Battery: Zn-Cu cell ("Daniell Cell")

At anode: oxidation (loss of electrons)
\[ \text{Zn} \rightarrow \text{Zn}^{++} + 2\text{e}^- \]

At cathode: reduction (gain of electrons)
\[ \text{Cu}^{++} + 2\text{e}^- \rightarrow \text{Cu} \]

- Zn electrode is eaten away as Cu electrode is plated.
- Screen allows SO₄²⁻ to pass, so charge neutrality is maintained, but it blocks Cu⁺⁺ from reaching Zn electrode. Otherwise direct transfer of electrons from Zn to Cu would short out the cell.
- The cell continues running until either Zn electrode is depleted or Cu⁺⁺ in solution is consumed.

Suppose switch is open, so no current flows. Consider the anode. The Zn atoms in electrode are in diffusive equilibrium with the Zn⁺⁺ ions in the electrolyte; hence both have the same total chemical potential.

\[ \mu(\text{Zn})_{(electrode)} \]
\[ \mu(\text{Zn}^{++})_{(electrolyte)} \]

But the internal chemical potentials are not equal. Zn atoms in metal electrode have higher \( \mu \) than Zn⁺⁺ ions in electrolyte.
What happens is that charge accumulates at the surface of an electrode, so there is an electrostatic potential difference between electrode and electrolyte.

\[(\mu_{\text{tot}})^{\text{electrode}} = (\mu_{\text{m+}} + 2eV)^{\text{electrode}} = (\mu_{\text{m+}} + 2eV)^{\text{solution}} = (\mu_{\text{tot}})^{\text{solution}}\]

\[\Rightarrow (\mu_{\text{m+}})^{\text{electrode}} - (\mu_{\text{m+}})^{\text{solution}} = 2e(V)^{\text{solution}} - 2e(V)^{\text{electrode}}\]

\[
\begin{align*}
\mu(Cu^{+2}) & \quad \text{The internal chemical potential difference favors } Cu^{+2} \text{ ions plating electrode, but the electrostatic potential step favors } Cu^{+2} \text{ staying in solution.}

\mu(Cu^{+2}) & \quad \mu(Cu) \quad (2eAV) \\
\mu_{\text{total}} & \quad (\mu_{\text{total}}) \\
(\text{electrode}) & \quad (\text{electrolyte})
\end{align*}
\]

Similarly, at the cathode, the internal chemical potential difference favors \(Cu^{+2}\) ions plating electrode, but the electrostatic potential step favors \(Cu^{+2}\) staying in solution.

Equilibrium is established at each electrode. In electrolyte, electrostatic potential is constant (no current flows).

The half-cell potentials are:

\[\Delta V_+ = 0.76 \text{ V (} Cu \text{)}\]
\[\Delta V_- = 0.34 \text{ V (} Cu\text{)}\]

Total potential difference between electrodes:

\[\Delta V = \Delta V_- + \Delta V_+ = 1.10 \text{ V}\]

The half-cell potentials drive current when switch closes.
Carbon Monoxide Poisoning

Adsorption site on hemoglobin (Hb) molecule can bind either O₂ molecule or CO molecule, but CO is more deeply bound:

\[
\frac{E_{CO} - E_{O2}}{\gamma} = -6.8 \text{ at } 37^\circ C
\]

(blood temperature).

The Hb site is system of the O₂ and CO in air as reservoir R, treated as ideal gas, with activity:

\[
\lambda = e^{n/\gamma} = n_{CO}/n_{O2} \Rightarrow \frac{n_{CO}}{n_{O2}} = \frac{1}{\lambda}
\]

Gibbs factor:

Site vacant: 1
Site binds O₂: \(X_{O2} = \lambda_{O2} e^{-E_{O2}/\gamma}\)
Site binds CO: \(X_{CO} = \lambda_{CO} e^{-E_{CO}/\gamma}\)

\[
P(\text{vacant}) = \frac{1}{1 + X_{O2} + X_{CO}}
\]

\[
P(O_{2}) = \frac{X_{O2}}{1 + X_{O2} + X_{CO}}
\]

\[
P(CO) = \frac{X_{CO}}{1 + X_{O2} + X_{CO}}
\]

Suppose \(n_{CO} = 0\). Fully oxygenated blood has \(P/\gamma = 0.9\)

\[
\Rightarrow P_{O2} = \frac{0.9}{1 + X_{O2}} \Rightarrow X_{O2} = \frac{P_{O2}}{1 - P_{O2}} = 0.9
\]

For what CO concentration will we have

\[P_{CO} = P_{O2}?\]
\[
\frac{PCO}{PO_2} = \frac{X_{CO}}{XO_2} = \frac{N_{CO}}{N_{O_2}} e^{(-E_{CO} - E_{O_2})/\gamma} = 1
\]

\[
\Rightarrow \frac{N_{CO}}{N_{O_2}} = e^{(E_{CO} - E_{O_2})/\gamma} = e^{-6.8} = \frac{1}{900}
\]

In this case, \( PO_2 = PCO = \frac{9}{1+9+9} = \frac{9}{19} = .47 \).

You'll get a headache.

If the concentration of CO is 10 times higher:

\[
\frac{N_{CO}}{N_{O_2}} = 90 \Rightarrow \frac{X_{CO}}{XO_2} = 10 \Rightarrow PO_2 = \frac{9}{1+9+90} = .09.
\]

You'll die in a couple of hours.

If the concentration of CO is

\[
\frac{N_{CO}}{N_{O_2}} = 18 \Rightarrow \frac{X_{CO}}{XO_2} = 50 \Rightarrow PO_2 = \frac{9}{1+9+180} = .02.
\]

You'll die in a couple of minutes.