - E_0(H_2O|O_2,H^+) \quad (3.37)$$

Given some estimates of ρ (0.3 Ω m for seawater, 50 Ω m for tap water, and 5000 Ω m for pure water) and l (1 cm).

This model shows

♦ Seawater (~550 mM NaCl) can support higher corrosion rates than fresh water due to higher ion conductivity. Temperature is also important.

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3.9 The Area Effect in corrosion models

When two different electrodes are connected, one will be cathodic while the other will be anodic.

- This situation can occur on a single metal surface. In the iron-acid and copper-oxygen examples above, the anode and cathode were treated as having the same area, since they took place on the same metal object. In reality, the surface would have hosted a mixture of 'anodic sites' and 'cathodic sites' due to concentration gradients.

- Often, corrosion takes place where two or more metals are joined together. In this situation, there is usually one dominant anode reaction, and one dominant cathode reaction, but they take place over different total areas.

Example

A zinc anode $(Zn|Zn^{2+})$ of area 1 m^2 is attached to a sheet of iron of area 10 m^2. This metal is entirely submerged in acid at pH 0, containing dissolved Zn^{2+} at <u>unit activity</u>. Given that the only significant reactions are a zinc anode $(Zn|Zn^{2+})$ and hydrogen evolution on the iron surface $(H^+|H_2)$, calculate the anode current density. Assume there is no mass transport limitation.

Data:

$E_0(Zn|Zn^{2+}) = -0.76$ V$_{SHE}$ $\qquad E_0(H_2|H^+) = +0.00$ V$_{SHE}$

$i_0(Zn|Zn^{2+}) = 10^{-8}$ mA/cm^2 $\qquad i_0(H_2|H^+) = 10^{-3}$ mA/cm^2 on iron

$\beta_a(Zn|Zn^{2+}) = +0.059$ V/decade $\qquad \beta_c(H_2|H^+) = -0.059$ V/decade

Solution

♦ The entire surface is at a potential E

♦ <u>No charge accumulation</u>, and Tafel-limited kinetics on both electrodes

$$A_a|i_a| = I_{cell} = A_c|i_c|$$

$$A_a i_0(Zn|Zn^{2+}).10^{\left(E-E_0\left(Zn|Zn^{2+}\right)\right)/\beta_a} = A_c i_0(H^+|H_2).10^{\left(E-E_0(H^+|H_2)\right)/\beta_c}$$

$$\frac{E-E_0\left(Zn|Zn^{2+}\right)}{\beta_a} - \frac{E-E_0\left(H^+|H_2\right)}{\beta_c} = \log_{10}\left(\frac{A_c i_0\left(H^+|H_2\right)}{A_a i_0\left(Zn|Zn^{2+}\right)}\right)$$

Since $\beta_c = -\beta_a$ this simplifies to

$$2E = \beta_a \log_{10}\left(\frac{A_c i_0\left(H^+|H_2\right)}{A_a i_0\left(Zn|Zn^{2+}\right)}\right) + E_0(Zn|Zn^{2+}) + E_0(H^+|H_2)$$

$$E = -0.203 \text{ V}_{SHE}$$

$$i_a(Zn|Zn^{2+}) = i_0(Zn|Zn^{2+}).10^{\left(E-E_0\left(Zn|Zn^{2+}\right)\right)/\beta_a} = 27.5 \text{ mA cm}^{-2}$$

… check that $|i_c|$ is 10% of this…

3.10 Summary of kinetic models

♦ We can predict corrosion rates for a single pair of corrosion half-reactions, using the Tafel approximation and either (a) algebra, or (b) plotting a suitable graph, called an Evans diagram, showing log of current density and potential.

♦ The rate of corrosion depends on:

  o The electrode equilibrium potentials of the reactions involved

  o The exchange current densities (which depend on surface chemistry)

  o The Tafel parameters

  o Any externally applied electronic currents

♦ The **charge conservation** condition, $A_a|i_a| = A_c|i_c|$, implies corrosion will be particularly rapid if $A_c \gg A_a$. A general principle in corrosion prevention is to avoid the situation of a large cathode and small anode area.

♦ More sophisticated corrosion models can explain: (a) **mass transport** or **diffusional** limitations and (b) **electrolyte ion resistance** limitations.

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3.11 Kinetics of Passivation

Passivation is the formation of a protective, solid oxidised layer.

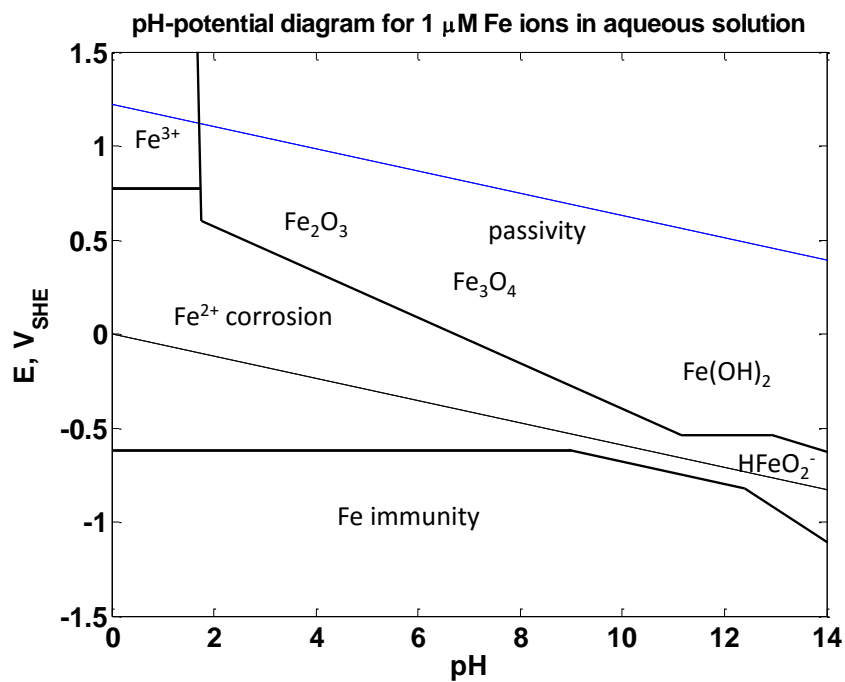**pH-potential diagram for 1 μM Fe ions in aqueous solution**

