

Electrochemical kinetics of corrosion

We now have a tool to predict if the corrosion reaction is possible, but it would also be handy to predict how fast the reaction will proceed. In theory, Faraday's law can be used do this. Faraday's first law stated as follows.

$$m = Zit$$

where: m = mass of metal lost to corrosion (grams)

I = corrosion current (amps)

z = electrochemical equivalent = $\frac{a}{nF}$ (g/A - s)

a = atomic weight of corroding metal (grams)

n = electrons transferred in oxidation reaction (mol e^-)

F = Faraday's constant (96,500 A - s/mol e^-)

t = time of reaction (seconds)

Example: A steel coupon with an anode surface area of 1000 cm² is placed in an electrolyte. The corrosion current is measured to be 1 mA. What mass of steel will be lost in 6 hours? What is the corrosion rate in $\mu\text{g}/\text{cm}^2/\text{day}$? In mpy? Assume valence of 2.

Solution

$$m = Izt$$

$$I = 0.001\text{A}$$

$$z = \frac{a}{nF} = \frac{55.847\text{g}}{(2 \text{ mol } e^-)(96,500 \text{ A - s/mol } e^-)} = 2.89 \times 10^{-4} \text{ g/A - s}$$

$$t = (6 \text{ hr}) \left(\frac{60 \text{ min}}{1 \text{ hr}} \right) \left(\frac{60 \text{ s}}{1 \text{ min}} \right) = 21,600 \text{ s}$$

$$m = (0.001A)(2.89 \times 10^{-4} \text{ g/A} \cdot \text{s})(21,600\text{s})$$

$$m = 6.255 \times 10^{-3} \text{ g}$$

To find the corrosion rate in $\mu\text{g}/\text{cm}^2/\text{day}$, first divide by anode area and time.

$$\text{rate} = \frac{m}{At} = \frac{6.255 \times 10^{-3} \text{ g}}{(1000 \text{ cm}^2)(21,600\text{s})} \left(\frac{10^6 \mu\text{g}}{1 \text{ g}} \right) \left(\frac{3600\text{s}}{1 \text{ hr}} \right) \left(\frac{24 \text{ hr}}{1 \text{ day}} \right) = 25.02 \mu\text{g}/\text{cm}^2/\text{day}$$

To find the corrosion rate in mpy, divide by the metal density.

$$\text{rate} = \frac{25.02 \mu\text{g}/\text{cm}^2/\text{day}}{\rho} = \frac{25.02 \mu\text{g}/\text{cm}^2/\text{day}}{7.20 \times 10^6 \mu\text{g}/\text{cm}^3} \left(\frac{365 \text{ days}}{\text{yr}} \right) \left(\frac{1 \text{ mil}}{2.54 \times 10^{-3} \text{ cm}} \right)$$

$$\text{rate} = 0.499 \text{ mpy}$$

The following table gives density, atomic mass, valence, and corrosion rate for various metals.

Corrosion data for various metals [from Swain Classnotes (1996)].

Element	Atomic Mass (g/mole)	Valence	Electrochemical Equivalent (g/coulomb)	Corr. rate equivalent to 1 $\mu\text{A}/\text{cm}^2$ (mm/yr)	Density (g/cm^3)
Magnesium	24.31	2	1.26E-04	0.023	1.74
Zinc	65.38	2	3.39E-04	0.015	7.13
Aluminum	26.98	3	9.30E-05	0.011	2.72
Iron	55.85	2	2.89E-04	0.013	7.20
Iron	55.85	3	1.93E-04	0.087	7.20
Copper	63.54	1	6.58E-04	0.023	8.94
Copper	63.54	2	3.29E-04	0.012	8.94
Nickel	58.71	2	3.04E-04	0.011	8.89

Corrosion thermodynamics

As we have observed, corrosion reactions inevitably involve electron transfer. For this reason, the reactions may be considered electrochemical in nature. Thermodynamics can provide a basis for the understanding of the energy changes associated with the corrosion reaction. It can, in general, predict when corrosion is possible. Thermodynamics cannot predict corrosion rates. The rate at which the reaction proceeds is governed by kinetics.

