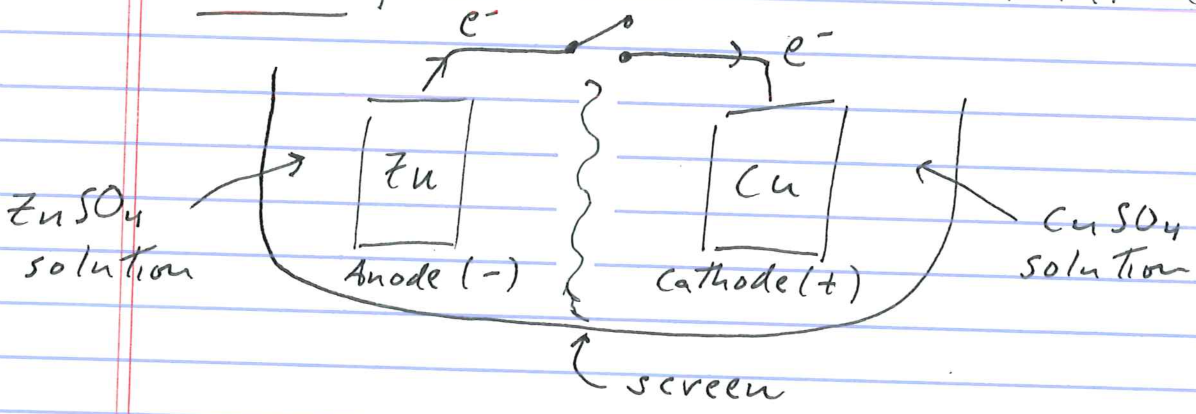
Battery: Zn-Cu cell ("Daniell Cell")



At anode: oxidation (loss of electrons)

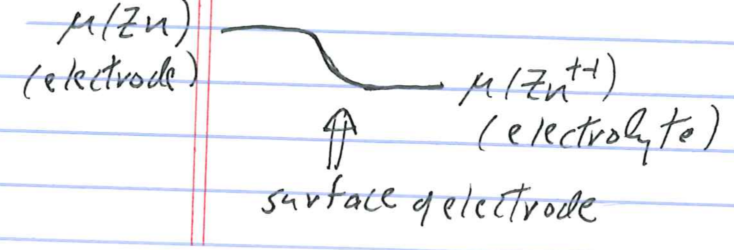
$$Zn \rightarrow Zn^{++} + 2e^-$$

At cathode: reduction (gain of electrons)

$$Cu^{++} + 2e^- \rightarrow Cu$$

- Zn electrode is eaten away as Cu electrode is plated.
- Screen allows SO_4^{--} 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.

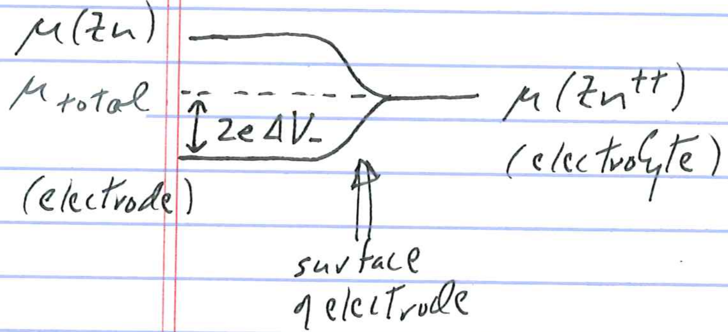


But the internal chemical potentials are not equal. Zn atoms in metal electrode have higher μ than Zn^{++} ions in electrolyte.

What happens is that charge accumulates at the surface of electrode, so there is an electrostatic potential difference between electrode and electrolyte.

