3.1.5.2.5 The Complete Diagram

Corresponding series of lines are drawn for Reactions 1–7. Since the reactions are mutually exclusive, they terminate at intersections, as illustrated in the full diagram given in Figure 3.2. The effect of the intersecting lines is to divide the diagram into several domains, within which one or another of the species is considered to be stable with respect to the soluble ion activity corresponding to any chosen set of lines.

Figure 3.2 illustrates the following features of Reactions 1–7:

1. Equilibria for Reactions 1 and 6 depend on \( a_{\text{Fe}^{2+}} \) and \( E \) but are independent of pH, because \( \text{H}^+ \) ions do not participate in the reactions. This yields a family of horizontal lines for the prescribed values of \( a_{\text{Fe}^{2+}} \).

2. Equilibria for Reaction 7 depend on \( a_{\text{Fe}^{3+}} \) and pH but are independent of \( E \), because electrons do not participate in the reaction, that is, it is not an electrode reaction. This yields a family of vertical lines for the prescribed values of \( a_{\text{Fe}^{3+}} \).

3. Equilibria for Reactions 3 and 4 depend on all three of the variables, \( E \), pH and \( a_{\text{Fe}^{2+}} \). This yields families of sloping lines for the prescribed values of \( a_{\text{Fe}^{2+}} \). The slopes are negative because \( \text{H}^+ \) ions are on the left side of the reactions as written, leading to negative pHs.

4. Equilibria for Reactions 2 and 5 depend on \( E \) and pH but are independent of \( a_{\text{Fe}^{2+}} \). This yields single sloping lines. The slopes are also negative for the reason given in 3 above.

**FIGURE 3.2**
Pourbaix diagram for the iron–water system at 25°C.
Labels: 0: \( a_{\text{Fe}^{2+}} = a_{\text{Fe}^{3+}} = 1 \)
-1: \( a_{\text{Fe}^{2+}} = a_{\text{Fe}^{3+}} = 10^{-2} \)
-4: \( a_{\text{Fe}^{2+}} = a_{\text{Fe}^{3+}} = 10^{-4} \)
-6: \( a_{\text{Fe}^{2+}} = a_{\text{Fe}^{3+}} = 10^{-6} \)
Domain for the stability of water shown by dotted lines.
3.1.5.3 The Domain of Stability for Water

Superimposing on a Pourbaix diagram the domain enclosing the combinations of the parameters, \( E \) and \( \text{pH} \) for which water is stable enhances its usefulness. This is defined by lines on the diagram representing the decomposition of water by evolution of hydrogen by Reaction 1 or of oxygen by Reaction 2:

\[
\text{Reaction 1. } \quad 2H^+ + 2e^- = H_2 \quad E^* = 0.000 \text{ V (SHE)} \\
\text{Reaction 2. } \quad \frac{1}{2}O_2 + 2H^+ + 2e^- = H_2O \quad E^* = +1.228 \text{ V (SHE)}
\]

Note that Reaction 2 is an alternative form of the equation introduced earlier:

\[
\frac{1}{2}O_2 + H_2O + 2e^- = 2OH^-
\]

but rewritten in terms of \( H^+ \) ions instead of \( OH^- \) ions, to permit plotting on the potential pH diagram. The gases are evolved against atmospheric pressure, so that \( a_{H_2} = a_{O_2} = 1 \).

Application of the Nernst equation yields:

**Reaction 1**

\[
E = 0.000 - \frac{0.0591}{2} \cdot \log \left( \frac{1}{(a_{H^+})^2} \right) \\
= -0.0591 \text{ pH} \quad (3.26)
\]

**Reaction 2**

\[
E = +1.228 - \frac{0.0591}{2} \cdot \log \left( \frac{1}{(a_{H^+})^2} \right) \\
= 1.228 - 0.0591 \text{ pH} \quad (3.27)
\]

Equations 3.26 and 3.27 are superimposed as dotted lines on Figure 3.2. The two lines enclose a domain within which water is stable. For combinations of potential and pH above the top line, water is unstable and decomposes evolving oxygen. For combinations below the bottom line, it is also unstable and decomposes evolving hydrogen.