The Gibb's free energy, given by the following equation, provides us a tool with which to predict if a corrosion reaction is thermodynamically possible:

$$\Delta G = -nFE$$

where: ΔG = Gibb's free energy (Joules)

n = electrons transferred in oxidation reaction (mol e^-)

F = Faraday's constant (96,500 J/v - mol e^-)

E = Standard emf potential = $E_{\text{ox}}^{\circ} + E_{\text{red}}^{\circ}$ (volts)

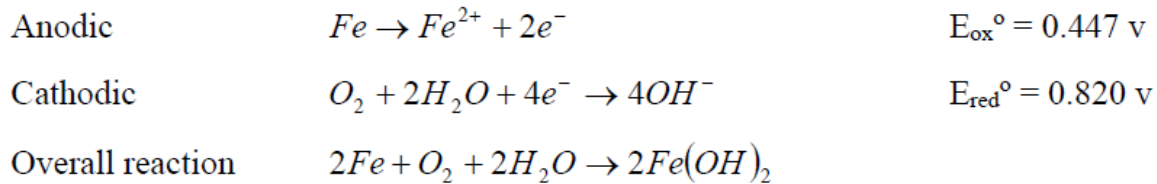
E_{red}° = Standard potential for cathode half cell (volts)

E_{ox}° = Standard potential for anode half cell (volts)

If ΔG is positive, the reaction will not proceed. If ΔG is negative, the reaction is possible.

Example: Steel is placed in aerated seawater with a neutral pH. Is corrosion of the steel possible, why? (Assume valence of 2)

Solution



$$E = E_{ox}^{\circ} + E_{red}^{\circ}$$

$$E = 1.267 \text{ v}$$

$$\Delta G = -nFE$$

$$\Delta G = -(2 \text{ mol } e^{-})(96,500 \text{ J/v} \cdot \text{mol } e^{-})(1.267 \text{ v})$$

$$\Delta G = -244,531 \text{ J}$$

negative sign indicates corrosion reaction, as written, is possible

It should be stated that potential values of a metal are modified by the environment. Concentrations of anodic and cathodic reactants will alter the balance between the oxidation and reduction reactions. The Nernst equation allows us to calculate metal potentials under differing metal ion or oxidation/reduction conditions. The Nernst equation may be stated as follows:

$$E_{cell} = E^{\circ} + 2.3 \frac{RT}{nF} \log_{10} \frac{[oxid.]}{[red.]}$$

where : E_{cell} = Cell potential under environmental conditions (volts)

E° = Standard reduction potential @ 25⁰ C and unit activity (volts)

R = Universal gas constant (8.3143 J/mol °K)

T = Absolute temperature (degrees Kelvin)

n = electrons transferred in the reaction (mol e⁻)

F = Faraday's constant (96,500 coulombs/mol e⁻)

$[oxid.]$ = activity of oxidized species (M)

$[red.]$ = activity of reduced species (M)

At standard temperature and pressure (25°C and 760mm Hg) this may be simplified to the following:

$$E_{cell} = E^{\circ} + \frac{0.059}{n} \log_{10} \frac{[oxid.]}{[red.]}$$

Derivation of Nernst Equation

Consider a metal in contact with its own salt aqueous solution. Reactions of metal losing an electron to become an ion and the ion gaining electron to return to the atomic state are equally feasible and are in an equilibrium state.



In the reduction reaction, 'n' moles of an electron is taken up by the ion against a reduction potential of E_{red} .

1. The work done in the movement of electron

$$W_{red} = nFE_{red}$$

Where,

- F is Faraday = 96485 coulomb = electrical charge carried by one mole of electrons

2. Change in the Gibbs free energy is an indication of the spontaneity and it is also equal to the maximum useful work (other than volume expansion) done in a process.

Combining work done and Gibbs free energy change:

$$W_{\text{red}} = nFE_{\text{red}} = -\Delta G \quad \text{or} \quad \Delta G = -nFE_{\text{red}}$$

3. Change in the free energy at standard conditions of 298K and one molar /one atmospheric pressure conditions is ΔG° . From the above relation, it can be written that

$$\Delta G^\circ = -nFE_{\text{red}}^\circ$$

Where,

- E_{red}° is the reduction potential measured at standard conditions.