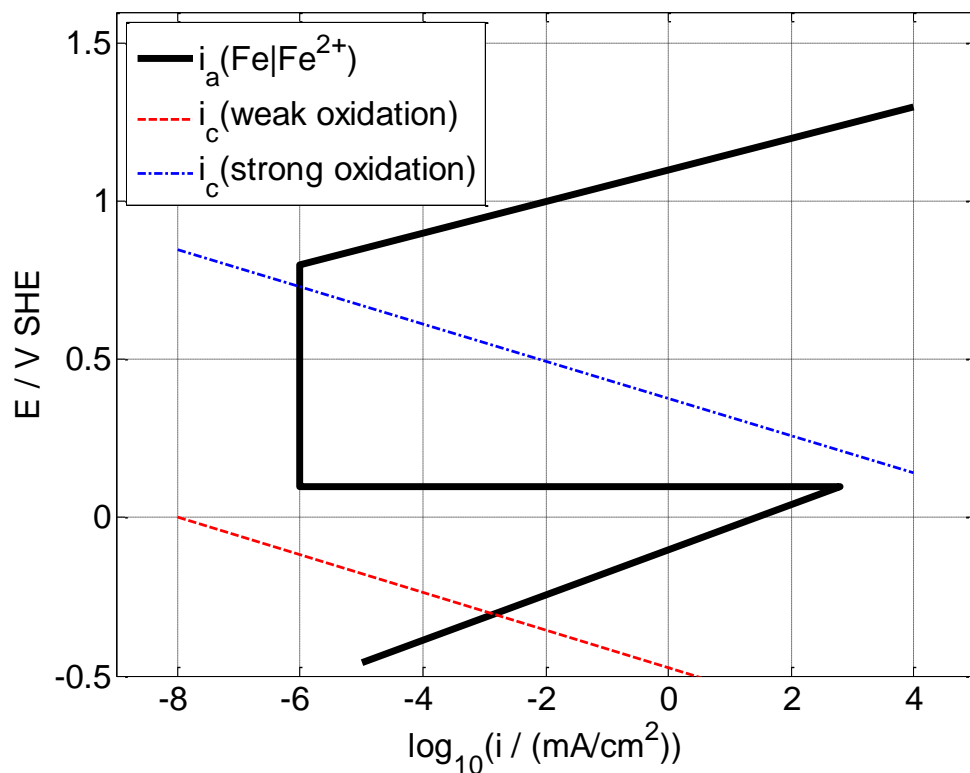Figure 3.8. A Pourbaix (pH-potential) diagram shows thermodynamic passivation.

Figure 3.9. An Evans diagram shows the kinetics of passivation.

- At low potentials "normal" corrosion occurs: active dissolution region

- At higher potentials, the corrosion products cause passivation, and so the rate of corrosion is reduced (or becomes negligible).

- At very high potentials, the corrosion products themselves undergo chemical reaction (the "transpassive" region).

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3.11.1 Factors affecting passivation

♦ Oxidation potential and pH of environment.

♦ Composition. Transition metals such as iron tend to have solid higher-oxides and so they can show active-passive behaviour. (I.e. they go from immune→ active → passive → transpassive with increasing oxidation potential and so can be 'anodically protected'). Other metals may just have immune→ active behaviour.

♦ Alloying. In passivated stainless steel, the surface is effectively chromium oxide. A (very simplified) description of chromium's effect is that it significantly expands the regions of passivity that are already present on the pH-potential diagram of iron, because the alloy will be passive if either the iron or the chromium are passive. In order for stainless steel to benefit from this property, the chromium content needs to be at least 11%, and is typically 18% to allow for local depletion.

♦ Aggressive chemicals. Chloride ions can cause breakdown of many passive oxides, shrinking the passive region on the pH-potential diagram, and increasing the passive current density.

♦ Abrasion and cracking. These processes may be the rate-limiting step for determining the passive current density.

Glossary of symbols for electrochemistry

Symbol	Description	Units	Section
i	Current density	A m^{-2}	3.11
i_0	Exchange current density	A m^{-2}	3.4
z	Electrons per reaction	-	2.6
A	Area	m^2	-
E	Potential	V$_{SHE}$	3.3
$E°$	Standard electrode potential	V$_{SHE}$	2.7
E_0	Equilibrium potential	V$_{SHE}$	2.10
F	Faraday constant	C mol^{-1}	-
I	Current	A	3.2
R	Universal gas constant	J mol^{-1} K^{-1}	-
T	Temperature	K	-
β	Tafel slope	V	3.5
η	Polarisation	V	3.3