3.1.5.4 Application of Pourbaix Diagrams to Corrosion Problems

The first requirement is to select the appropriate lines from the Pourbaix diagram. By international convention, a metal is considered to be actively corroding if the equilibrium activity of a soluble ion derived from it, for example, \( a_{Fe^{2+}} \) or \( a_{Fe^{3+}} \) exceeds \( 10^{-6} \). The diagram selected from Figure 3.2 for \( a_{Fe^{2+}} = a_{Fe^{3+}} = 10^{-6} \), is given in Figure 3.3. Domains of stability for the species with respect to \( a_{Fe^{2+}} = a_{Fe^{3+}} = 10^{-6} \), are labelled.

As explained later in discussing kinetics, a metal exposed to an aqueous medium acquires a potential from coupled electrode processes such as those represented in Equations 3.2 and 3.3 that prevail at its surface. This establishes one of the parameters plotted in a Pourbaix diagram. The other parameter is the pH of the aqueous medium. The two parameters define a point in the diagram and the probable response of the metal is indicated by the nature of the stable species within the domain containing the point, as follows:
1. Domains in which the metal is the stable species so that it is immune to corrosion in the terms for which the diagram is drawn: These domains are zones of immunity.

2. Domains in which a soluble ion is the stable species: Provided that the kinetics are favourable the metal is expected to corrode. These domains are zones of corrosion.

3. Domains in which an insoluble solid, for example, an oxide or hydroxide is the stable species: If the solid product is formed as an adherent layer, impervious to one or more of the reacting species, it can protect the metal. These domains are zones of passivity.

3.1.5.5 Pourbaix Diagrams for Some Metals of Interest in Corrosion

Figures 3.4 to 3.10 give Pourbaix diagrams for the aluminium, zinc, copper, tin, nickel and titanium water systems, with the domain of stability for water superimposed, constructed using the equations given in the Appendix to this chapter.

Species in the aluminium, zinc, tin and nickel systems relevant to corrosion issues are readily identified, but the selection of appropriate species in copper and titanium must take account of the special features of their aqueous chemistries.

3.1.5.5.1 Species in the Copper-Water System

In the Pourbaix diagram of the copper-water system for $a_{\text{Cu}^{2+}} = 10^{-6}$ at 25°C, given in Figure 3.6, the +II oxidation state is represented by both a soluble ion $\text{Cu}^{2+} \text{(aq)}$ and an oxide, $\text{CuO}$, but the +I state is represented only by the oxide $\text{Cu}_2\text{O}$. An associated feature is the retrograde boundary between the domains for $\text{Cu}^{2+}$ and $\text{Cu}_2\text{O}$. This is because the stability of the $\text{Cu}^+$ ion is sensitive to its chemical environment as illustrated in the following calculations showing that the activity of the $\text{Cu}^+ \text{(aq)}$ ion is unsustainable at the value, $10^{-6}$, for which the diagram is prepared, whereas the oxide $\text{Cu}_2\text{O}$ has a domain of stability.
FIGURE 3.4
Pourbaix diagram for the aluminium–water system at 25°C.

\[ a_{\text{Al}^{3+}} = a_{\text{AlO}_2^-} = 10^{-6}. \]

Domain for the stability of water shown by dotted lines.

FIGURE 3.5
Pourbaix diagram for the zinc–water system at 25°C.

\[ a_{\text{Zn}^{2+}} = a_{\text{Zn(OH)}_2} = a_{\text{ZnO}_2^{2-}} = 10^{-6}. \]

Domain for the stability of water shown by dotted lines.
FIGURE 3.6
Pourbaix diagram for the copper–water system at 25°C.

\[ a_{\text{Cu}^{2+}} = 10^{-6}. \]
Domain for the stability of water shown by dotted lines.

