Chapter 15  Fundamentals of Aqueous Corrosion

15.1 Introduction..................................................................................................................................1

15.2 Thermodynamics of corrosion.....................................................................................................2
  15.2.1 The overall reaction..................................................................................................................2
  15.2.2 Pourbaix diagrams...................................................................................................................3

15.3 Electrostatics - the electric potential and the electric field.......................................................5

15.4 Driving force for corrosion - the interface potential difference ..............................................6
  15.4.1 The electric double layer.........................................................................................................6
  15.4.2 The Electrode potential at equilibrium....................................................................................7
  15.4.3 Electrode potential during corrosion.......................................................................................7

15.5 Corrosion kinetics - the Butler-Volmer equation........................................................................9
  15.5.1 Microscopic effect of the interface potential..........................................................................9
  15.5.2 Rate equations.......................................................................................................................11

15.6 Tafel Diagrams..............................................................................................................................12
  15.6.1 The exchange current density...............................................................................................12
  15.6.2 for half-cell reactions.............................................................................................................13
  15.6.3 for overall cell reactions.........................................................................................................14
  15.6.4 for multiple cathodic reactions...............................................................................................17
  15.6.5 for multiple anodic reactions.................................................................................................18
  15.6.6 with concentration polarization.............................................................................................18
  15.6.7 for actual systems...................................................................................................................20

15.7 Scales on structural metals...........................................................................................................22
  15.7.1 Corrosion properties...............................................................................................................22
  15.7.2 Parabolic scale-growth law.....................................................................................................24
  15.7.3 Effect of the ionic character of the oxide ..............................................................................25
  15.7.4 An Illustrative System - an oxide scale on a divalent metal.................................................26
  15.7.5 Position-independent electric field.........................................................................................29
  15.7.6 Nonparabolic scaling kinetics - constant electric field.........................................................30
  15.7.7 The effect of space charge in the oxide scale.........................................................................30
  15.7.8 Solution of the equations for film growth with space charge..............................................31
  15.7.9 Scale growth rate...................................................................................................................35

15.8 Passivity .......................................................................................................................................36

15.9 Localized Corrosion......................................................................................................................38
  15.9.1 Pitting.........................................................................................................................................39
  15.9.2 Crevice corrosion.....................................................................................................................43

References............................................................................................................................................50
15.1 Introduction

Metallic iron was first produced about 2000 years ago and has been corroding ever since. One type of corrosion is reaction of a metal with water that converts the surface to an oxide or hydroxide by reactions such as:

\[ M + \frac{1}{2} z \ H_2O \rightarrow \text{MO}_{z/2} + \frac{1}{2} z \ H_2 \quad \text{or} \quad M + z \ H_2O \rightarrow \text{M(OH)}_z + \frac{1}{2} z \ H_2 \]  

(15.1)

For most metals, the oxide or hydroxide is thermodynamically more stable than the elemental metal. This is the case for iron, nickel, chromium, aluminum, zinc, uranium, and very importantly for this book, zirconium. It is not so for the noble metals, notably gold and platinum.

When a metal corrodes, the corrosion product behaves in one of several ways: i) the corrosion product may flake off the metal's surface, exposing fresh metal for continuation of the process; this is the case for pure iron and zirconium alloys; ii) the corrosion product may adhere to the metal but continue to grow, as with ????; iii) a very thin corrosion-product layer may adhere to the surface of the metal but act protectively and greatly slow the corrosion rate. This phenomenon is called passivity and fortunately for modern society, applies to aluminum and chromium and their alloys with other metals. Corrosion is said to be uniform if the product layer is roughly the same thickness over the entire metal surface. If only special spots on the metal are susceptible to oxidation, corrosion is termed localized. The latter form of corrosion may respond to a tensile stress parallel to the metal surface.

Alternatively, the metal may corrode by effectively dissolving in the aqueous solution by a reaction such as:

\[ M + z \ H^+ \rightarrow M^{z+} + \frac{1}{2} z \ H_2 \]  

(15.2)

This mode of corrosion, called active corrosion, is particularly common in highly-acidic solutions. It is not a practical concern since the process is fast and such a combination would render useless the component in such an environment. However, the basic theory of corrosion is developed in Sects 15.2 - 15.6 based on this type.

In reactions (15.1) and (15.2), \( z \) designates the valence or oxidation state of the metal. Some metals, aluminum being one, have only a single oxidation state. Others such as iron have multiple oxidation states, all or some of which may be present as solid oxides or hydroxides coating the metal or as ions dissolved in the aqueous phase.

This chapter explores the thermodynamics, kinetics and mechanical aspects of corrosion. The thermodynamic aspects of corrosion are twofold: First, it determines whether a particular metal is susceptible to corrosive attack by a particular aqueous solution. Second, if a metal is susceptible to corrosion, approximate thermodynamically-based constructions called Pourbaix diagrams show the range of conditions under which corrosion does or does not occur and which of reactions (15.1) and (15.2) is the route. These diagrams recognize the dependence of the corrosion process on the pH and the electric potential of the aqueous phase (see Sect 2.9.1).

The above corrosion processes are called overall reactions. They do not explicitly show the transfer of electrons from one element to another. To do so requires splitting them up into
**Half-cell reactions**, which clearly show the electron transfer process. As discussed in Sect. 2.9, for reaction (15.2), these are:

\[
M = M^{z+} + ze^- \quad 2H^+ + 2e^- = H_2
\]  

(15.3)

where \(e^-\) denotes an electron. These electrons are not found floating around in the solution like the ions; they are transferred directly from one species to another. In reaction (15.3), each metal atom \(M\) donates \(z\) electrons to \(z\) hydrogen ions to effect the conversion to aqueous ions of \(M^{z+}\) and hydrogen gas.

The \(\rightarrow\) signs in reactions (15.1) and (15.2) indicate that the reaction is proceeding from left to right. The equal signs in reaction (15.3) signify that both the forward and reverse processes occur, and moreover, that they are of equal speed. That is, the reaction is in equilibrium. This is not always true as half-cell reactions can proceed at finite rates. This kinetic aspect of corrosion is expressed by *Tafel diagrams*. Analysis of the kinetic mechanisms can explain the origin of these diagrams.

Localized corrosion is attack of the metal in penetrations called *pits* or *crevices*. The former look like holes dug in the ground, and can often be seen on stainless steel tableware. Crevices, on the other hand, resemble clean cracks. Crevice corrosion most frequently occurs in metals under stress, which is the origin of the name stress-corrosion cracking (SCC). This phenomenon is sensitive to the pH, the electric potential and the presence of other ions in the aqueous solution. In certain alloys, chloride ions in solution significantly affect SCC. Cracks can penetrate a specimen either through the grains of the metal or follow grain boundaries. The latter is most common and is called *intergranular stress-corrosion cracking*, which is shortened to IGSCC. A special variant of IGSCC occurs in the coolant of nuclear reactors, in which neutron or gamma irradiation creates a variety of radiolysis products that significantly accelerate the corrosion process. The term for this effect is *irradiation-assisted stress-corrosion cracking*, or IASCC.

The thermodynamics and kinetics of corrosion reactions depend on temperature. Because the liquid phase is water, 25\(^\circ\)C is the most common temperature considered. The notable exception is the water coolant of a nuclear reactor, which is within ±20\(^\circ\)C of 300\(^\circ\)C.

### 15.2 Thermodynamics of corrosion

#### 15.2.1 The overall reaction

Whether corrosion of a metal is thermodynamically possible depends on the free-energy change of the overall reaction. For the first of reaction (15.1), for example, this is:

\[
\Delta g = g^o_{\text{Mo}_2} + z(g^o_{\text{H}_2} + RT\ln p_{\text{H}_2}) - g^o_M - zg^o_{\text{H}_2O}
\]  

(15.4a)

where the superscript \(^o\) indicates that the substance is in its *standard state*, which is pure, at the temperature of the reaction, and at 1 atm pressure. The two solids and water are pure (or in the latter case, nearly pure) and so are in their standard states. Hydrogen gas may be present at a pressure different from 1 atm, which accounts for the second term in parentheses in Eq (15.4a).

Equation (15.4a) can be written as:

\[
\Delta g = \Delta g^o + RT\ln p^z_{\text{H}_2}
\]  

(15.4b)

where \(\Delta g^o\) is the *standard-state free-energy change* of the reaction. It depends on temperature
only. Reactions take place if $\Delta g$ is negative, which almost always means that $\Delta g^\circ$ is negative. For example, if $M = \text{Fe}$ and $z = 2$, in the first of reactions (15.1), $\Delta g^\circ = -7.7 \text{ kJ/mole}$ at 25°C. Forming the equilibrium constant of the reaction as:

$$K = P_{H_2} = \exp(-\Delta g^\circ/RT) = \exp[-(-7700)/8.314 \times 298] = 460 \text{ atm}$$

means that the hydrogen pressure must be greater than 460 atm in order to prevent all Fe from becoming oxidized to FeO in water. On the other hand, if $M = \text{Pb}$, $\Delta g^\circ = 20 \text{ kJ/mole}$ and lead contacting water could not be converted to PbO unless the H$_2$ pressure were less than 3x$10^{-8}$ atm. The standard-state free energy simply indicates whether the left-hand side or the right-hand side of the written reaction, of which (15.1) and (15.2) are examples, is favored.

### 15.2.2 Pourbaix diagrams

More detailed information about the thermodynamics of a particular metal in water is contained in Pourbaix diagrams, named after the Russian chemist who, while studying in Belgium, produced a PhD thesis on the graphical representation of the role of the pH and electric potential of an aqueous solution on the stable states of the contained metal. Pourbaix diagrams are also known as $pH$-potential diagrams. They are analogous to binary phase diagrams (Sect. 2.7), which are also called temperature-composition diagrams.

Pourbaix diagrams are constructed from Nernst equations of Eq (2.77a). For the M/M$^{2+}$ half cell at 25°C, this is:

$$\phi = \phi^o - \frac{0.059}{z} \log[M^{z+}]$$  \hspace{1cm} (15.5)

where $\phi^o$ is the standard electrode potential (Table 2.2), $z$ is the number of electrons transferred in the half-cell reaction and $[M^{z+}]$ is the molar concentration of the metal ion. Solid M does not appear since activity is unity because it is assumed to be pure.

The rules for using other Nernst equations to construct Pourbaix diagrams are:

i) the pressures of the gases H$_2$ and O$_2$ (if they appear in the equation) are set equal to 1 atm

ii) the concentrations of all ions (excepting H$^+$) are fixed at 10$^{-6}$ M.

The latter condition is intended to separate regions in which the individual species predominate. As in the Nernst equations, the anion that accompany the various cations (e.g., Cl$^-$, SO$_4^{2-}$) are ignored, although the diagram is slightly dependent on these species.

The two states of the metal in Pourbaix diagrams are dissolved (as ions) or solid, including metal: metal oxide(s), hydroxides and oxy-hydroxides. For iron, the important species are the ions Fe$^{2+}$, Fe$^{3+}$, Fe(OH)$_2^+$, Fe(OH)$_4^-$ and FeO$_2^{2-}$ and the solids Fe, Fe$_3$O$_4$ and Fe$_2$O$_3$.

To account for the different sign convention used in Table 2.2 and Eq (2.77a) from the convention used in corrosion analyses, the Nernst potential in Sect. 2.9.3 ($\phi$) is the negative of equilibrium electrode potential, $\varepsilon^{eq}$ in the present notation:

$$\varepsilon^{eq} = -\phi \text{ (Sect. 2.9)}$$  \hspace{1cm} (15.5a)

An example of constructing the Pourbaix for iron is shown in Table 15.1.
The two horizontal lines (nos. 1 and 2) and the vertical line (no. 4) and the sloped line (no.3) are shown on the Fe/H₂O Pourbaix diagram of Fig. 15.1 along with the remainder of the iron-water lines.

**Table 15.1 Construction of the iron Pourbaix diagram at 25°C**

<table>
<thead>
<tr>
<th>Line No.</th>
<th>couple</th>
<th>Half-cell reaction</th>
<th>Standard potential, V</th>
<th>Log (ion concentration ratio)</th>
<th>Pourbaix line</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe/Fe²⁺</td>
<td>Fe = Fe²⁺ + 2e⁻</td>
<td>0.44</td>
<td>log[Fe²⁺] = log[10⁻⁶]</td>
<td>εeq = - 0.62</td>
</tr>
<tr>
<td>2</td>
<td>Fe²⁺/Fe³⁺</td>
<td>Fe²⁺⁰ = Fe³⁺⁰ + e⁻</td>
<td>-0.77</td>
<td>log[Fe³⁺⁰]/[Fe²⁺⁰] = 0</td>
<td>εeq = +0.77</td>
</tr>
<tr>
<td>3</td>
<td>Fe²⁺/Fe₂O₃</td>
<td>2Fe²⁺ + 3H₂O = Fe₂O₃ + 6H⁺ + 2e⁻</td>
<td>-0.68*</td>
<td>log[H⁺⁰⁰]/[Fe²⁺⁰]² = -6pH - 2log[10⁻⁶]</td>
<td>εeq = 1.03 - 0.18pH</td>
</tr>
<tr>
<td>4</td>
<td>Fe³⁺/Fe₂O₃</td>
<td>2Fe³⁺ + 3H₂O = Fe₂O₃ + 6H⁺</td>
<td>#</td>
<td>#</td>
<td>pH=1.52⁷</td>
</tr>
<tr>
<td>a</td>
<td>H₂/H₂O</td>
<td>2OH⁻ + H₂ = 2H₂O + 2e⁻</td>
<td>0.83</td>
<td>log(pH/H₂)[OH⁻]² = 2log10⁻¹⁴ + 2pH</td>
<td>εeq = - 0.059pH</td>
</tr>
<tr>
<td>b</td>
<td>O₂/H₂O</td>
<td>H₂O = 1/2O₂ + 2H⁺ + 2e⁻</td>
<td>-1.23</td>
<td>log(pH/O₂)[H⁺]² = 2pH</td>
<td>εeq = 1.23 - 0.059pH</td>
</tr>
</tbody>
</table>