4. During the reaction, concentration keeps changing and the potential also will decrease with the rate of reaction.

To get the maximum work or maximum free energy change, the concentrations have to be maintained the same. This is possible only by carrying out the reaction under a reversible equilibrium condition.

For a reversible equilibrium reaction, vant Hoff isotherm says:

$$\Delta G = \Delta G^\circ + RT \ln K$$

Where,

- K is the equilibrium constant
-

- $K = \text{Product/Reactant} = [M]^n/[M]^{n+}$
- R is the Gas constant = 8.314 J/K mole
- T is the temperature in Kelvin scale.

5. Substituting for free energy changes in ant Hoff equation,

$$-nFE_{\text{red}} = -nFE_{\text{red}}^{\circ} + RT \ln [M]/[M]^{n+} = -nFE_{\text{red}}^{\circ} + 2.303 RT \log [M]^n/[M]^{n+}$$

Dividing both sides by $-nF$,

$$E_{\text{red}} = E_{\text{red}}^{\circ} - \frac{2.303RT}{nF} \log \frac{[M]^+}{[M]^{n+}}$$

Or
$$EM^{n+}/M = E^{\circ}M^{n+}/M - \frac{2.303RT}{nF} \log \frac{[M]^+}{[M]^{n+}}$$

The activity of the metal is, always considered as equal to unity.

This relation connecting reduction potential measurable at conditions other than standard conditions to the standard electrode potential is the Nernst equation.

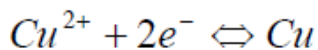
For reaction conducted at 298K but at different concentrations, Nernst Equation is;

$$\begin{aligned} EM^{n+}/M &= E^{\circ}M^{n+}/M - \frac{2.303 \times 8.314 \times 293}{n \times 96485} \log \frac{1}{[M]^{n+}} \\ &= E^{\circ}M^{n+}/M - \frac{0.0591}{n} \log \frac{1}{[M]^{n+}} \end{aligned}$$

The Nernst equation can also be written for each half cell as is shown in the following metal ion concentration cell example.

Example: A circular copper coupon is rotated in seawater. A gradient in the metal ion concentration is set up on the disk surface. On periphery of the disk copper ion concentration is 0.001 M. Near the center of the disk the copper ion concentration is 10 M. What are the potentials of anodic and cathodic sites on copper? Where will the metal loss occur? Assume STP.

In this case we find the standard EMF for the following equation:



$$E^{\circ} = 0.342 \text{ volts}$$

$$E_{\text{outside}} = E^{\circ} + \frac{0.059}{n} \log_{10} \left(\frac{[10^{-3}]}{[1]} \right)$$

$$E_{\text{center}} = E^{\circ} + \frac{0.059}{n} \log_{10} \left(\frac{[10^1]}{[1]} \right)$$

$$E_{\text{outside}} = 0.342\text{v} + \frac{0.059}{2 \text{ mol } e^{-}} \log_{10} (10^{-3}) = 0.2535\text{v}$$

$$E_{\text{center}} = 0.342\text{v} + \frac{0.059}{2 \text{ mol } e^{-}} \log_{10} (10^1) = 0.3715\text{v}$$

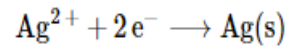
Metal will be lost from the outside of the disk (it is more negative)

$$E_{\text{overall}} = E_{\text{center}} - E_{\text{outside}} = 0.118\text{v}$$

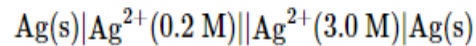
Example:

1) Calculate cell potential for a concentration cell with two silver electrodes with concentrations 0.02 M and 3.0 M.