FIGURE 3.7
Pourbaix diagram for the tin–water system at 25°C.

\[ a_{\text{Sn}^{2+}} = a_{\text{Sn}^{4+}} = a_{\text{SnO}_3^{2-}} = 10^{-6}. \]
Domain for the stability of water shown by dotted lines.
FIGURE 3.8
Pourbaix diagram for the nickel–water system at 25°C.

\[ a_{\text{Ni}^{2+}} = 10^{-6}. \]

Domain for the stability of water shown by dotted lines.

FIGURE 3.9
Pourbaix diagram for the titanium–water system at 25°C considering anhydrous oxides, TiO, TiO_2 and Ti_2O_3.

Notional activities \[ a_{\text{Ti}^{2+}} = a_{\text{Ti}^{3+}} = a_{\text{Ti}^{4+}} = 10^{-6}. \]

Domain for the stability of water shown by dotted lines.
First consider equilibrium between oxidation states I and II for the ions, Cu\(^+\)\(_{(aq)}\) and Cu\(^{2+}\)\(_{(aq)}\):

\[
2\text{Cu}^{+}\(_{(aq)}\) = \text{Cu}^{2+}\(_{(aq)}\) + \text{Cu} \quad \text{(Reaction 1)}
\]

The Van’t Hoff isobar yields the equilibrium constant from the standard Gibbs free energy:

\[
\ln K = -\frac{\Delta G^o}{RT}
\]

The Gibbs free energy for Reaction 1, \((\Delta G^o)_1\), is the weighted sum of the Gibbs free energies for the reactions:

\[
\text{Cu}^+ + \text{e}^- = \text{Cu} \quad \text{(Reaction 2)}
\]

and:

\[
\text{Cu}^{2+} + 2\text{e}^- = \text{Cu} \quad \text{(Reaction 3)}
\]

that is

\[
(\Delta G^o)_1 = 2(\Delta G^o)_2 - (\Delta G^o)_3
\]

\((\Delta G^o)_2\) and \((\Delta G^o)_3\) are obtained from standard electrode potentials for Reactions 2 and 3, given in Table 3.3, using the relation, \(\Delta E^o = -zFE^*\).

Thus:

\[
(\Delta G^o)_2 = -(1 \times 96490 \times 0.520) = -50180 \text{J}
\]
and:

\[
\Delta G^\circ \text{J} = -(2 \times 96490 \times 0.337) = -65040 \text{ J}
\]

Hence:

\[
\Delta G^\circ \text{J} = 2 \times (-50180) - (-65040) = -35320 \text{ J}
\]

The negative value \(\Delta G^\circ \text{J}\) indicates that the reaction is spontaneous.

Inserting this value and \(R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}\) into the Van't Hoff isobar applied to Reaction 1 at \(T = 25^\circ \text{C} (\equiv 298 \text{ K})\), assuming unit activity for the metallic copper:

\[
\ln K = \ln \left( \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}^+}^2} \right) = \frac{-(-35320)}{8.314 \times 298} = 14.256
\]

whence:

\[
\frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}^+}^2} = 1.55 \times 10^6
\]

Consider a solution in which all of the copper, \(\text{Cu}_\text{f}\), is assumed to be present initially as \(\text{Cu}^+\). On equilibration, every mole of \(\text{Cu}^+\) eliminated produces 0.5 mole of \(\text{Cu}^{2+}\) that is

\[
[\text{Cu}^{2+}] = 0.5(\text{Cu}_\text{f} - [\text{Cu}^+])
\]

where square brackets are concentrations. In dilute solution, \(a_{\text{Cu}^+} \rightarrow [\text{Cu}^+]\) and \(a_{\text{Cu}^{2+}} \rightarrow [\text{Cu}^{2+}]\). Therefore:

\[
0.5(\text{Cu}_\text{f} - [\text{Cu}^+])/[\text{Cu}^+]^2 = 1.55 \times 10^6
\]