(⁷) From Table 2.2
* see example in Sect. 2.9.2

# line No. 4 does not involve electrons, so must be treated like reaction (b) in the example in Sect. 2.9.2:
In Table 2.2, half-cell reactions (15) - 2×(9) give reaction No. 4 in the above table. Using Eq (2.75):

\[
\Delta \mu_4^o = \Delta \mu_{17}^o - 2\Delta \mu_9^o = (-2)(96.5)\phi_{15}^o - (-2)(96.5)\phi_9^o = (-2)(96.5)(-0.68) - (-2)(96.5)(-0.77) = -16.6 \text{ kJ/mole}
\]

\[
\Delta \mu_4^o = -RT \ln([H⁺][Fe³⁺]) = -8.314 \times 0.298 \ln([H⁺][Fe³⁺]) = -5.75 \log([H⁺][Fe³⁺])
\]

\[
= -5.75 \left(6 \log[H⁺] - 2 \log[Fe³⁺]\right) = -5.75(-6 \text{pH} - 2 \log(10^{-6})) = -5.75(-6 \text{pH} + 12)
\]

Equating the right-hand sides of the above equations:

\[
-5.75(-6 \text{pH} + 12) = -16.6. \text{ Solving: } \text{pH} = 1.52.
\]

The lines a and b in Fig. 15.1 encompass the zone of stability of water. For potentials less than line a, water decomposes into H₂ and OH⁻ by the reverse of half-cell reaction 3a in Table 2.2. The standard electrode potential of this half-cell reaction is \(\phi_{3a}^o = 0.83\) V (see problem 2.1). Its Nernst equation (with 10⁻⁶ M concentrations for ions and 1 atm pressure for gases) is obtained from:

\[
\phi_{3a} = \phi_{3a}^o - \frac{0.059}{2} \log \frac{1}{[OH⁻]^2} = 0.83 + 0.059 \log \frac{10^{-14}}{[H⁺]} = 0.059\text{pH}
\]

Because of this restriction, metallic iron is not stable in water under any accessible conditions. For potentials greater than line b in Fig. 15.1, water decomposes into O₂ and H⁺ by half-cell reaction 2 in Table 2.2, for which the standard electrode potential is \(\phi_i^o = -1.23\) V. This leads to

\[\]

1 The minus signs on the potentials in the last column account for the different sign conventions used for the standard electrode potentials (Table 2.2) and the associated Nernst equation (Eq (2.77a)) and that adopted for the Pourbaix diagrams.
the Nernst equation shown in the last row of the last column in the above table (with the sign change to conform to the convention).

![Pourbaix diagram for iron/water at 25°C](image)

**Fig. 15.1** Pourbaix diagram for iron/water at 25°C

### 15.3 Electrostatics - the electric potential and the electric field

The *electric potential* plays a central role in corrosion. It is analogous to the chemical potential, the thermal potential and the mechanical potential; all of these have in common that a gradient of the potential causes motion of some quantity: the chemical potential drives material species; the thermal potential drives heat; the mechanical potential drives objects. The electric potential drives charged species, either electrons in a wire or ions in an aqueous solution.

Consider two point charges, $q$ and $q'$ separated by a distance $r$ in a some medium.

![Charge arrangement](image)

Charge $q$ is fixed in space but charge $q'$ is moveable. The force acting on $q'$ in the positive $r$ direction (to the right in the diagram) due to the presence of $q$ is:

$$F = \frac{q \times q'}{4\pi K_r \varepsilon_0 r^2}$$  \hspace{1cm} (15.6)

$\varepsilon_0$ is the vacuum permittivity, $8.85 \times 10^{-14}$ C/Volt-cm and $K_r$ is the *dialectic constant* of the medium. For a nonpolar medium such as liquid helium, $K_r = 1$, meaning that the force in this
medium is the same as if the two charges were in vacuum. In general, $K_r$ is a measure of how much the force is reduced by the presence of the medium. The magnitude of $K_r$ is $\geq 1$, by how much depends on the dipole moment of the molecules in the medium. For polar molecules such as water, positive and negative charges each of magnitude $\sigma$ are separated by a distance $d$, the dipole moment is $\sigma d$. Most molecules have dipole moments somewhat greater than unity. Very polar molecules such as HF and H$_2$O have large dipole moments, and as a result, their dielectric constants are $\sim 30$ and 80, respectively. By aligning their dipoles in the $r$-direction they effectively reduce the force $F$ acting between the two charges.

If the charges $q$ and $q'$ are of the same sign, the force on $q'$ is in the $+r$ direction, as shown in the above diagram. The work done in bringing $q'$ from infinity to $r$ is:

$$W = -\int_{\infty}^{r} F(r')dr' = -\frac{q \times q'}{4\pi K_r \varepsilon_o} \frac{1}{r}$$

(15.7)

The negative sign in front of the integral is because the charge $q'$ is moved in the $-r$ direction.

If $q' = +1$, the force is called the electric field:

$$E = \frac{q}{4\pi K_r \varepsilon_o} \frac{1}{r^2} = -\frac{d\phi}{dr}$$

(15.6a)

and the work is the electrostatic (or electric) potential:

$$\phi = \frac{q}{2\pi K_r \varepsilon_o} \frac{1}{r}$$

(15.8)

The units of $\phi$ are volts and those of $E$ are volts/m. $q$ in Eqs (15.6a) and (15.8) need not be a point charge; in general it is a distribution of charges such as those that gather at the surface of a metal immersed in a solution containing positive and negative ions.

The variation of electrostatic potential ($\phi$) across an interface for the case of excess negative charge on the aqueous solution side of the interface and excess positive charge in the metal is shown on the left in Fig 15.2. The right-hand sketch shows the variation of electric field across the interface.

**Example:** What is the potential difference between two hollow, initially-neutral metal spheres each 2 cm diameter after 125 $\mu$C of electrons have been moved from one sphere to the other? The center-to-center separation of the two spheres is 10 cm. The capacitance of the two-sphere system is $\sim 6 \times 10^{-13}$ Coulombs/Volt. The capacitance (cap) is defined as $\text{cap} = q/\Delta \phi$, where the charges are $+q$ on one sphere and $-q$ on the other. For this situation, $q = 125 \mu$C, so $\Delta \phi = q/\text{cap} = 125 \times 10^{-6}/6 \times 10^{-13} = 2 \times 10^8$ Volts.

**15.4 Driving force for corrosion - the interface potential difference**

**15.4.1 The electric double layer**

When a metal is inserted into an aqueous solution containing anions and cations, a redistribution of charges at the metal-solution interface takes place. Figure 15.3 shows a representation of this effect. In this example, the metal is assumed to be negatively-charged with respect to the solution. The inner layer in the solution shows water molecules lined up at the metal surface. The outer solution layer shows solvated cations, anions and randomly-oriented water molecules. No attempt has been made to show hydrogen bonding of the water molecules. Because the metal at
the interface is negative, the solution at the interface has an excess of positive ions. The bulk metal and the bulk solution are electrically neutral. The situation shown in Fig. 15.3 could have been reversed, with the metal positive and the solution negative (excess of anions in the layer). One can imagine separating the metal and the solution without disturbing the charge distributions, then measuring the electric potential of each surface by recording the work required to move a positive single charge from far away towards each of the surfaces. This experiment is not possible, so the difference in the potentials across the interface,

\[ \Delta \phi = \phi_M - \phi_S \]  

(15.9)
cannot be measured.

15.4.2 The electrode potential at equilibrium
The electrochemical cell shown in Fig. 15.4 provides information on the equilibrium electrode potential, \( \varepsilon^{eq} \). For fixed concentrations of M\(^{z+} \) in the solution (and no current flow), the measured cell potential contains other contributions:

\[ \varepsilon^{eq} = \Delta \phi + \text{other} \]  

(15.10)
where "other" includes potential changes in the measurement apparatus. The cell in Fig. 15.4 is similar to that in Fig. 2.9. The M/M\(^{z+} \) half-cell reaction does not depend on the pH and the H\(_2\)/H\(^+\) half-cell reaction does not involve M\(^{z+} \), so the cells in Figs. 2.9 and 15.4 measure the same thing.

15.4.3 Electrode potential during corrosion
In analyzing corrosion kinetics, the quantity appearing in the rate equations (Sect. 15.5.2) is the difference \( \varepsilon - \varepsilon^{eq} \), where \( \varepsilon \) is the electrode potential for metal M and a solution wherein the rates of the reverse and forward reactions of \( M \leftrightarrow M^{z+} + ze^- \) are not equal (i.e., a corrosion current flows). For the purpose of measuring \( \varepsilon \), a somewhat more complex setup, such as the one shown in Fig 15.5, is needed. Here the voltmeter measures the electrode potential \( \varepsilon \) while corrosion is occurring in the test electrode M. The right-hand side of the system establishes a

**Fig. 15.2 Electric properties of a metal/solution interface**
current $i$ that is measured by an ammeter. This represents the corrosion rate, which is a function of the current and the concentration of $M^{z+}$.

![Electric double layer at a metal-solution interface](image1)

**Fig. 15.3** Electric double layer at a metal-solution interface

![Electrochemical cell to measure $\varepsilon^\text{eq}$ of the M/M$^{z+}$ half cell](image2)

**Fig. 15.4** Electrochemical cell to measure $\varepsilon^\text{eq}$ of the M/M$^{z+}$ half cell
If the metal half-cell reactions are pH-sensitive, a bridge (shown) is needed to allow separate solution compositions around the Pt electrode to the left and the M/Pt cell to the right.

Fig. 15.5 Electrochemical cell for measuring the electrode potential of a nonequilibrium (corroding) half cell

15.5 Corrosion kinetics - the Butler-Volmer equation

The active corrosion process consists of two half-cell reactions: anodic (oxidation), \( M \rightarrow M^{z+} + ze^- \) and cathodic (reduction), \( M^{z+} + ze^- \rightarrow M \). The difference between the rates of these two half-cell reactions is the overall oxidation rate:

\[
j_{ox} = j_a - j_c
\]  

(15.11)

\( j \) is the flux of the species moving to and from the metal surface and the bulk solution. The units of \( j \) are moles of ions per unit time per unit area. The right-pointing arrow above the \( j \) indicates the metal-to-solution direction and the subscript \( a \) means anodic. Similarly, the left-pointing arrow signifies transfer of the ion from the solution to the metal, which is a cathodic reaction indicated by the subscript \( c \).

15.5.1 Microscopic effect of the interface potential

For a atoms in a metal to be converted to the ion in solution in the absence of an interface potential, not only must the standard free-energy change of the half-cell reaction be negative (the thermodynamic requirement) but the activation energy of the reaction (the kinetic requirement) must be accounted for. The solid curve in Fig. 15.6 shows the changes in free energy of a metal atom as it is removed from the solid, converted to an ion and transferred to the bulk solution. In the diagram, \( \Delta g^0 \) is the negative of the standard-state free energy change for \( M \rightarrow M^{z+} + ze^- \) and \( \Delta g^* \) is the activation energy. \( \Delta \phi \) is the potential change across the double layer at the metal/solution interface (Sect. 15.4.1).
Fig. 15.6 free energy barrier for $M \rightarrow M^{z+} + 2e^-$ in the absence of electrical effects (solid curve) and with the metal positively charged (dashed curve).

(The extent of the curves is about 10 nm.)
15.5.2 Rate equations

The rate (flux) of the $M \rightarrow M^{z+} + ze^{-}$ half-cell reaction is:

$$\tilde{j}_a = \tilde{k}_a^o \exp(-\Delta g^*/RT)$$

$\tilde{k}_a^o$ is the pre-exponential factor of the rate constant for this step. The activation energy is due to the energy barrier presented by the solid curve in Fig. 15.6.

The dashed curve in Fig. 15.6 shows the reaction barrier with the interface potential difference of Sect. 15.4 taken into account. This curve starts out at the metal surface with a potential (now electrochemical) at a free energy $zF\Delta\phi$ higher than the electrically-neutral value of $\Delta g^o$ (see Eq (2.71))$^2$. This added potential decreases with distance into the solution so that after a few nanometers, none of it remains. The dashed and solid curves at the maximum differ from the value at the interface by a fraction $1-\alpha$, where $\alpha < 1$. The activation energy for the forward step with the interface potential is obtained from the plot as:

$$zF\Delta\phi + \varepsilon^* = \Delta g^* + zF[(1-\alpha)\Delta\phi]$$

At this point, $\Delta\phi$ in the above equation is replaced by $\varepsilon^{eq}$. Although according to Eq (15.9a), these two measures of the potential differ by an unknown constant, the term this introduces into the rate equation is simply absorbed into the unknown rate constant $\tilde{k}_a^o$. With this change, the anodic rate becomes:

$$\tilde{j}_a = \tilde{k}_a^o \exp(-\varepsilon^*/RT) = \tilde{k}_a^o \exp(-\Delta g^*/RT) \exp\{\alpha zF\varepsilon^{eq}/RT\}$$  \hspace{1cm} (15.12a)

The rate of the cathodic step, $M^{z+} + 2e^- \rightarrow M$, in the absence of an electric potential is given by:

$$\tilde{j}_c = \tilde{k}_c^o [M^{z+}] \exp[-(\Delta g^o + \Delta g^*)/RT]$$

Including the interface potential, Fig. 15.6 gives the new activation energy as $\Delta g^o + \Delta g^* + (1-\alpha)zF\Delta\phi$. Again replacing $\Delta\phi$ with $\varepsilon^{eq}$ gives the interface-potential-modified cathodic rate:

$$\tilde{j}_c = \tilde{k}_c^o [M^{z+}] \exp[-(\Delta g^o + \Delta g^*)/RT] \exp\{-\alpha zF\varepsilon^{eq}\}$$  \hspace{1cm} (15.12b)

In this electrochemical equilibrium situation, the anodic and cathodic rates are equal to each other and are called the equilibrium rate because there is no net flux: $j_{eq} = j_a = j_c$, or:

$$j_{eq} = \tilde{k}_a^o \exp(-\Delta g^*/RT) \exp\{\alpha zF\varepsilon^{eq}/RT\} = \tilde{k}_c^o [M^{z+}] \exp[-(\Delta g^o + \Delta g^*)/RT] \exp\{-\alpha zF\varepsilon^{eq}/RT\}$$

With an applied potential $\varepsilon \neq \varepsilon^{eq}$, the net oxidation rate is $j_{ox} = \tilde{j}_a - \tilde{j}_c$, and $\varepsilon^{eq}$ in Eqs (15.12a) and (15.12b) is replaced by $\varepsilon$. Dividing Eq (15.12a) by the first equality in Eq (15.13) and Eq (15.12b) by the second equality yields the *Butler-Volmer equation*:

$$\frac{j_{ox}}{j_{eq}} = \exp\left[\frac{\alpha zF\eta}{RT}\right] - \exp\left[-\frac{(1-\alpha)zF\eta}{RT}\right]$$  \hspace{1cm} (15.14)

where $\eta$ is the *overpotential*.

