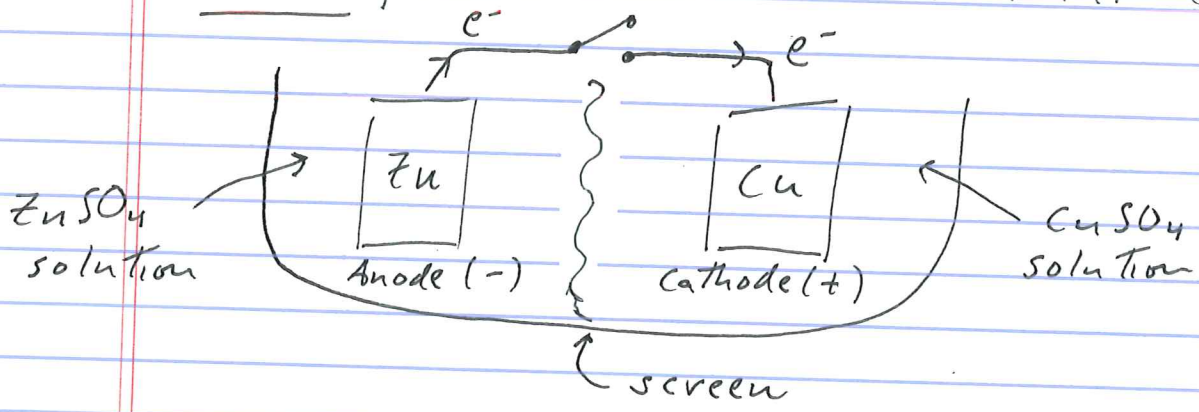
Battery: Zn-Cu cell ("Daniell cell")



At anode: oxidation (loss of electrons)

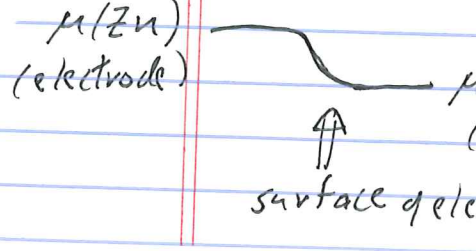
$$Zn \rightarrow Zn^{++} + 2e^-$$

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.

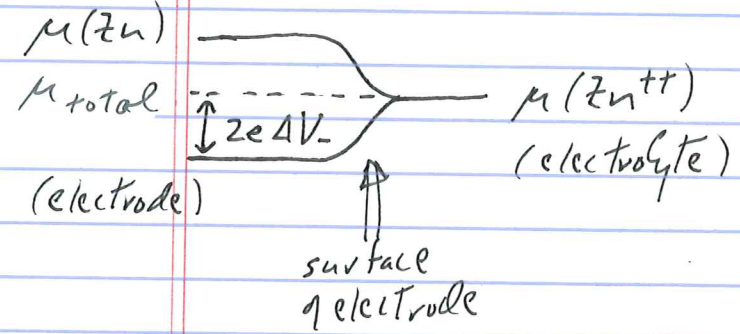


But the internal chemical potentials are not equal. Zn atoms in metal electrode have higher μ than Zn^{++} ions in electrolyte.

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

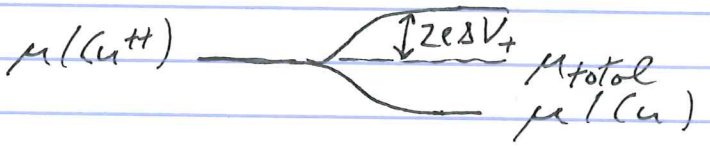
$$(\mu_{tot})_{electrode} = (\mu_{int} + 2eV)_{electrode} = (\mu_{int} + 2eV)_{solution} = (\mu_{tot})_{soln.}$$

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

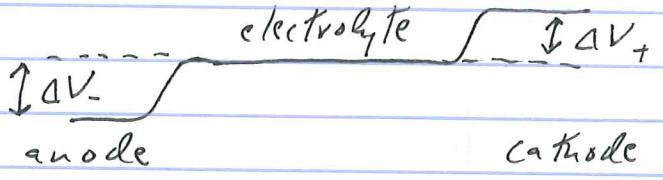


The internal chemical potential difference favors Zn atoms dissolving and joining electrolyte, but electrostatic potential step favors Zn staying in electrode.

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).



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

"half-cell potentials" are
$\Delta V_- = 0.76\,V$ (Zn)
$\Delta V_+ = 0.34\,V$ (Cu)