Rearranging yields:

\[
3.1 \times 10^6 \times [\text{Cu}^+]^2 + [\text{Cu}^+] - \text{Cu}_\text{f} = 0
\]

which can be solved to give the concentration of \(\text{Cu}^+\) ions in solution for various values of \(\text{Cu}_\text{f}\). For \(\text{Cu}_\text{f} = 10^{-6} \text{ mol dm}^{-3}\), the standard quadratic formula gives:

\[
[\text{Cu}^+] = \left\{ -1 + (1^2 + 4 \times 3.1 \times 10^6 \times 10^{-6})^{1/2} \right\}/[2 \times 3.1 \times 10^6] = 4.3 \times 10^{-7} \text{ mol dm}^{-3}
\]

Since 57% of the \(\text{Cu}^+\) disproportionates at the activity that would be specified in the Pourbaix diagram, it cannot be considered a stable species and no domain can be assigned to it. The disproportionation increases with rising concentrations of copper ions, for example, it is 80% at \(\text{Cu}_\text{f} = 10^{-3} \text{ mol dm}^{-3}\), for which \([\text{Cu}^+] = 0.02 \times 10^{-3} \text{ mol dm}^{-3}\).

Now consider equilibrium between oxidation states I and II for the oxides, \(\text{Cu}_2\text{O}\) and \(\text{CuO}\). A hypothetical disproportionation reaction for \(\text{Cu}^+\) in \(\text{Cu}_2\text{O}\), corresponding to Reaction 1 would be:

\[
\text{Cu}_2\text{O} = \text{CuO} + \text{Cu} \quad \text{(Reaction 4)}
\]

which is half the difference between the reactions:

\[
\text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{e}^- = 2\text{Cu} + \text{H}_2\text{O} \quad \text{(Reaction 5)}
\]
2CuO + 2H⁺ + 2e⁻ = Cu₂O + H₂O  \hspace{1cm} \text{(Reaction 6)}

Proceeding as before, using data from calculations for the copper–water system given in the Appendix to this chapter:

\[ (E' \text{S})(\text{for Reaction 5}) = 0.471 - 0.0591 \text{ p}\text{H (SHE)} \]

\[ (E' \text{S})(\text{for Reaction 6}) = 0.669 - 0.0591 \text{ p}\text{H (SHE)} \]

\[ (\Delta G \text{S})(\text{for Reaction 4}) = ½\{-zFE'_5\} - ½\{-zFE'_6\} \]

\[ = ½\{-2 \times 96490 \times (0.471 - 0.0591 \text{ p}\text{H})\} - ½\{-2 \times 96490 \times (0.669 - 0.0591 \text{ p}\text{H})\} \]

\[ = +19100 \text{ J mol}^{-1} \]

Since all species participating in Reaction 4 are solid substances, assumed pure, all activities are unity and the free energy of the reaction is the standard free energy \[ \Delta G \text{S}. \] Since its value is positive, the reaction is not spontaneous so that there is a domain of stability for Cu₂O.

3.1.5.5.2 Species in the Titanium–Water System

Alternative versions of the Pourbaix diagram for the titanium–water system differ in the state of the oxide species considered, that is, either the anhydrous oxides TiO₂ and Ti₂O₃ or the hydrous oxides derived from them, TiO₂ · H₂O and Ti(OH)₃. These versions are illustrated in Figures 3.9 and 3.10, respectively.