---

$^2$ F is Faraday’s constant: 96,500 J/mole-Volt
When $\eta=0$, there is no net consumption of metal, or $j_{\text{ox}} = 0$. Given the corrosion conditions (the overpotential $\eta$ and the cation concentration $[M^{z+}]$ to fix $\varepsilon^{eq}$), the net or oxidation rate $j_{\text{ox}}$ can be calculated from Eq (15.14) if $j_{\text{eq}}$ is known.

### 15.6 Tafel Diagrams

From here on reaction rates are expressed in terms of current density instead of the flux:

$$i = zFj$$  
(15.16)

Both the rate $j$ and the current $i$ are per unit area. In this application, Faraday’s constant is 96,500 Coulombs/mole.

#### 15.6.1 The exchange current density

$j_{\text{eq}}$ corresponds to the exchange current density $i_{\text{o}} = zFj_{\text{eq}}$. Observing the sign convention in using the Nernst equation, the equilibrium electrode potential from Eq (2.77a) for the M/M$^{z+}$ half-cell is:

$$\varepsilon^{eq} = -\phi^o + \frac{RT}{zF} \ln[M^{z+}]$$  
(15.18)

The first equality of Eq (15.13) becomes:

$$i_{\text{oM}} = zFk^{oM} \exp(-\Delta g^o / RT) \exp\{\alpha zF(-\phi^o) / RT\}[M^{z+}]^\alpha$$  
(15.18a)

and the second equality gives:

$$i_{\text{oM}} = zFk^{cM} \exp\{-(1-\alpha)zF(-\phi^o) / RT\}[M^{z+}]^\alpha$$  
(15.18b)

Both of the above equations are of the form

$$i_{\text{oM}} = Q_M[M^{z+}]^\alpha$$

where $Q_M$ is the collection of constants, which, for these two expressions for $i_{\text{oM}}$, must be equal. (this simply provides a relation between $k^{oM}_a$ and $k^{cM}_c$, which is not of interest). What is important is the dependence of $i_{\text{oM}}$ on the concentration of metal ions in solution raised to a power $\alpha \sim 0.5$.

For the hydrogen half-cell reaction, $H_2 = 2H^+ + 2e$

the exchange current density is:

$$i_{\text{oH}} = Q_H[H^+]^\alpha [p_{H_2}]^{(1-\alpha)}$$  
(15.19)

In neutral water with the $H_2$ pressure $\sim 1$ atm, the exchange current densities are:

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$i_{\text{o}}$ A/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>Fe</td>
<td>$10^{-6}$</td>
</tr>
<tr>
<td>Hg</td>
<td>$10^{-12}$</td>
</tr>
</tbody>
</table>

The exchange-current-density concept is applicable to any combination of half-cell reaction and electrode. In general,

$$i_{\text{o}} = Q[\text{oxid}]^\alpha[\text{red}]^{(1-\alpha)}$$  
(15.19a)

where oxid and red are the ions in solutions or the gases taking part in the half-cell reaction:

$$\text{red} = \text{oxid} + ze^-$$
15.6.2 Tafel diagram for half-cell reactions
A Tafel diagram is a plot of the Butler-Volmer equation. For the half-cell reaction
\[ M \leftrightarrow M^{2+} + 2e^- \]
with the following numerical values:
\[ \alpha = 0.5; \ z = 2; \ F/RT = 96.5/8.314 \times 0.298 = 39 \]
and replacing the fluxes (j) with the current densities (i), Eq (15.14) becomes:
\[ \frac{i}{i_0} = e^{39\eta} - e^{-39\eta} \] (15.14a)

Figure 15.7 is a plot of Eq (15.14a) with the alteration of changing the ratio \( i/i_0 \) to its absolute value. This is needed because at negative overpotentials, the current changes from anodic to cathodic, so the second term in Eq (15.14a) dominates the first. Because negative values cannot be plotted on a logarithmic scale, the absolute value of the cathodic current is reported.

At large absolute values of the overpotential, either the first or the second term in Eq (15.14a) predominates. The slopes of the two branches are equal in Fig. 15.7 because \( \alpha = 0.5 \). This is not generally the case, and for \( \alpha \neq 0.5 \), the slopes of the two branches differ.

The curvature of the two branches at small overpotentials is due to the two terms in Eq (15.14a) having the same order of magnitude. As \( \eta \to 0 \), the current density \( i \) approaches zero. However, for large overpotentials, only one of the two terms is important. The intercept of the extrapolation of dominant term at \( \eta = 0 \) is \( i/i_0 = 1 \) (dotted lines in Fig. 15.7).

![Tafel diagram for active corrosion](image)

**Fig. 15.7 Generic Tafel diagram for active corrosion**

The Tafel diagram can be determined experimentally with the electrochemical cell shown in Fig. 15.5. Provided by this apparatus is the current density \( i \) flowing from the metal electrode \( M \) to the right-hand Pt electrode where the cathodic half-cell reaction \( 2H^+ + 2e^- \to H_2 \) takes place. The current density can be changed with the variable resistor in the diagram. For each current density setting, the standard hydrogen electrode (SHE) on the left in the diagram measures the electrode potential. When the current is zero, the SHE measures the equilibrium potential.
overpotential ($\eta$) is then determined by Eq (15.15). The data from this experiment is sufficient to extract the parameters $\alpha$ and $i_0$.

**Example**  The plot below shows the data from the apparatus of Fig. 15.5 for the half-cell $\text{Fe} = \text{Fe}^{2+} + 2\text{e}^-$ in acid of pH 2 at 25°C. What are the best-fitting values of $\alpha$ and $i_0$?

For this half-cell, $z = 2$ and the hydrogen ion concentration does not enter. The extrapolations of the single-exponential portions of the plots (dashed portions) intersect zero overpotential at a current density of 1 $\mu$A/cm$^2$, so this is $i_0$.

The slope of the linear portion of the anodic curve is $\log(i/i_0)/\eta = 1.86/0.1 = 18.6$. From Eq (15.4) with $j_{ox}/j_{eq}$ replaced by $i/i_0$, the slope is:

$$\text{slope} = \frac{\alpha}{2.3} \frac{F}{RT}, \quad \text{or} \quad \alpha = \frac{2.3 \times \text{slope}}{z \times (F/RT)} = \frac{2.3 \times 18.6}{2 \times 38.9} = 0.55$$

The slope of the cathodic branch is $-\log(i/i_0)/\eta = 1.90/(-0.126) = -15.1$. But:

$$\text{slope} = -\frac{1 - \alpha}{2.3} \frac{z F}{RT} \quad \text{or} \quad \alpha = 1 - \frac{2.3 \times \text{slope}}{z \times (F/RT)} = 1 - \frac{2.3 \times 15.1}{2 \times 38.9} = 0.55$$

Agreement between the values of $\alpha$ from the anodic and cathodic polarization curves is excellent.

---

**15.6.3 Tafel diagram for overall cell reactions**

The previous section dealt with individual half-cell reactions, which were caused to proceed in either the anodic or cathodic direction by application of the appropriate overpotential (positive or negative) to the electrochemical apparatus shown in Fig. 15.5. However, in actual corrosion situations, a metal (e.g., a pipe or tubing through which water flows) supports the anodic reaction $\text{M} \rightarrow \text{M}^{z+} + z\text{e}^-$ along with a cathodic reaction, which can be the reverse of any one of the first four half-cell reactions in Table 2.2. The cathodic half-cell reaction $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ will be employed for purposes of illustrating how both half-cell reactions operate together spontaneously.
Figure 15.8 is a schematic of water flowing through a pipe. The water is sufficiently acidic that the metal of the pipe wall undergoes active corrosion (i.e. without formation of an oxide scale on the surface). The anodic and cathodic half-cell reactions take place on different parts of the pipe inside surface. Electrons produced by the anodic reaction flow through the pipe wall to the zone where the cathodic reaction is occurring. One section of the pipe is connected to a standard hydrogen electrode (SHE) for the purpose of measuring the overpotential (i.e., the pipe is corroding). The pH 1 acid of the SHE is connected to the pipe water by a salt bridge, the function of which is to complete the electrical circuit of the measuring cell.

![Fig. 15.8 Corrosion of a pipe in flowing water.](image)

The Tafel diagram for this overall-cell process is shown schematically in Fig. 15.9. It is based on simplified forms of the Butler-Volmer equation of Eq (15.14) for large overpotentials where only the first exponential term is needed for the anodic line and the second exponential term applies to the cathodic reaction. The lines in the diagrams are called polarization curves, although the curvature does not appear in the simplified diagrams of Figs. 15.9, 15.10 and 15.11.

The Tafel diagrams in Fig. 15.9 differ from the half-cell diagram of Fig. 15.7 in the definition of the overpotential. In Fig. 15.9, two half-cell polarization curves (lines) are superposed, each with its own overpotential defined by \( \eta \) of Eq 15.15. However, the equilibrium potential \( \varepsilon_{\text{eq}} \) for the cathodic and anodic reactions are different, yet the reference potential must be the same for both half-cells in order to properly use them together.

In Fig. 15.9, the reference potential has been chosen as the equilibrium electrode potential of the anode metal M, \( \varepsilon_{\text{eq}}^M \). Ignoring the curvature near the equilibrium potential seen in Fig 15.6, the anodic line for the metal is given by:

\[
\varepsilon - \varepsilon_{\text{eq}}^M = b_M \left[ \log i - \log i_{\text{oM}} \right]
\]

(15.19a)

where \( i_{\text{oM}} \) is the exchange current density for the anodic half-cell reaction \( M \rightarrow M^{z+} + ze^- \) at a metal ion concentration of \([M^{z+}]\) from Eq (15.18a). The parameter \( b_M \) is:

\[
b_M = \frac{2.3RT}{\alpha_M z_F} = \frac{0.059}{\alpha_M z_M}
\]

(15.20a)

When coupling the anodic line of the metal diagram to the cathodic portion of the hydrogen diagram, the reference potential must be the same for both diagrams. The overpotential is with respect to \( \varepsilon_{\text{eq}}^M \). The cathodic portion of the Butler-Volmer equation contains only the second exponential term in Eq (15.14). For the \( \text{H}^+/\text{H}_2 \) half-cell reaction it can be written as:

\[
\varepsilon - \varepsilon_{\text{eq}}^M = \delta_{\text{HM}} - b_H (\log i - \log i_{\text{oH}})
\]

(15.19b)
where

\[ b_H = \frac{2.3RT}{(1 - \alpha_H)zF} \]

(15.20b)

and

\[ \delta_{HM}^{eq} = \epsilon_H^{eq} - \epsilon_M^{eq} \]

(15.21)

At the intersection in Fig. 15.9, the current densities of the two half-cell reactions are equal. An analytic version of Fig. 15.9 is based on Eq (15.19a) for the metal anodic reaction and Eq (15.19b) for the hydrogen cathodic reaction. Setting \( i = i_{corr} \) and \( \epsilon = \epsilon_{corr} \) in Eqs (15.19a) and (15.19b), equating their right-hand sides at the intersection and solving for \( \log i_{corr} \) yields:

\[ \epsilon_{corr} - \epsilon_M^{eq} = \eta_{corr} = b_M (\log i_{corr} - \log i_{oM}) = \delta_{HM}^{eq} - b_H (\log i_{corr} - \log i_{oH}) \]

(15.22a)

solving the last equality for \( \log i_{corr} \):

\[ \log i_{corr} = \frac{\delta_{HM}^{eq} + b_M \log i_{oM} + b_H \log i_{oH}}{b_M + b_H} \]

(15.22b)

**Fig. 15.9 The corrosion potential and corrosion current from the intersection of cathodic and anodic polarization lines**

**Example** Determine the overpotential \( \eta_{corr} \) and the corrosion current density \( i_{corr} \) when \( M = Ni \) and: \( \alpha_{Ni} = 0.55, \alpha_H = 0.20, [Ni^{2+}] = 0.02 M, pH = 1, p_{H2} = 0.1 \text{ atm}, i_{oNi} = 10^{-6} \text{ A/cm}^2, i_{oH} = 6 \times 10^{-9} \text{ A/cm}^2 \)

Nernst potentials from Table 2.2 and Eq (2.77a):

\( \phi_{Ni} = 0.25 - (0.059/2)\log(0.02) = 0.30 \text{ V}; \quad \phi_H = 0 - (0.059/2)\log([10^{-1}]^2/0.1) = 0.19 \text{ V} \)

Applying the sign convention: \( \epsilon_{Ni}^{eq} = -0.30 \text{ V} \quad \epsilon_H^{eq} = -0.19 \text{ V} \quad \delta_{H,Ni} = -0.19 - (-0.30) = 0.11 \text{ V} \)

From Eqs(15.20ab):

\[ b_{Ni} = \frac{0.059}{2 \times 0.55} = 0.054 \text{ V} \quad b_H = \frac{0.059}{2 \times (1 - 0.2)} = 0.037 \text{ V} \]

From Eq

\[ (15.22b): \log(i_{corr}) = \frac{0.11 + 0.054 \log(10^{-6}) + 0.037 \log(6 \times 10^{-9})}{0.054 + 0.037} = -5.69 \quad \text{or} \quad i_{corr} = 2 \times 10^{-9} \text{ A/cm}^2 \]

Use \( \log(i_{corr}) \) in Eq (15.22a):

\[ \eta_{corr} = 0.054(-5.69 - \log(10^6)) = 0.017 \text{ Volts} \]

\[ \eta_{corr} = 0.11 - 0.037(-5.69 - \log(6 \times 10^9)) = 0.016 \text{ Volts} \]
15.6.4 Tafel diagram for multiple cathodic reactions

In many situations, active corrosion is driven by more than a single cathodic reaction. For example, under neutron or gamma radiation, water radiolysis produces substantial quantities of hydrogen peroxide, which decomposes according to \( \text{H}_2\text{O}_2 + 2e^- \rightarrow 2\text{OH}^- \). This half-cell reaction acts in concert with the proton reduction reaction to increase the corrosion rate. The two cathodic lines and the anodic metal dissolution line are shown in Fig. 15.10. The condition requiring equal rates of production and consumption of electrons are:

\[
i_{c}(\text{H}_2\text{O}_2) + i_{c}(\text{H}) = i_{a}(\text{M})
\]

To determine the state of corrosion, the dashed line must be moved up from its location without \( \text{H}_2\text{O}_2 \) (point E), past the corrosion condition if only \( \text{H}_2\text{O}_2 \) were present (point D) until the combined cathodic lines satisfy the above equation, or:
The corrosion current density (point C) is larger than either of the cathodic rates.

