Corroding Metals: Potential-pH (Pourbaix) Diagrams

There are three general reactions by which a metal, M, may react anodically with water:

1. Oxidation to aqueous cations:

   \[ M = M^{n+} + ne^- \]

2. Oxidation to metal oxide or hydroxide:

   \[ M + nH_2O = M(OH)_n + nH^+ + ne^- \]

3. Oxidation to aqueous anions:

   \[ M + nH_2O = MO_n^{-(2n-l)} + 2nH^+ + le^- \]
Cathode reactions Supporting Corrosion

**Hydrogen reduction**

\[
E = E^0 + \frac{0.059}{n} \log \left( \frac{[A]^a}{[B]^b} \right) - \frac{m}{n} 0.059 pH
\]

\[
2H^+ + 2e^- = H_2
\]

\[
E_{H^+/H_2}^0 = E_{H^+/H_2}^0 - 0.059 pH
\]

The above reaction occurs in an acid solution.

An equivalent reaction in neutral or alkaline solutions is:

\[
2H_2O + 2e^- = H_2 + 2OH^- \quad E_{H^+/H_2}^0 = E_{H^+/H_2}^0 - 0.059 pH
\]

\[
E_{H^+/H_2}^0 = 0 - 0.059 pH
\]
Cathode reactions Supporting Corrosion

$$E = E^0 + \frac{0.059}{n} \log \left[ \frac{A}{B} \right]^a - \frac{m}{n} \cdot 0.059 \cdot pH$$

Oxygen reduction (dissolved $O_2$ in the electrolyte)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E_{O_2/H_2O} = E_{O_2/H_2O}^0 - 0.059 \cdot pH$$

The above reaction occurs in an acid solution.

An equivalent reaction in neutral or alkaline solutions is:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad E_{O_2/H_2O} = E_{O_2/H_2O}^0 - 0.059 \cdot pH$$

$$E_{O_2/H_2O} = 1.229 - 0.059 \cdot pH$$
Potential/pH (Pourbaix) Diagram

It turns out to be very convenient to represent the results of all these anodic metal oxidation processes and cathodic reduction process on a map-like “phase diagram”.

The map considers the parameters of voltage and solution pH as parameters and shows the thermodynamically possible electrochemical/corrosion reactions that can occur for a particular metal such as Fe, Al, Cd, Zn, … and water.
Potential/pH (Pourbaix) Diagram

Water

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O} \quad \text{oxygen evolution and acidification} \]

\[ \text{OH}^- + \text{H}^+ = \text{H}_2\text{O} \quad \text{water thermodynamically stable} \]

\[ 2\text{H}^+ + 2\text{e}^- = \text{H}_2 \quad \text{hydrogen evolution and alkalization} \]

\[ E_{\text{O}_2/\text{H}_2\text{O}} = 1.229 - 0.059 \text{pH} \]

\[ E_{\text{H}^+/\text{H}_2} = 0 - 0.059 \text{pH} \]
Potential/pH (Pourbaix) Diagram

**Generic diagram for a metal**

- **Corrosion**: soluble ions of the metal are stable.
- **Passivation**: oxides are stable.
- **Immunity**: reduced form of the metal is stable.

The diagram illustrates the stability regions for different potential (E(V)) and pH values.
Potential/pH (Pourbaix) Diagram

Pourbaix diagram for Al

Reaction 1: Metal oxidizes to aqueous cations

\[ M = M^{n+} + ne^- \]
\[ Al = Al^{3+} + 3e^- \]

\[ e_{Al/Al^{3+}} = e^0 + \frac{0.059}{n} \log \left( \frac{A}{B} \right)^a - \frac{m}{n} \cdot 0.059 \cdot pH \]

\[ e_{Al/Al^{3+}} = -1.662 + \frac{0.059}{3} \log(Al^{3+}) \]

Independent of pH since no H\(^+\) is involved.

Only depends on Al\(^{3+}\) activity.
Potential/pH (Pourbaix) Diagram

Pourbaix diagram for Al

\[ E = E^0 + \frac{0.059}{n} \log \left( \frac{[A]^a}{[B]^b} \right) - \frac{m}{n} 0.059 \text{pH} \]

Reaction 2: Metal reacts to metal hydroxide or oxide

\[ M + nH_2O = M(OH)_n + nH^+ + ne^- \]

\[ 2Al + 3H_2O = Al_2O_3 + 6H^+ + 6e^- \]

\[ E_{Al/Al_2O_3} = -1.55 - 0.059 \text{pH} \]

At higher pH \( Al_2O_3 \) is formed. At lower pH \( Al_2O_3 \) chemically dissolves to \( Al^{3+} \)

Intersection depends on \( Al^{3+} \) activity (dashed lines are portions of the reactions with no significance)
Potential/pH (Pourbaix) Diagram

Pourbaix diagram for Al

Chemical equilibrium between $\text{Al}_2\text{O}_3$ and $\text{Al}^{3+}$

$$2 \text{Al}^{3+} + 3 \text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 6 \text{H}^+$$

$$\Delta G^o = \mu^o_{\text{Al}_2\text{O}_3} + 6\mu^o_{\text{H}^+ (aq)} - 2\mu^o_{\text{Al}^{3+}} - 3\mu^o_{\text{H}_2\text{O}}$$

$$\Delta G = -65019 \ J = -2.303RT \log K$$

$$\log K = -11.4$$

$$K = \frac{[\text{H}^+]^6}{[\text{Al}^{3+}]^2}$$
Pourbaix diagram for Al

The chemical reaction rate constant for

$$2Al^{3+} + 3H_2O = Al_2O_3 + 6H^+$$

$$K = \frac{(H^+)^6}{(Al^{3+})^2} = 10^{-11.4}$$

Independent of potential

$$\log K = 6\log(H^+) - 2\log(Al^{3+}) = -6pH - 2\log(Al^{3+})$$

$$pH = -1/6 \log K - 2\log(\text{Ag}^{3+})$$

$$K = 10^{-11.4}; [\text{Ag}^{3+}] = 10^{-6} \ M$$

pH = 3.9
Potential/pH (Pourbaix) Diagram

Pourbaix diagram for Al

Reaction 3: Metal reacts to form soluble aqueous anions

\[
E = E^0 + \frac{0.059}{n} \log \left( \frac{[A]^n}{[B]^m} \right) - \frac{m}{n} 0.059 \text{pH}
\]

\[
Al + 2H_2O = AlO_2^- + 4H^+ + 3e^-
\]

\[
E_{Al/AlO_2^-} = -1.262 + 0.020 \log(AlO_2^-) - 0.079 \text{pH}
\]

At higher pH, Al$_2$O$_3$ dissolves to AlO$_2^-$

\[
Al_2O_3 + H_2O = 2AlO_2^- + 2H^+ \quad K = (H^+)^2 (AlO_2^-)^2 = 10^{-29.2}
\]

\[
pH = 14.6 + \log[AlO_2^-]
\]