The stability of oxidation states II, III and IV for titanium in compounds and complex ions suggests the possible existence of domains for the simple aquo ions, Ti²⁺, Ti³⁺ and Ti⁴⁺, but in practice, only the trivalent ion Ti³⁺ can exist in aqueous solution and even so it is confined to a narrow potential range in highly acidic media. The energy to form a simple tetravalent ion, Ti⁴⁺, would be prohibitive due to its high charge density. Cations with tetravalent titanium can exist in oxidizing strongly acidic conditions, but only as oxo ions, for example TiO²⁺, which is stabilized by the lower charge density due to its greater size and reduced charge. The tetravalent state can be similarly stabilized in complex ions formed in multicomponent aqueous media that by definition do not appear in diagrams for the binary titanium–water system. It is true that there are notional domains for a divalent aquo ion, Ti²⁺, in the diagrams given in Figures 3.9 and 3.10, but they have no physical reality because they lie well below the domain of stability for water so that there is no aqueous chemistry for this ion.

The principal difference between the diagrams given in Figures 3.9 and 3.10 is that the domain of stability of the passivating anhydrous tetravalent oxide, TiO₂, in Figure 3.9 is much larger than the domain for the corresponding hydrous oxide, TiO₂ · H₂O in Figure 3.10 that is also passivating but which can dissolve in acidic solutions as the oxo ion TiO²⁺, sometimes considered in association with a water molecule and written [Ti(OH)₄]²⁺. Whichever of the diagrams is most appropriate for any particular application is decided empirically from experience and foreknowledge of the prevailing conditions.

The most impressive feature of titanium is the exceptionally wide range of pH and potential over which it can passivate within the domain of stability for water. These characteristics underlie its outstanding corrosion resistance and its suitability for use in severe conditions.
that are considered in greater detail together with its metallurgical characteristics in Chapter 12 and which are related to some marine applications in Chapter 25.

3.1.5.6 Limitations of Pourbaix Diagrams

Pourbaix diagrams can be of great utility in guiding consideration of corrosion and other problems, but they apply only for the conditions assumed in their construction and they are not infallibly predictive because they have limitations, as follows:

1. The diagrams are derived from thermodynamic considerations and yield no kinetic information. There are situations in which zones of corrosion suggest that a metal dissolves and yet it does not, due, for example, to the formation of a metastable solid phase or to kinetic difficulties associated with a complementary cathodic reaction. In extremis, some binary systems include species that are ambiguous or so kinetically inert that they can persist almost indefinitely under conditions in which they are thermodynamically very unstable, thereby defeating the purpose of the diagrams. Fortunately, few such systems are important in the present context except for the chromium–water system, which is considered empirically later in relation to electrodeposited coatings and stainless steels.

2. Domains in which solid substances are considered to be stable species relative to arbitrary soluble ion activities \(<10^{-6}\) give good indications of conditions in which a metal may be passive. Whether particular metals are actually passivated within these nominal domains and to what extent a useful passive condition can extend beyond their boundaries depends on the nature, adherence and coherence of the solid substance. This reservation is considered further in Sections 9.2.1 and 9.2.2 with respect to the development of passivity on aluminium.

3. The diagrams yield information only on the reactions considered in their construction and take no account of known or unsuspected impurities in the aqueous phase or of alloy components in the metal that may modify the reactions. For example, \(\text{Cl}^-\) or \(\text{SO}_4^{2-}\) ions present in solution may attack, modify or replace oxides or hydroxides in domains of passivity, usually diminishing but occasionally enhancing the protective power of these substances. Alloy components can modify surface conditions or introduce microstructural features into the metal that may enhance or destroy passivation according to circumstances.

4. The form and interpretation of a Pourbaix diagram are both temperature dependent, the form because \(T\) appears in Equation 3.10 and the interpretation because pH is temperature dependent, as shown in Table 2.5.

3.2 Kinetics of Aqueous Corrosion

In the long term, the degradation of engineering metals and alloys by corrosion is inevitable and so resistance to it is essentially concerned with the rates of corrosion. Reaction rate theory can be quite complicated and is dealt with in specialized texts*, but the following

* For example, Hinshelwood, cited in Further Reading.