15.6.5 Tafel diagram for multiple anodic reactions

A common case of two anodic reactions and one cathodic reaction is zinc plated on iron, which constitutes galvanic protection. Figure 15.11 is an example wherein these two metals exist in the presence of oxygenated neutral water, which provides the cathodic half-cell:

\[ \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^- . \]

The areas of the two metals exposed to water may be different, so the electron-production/electron consumption balance is:

\[ (A_{\text{Fe}} + A_{\text{Zn}}) i_{\text{O}_2} = A_{\text{Fe}} i_{\text{Fe}} + A_{\text{Zn}} i_{\text{Zn}} \]

where \( A_{\text{Fe}} \) and \( A_{\text{Zn}} \) are the areas of the two metals exposed to water. The above charge balance assumes that the cathodic reaction takes place over the entire exposed metal area and that the rates are the same on both metals. With reference to Fig. 15.11, the relevant terms in the above equation are:

\[ i_{\text{O}_2} = 10^{0\text{C}} \quad i_{\text{Fe}} = 10^{0\text{A}} \quad i_{\text{Zn}} = 10^{0\text{B}} \]

The corrosion rate of the iron component is \( A_{\text{Fe}} i_{\text{Fe}} \) is approaching the exchange-current density, which is \( i_{\text{Fe}} \sim 1 \mu\text{A/cm}^2 \). As an example, if the corrosion current density at point A in Fig. 15.11 is 10 \( \mu\text{A/cm}^2 \), the dissolution rate of the metal can be calculated from Eq (15.16). \( j_{\text{corr}} \) can be converted to a loss rate by:

\[
\text{metal loss rate} = \frac{10^{-5} \ \text{A/cm}^2}{2 \times 96,500 \ \text{C/mole}} \times \frac{56 \ \text{g}}{\text{mole}} \times \frac{\text{cm}^3}{7.9 \ \text{g}} \times \frac{3.14 \times 10^7 \ \text{s}}{\text{yr}} = 10^{-2} \ \text{cm}^2/\text{yr}
\]

which is a significantly smaller loss rate than would afflict unprotected iron.

15.6.6 Concentration polarization

The cathodic polarization curves heretofore represented as straight lines with a negative slope are surface reactions whose rates depend upon delivery of a dissolved species from the bulk solution to the interface. Like any other reaction at a surface supplied with reactants from a fluid, they are potentially mass-transfer limited. Consider the cathodic half-cell reaction \( 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \). The
transport rate of $H^+$ to the surface depends on the hydrodynamic boundary layer in the water adjacent to the metal and on the diffusivity of $H^+$ in water. Figure 15.12 is a sketch of the $H^+$ concentration close to the surface.

![Diagram of H+ concentration close to the surface]

Fig. 15.12 Concentration of $H^+$ adjacent to the metal surface during active polarization

The flux of $H^+$ to the interface and the equivalent current density are:

$$j_{MT} = k_{MT}([H^+]_b - [H^+]_{int}) = \frac{i}{F}$$ (15.23)

Since $i_{MT} = i_c$, the cathodic current density, the entire process becomes mass-transfer limited when attains a limiting value $i_L$ which reduces $[H^+]_{int}$ to zero. The behavior of the cathodic polarization curve with a mass-transfer limitation is shown in Fig. 15.13. The potentials are reported with respect to $\Delta \phi_{eq}^H$, the equilibrium interfacial potential difference of the hydrogen half-cell having the bulk hydrogen ion concentration and $H_2$ partial pressure. The overpotential under these conditions is $\eta = 0$. The equilibrium interface potential difference for the bulk solution conditions is the Nernst potential$^3$:

$$\Delta \phi_{eq}^H = 0.059 \log \left( \frac{[H^+]_b}{p_{H_2}^{1/2}} \right)$$

where $[H^+]_b$ is the bulk concentration of hydrogen ions and $p_{H_2}$ is the $H_2$ partial pressure with which the solution is in equilibrium (it need not be 1 atm). Under these conditions, there is no net current but the exchange current density, $i_{0H}$, prevails at the interface. When a net current is drawn (e.g., by reducing the overpotential), the $H^+$ concentration at the interface, $[H^+]_{int}$, is no longer the bulk value. The interface potential difference is not:

$$\Delta \phi_H = 0.059 \log \left( \frac{[H^+]_{int}}{p_{H_2}^{1/2}} \right)$$

The concentration overpotential is defined by:

$$\eta_{conc} = \Delta \phi_H - \Delta \phi_{eq}^H = 0.059 \log \left( \frac{[H^+]_{int}}{[H^+]_b} \right)$$

Eliminating $[H^+]_{int}$ by use of Eq (15.23):

$$\eta_{conc} = 0.059 \log \left( 1 - \frac{i}{k_{MT} F [H^+]_b} \right) = 0.059 \log \left( 1 - \frac{i}{i_L} \right)$$ (15.24)

Where $i_L$ is the limiting current density, meaning that the current density is so large that the entire kinetics is limited by mass transport. This means that $[H^+]_{int}$ is reduced to zero.

$$i_L = k_{MT} F [H^+]_b$$ (15.25)

$^3$ See first paragraph of Sect. 15.6.1 for an explanation of the signs
The exchange-current density also reflects the interface conditions. From Eq (15.19):

\[ i_{oH} = Q_H[H^+]^{(1-\alpha)}[p_{H2}]^{\alpha} = Q_H[H^+]^{(1-\alpha)} \left(1 - \frac{i}{i_L}\right)^{(1-\alpha)}[p_{H2}]^{\alpha} \]  

(15.26)

\(Q_H\) is the collection of constants in Eq (15.18a) for the hydrogen half-cell reaction. \(\alpha\) is also a property of the hydrogen half-cell. However, the \(H^+\) concentration and \(p_{H2}\) are the actual conditions of the aqueous phase.

From Eq (15.19b) the overpotential without mass transfer limitation, \(\eta_c\) (AB on the dashed line in Fig. 15.13), is

\[ \eta_c = -b_{HH} \left(\log i - \log i_{oH}\right) \]  

(15.27)

The overpotential that appears on the ordinate of Fig. 15.13 is the sum:

\[ \eta = \eta_{conc} + \eta_c \]  

(15.28)

**Example**: show how \(i\) and \(\eta\) are related when the concentration overpotential is significant. \([H^+]_b\) and \(p_{H2}\) are specified. Let \(i\) be the independent variable and \(\eta\) the dependent variable.

1. The mass-transfer coefficient \(k_{MT}\) must be known in order to fix \(i_L\) by Eq (15.25).
2. Given \(i\), calculate:
   (a) \(i_{oH}\) from Eq (15.26)
   (b) \(\eta_c\) from Eq (15.27)
   (c) \(\eta_{conc}\) from Eq (15.24)
   (d) \(\eta\) from (15.28)

**15.6.7 Actual Tafel diagrams**

Figure 15.14 is a sketch of a realistic Tafel diagram for a metal like iron. Three regions with cathodic polarization curves are depicted. In the bottom of the sketch is the active corrosion region, which has been the sole mechanism dealt with up to this point. Activate corrosion ends at the peak of the anodic curve, for which the coordinates are the critical current density and an

---

4 The first term on the right-hand side of Eq (15.19b) vanishes because the two equilibrium interface potential differences in Eq (15.21) are both that for \(H^+\).
overpotential termed the *passivation potential*. In the middle is a region called *passive* because the corrosion rate is very low. This is the subject of Sect. 15.7. The region at high overpotential is termed *transpassive*. It is similar to active corrosion in that the corrosion product is a soluble ionic species. We do not review this type of corrosion because the overpotentials are above that at which water decomposes into \( \text{O}_2 \).

Two cathodic polarization curves are shown in the active and transpassive corrosion zones. For branches 1 and 5, the intersection with the anodic branch of iron lies on exchange-current-density lines. It was shown in Sect. 15.6.1 that \( i_0 \) represents equal anodic and cathodic currents and an interface potential difference that is the equilibrium (or Nernst) value. This combination of anodic and cathodic polarization curves is termed *thermodynamic control* of the corrosion rate. These polarization-curve intersections are also the corrosion potentials.

It may seem illogical that the corrosion current density should coincide with an exchange-current density, which by definition has zero net current drawn from the equal anodic and cathodic current densities. However, cathodic branches 2 and 4 in Fig. 15.14 are examples of *kinetic* control of the corrosion process. These are the type that have been discussed at length in the preceding sections. The maximum labeled \( \log i_{\text{crit}} \) on the anodic curve represents a point of instability.

The numbering of the red lines assumes that the cathodic reaction is \( \text{H}^+ + \varepsilon^- \rightarrow \frac{1}{2} \text{H}_2 \). At 1 atm \( \text{H}_2 \), Eq (2.77a) gives the Nernst potential: \( \phi = 0 - 0.059\log[\text{H}^+] = 0.059\text{pH} \). Changing signs to adhere to the convention used in this chapter and Sect. 2.9, the equilibrium electrode potential is \( \varepsilon_{\text{eq}} = -\phi = -0.059 \text{pH} \). The overpotential given by Eq (15.15) is \( \eta = \varepsilon - \varepsilon_{\text{eq}} \) or \( \eta = \varepsilon + 0.059\text{pH} \). This is a useful overpotential if the pH is constant and \( \varepsilon \) is variable. However, when comparing the effect of pH, an arbitrary reference potential \( \varepsilon_{\text{ref}} \) is employed: \( \sigma = \eta - \varepsilon_{\text{ref}} \), or

\[
\sigma = \varepsilon + 0.059\text{pH} - \varepsilon_{\text{ref}}
\]

Thus, increasing acidity (lower pH) reduces the overpotential. The anodic lines 1 - 3 correspond to basic solutions and lines 4 and 5 represent acidic solutions.

If the current density is increased from zero using the cell configuration of Fig. 15.5, the overpotential follows the active corrosion segment of the portion of the curve intersected by
cathodic branches 2 and 4. When the critical current density \( i_{\text{crit}} \) is reached, the overpotential jumps to the transpassive portion of the anodic polarization curve. If the overpotential (rather than the current density) is controlled, again the section from the critical current density to the start of the passification portion of the polarization curve cannot be measured. If the overpotential is raised slightly above the value corresponding to \( \log i_{\text{crit}} \), the system again jumps to the transpassive section of the anodic polarization curve.

The region of the anodic polarization curve represented by the vertical straight line in Fig. 15.11 is the region of passivity, so named because of the very low corrosion current density. In this region the low corrosion rate, for example at the intersection with cathodic branch 3, a protective oxide or hydroxide scale is present on the metal surface. This phenomenon is treated in Sect. 15.7.

Quantitative curves of the anodic polarization curves for iron and stainless steel are shown in Fig. 15.15. Stainless steel is represented by chromium, since this metal is the primary chemical actor for the surface of this alloy in water. Despite the general chemical similarity of Fe and Cr, their anodic polarization curves are vastly different. The primary difference is the critical current densities of the two metals. The very large value of \( i_{\text{crit}}(\text{Fe}) \) make iron very difficult to passivate. The overpotential corresponding to the critical current density of Cr is an order-of-magnitude lower than that of Fe, which also makes the former easier to passivate. This difference in corrosion behavior between the two metals is the reason that the iron age morphed into the age of stainless steel and chrome plating.

![Fig. 15.15 The anodic polarization curves of iron and chromium (stainless steel)](image)

15.7 Scales on structural metals

15.7.1 Corrosion Properties

By structural metals we mean the iron-nickel-chromium alloys which provide the majority of the high-strength, elastic support of modern society's edifices. Nearly all of these applications exist at ambient temperatures, with the notable exceptions of fossil-fired and nuclear power plants, where temperatures up to 850°C are involved. The compositions of the three most common alloys are listed in Table 15.2. There is a goodly spread in the
compositions and the table gives rough averages. These alloys have somewhat different corrosion resistance to water and different strength versus temperature dependences. In what follows, only the properties of stainless steel are reviewed.

The result of metal corrosion in water (or air) are oxide scales, which are also called films or barriers.