Reaction:



Cell Diagram:



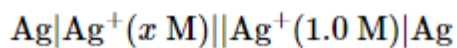
Nernst Equation:

$$E = E^{\circ} - \frac{0.0592}{2} \log \frac{0.02}{3.0}$$

** $E^{\circ} = 0$ for concentration cells

$$E = 0.0644\text{ V}$$

2) Calculate the concentration of the oxidation, given the equation below and a cell potential of 0.26 V



$$E = E^{\circ} - \frac{0.0592}{1} \log \frac{x}{1.0}$$

$$0.26 = 0 - 0.0592 \log \frac{x}{1.0}$$

$$4.362 = -\log(x) + \log(1.0)$$

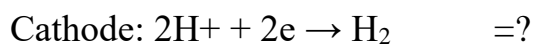
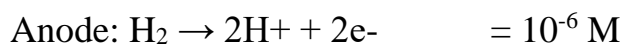
$$\log(x) = \log(1.0) - 4.362$$

$$x = 4.341 \times 10^{-5}\text{ M}$$

Example: cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The emf of the cell is 0.118 volt at 25° C. Calculate the concentration of hydrogen ions at the positive electrode.

Solution

The cell may be represented as



$$E_{\text{cell}} = 0.0592/2 \log [10^{-6}] / ([\text{H}^+]_{\text{cathode}})^2$$

$$0.118 = (0.0591) \log 10^{-6} / ([\text{H}^+])$$

$$\log 10^{-6} / [\text{H}^+]_{\text{cathode}} = 0.118/0.0591$$

$$\log 10^{-6} / [\text{H}^+]_{\text{cathode}} = 2$$

$$10^{-6} / [\text{H}^+]_{\text{cathode}} = 10^2$$

$$[\text{H}^+]_{\text{cathode}} = 10^{-8} \text{ M}$$

Example: The standard electrode potential of zinc ions is 0.76V. What will be the potential of a 2M solution at 300K?

Solution:

The Nernst equation for the given conditions can be written as follows;

$$E_{\text{M}^{n+}/\text{M}} = E^\circ - [(2.303RT)/nF] \times \log 1/[\text{Mn}^+]$$

Here,

- $E^\circ = 0.76\text{V}$
- $n = 2$
- $F = 96500 \text{ C/mole}$
- $[\text{Mn}^+] = 2 \text{ M}$
- $R = 8.314 \text{ J/K mole}$
- $T = 300 \text{ K}$

Substituting the given values in Nernst equation we get,

$$E_{\text{Zn}^{2+}/\text{Zn}} = 0.76 - [(2.303 \times 8.314 \times 300) / (2 \times 96500)] \times \log 1/2 = 0.76 - [0.0298 \times (-0.301)]$$

$$= 0.76 + 0.009 = \mathbf{0.769V}$$

Therefore, the potential of a 2M solution at 300K is 0.769V.

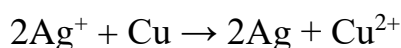
Example: The Cu^{2+} ion concentration in a copper-silver electrochemical cell is 0.1M. If $E^\circ(\text{Ag}^+/\text{Ag}) = 0.8\text{V}$, $E^\circ(\text{Cu}^{2+}/\text{Cu}) = 0.34\text{V}$, and Cell potential (at 25°C) = 0.422V, find the silver ion concentration.

Solution

Here, the silver electrode acts as a cathode whereas the copper electrode serves as the anode. This is because the standard electrode potential of the silver electrode is greater than that of the copper electrode. The standard electrode potential of the cell can now be calculated, as shown below.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.8\text{V} - 0.34\text{V} = 0.46\text{V}$$

Since the charge on the copper ion is +2 and the charge on the silver ion is +1, the balanced cell reaction is:



Since two electrons are transferred in the cell reaction, $n = 2$. Now, the Nernst equation for this electrochemical cell can be written as follows.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0592/2) \times \log(0.1/[\text{Ag}^+])$$

$$0.422\text{V} = 0.46 - 0.0296 \times (-1 - \log[\text{Ag}^+])$$

$$\text{Therefore, } -\log[\text{Ag}^+] = 1.283 + 1 = 2.283$$

$$\text{Or, } \log[\text{Ag}^+] = -2.283$$

$$[\text{Ag}^+] = \text{antilog}(-2.283) = \mathbf{0.00521\text{ M}}$$