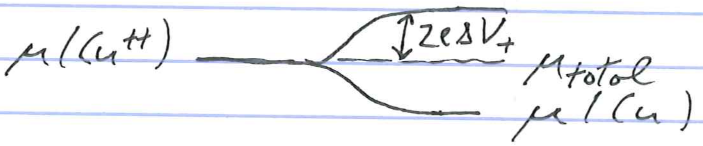
$$(\mu_{tot})_{electrode} = (\mu_{int} + 2eV)_{electrode} = (\mu_{int} + 2eV)_{solution} = (\mu_{tot})_{soln.}$$

$$\Rightarrow (\mu_{int})_{electrode} - (\mu_{int})_{solution} = 2e(V)_{soln} - 2e(V)_{electrode}$$

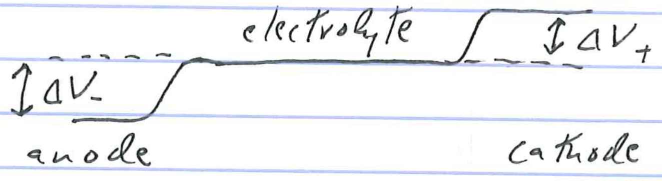


The internal chemical potential difference favors Zn atoms dissolving and joining electrolyte, but electrostatic potential step favors Zn staying in electrode.

Similarly, at the cathode, the internal chem. potential difference favors Cu⁺⁺ ions plating electrode, but the electrostatic potential step favors Cu⁺⁺ staying in solution.



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



The "half-cell potentials" are

$\Delta V_- = 0.76\,V$ (Zn)

$\Delta V_+ = 0.34\,V$ (Cu)

Total potential difference between electrodes, $\Delta V = \Delta V_- + \Delta V_+ = 1.10\,V$ drives current when switch closes.

Carbon Monoxide Poisoning

Adsorption site on hemoglobin (Hb) molecule can bind either O_2 molecule or CO molecule, but CO is more deeply bound:

$$\frac{\varepsilon_{CO} - \varepsilon_{O_2}}{\tau} = -6.8 \quad \text{at } 37^\circ C$$

(body temperature).

The Hb site is system $\mathcal{S}$, the O_2 and CO in air are reservoir $\mathcal{R}$, treated as ideal gas, with activity

$$\lambda \equiv e^{\mu/\tau} = n/n_Q \Rightarrow \frac{\lambda_{CO}}{\lambda_{O_2}} = \frac{n_{CO}}{n_{O_2}}$$

Gibbs factor:

Site vacant: 1

Site binds O_2: $X_{O_2} = \lambda_{O_2} e^{-\varepsilon_{O_2}/\tau}$

Site binds CO: $X_{CO} = \lambda_{CO} e^{-\varepsilon_{CO}/\tau}$

$$\Rightarrow \mathcal{Z} = 1 + X_{O_2} + X_{CO}$$

$$P(\text{vacant}) = \frac{1}{1 + X_{O_2} + X_{CO}}$$

$$P(O_2) = \frac{X_{O_2}}{1 + X_{O_2} + X_{CO}}$$

$$P(CO) = \frac{X_{CO}}{1 + X_{O_2} + X_{CO}}$$

Suppose $n_{CO} = 0$. Fully oxygenated blood has $P(O_2) = .9$

$$\Rightarrow P_{O_2} = .9 = \frac{X_{O_2}}{1 + X_{O_2}} \Rightarrow X_{O_2} = \frac{P_{O_2}}{1 - P_{O_2}} = 9$$

For what CO concentration will we have $P_{CO} = P_{O_2}$?

$$\frac{P_{CO}}{P_{O_2}} = \frac{X_{CO}}{X_{O_2}} = \frac{n_{CO}}{n_{O_2}} e^{-(\varepsilon_{CO} - \varepsilon_{O_2})/\tau} = 1$$

$$\Rightarrow \quad \frac{n_{CO}}{n_{O_2}} = e^{(\varepsilon_{CO} - \varepsilon_{O_2})/\tau} = e^{-6.8} = \frac{1}{900}$$

In this case, $P_{O_2} = P_{CO} = \frac{9}{1+9+9} = \frac{9}{19} = .47.$

You'll get a headache.

If the concentration of CO is 10 times higher:

$$\frac{n_{CO}}{n_{O_2}} = \frac{1}{90} \Rightarrow \frac{X_{CO}}{X_{O_2}} = 10 \Rightarrow P_{O_2} = \frac{9}{1+9+90} = .09.$$

You'll die in a couple of hours.

If the concentration of CO is

$$\frac{n_{CO}}{n_{O_2}} = \frac{1}{18} \Rightarrow \frac{X_{CO}}{X_{O_2}} = 50 \Rightarrow P_{O_2} = \frac{9}{1+9+450} = .02.$$

You'll die in a couple of minutes.