When a nearly-pure alloy such as Zircaloy corrodes, a single oxide scale is formed. Stainless steel corrosion in ambient-temperature water, which is very slow, results in a two-layer scale, which is seen in Fig. 15.16.

| Table 15.2 Compositions of Fe, Cr, Ni alloys |
|----------------|-----|-----|-----|
| Alloy          | Ni % | Cr % | Fe% |
| stainless steel (304 & 316) | 10   | 18  | 72  |
| Inconel 600    | 76   | 16  | 8   |
| Inconel 625*   | 68   | 21  | 5   |

*balance Mo, Ta

The actual corrosion layer (i.e, that controls the growth rate) is the sub-layer rich in chromite, or in general an oxide whose main metal component is Cr. Lying on top of this corrosion barrier is a collection of particles rich in ferrite. These scales are a class of mixed double oxides AB₂O₄ called spinels, where A and B denote mixtures of Fe, Ni and Cr. The sublayer Cr-rich spinel grows into the base metal while the ferrite chunks are deposited from the liquid as recrystallized particles. The reason for this difference is the very low solubility of Cr in water compared to that of Fe and Ni. This is seen in the compositions of the two layers on various alloys collected in Table 15.3.
The upper (ferrite) layer contains little chromium, in keeping with the latter's low solubility in water. The A part of the spinels consists only of Ni and Fe, while the B component contains no Ni. In these compounds, nickel has a valence of 2+ while Cr is in the 3+ oxidation state. Iron has a valence of 2+ in the A part and in the B portion, the valence is 3+. The range of compositions in corrosion-products spinels is shown below

Table 15.3 Corrosion-films AB₂O₄, on Fe, Ni, Cr alloys in hydrogenated water at 200°C

<table>
<thead>
<tr>
<th>Chromite (lower) layer</th>
<th>Ferrite (upper) layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy</td>
<td>A</td>
</tr>
<tr>
<td>304 SS</td>
<td>NiₐFe₀.₈</td>
</tr>
<tr>
<td>Inconel 600</td>
<td>Ni₀.₇Fe₀.₃</td>
</tr>
<tr>
<td>Inconel 625</td>
<td>Ni₀.₇Fe₀.₃</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
(Ni_mFe_{1-m})(Cr_nFe_{1-n})O_4 & \quad m = 1 \\
Ni(Cr_nFe_{1-n})O_4 & \quad n = 1 \\
NiCr_2O_4 & \quad (n i c k e l \, c h r o m i t e) \\
& \\
(Ni_mFe_{1-m})(Cr_nFe_{1-n})O_4 & \quad m = 0 \\
Fe(Cr_nFe_{1-n})O_4 & \quad n = 1 \\
FeCr_2O_4 & \quad (f e r r o u s \, c h r o m i t e) \\
& \\
& \quad n = 0 \\
& \quad (n i c k e l \, f e r r i t e) \\
& \quad (f e r r o u s \, c h r o m i t e) \\
& \quad (m a g n e t i t e)
\end{align*}
\]

Recrystallization of a ferrite layer occurs on the zirconium oxide scale growing on reactor fuel-element cladding, with deleterious consequences (see Chap. 21)

15.7.2 Parabolic scale growth kinetics
There two mechanisms by which a metal oxidizes. i) metal ions migrate from the metal/scale interface to the scale/solution interface where the ions are converted to an oxide by reaction with H₂O or O₂ dissolved in water. ii) oxygen ions produced at the scale-solution interface diffuse through the scale to the metal-scale interface where they extract metal atoms and convert them to metal ions in the scale. Only the second of these possibilities is considered in what follows.

The simplest rate law for growth of a corrosion scale (oxide or hydroxide) on a metal is the parabolic growth law. This law is based on the flux of a species of the solid diffusing through the scale according to Fick's law:

\[
J = -D \frac{dC}{dx} = D \frac{C_o - C_L}{L} = C_m \frac{dL}{dt}
\]

D = diffusion coefficient of species transferring (oxygen ions) in the scale, cm²/s
Cₗ = concentration of O²⁻ at the scale/solution interface, moles/cm³
L = thickness of scale, cm
C₀ = concentration of O²⁻ at the scale/metal interface, moles/cm³
\( C_M = \text{molar density of the metal, moles/cm}^3 \)

\( C_M = \text{molar density of the metal element in the scale, moles/cm}^3 \)

\( x = \text{distance from the metal/scale interface (see Fig. 15.2)} \)

The last equality in Eq (15.29) can be integrated to give the scale thickness as a function of time, which is the desired end result for all of the analyses of corrosion scales. Integrating from \( L = 0 \) at \( t = 0 \) yields:

\[
L^2 = \left[ \frac{2D}{C_{tot}} (C_o - C_1) \right] t \tag{15.29a}
\]

which is the parabolic growth law. This law, however, is not consistent with the empirical oxide scaling laws observed on most metals, which are:

\[
L = A + B \times \ln(t) \quad \text{or} \quad L = \text{const} \times t^{1/n} \tag{15.29b}
\]

where \( A \) and \( B \) are constants in the first form and \( n \) is an integer >2 in the second form.

15.7.3 Effect of the ionic character of the metal

The above simple analysis does not apply to the oxide scales on metals because of: i) the ionic character of the species involved in forming oxide scales on metals and ii) the potential difference between the metal and the aqueous solution analyzed in Sect. 15.4. These electrical effects influence the corrosion rate.

In the usual form of Fick’s first law, as used in deriving Eq (15.29), the flux is driven only by the chemical potential gradient:

\[
J_{chem} = -\frac{D C}{RT} \frac{d\mu}{dx}
\]

where \( \mu \) is the chemical potential of the moving species in the solid.

According to Eq (2.71), a position-dependent electric potential provides a gradient which generates a species flux of:

\[
J_{elec} = -\frac{zF}{RT} DC \frac{d\phi}{dx}
\]

where \( \phi \) is the electric potential, \( F \) is the Faraday (96,500 Coulombs/mole or 96.5 kJ/mole-Volt) and \( z \) is the charge on the moving species. The total flux (moles/cm\(^2\)-s) is the sum of the above two contributions:

\[
J = J_{chem} + J_{elec} = -\frac{D C}{RT} \frac{d\mu}{dx} - \frac{zF}{RT} DC \frac{d\phi}{dx} \tag{15.30}
\]

In an ideal solution, the chemical potential is related to the concentration by Eqs (2.36) and (2.37): \( \mu = g^o + RT \ln(C/C_M) \), where \( g^o \) is the free energy of the species in a standard state. The gradient of \( \mu \) is:

\[
\frac{d\mu}{dx} = \frac{RT}{C} \frac{dC}{dx}
\]

The electric potential gradient is expressed in terms of the electric field (Volts/cm):

---

5 The oxide formula is MO\(_{1-y}\), where \( y \) is the deviation from exact stoichiometry, so \( C_M \) is the molar density of the oxide as well as of the metal. It is obtained from the oxide density \( \rho_{ox} \) g/cm\(^3\) and the molecular weight \( M_{ox} \):

\[
C_M = \frac{\rho_{ox}}{M_{ox}}.
\]

For NiO, for example, \( C_M = 6.67/74.7 = 0.089 \) moles/cm\(^3\)
Replacing $d\mu/dx$ in terms of $dC/dx$ and the electric potential gradient in terms of the electric field, Eq (15.30) becomes:

$$J = -D \frac{dC}{dx} + u CE$$  \hspace{1cm} (15.30a)

where

$$u = \frac{D zF}{RT}$$  \hspace{1cm} (15.32)

is the mobility of the moving species (cm²/Volt-s).

Note the fundamental difference between Eq (15.30a) and the Butler-Volmer equation, (15.14). The latter deals with the rates of half-cell reactions, the first term for the anodic (oxidizing) half-cell and the second term for the cathodic (reducing) step. These processes are driven by differences between an applied potential and the Nernst equilibrium potential. Equation (15.30a), on the other hand, describes the flux of a species through an oxide film. The movement is driven by spatial gradients of the potentials.

15.7.4 An Illustrative System - the oxide scale on a divalent metal

The reason for choosing a divalent metal, which could be (among many others) Fe or Ni, is to keep the notation simple. The oxide is written as MO and is stable on the metal (i.e., does not dissolve in the aqueous phase) because the metal concentration in the solution is at or above the solubility limit (Sect. 2.9.5):

$$\text{MO} (s) + \text{H}_2\text{O} = \text{M}^{2+} (\text{sol'en}) + 2\text{OH}^-$$

Allowing for deviations from exact stoichiometry, the oxide has the formula MO$_{1-y}$. For simplicity, only hypostoichiometry is allowed. The nonstoichiometry parameter $y$ is equal to the fraction of anion lattice sites that are vacant. If anions are missing but all cation sites are filled (as assumed here), electrical neutrality is maintained by leaving behind the two electrons formerly associated with the missing oxygen ions. Where do these electrons go? As shown in Fig. 15.17, they move to the oxide/solution surface where they reduce neutral oxygen in the solution to anions (O$^{2-}$).

In nearly all cases, oxygen ions migrate by the vacancy mechanism, which means that the flux of oxygen ions through the oxide can equally well be considered to be movement of anion vacancies in the opposite direction. Vacancies cannot be the sole species migrating from the oxide-metal interface to the solution-oxide interface, for this would be equivalent to removal of positive charges from the metal. The resulting buildup of the negative charges in the metal would eventually stop the movement of O$^{2-}$ and corrosion would cease. This charge flux is counteracted by the equal and opposite flux of diffusing electrons.

This illustrative corrosion mechanism can be described by the following electronic processes:

at the metal/oxide-scale interface $(x = 0)$: \hspace{1cm} M(met) $\rightarrow$ M$_m + V_o$ (met/ox) $+ 2e'$ (met/ox)
in the oxide film (or scale):

\[ \text{e}^- (\text{met/ox}) \rightarrow \text{e}^- (\text{ox/sol'n}) \]

and

\[ \text{V}_O^\circ (\text{met/ox}) \rightarrow \text{V}_O^\circ (\text{sol'n/ox}) \]

at the oxide-scale/sol'n interface \((x = L)\):

\[ \frac{1}{2} \text{O}_2 (\text{sol'n}) + 2 \text{e}^- (\text{ox/sol'n}) + \text{V}_O^\circ (\text{ox/sol'n}) \rightarrow \text{O}_O (\text{ox/sol'n}) \]

*Kroger-Vink notation*

Identification of the defects in the above reactions follows *Kroger-Vink* notation. In this method, the letter signifies the type of defect: \(V\) for vacancy, \(I\) for interstitial. The subscript indicates the location of the entity: \(O\) means on the anion (oxygen) sublattice, \(M\) means the cation (metal) sublattice, etc. The superscript indicates the charge deviation from the perfect lattice, dots \(\cdot\) for positive charge and apostrophe \(\prime\) for negative charge. Accordingly, the symbol \(V_O^-\) in the above reactions and in Fig. 15.17 identifies a vacancy \((V)\) on the anion sublattice \((\text{sub } O)\) which is doubly-positively-charged relative to the same site occupied by \(O_2^-\) (superscript \(\cdot\)). \(\text{e}^-\) symbolizes an electron with a single negative charge. A missing charge symbol indicates species on normal lattice positions \((\text{MM means a cation on the cation sublattice and } \text{OO denotes an anion on the anion sublattice})\). The terms in parentheses give the macroscopic location of the defect.

Whatever the mechanism\(^6\), the overall corrosion reaction in this example is the sum of the three steps:

\[ \text{M(met)} + \frac{1}{2} \text{O}_2 (\text{sol'n}) = \text{MO (ox)} \]

A key step that requires elucidation is the movement of \(O_2^-\) from the scale/sol'n interface to the metal/scale interface so that it can occupy a lattice position adjacent to an \(M^{2+}\) ion.

If oxygen diffuses by a vacancy mechanism (Chapter 5, section 5.4) on the anion sublattice, the anion diffusion coefficient is \(D_O = D_{V_0} \chi_{V_0}\), where \(D_{V_0}\) is the diffusivity of the anion vacancies and \(\chi_{V_0}\) is the vacancy fraction in the anion sublattice. The sum of the vacancy fraction and the \(O_2^-\) fraction equals one. Hence a gradient in the \(O_2^-\) concentration generates an opposing gradient of the anion vacancies. If \(\chi_{V_0}\) varies through the scale, the oxygen diffusivity \(D_O\) is position-dependent as well. This would complicate the analysis. However, the vacancy diffusivity \(D_{V_0}\) is constant throughout the scale, so in the present analysis, the anion vacancy is chosen as the moving species instead of oxygen ions. However, anion vacancy diffusion from the met/ox interface to the ox/sol'n interface is equivalent to anion diffusion in the opposite direction, so the choice of the former is merely a matter of convenience.

The remaining question is how the anion vacancies are produced at the metal/oxide interface. Formation of this point defect at first seems counterintuitive, given that \(O_2^-\) ions are moving towards this interface. The explanation is twofold: i) the \(O_2^-\) anions move by hopping into existing vacant anion sites, which are those moving in the opposite direction, as explained in the previous paragraph; ii) the very act of creating \(M^{2+}\) cations in the lattice structure automatically

---

\(^6\) the actual mechanisms of these interface reactions are more complex than the simple one-step processes shown here.
creates vacant anion sites in order to preserve the crystal structure. This step is illustrated in Fig. 15.18, where again for the purpose of illustration, the MO crystal is assumed to be the NaCl-type (Fig. 2.9).

Figure 15.17 includes a sketch of the variation of the electric potential, $\phi$, in the three phases. Note the discontinuities at the two interfaces, which are due to unequal charges on either side of the interfaces. Also, the variation of the potential in the scale is not a straight line, as assumed for the double layer in the absence of the intervening oxide (Fig. 15.2). As we shall see, this curvature causes severe complications in the analysis of the corrosion process.

Electrons can move through an oxide scale by the quantum-mechanical process called tunneling, whereby an electron "passes through" an energy barrier that it could not surmount by the usual thermal agitation. At higher temperatures and thicker scales, the electrons move by hopping from one energy minimum to an adjacent one. This process is essentially diffusion, and is described by the same equations as diffusion of atomic species (i.e., Eq (15.30a)).

The objective of the following analyses is to calculate the flux of species (oxygen vacancies in this case) that is responsible for growth of the scale. The rate of film growth is determined from:
\[
\frac{dL}{dt} = \frac{J_{VO}}{C_M}
\]  

(15.33)

where \(C_M\) is the molar density of the cations in MO, which is equal to the sum of the anion vacancy and filled anion-site concentrations. The subscript VO means vacancy on the oxygen sublattice, or anion vacancy. \(C_M\) is the density of the metal component (cation) of the oxide.

Once \(J_{VO}\) is known as a function of \(L\), Eq (15.33) can be integrated to give the growth law, \(L = f(t)\).

15.7.5 Position-independent electric field

For the electric field to be constant throughout the scale, Eq (15.31) requires that the electric potential vary linearly with position in the scale. At steady-state, the flux of anion vacancies through the scale \((J_{VO})\) is a constant, and provided that the electric field \(E\) does not depend on \(x\), Eq (15.30a) can be integrated with the boundary condition \(C_{VO} = C_{VO}(0)\) at \(x = 0\) (the scale/metal interface):

\[
\frac{C_{VO} - J_{VO} / u_{VO}E}{C_{VO}(0) - J_{VO} / u_{VO}E} = e^{\alpha x}
\]

(15.34a)

where \(u_{VO} = \frac{z_{VO}F}{RT} D_{VO}\)

\(\alpha = \frac{z_{VO}F}{RT} E\)

(15.34b)

\(z_{VO} = +2\) is the charge on anion vacancies (relative to the perfect lattice) \(F = 96.5 \text{ kJ/mole-Volt}\) is Faraday's constant. With the boundary condition \(C_{VO} = C_{VO}(L)\) at \(x = L\) (the scale/sol'n interface) in Eq (15.34a), solving for \(J_{VO}\) yields:

\[
J_{VO} = u_{VO} E \left( \frac{C_{VO}(0)e^{\alpha L} - C_{VO}(L)}{e^{\alpha L} - 1} \right)
\]

(15.35)

In the limit as \(\alpha \rightarrow 0\) (or \(E \rightarrow 0\)), Eq (15.35) reduces to Eq (15.29).

Using Eq (15.33) the growth rate of the scale is:

\[
\frac{dL}{dt} = \frac{u_{VO} E}{C_M} \left( \frac{C_{VO}(0)e^{\alpha L} - C_{VO}(L)}{e^{\alpha L} - 1} \right)
\]

(15.36)

Time-integration of Eq (15.36) hinges on how the electric field varies with \(L\). Since \(E\) is constant across the scale, the electric condition of solid scale is analogous to that across the double layer as depicted in Fig. 15.2. This condition is described by:

\[
E = -\frac{\phi_M - \phi_S}{L} = -\frac{\Delta \phi}{L}
\]

(15.37)

If the electric potential difference (the numerator of the above equation) is independent of scale thickness, \(E\) varies as \(L^{-1}\). With \(\alpha\) given by Eq (15.33b), the argument of the exponential functions in Eq (15.36) is not a function of \(L\). However, the coefficient varies as \(L^{-1}\). Integrating
Eq (15.36) with \( L = 0 \) at \( t = 0 \) yields the parabolic growth law but with a different coefficient from that of Eq (15.29a):

\[
L^2 = \left[ \frac{2u_{vo} \Delta \phi C_{vo}(0)}{C_M} \right] \exp \left( \frac{u_{vo} \Delta \phi}{D_{vo}} \right) \frac{C_{vo}(L)}{C_{vo}(0)} \exp \left( \frac{u_{vo} \Delta \phi}{D_{vo}} - 1 \right) \times t
\]

(15.38)

As \( \Delta \phi \to 0 \), Eq (15.38) reverts to Eq (15.29a). Problem 15.2 compares rate constants for the two cases.

15.7.6 Nonparabolic scaling kinetics - constant electric field

If instead of holding \( \Delta \phi \) constant as the scale grows, the electric field \( E \) retains a fixed value, integration of Eq (15.36) gives:

\[
\alpha L - (1 - \xi) \ln \left( \frac{e^{\alpha L} - \xi}{1 - \xi} \right) = \left( \frac{\alpha u_{vo} E C_{vo}(L)}{C_M} \right) \times t
\]

(15.39)

where \( \xi = C_{vo}(L) / C_{vo}(0) \). Even for small values of \( L \), the exponential term in this equation is much larger than \( \xi \), so the Eq (15.39) reduces to:

\[
\alpha L - (1 - \xi)[\alpha L - \ln(1 - \xi)] = \left( \frac{\alpha u_{vo} E C_{vo}(L)}{C_M} \right) \times t
\]

(15.39a)

According to this equation, \( L \) should increase linearly with time. This is contrary to experimental observations of corrosion kinetics, so the constant-field model is rejected.

15.7.7 The effect of space charge in the oxide scale

If the electric potential does not vary linearly through the scale, integration of Eq (15.30a) becomes considerably more complex.

To avoid continual charge buildup or depletion in portions of the scale, the net charge crossing any plane parallel to the interfaces must be zero, or at all \( x \):

\[
J_e = 2J_{vo}
\]

(15.40)

In the notation of Eq (15.34b), the flux of anion vacancies is given by Eq (15.30a) as:

\[
J_{vo} = -D_{vo} \frac{dC_{vo}}{dx} + u_{vo} E C_{vo}
\]

(15.41)

The electric current flowing through the scale consists of components due to the diffusing \( O^{2-} \) (or, what is equivalent, the oppositely-directed anion vacancies as expressed by Eq (15.41)) and that of the electrons (subscript \( e \)). The latter is:

\[
J_e = -D_e \frac{dC_e}{dx} - u_e E C_e
\]

(15.42)

Although the net charge flux is zero (Eq (15.40)), sections of the scale perpendicular to the interfaces may build up a net electrical charge. This is termed the space charge, and is related to the electric field by Poisson's equation.
\[
\frac{dE}{dx} = \frac{F'}{\varepsilon} (2C_{VO} - C_{e}) \tag{15.43}
\]

Here Faraday's constant is \( F' = 96,500 \) Coulomb/mole. \( \varepsilon \) is the permittivity of the oxide, \( \sim 10^{-12} \) Coulomb/Volt-cm. The term in parentheses multiplied by \( F' \) is the space charge (units of Coulombs/cm\(^3\)).

The three coupled first-order ordinary differential equations, Eqs(15.41), (15.42) and (15.43) require initial conditions (at \( x = 0 \), the metal/scale interface). To this end, it is assumed that structural equilibrium (i.e., the M/O ratio) between adjacent phases prevails at both interfaces.

In terms of the deviation from exact stoichiometry \( MO_1-y \), the relation between the O/M ratio \( 1-y \) and the anion vacancy concentration is \( C_{VO} = yC_M \). The stoichiometry deviations at the two interfaces can be obtained from the M-O phase diagram, as shown pictorially in Fig. 15.19. The intersection of the isotherm with the lower phase boundary of the \( MO_1-y \) phase (point A) is the \( y \)-value at the metal/oxide interface. The intersection of the isotherm with the isobar representing the system's \( O_2 \) pressure (point B) is the corresponding value at the oxide/solution interface. These give \( C_{VO} (0) = y_A C_M \) and \( C_{VO}(L) = y_B C_M \), respectively, for the bounding anion-vacancy concentrations for Eq (15.41).

\( C_e(x) \) and \( E(x) \) need to be provided with values at \( x = 0 \). What then remains is a solution method, which is inevitably numerical. Below we simplify the system as much as possible and provide such a solution.

**15.7.8 Solution of the equations for oxide-scale growth with space charge**

The relation of the various quantities derived in the previous section are best seen if cast in dimensionless form. The dependent variables are:

\[
\theta_{vo} = \lambda \delta C_M y L^2 \quad \theta_e = \lambda \delta C_M (C_e/C_M) L^2 \quad \Psi = \lambda E L \tag{15.44}
\]

The constants in the above definitions are:

\[
\lambda = \frac{2F}{RT} = 36 \text{ Volt}^{-1} \text{ at room temperature} \quad \delta = \frac{F'}{\varepsilon} = \frac{96,500}{10 \times 8.9 \times 10^{-14}} = 1.1 \times 10^{17} \text{ Volt} \cdot \text{cm/mole} \tag{15.45}
\]

The dimensionless forms of the anion-vacancy flux through the oxide scale and its thickness are:

\[
j = \frac{\lambda \delta}{D_{vo}} L^3 J_{vo} \quad X = \frac{x}{L} \tag{15.46}
\]

In terms of the above dimensionless variables, Eqs (15.41) - (15.43) are:

\[
j = -\frac{d\theta_{vo}}{dX} + \Psi \theta_{vo} \tag{15.41a}
\]

\[
4j = -\frac{d\theta_e}{dX} - \frac{1}{2} \Psi \theta_e \tag{15.42a}
\]

\[
d\Psi / dX = 2\theta_{vo} - \theta_e \tag{15.43a}
\]
The factor of 4 in Eq (15.42a) is twice the ratio $D_{\text{VO}}/D_e$, with the diffusivities estimated by Fromhold\textsuperscript{7}.

The boundary conditions for Eq (15.41a) are:

$$
\theta_{\text{VO}}(0) = \lambda \delta C_M y_A L^2 \quad \theta_{\text{VO}}(1) = \lambda \delta C_M y_B L^2
$$

where $y_A$ and $y_B$ are the nonstoichiometry parameters characterizing the oxide at its two extremities (Fig. 15.19). Generic concentrations at these locations used by Fromhold\textsuperscript{7} are:

$$
y_A = 4 \times 10^{-6} \quad y_B = 4 \times 10^{-7}
$$

When inserted into the first equality of Eqs (15.44) the bounding conditions on the anion vacancy concentrations are:

$$
\theta_{\text{VO}}(0) = (36)(1.1 \times 10^{17})(0.1)(4 \times 10^{-6})(10^{-14}) = 0.015L^2 \quad \text{and} \quad \theta_{\text{VO}}(1) = 0.0015L^2
$$

The unit of the oxide scale thickness $L$ is nanometers. The factor of $10^{-14}$ converts nm$^2$ to cm$^2$.

Initial conditions for Eqs (15.42a) and (15.43a) are also required. For the former, Fromhold\textsuperscript{7} recommends $C_e(0)/C_M = 4 \times 10^{-5}$, although this is not an experimentally-determined value. Consequently, this ratio needs also to be treated as an undetermined condition.

Finally, the initial condition for Eq (15.43a) is given by the last equality of Eq (15.44) with $E = E_0$. This electric field depends on the separation of charges between the metal and the oxide at their common interface. There is no \textit{a priori} method of assessing this quantity, although many sources argue that $E_0 \sim 10^5 - 10^6$ Volts/cm. Once a value of this parameter is specified, the initial condition for Eq (15.43a) is

$$
\Psi(0) = \lambda E_0 L
$$

Solution of the three coupled ordinary differential equations is accomplished by a trial-and-error method: for a fixed $L$, $J_{\text{VO}}$ (in its dimensionless form $j$ from Eq (15.46)) is guessed and integration is performed numerically starting from $\eta = 0$. When $\eta = 1$ is reached, the calculated $\theta_{\text{VO}}(1)$ is compared to the value given in Eq (15.49). When the two agree, the correct value of $J_{\text{VO}}$ has been chosen.

However, the presence of the poorly-known parameters $\theta_e(0)$ and $E_o$ greatly complicates this procedure. In actuality, all three unknowns, the above two quantities and $J_{\text{VO}}$, must be simultaneously guessed. After integration, the error measure:

$$\text{error} = \frac{|\theta_{\text{VO}}(1)(\text{calc}) - \theta_{\text{VO}}(1)|}{\theta_{\text{VO}}(1)}$$

is computed. When this is less than 5%, the trio of parameters forms an acceptable solution to the three equations.

As expected, at a fixed value of the scale thickness $L$, this procedure results in a large number of acceptable parameter combinations. However, these all fall within finite ranges, and when plotted as distributions, provide average values that appear reasonable. For example, Fig. 15.19 shows the results of the parameter search for $L = 5$ nm for the anion vacancy flux $J_{\text{VO}}$ (or $j$ of Eq (15.46)). From Fig. 15.19, the weighted average value of the dimensionless flux,

$$\bar{j} = \frac{\sum n j(n)}{\sum n}$$

is $\bar{j} = 0.082 \pm 0.4$. While not particularly accurate, the 50% error is the best that can be obtained for a single specified parameter ($\theta_{\text{VO}}(1)$) fitted by selection of three parameters.

When the $\bar{j}$ values for other scale thicknesses are computed in the same manner and converted to $J_{\text{VO}}$ values using Eq (15.46), the $J_{\text{VO}}$ vs $L$ plot shown in Fig. 15.20 results. In converting $\bar{j}$ to $J_{\text{VO}}$, the anion vacancy diffusivity was taken to be $D_{\text{VO}} = 4 \times 10^{-11}$ cm$^2$/s at 300 K.

The best-fitting line through the points is:

$$J_{\text{VO}} = A e^{-bL} \quad (15.51)$$

where $A = 7.5 \times 10^{-11}$ moles/cm$^2$-s and $b = 0.47$ nm$^{-1}$. $L$ is in nm.

The thickness dependences of the other two fitted parameters are shown in Table 15.4

<table>
<thead>
<tr>
<th>$L$, nm</th>
<th>$C_e(0)/C_M \times 10^5$</th>
<th>$E_o$, Volt/cm $\times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>5.0 $\pm$ 2.3</td>
<td>2.2 $\pm$ 3.9</td>
</tr>
<tr>
<td>5.0</td>
<td>4.8 $\pm$ 0.3</td>
<td>2.6 $\pm$ 1.0</td>
</tr>
<tr>
<td>7.5</td>
<td>3.3 $\pm$ 0.3</td>
<td>3.1 $\pm$ 0.8</td>
</tr>
<tr>
<td>10.0</td>
<td>3.5 $\pm$ 0.5</td>
<td>7.2 $\pm$ 1.7</td>
</tr>
</tbody>
</table>

**Table 15.4** Fitted parameters in the oxide at the metal/oxide interface; electron concentration (2nd column) and the electric field (3rd column)

The fitted values of the electron concentration at $x = 0$ (2nd column) is very close to Fromhold's guess. In addition, it is nearly independent of scale thickness. The metal/oxide interface electric field is below the commonly-reported value of $10^5$-$10^6$ Volt/cm and is also essentially independent of scale thickness.
Lastly, Fig. 15.21 shows the spatial distributions at \( L = 3.3 \) nm of the three properties that characterize the oxide scale. The anion-vacancy concentration \((C_{\text{VO}}/C_M)\) decreases from the oxide/metal interface \((x/L = 0)\) to the oxide/solution interface \((x/L = 1)\). This behavior is forced on the solution as the conditions at these two locations are prescribed.

The initial values of the electron concentration and the electric field, on the other hand, are chosen as part of the random parameter-search process. The electron concentration at \( x = 0 \) is very close to the value suggested by Fromhold\(^7\). The \( x \)-variation of this concentration, however, requires some explanation. In order for electrons to move from the metal/oxide interface to the
oxide/solution interface, Eq (15.42a) suggests that the concentration gradient should be the opposite of that shown in Fig. 15.21; that is, the electrons move up their concentration gradient instead of down it. The reason for this behavior is the strong coupling between Eqs (15.42a) and (15.43a); \( \theta_e \) starts out about an order-of-magnitude larger than \( \theta_{VO} \), so that the latter can be neglected in Eq (15.43a). Thus the gradient of the dimensionless field \( \Psi \) is always negative. As a result, the second term on the right-hand-side of Eq (15.42a) quickly dominates the \( 4j \) term and the gradient of \( \theta_e \) becomes positive. As \( \theta_e \) grows ever more positive, \( \Psi \) becomes increasingly negative, which, according to Eq (15.42a), accelerates the rise of \( \theta_e \) with distance into the scale. This feedback phenomenon is clearly evident in the two dashed curves in Fig. 15.21 and is observed for all scale thicknesses.

15.7.9 Scale growth rate
Having determined the dependence of the anion-vacancy flux on scale thickness (Eq (15.51)), we are now able to integrate Eq (15.33):

\[
L(\text{nm}) = 2.1 \times \ln(3.6 \times 10^{-3} t + 1)
\]

(15.52)

\( t \) is in seconds. This equation is plotted in Fig. 15.22. For the anion-vacancy diffusivity assumed for this calculation (\( D_{VO} = 4 \times 10^{-11} \text{ cm}^2/\text{s} \)), a scale thickness of 10 nm is achieved in \( \sim 10 \) hours. For comparison, a parabolic scale-growth curve from Eq (15.29a) is plotted in Fig. 15.22. The sharper curvature of the solid curve more closely resembles experimental data for scales in the size range of the graph and formulae such as Eq (15.29b). Figure 15.22 shows that the magnitude of the parabolic line is everywhere much greater than that from Eq (15.52). The reason for the inhibiting effect of the electric field on the corrosion rate lies in the second term of Eq (15.30a). The electric field curve in Fig. 15.21 is negative over 90% of the scale thickness, which means that the second term in Eq (15.30a) diminishes rather than increases the flux of anion vacancies.
from the metal/oxide interface to the oxide/solution interface. This is equivalent to reducing the flux of oxygen ions in the opposite direction, and hence decreases the rate of formation of metal oxide.

Fig. 15.22 Scale growth according to Eq (15.52) (solid curve); parabolic (dashed line)

15.8 Passivity

A scale forms on a metal when solution conditions (i.e., pH and overpotential) are in the passivity region of the polarization curve of Fig. 15.14. The film is called "passive" because it persists indefinitely and protects the metal from rapid corrosion. The phenomenon is extremely important for structural metals, all of which, in air or water, should (thermodynamically) be converted back to the ore whence they originated. In particular, chemical immunity of aluminum, chromium and stainless steel from attack by water, even at room temperature, is due to the formation of passive films. Because these scales are no more than a few nanometers thick, they can only be seen with appropriate microscopes.

Instead of ascribing the onset of formation of an oxide scale to the metal ion in solution reaching its solubility limit (Sect. 15.7.4), connection to Tafel diagrams is made by considering the appropriate half-cell reaction. For the MO solid oxide treated in Sect. 15.7, this is:

\[
M + H_2O = MO + 2H^+ + 2e^- \quad (15.52)
\]

The maxima in the polarization curves in Fig. 15.15 (at log_{crit}) are reached at the passivation overpotential\(^9\). For the half-cell reaction (15.52), this is:

---

\(^8\) The actual mechanism of which Reaction (15.52) is the overall description is the 3-step sequence: 
M + H_2O = MOH + H^+ + e^- , followed by: MOH + H_2O = M(OH)_2 + H^+ + e^- and finally: M(OH)_2 = MO + H_2O

\(^9\) The electric potential of the water in a complex industrial system, such as the coolant for a light-water nuclear reactor, can be measured with the standard hydrogen electrode, as shown in Fig. 15.8.
\[ \eta_{\text{pass}} = \eta_{\text{pass}}^o + 0.059\log[H^+]^2 = \eta_{\text{pass}}^o - 0.118pH \]  

(15.53)

\( \eta_{\text{pass}}^o \) is the passivation overpotential at pH = 0. Note that for the pH, the H\(^+\) concentration is in units of molarity, or moles per 10\(^3\) cm\(^3\) (a liter). Thus, in a solution with pH = 7, the H\(^+\) concentration is 10\(^{-10}\) moles/cm\(^3\).

Description of passivation by a Butler-Volmer equation (also called the Tafel equation) such as Eq (15.14) applies to an electrochemical cell in a laboratory in which the overpotential given by Eq (15.53) is applied and the current measured (or vice versa). However, the application with which we are concerned is an aqueous phase in an industrial device, where the electric potential is determined by many factors that cannot be controlled. In this case, scale growth (corrosion) and passivation are treated as kinetic phenomena, which are best described by the methods in Sect. 15.7.

The mechanism is straightforward: scale growth stops at a thickness where the rate of the scale-growth reaction at the metal/oxide interface equal the rate at which the oxide dissolves at the oxide/solution interface. The former is given by the combination of Eqs (15.43) and (15.51):

\[
\left( \frac{dL}{dt} \right)_{\text{corr}} = \frac{A}{C_M} e^{-bL} \]  

(15.54)

Dissolution is assumed to proceed at the oxide/scale interface by the reaction:

\[ \text{MO} + 2\text{H}^+ \rightarrow \text{M}^{2+}(\text{sol'n}) + \text{H}_2\text{O} \]  

(15.55)

at a rate given by:

\[ \text{rate} = k_{\text{rxn}}[\text{H}^+]^2, \text{ moles/cm}^2\text{-s} \]  

(15.56)

where \( k_{\text{rxn}} \) is the rate constant for reaction (15.54). In this equation, the concentration must be expressed in units of moles/cm\(^3\).

The rate of shrinkage by dissolution of the scale is:

\[
\left( \frac{dL}{dt} \right)_{\text{diss}} = -\frac{k_{\text{rxn}}}{C_M}[\text{H}^+]^2
\]  

(15.57)

The scale achieves a steady-state thickness, \( L_{\text{SS}} \) given by the condition that the net rate of change is zero:

\[
\left( \frac{dL}{dt} \right)_{\text{corr}} + \left( \frac{dL}{dt} \right)_{\text{diss}} = 0
\]

from which \( L_{\text{SS}} \) is found to be:

\[
L_{\text{SS}} = \frac{1}{b} \left[ \ln\left( \frac{A}{k_{\text{rxn}}} \right) - 2\ln[\text{H}^+] \right]
\]  

(15.58)
Example: a piece of the metal is immersed in a solution of pH = 10
The rate constant of reaction (15.54) for a particular metal is \( k_{\text{rxn}} = 2 \times 10^9 \)

(a) what are the units of \( k_{\text{rxn}} \)?
(b) what is the thickness of a passive scale on the metal?
(c) at what rate does the scale penetrate the underlying metal?

(a) With the H\(^+\) concentration in units of moles/cm\(^3\), Eq (15.56) gives:

\[
\text{units of } k_{\text{rxn}} = \frac{\text{moles}}{\text{cm}^2 \cdot \text{s}} \times \frac{\text{cm}^3}{\text{mole}} = \frac{\text{cm}^{-4}}{\text{mole} \cdot \text{s}}
\]

(b) From Eq (15.58):

\[
L_{\text{ss}} = \frac{1}{0.47} \left[ \ln \left( \frac{7.5 \times 10^{-11}}{2 \times 10^{-9}} \right) - 2 \times 2.3 \log 10^{-10} \right] = 3.0 \text{ nm}
\]

(c) from Eq (15.54)

\[
\left( \frac{\text{d}L}{\text{d}t} \right)_{\text{corr}} = \frac{7.5 \times 10^{-11}}{0.1} e^{-0.47 \times 3.0} = 1.8 \times 10^{-10} \text{ nm/s}
\]

or, the metal is corroded at a rate of only \( \sim 0.006 \text{ nm/yr} \)! The passive scale on this particular metal is indeed very protective.

The corrosion current density is associated with the flux of oxygen ions through the scale to the metal/oxide interface, which is where the conversion of metal to metal oxide occurs. With the oxygen ion flux given by Eq (15.51), the corrosion current density is also equal to the rate at which electrons arrive at the oxide/solution interface:

\[
i_{\text{corr}} = 2F'J_{\text{VO}} = 2F'A\exp(-bL_{\text{ss}}) \quad \text{A/cm}^2
\]

where \( F' = 96,500 \text{ Coulombs/mole} \) is Faraday's constant. For the 3-nm-thick passive scale of the preceding example, the corrosion current is 3.5 \( \mu \text{A/cm}^2 \).

15.9 Localized corrosion

Until now, only uniform corrosion has been treated. If this were the only form of the electrochemical attack of metals, our industrial society would be relieved of an significant portion of its problems. Not all uniform scales are as protective as passive films. One exception are oxide scales that reach a thickness where they crack because of stresses arising from the difference in the metal-component density between the metal and the oxide. Cracking allows the solution ingress to the bare metal, and corrosion resumes. Zirconium alloys (e.g., Zircaloy) exposed to 300\(^\circ\)C exceptionally-clean water in water-cooled nuclear reactors suffer from this problem.

All structural metals (iron, nickel, chromium, aluminum, titanium, zirconium, etc) are chemically reactive and when exposed to water or air, would much prefer to obey their thermodynamic tendency and convert back to the oxides whence they came. It is only a matter of time that they do so. The challenge is to find ways of deferring this conversion as long as possible. Several means of so doing include:
1. keep the temperature as low as possible. Sometimes high temperatures cannot be avoided.
   (e.g., piping in electric power plants)
2. develop alloys of the metals that are more resistant to corrosion than the elemental metal.
   Adding chromium to iron produces stainless steel, so named because of this property. Alloying
   additions improve the corrosion resistance of pure zirconium metal (see Chap. 17).
3. avoid aggressive anions (e.g., Cl\(^-\)) in the water.
4. Galvanic protection\(^{10}\)

A particularly uncompromising form of attack is called localized corrosion. As the name implies
dissolution of the metal occurs in isolated spots. Also, the direction of the process is into the,
metal, rather than on its surface which is the result of uniform corrosion. There are two distinct
forms of localized corrosion, pitting and crevice corrosion.

15.9.1 Pitting
Pitting is initiated by penetration of the passive film on the surface of the metal by one of three
mechanisms:
1. movement of an aggressive anion (esp. Cl\(^-\)) through the passive scale by diffusion, without
   leaving macroscopic signs. This process is facilitated by high electric potential differences across
   the scale and/or a scale which is amorphous rather than crystalline
2. breakage of the passive scale by any one of a number of causes, including metal
   nonuniformities, grain boundaries, surface roughness which are mimicked by the scale. Weak
   points in the passive scale can progress to local rupture by temperature or stress changes of the
   component. Penetration of reactive anions initiate pit growth
3. adsorption of aggressive anions on the surface of the passive film. Their negative charge pulls
   metal ions from the inside of the film. In addition this mechanism tends to thin the scale locally,
   eventually forming an embryo pit.

There is no established theory that would enable analysis of pit initiation, nor is there any for pit
growth. The reasons are twofold: first, the geometry of pits is so variable that no single shape
fits; second, the diameter-to-depth ratio is near unity, which means that convection due to
moving water influences their growth. These difficulties are illustrated by the large range of pits
observed on metals that are shown in Fig. 15.23.

Perhaps the most astounding corrosion pit was found in the pressure-vessel head (top lid) of the
Davis-Besse nuclear power plant in 2002. A drawing of the head and a sketch of the hole are
shown in Fig. 15.24. A leak of the reactor coolant (high-purity water with boric acid) through
fittings in the control-rod drives initiated the pit. A crust of solid boric acid on the outer surface
of the head hid the corrosive attack from inspection. Over a period of several years, the
concentrated boric acid solution inside the hole generated the pit in the carbon-steel main body
of the pressure-vessel head. Corrosion ceased when the pit reached the stainless-steel liner on the
inner surface of the head. The purpose of this liner is to prevent pitting corrosion of the head
from the high-pressure (15 MPA), high-temperature (300\(^\circ\)C) coolant water with as much as 0.2 M
dissolved H\(_3\)BO\(_3\) filling the inside of the vessel. This gigantic pit is shown in Fig. 15.25.

---

\(^{10}\) Coating a structural metal (e.g., iron) with a sacrificial metal (e.g., zinc) that has a higher standard electrode
potential and so corrodes first
Fig. 15.23 Pits in metals (from Ref. 1). (a) Scanning-tunneling microscope image of a pit on single-crystal Ni in 0.2 M NaCl; (b) optical micrograph of pits on polycrystalline Fe in 0.1 M K$_2$SO$_4$; (c) Scanning-electron micrograph of pits in polycrystalline Ni in 0.2 M NaCl; (d) Optical micrograph of a pit in polycrystalline Ni in 0.1 M K$_2$SO$_4$. 
In view of the enormous range of sizes and shapes and the complexity of the electrochemistry involved, it is no surprise that no quantitative modeling of the growth kinetics of pit corrosion exists. However, detailed qualitative accounts of pitting corrosion can be found in Ref. 2.
Fig. 15.24(b) Corrosion pit. from: Davis-Besse Reactor Vessel Head Degradation Lessons-Learned Task Force Report, September 20, 2002

Fig. 15.25. Corrosion hole (pit) in the pressure-vessel head of the Davis-Besse reactor.
15.9.2 Crevice corrosion

Crevice corrosion, a close cousin of pitting corrosion, occurs in geometrically simple confines, and so is a favorite target of corrosion modelers. This form of corrosion occurs on close-fitting metal parts that are purposely or accidentally exposed to water containing aggressive anions. Typical venues for crevice corrosion include bolts, valves, tube holders (as in steam generators) and welded joints. The flat sides of a crevice are usually the same metal. However, there are crevices formed from two dissimilar metals or with on side a metal and the other a nonmetal. Examples of the latter are a gasket pressed against a flange or a metal piece pressed against a metal coated with an oxide.

As opposed to the variety of irregular shapes of pits, the geometry of crevices is regular and well-suited to analytical modeling. Crevices have a well-defined depth (or length L), a constant width (w), or other simple shape and a straight third dimension with no property or condition variations. The crevice opens to the bulk water at its mouth. A generic crevice is shown in Fig. 15.26.

![Diagram of a crevice in a metal under water](image)

The sequence of steps that drives the corrosion processes inside a water-filled crevice include:

1. O₂ in the water in the crevice is depleted by reaction with the metal. The close proximity of the metal sides means that replenishment of O₂ requires molecular diffusion from the crevice.
mouth through the stagnant water filling the length of the crevice, which is slow compared to the corrosion reactions.

2. Due to the restricted geometry, dissolution of the passive oxide film by reaction (15.55) on the sides and bottom of the crevice builds up the concentration of $M^{2+}$ in the crevice. Because of the slow transport by diffusion to the crevice mouth the metal ions cannot easily escape to the bulk water.

3. The high concentration of metal ions drives hydrolysis reactions, such as $M^{2+} + H_2O \rightarrow M(OH)^+ + H^+$ eventually leading to precipitation of a solid hydroxide or oxide when the ion reaches its solubility limit, e.g., $M(OH)^+ + H_2O \rightarrow M(OH)_2 + H^+$. The net result of these reactions is twofold: i) the solid that precipitates inside the crevice increases the resistance to transport to and from the crevice mouth. ii) $H^+$ ions are produced with consequent decrease in the pH of the solution at the base of the crevice. The period between the time of $O_2$ depletion and generation of a low-pH electrolyte in the crevice by this mechanism is termed *incubation*.

4. The net result of metal dissolution in the crevice is generation of an excess of positive ions ($M^{2+}$ and $H^+$). Unless these are electrically neutralized by anions, dissolution ceases. This is where the "aggressive" anions in the bulk solution come in; if the bulk solution contains a significant concentration of NaCl, for example, $Cl^-$ is available to diffuse down the crevice to neutralize the excess of cations. This permits the corrosion reaction to continue.

5. The high acidity in the crevice moves the solution in the crevice to the low-pH end of the Pourbaix diagram (Fig. 15.1), where the stable corrosion product is $M^{2+}$, not an oxide or hydroxide that would passivate the metal. This can be also be shown for the half-cell reaction $\frac{1}{2}H_2 = H^+ + e^-$ for which Nernst potential is given by Eq (2.77a). According to the note adjacent to Fig 15.14, decreasing the pH moves the cathodic line so that it crosses the metal's anodic polarization curve in the active corrosion zone. As a result, the corrosion mechanism changes from passive to active, with the concomitant increase in the rate of attack of the metal.

6. The electrons produced by the anodic half-cell reactions on the crevice walls or at the bottom of the crevice are conducted through the metal to a surface contacted by the bulk water. Here $O_2$ is readily available to the metal from the bulk water, so the electrons are consumed by the usual cathodic half-cell reaction: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$. For the following analysis$^{11}$, the crevice processes are simplified as shown in Fig. 15.26.

1. The width of the crevice is constant

2. The external surface of the metal and the walls of the crevice corrode in the passive mode, but this source of metal ions in solution is neglected here.

3. Only the bottom of the crevice is actively corroding - this is the locale of the anodic reaction $M \rightarrow M^{2+} + 2e^-$

4. The electrons generated at the crevice bottom are conducted to the external surface of the metal where there is sufficient O$_2$ in the water to permit removal of the electrons by the cathodic reaction.

5. The electric potential (charge) of the metal is $\phi_M$ and that of the bulk solution is $\phi_{\text{bulk}}$. The electrode potential is the difference between the charge on the metal and the charge in the solution. When measured by a standard hydrogen electrode (SHE), as shown in Fig. 15.8, the corrosion potential of the bulk water is: $\varepsilon_{\text{corr}} = \phi_M - \phi_{\text{bulk}}$

6. The corrosion potential is constant throughout the bulk water (outside of the crevice); specifically it persists over the crevice mouth

7. All processes are in steady-state

8. The problem contains seven unknowns, six concentrations:
   a). M$^{2+}$ b.) M(OH)$^+$ c.) Cl$^-$ d.) Na$^+$ e) H$^+$ f.) OH$^-$
   and the electric potential of the solution in the crevice, $\phi_{\text{soln}}$. These variables are functions of depth in the crevice (x) only

9. Precipitation of solid corrosion product by the reaction: M(OH)$^+$ + H$_2$O $\rightarrow$ M(OH)$_2$ + H$^+$ is neglected.

Mass transport of ions in the crevice solution (letter designation in No. 8 above)
The fluxes of the six species in the crevice solution are generated by both concentration gradients and an electric potential gradient. The transport equation for ions in the liquid is the same as that in solids (Eq (15.30). With the electric field replaced by the gradient of the potential in Eq (15.31), the flux of species i is:

$$j_i = -D_i \frac{dC_i}{dx} - u_i C_i \frac{d\phi_{\text{soln}}}{dx}$$

(15.60)

and $u_i$ is the mobility of species i:

$$u_i = D_i \frac{z_i F}{RT}$$

(15.32)

F is Faraday's constant in units of J/mole-Volt. $C_i$ is the molar concentration of i (used in place of [i] for convenience)

Relations between fluxes:
metal (as M$^{2+}$ or M(OH)$^+$):

$$j_M = j_a + j_b$$

(M)

$j_M$ is the flux of ions containing M$^{2+}$, which, as shown below, is obtained from the Tafel equation for active corrosion at the crevice tip.

Water: all hydroxyl (as OH$^-$ or M(OH)$^+$) and H$^+$ originate as H$_2$O:

$$j_b + j_r = j_e$$

(HOH)
Relations between electric potentials

In the bulk water outside the crevice (and at the crevice tip \( x = 0 \)), the electrode potential is:

\[
\varepsilon_{\text{corr}} = \phi_M - \phi_{\text{bulk}} \tag{15.33a}
\]

\( \varepsilon_{\text{corr}} \) is measured by a cell such as the one shown in Fig. 15.8. In the crevice, the electrode potential is:

\[
\varepsilon_{\text{soln}} = \phi_M - \phi_{\text{soln}} = \varepsilon_{\text{corr}} + (\phi_{\text{bulk}} - \phi_{\text{soln}}) \tag{15.33b}
\]

In principle, \( \varepsilon_{\text{soln}} \) could be measured by connecting the liquid in the crevice at depth \( x \) to an SHE via a liquid bridge, but of course this is not possible.

Electrochemistry in the crevice

Substituting Eq (15.60) and Eq (15.33b) into the metal flux relation, Eq (M), gives:

\[
D_a \frac{dC_a}{dx} + D_b \frac{dC_b}{dx} - (u_a C_a + u_b C_b) \frac{d\varepsilon_{\text{soln}}}{dx} = j_M \tag{15.61}
\]

In our simplified crevice-corrosion model, active corrosion takes place only at the crevice tip. Here, the Tafel equation for the metal corrosion current generated by the half-cell reaction \( M \rightarrow M^{2+} + 2e^- \) is obtained from Eq (15.19a) with the overpotential given by \( \varepsilon_{\text{soln}} \) as defined above:

\[
j_M = \left( \frac{i_{\text{soM}}}{2F'} \right) \exp \left( \frac{2.3 \varepsilon_{\text{soln}}(L)}{b_M} \right) \tag{15.62}
\]

where \( \varepsilon_{\text{soln}}(L) \) is the electrode potential at the crevice tip (\( x = L \)). \( j_M \) is negative because dissolution of the metal creates a flux directed away from the crevice tip, or in the negative \( x \) direction. The exchange current density \( i_{\text{soM}} \) is converted to a metal flux by the factor \( 2F' \), where \( F' \) is Faraday's constant in units of Coulombs/mole. The factor of 2 accounts for the valence of the metal in this example. \( j_M \) is independent of \( x \), which means that the metal-containing ions are leaking out of the crevice into the bulk solution.

The second equation of the required seven is obtained by substituting Eq (15.60) into Eq (HOH) and replacing \( \phi_{\text{soln}} \) with \( \varepsilon_{\text{soln}} \) using Eq (15.33b) above. The result is:

\[
D_b \frac{dC_b}{dx} + D_f \frac{dC_f}{dx} - (u_b C_b - u_f C_f) \frac{d\varepsilon_{\text{soln}}}{dx} = D_c \frac{dC_c}{dx} - u_c C_c \frac{d\varepsilon_{\text{soln}}}{dx} \tag{15.63}
\]

For the \( \text{Na}^+ \) and \( \text{Cl}^- \) ions, the flux equations are:

\[
D_c \frac{dC_c}{dx} + u_c C_c \frac{d\varepsilon_{\text{soln}}}{dx} = 0 \tag{15.64a}
\]

and

\[
D_d \frac{dC_d}{dx} - u_d C_d \frac{d\varepsilon_{\text{soln}}}{dx} = 0 \tag{15.64b}
\]

Note: the signs before the mobilities reflect their valences (+ or -).
Because neither of these ions takes part in an electrochemical reaction with the metal at the crevice tip, the right hand sides of these two equations are zero.

Additional flux equations are not necessary because chemical equilibrium relates concentrations. The first reaction is:

\[ M^{2+} + H_2O = M(OH)^+ + H^+ \]

for which the law of mass action is:

\[ K_M = \frac{C_b C_e}{C_a} \]  

(15.65M)

The second is the usual equilibrium between \( H^+ \) and \( OH^- \):

\[ H_2O = H^+ + OH^- \]

for which:

\[ K_W = C_c C_f \]  

(15.65W)

The final equation is a consequence of the requirement of electrical neutrality:

\[ 2C_a + C_b - C_c + C_d + C_e - C_f = 0 \]  

(15.66)

The boundary conditions at the crevice mouth require the concentrations to reflect the composition of the bulk water:

\[ C_a(0) = C_b(0) = 0 \]  

(15.67a)

\[ C_e(0) = C_d(0) = C_{NaCl} \]  

(15.67b)

\[ C_e(0) = 10^{-pH} \]  

(15.67c)

\[ \varepsilon_{soln}(0) = \varepsilon_{corr} \]  

(15.67d)

**Input information**

i) The salt concentration \( C_{NaCl} \) and the pH of the bulk solution.

ii) Equation (15.65W) provides \( C_f(0) \).

iii) The corrosion potential of the bulk water, \( \varepsilon_{corr} \).

iv) The diffusivities of the ionic species in water are reasonably well known, as are v) The equilibrium constants \( K_M \) and \( K_W \).

vi) The shape of the crevice (width \( w \) and length \( L \) )

vii) metal composition and electrochemical properties

**Solution method**

The system of 7 equations is highly nonlinear and must be solved numerically. In addition, trial-and-error is necessary. Specifically, the electrode potential at the bottom of the crevice, \( \varepsilon_{soln}(L) \) is not known \textit{a priori} and must be guessed before the numerical solution can be applied. Sequential guessing of this quantity continues until the guesses converge.
Computational results

Figures 15.27 and 15.28 present typical results of the above analysis of the pertinent features of the crevice. Figure 15.27 shows all ion concentrations as a function of distance from the crevice tip (direction opposite to that of x used above). The OH\(^{-}\) concentration is obtained from the H\(^{+}\) concentration with the aid of Eq 15.65M. The calculations behind the curves in this plot included active corrosion along crevice walls, which was neglected in the model presented in this section. The important features of the curves in Fig. 15.27 are:

(a) sharp changes occur within 0.1 mm of the crevice mouth; by 0.2 mm the curves become essentially flat, indicating no further concentration changes.
(b) The pH is ~ 4.5 over most of the length of the crevice.
(c) The combination of the increases in the concentrations of Fe\(^{2+}\) and Fe(OH)\(^{+}\) along the crevice causes a high Cl\(^{-}\) concentration to provide solution neutrality. Na\(^{+}\) has been pushed out of the crevice.

![Diagram](image_url)

**Fig. 15.27** Concentration profiles in a 2 mm long crevice with the following conditions:

- \(\varepsilon_{\text{mouth}} = 0\) Volts; \(C_{\text{NaCl}} = 0.02\) M; pH = 7. Active corrosion on walls permitted.

From Sharland (footnote 11)

The profiles of the electric potential in the cavity in Fig. 15.28 show a decrease of ~ 0.3 Volts moving from the crevice mouth to the tip, with the drop larger for active walls because of the faster corrosion rate than for passive walls. The consequence of the simultaneous decreases in pH and potential can be seen on the Pourbaix diagram. If the initial condition of the water in the crevice were pH = 7 and a potential of +0.2 V, the point with these coordinates in Fig. 15.1 would lie in the Fe\(_2\)O\(_3\) region. In the crack, the pH drops to 4.3 and the potential to -0.1 V, which moves the point into the Fe\(^{2+}\) region. This is what permits active corrosion on both the crevice tip and the walls.
Fig. 15.27 Potential profiles in a 2 mm long crevice with the following conditions: \( \epsilon_{\text{mouth}} = 0 \) Volts; \( C_{\text{NaCl}} = 0.02 \) M; pH = 7. Active corrosion and passive walls. From Sharland (footnote 11)

**Improvements of the model to account for:**

i) a passive-corrosion flux from the crevice walls that supplies \( M^{2+} \) to the liquid (Eq (15.55));

ii) cathodic half-cell reactions (e.g., \( H^+ + e^- \rightarrow \frac{1}{2} H_2 \)) along the crevice walls

iii) breakdown of passive corrosion on the walls which then undergo active corrosion (e.g. \( M \rightarrow M^{2+} + 2e^- \));

iv) aggressive anions other than \( Cl^- \) in the bulk water (e.g., \( SO_{4}^{2-} \));

v) impeding diffusion of ions in the water in the crevice by precipitation of metal hydroxides (e.g. by the reaction \( M(OH)^+ + H_2O \rightarrow M(OH)_2 + H^+ \)) - the solubilities in 25°C water of ionic species of iron, nickel and chromium are very low;

vi) concentration and electric potential gradients in the bulk water, meaning that Eq (15.67d) is no longer valid.

vii) trapezoidal rather than the rectangular crevice shape shown in Fig. 15.26. This modification is necessary when the method is applied to a crack in the metal rather to a crevice formed by a gap between two metal pieces.

viii) transient crevice corrosion

ix) additional homogeneous reaction than (15.65M) and (15.65W) (e.g., \( M^{2+} + 2Cl^- = MCl_2 \))
References


