

Topic 6L - Galvanic Cells

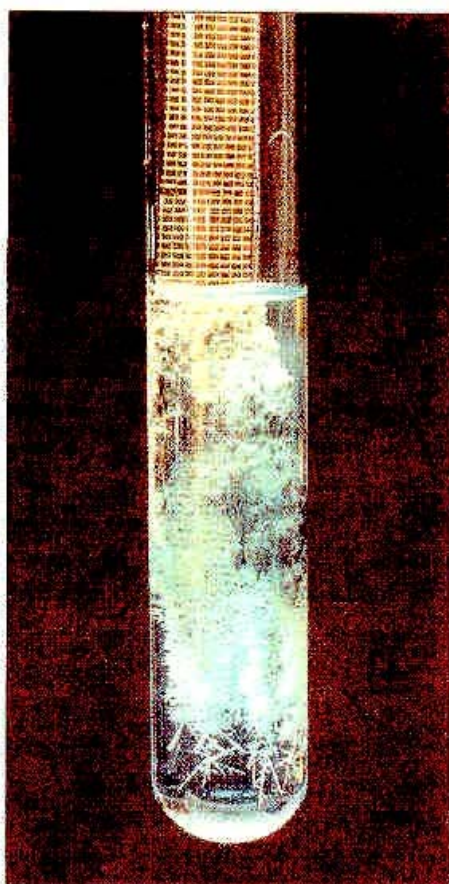


FIGURE 6.7 When a piece of copper screen is inserted into a solution of silver nitrate, silver forms in a tree-like structure and the solution turns blue as Cu^{2+} ions form.
(Charles D. Winters)



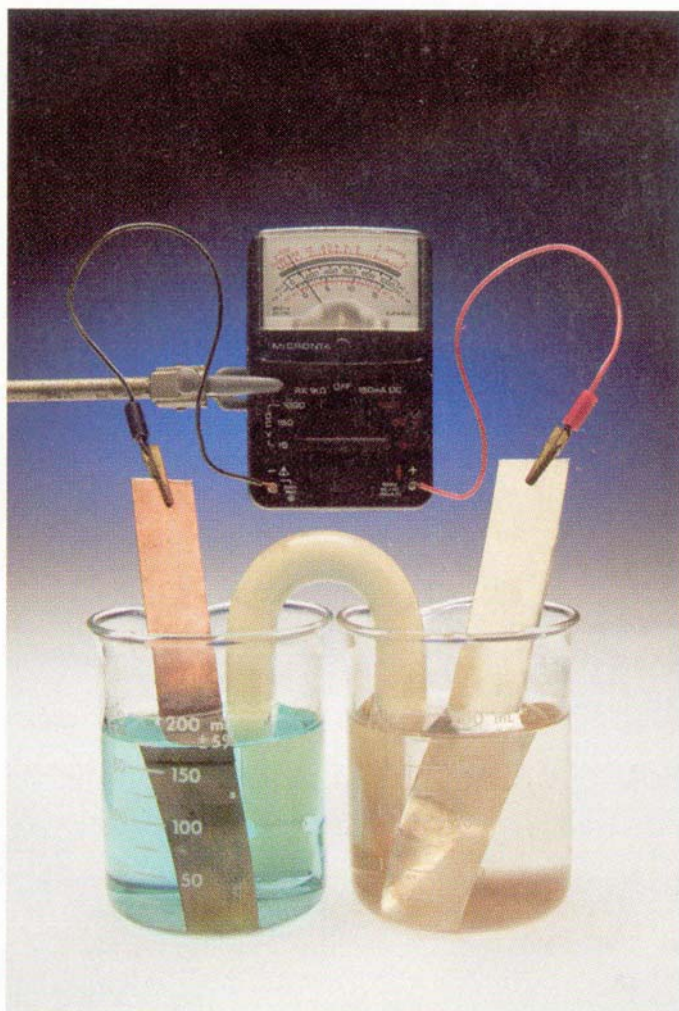


FIGURE 17.1 A metallic copper anode reacts to give a blue solution containing copper(II) ions as silver ions plate out on a silver cathode in a galvanic cell.

Electrochemical Cells

Galvanic (spontaneous)



Electrolytic (non-spontaneous)

Reverse of Above Reactions



Methods of Reaction

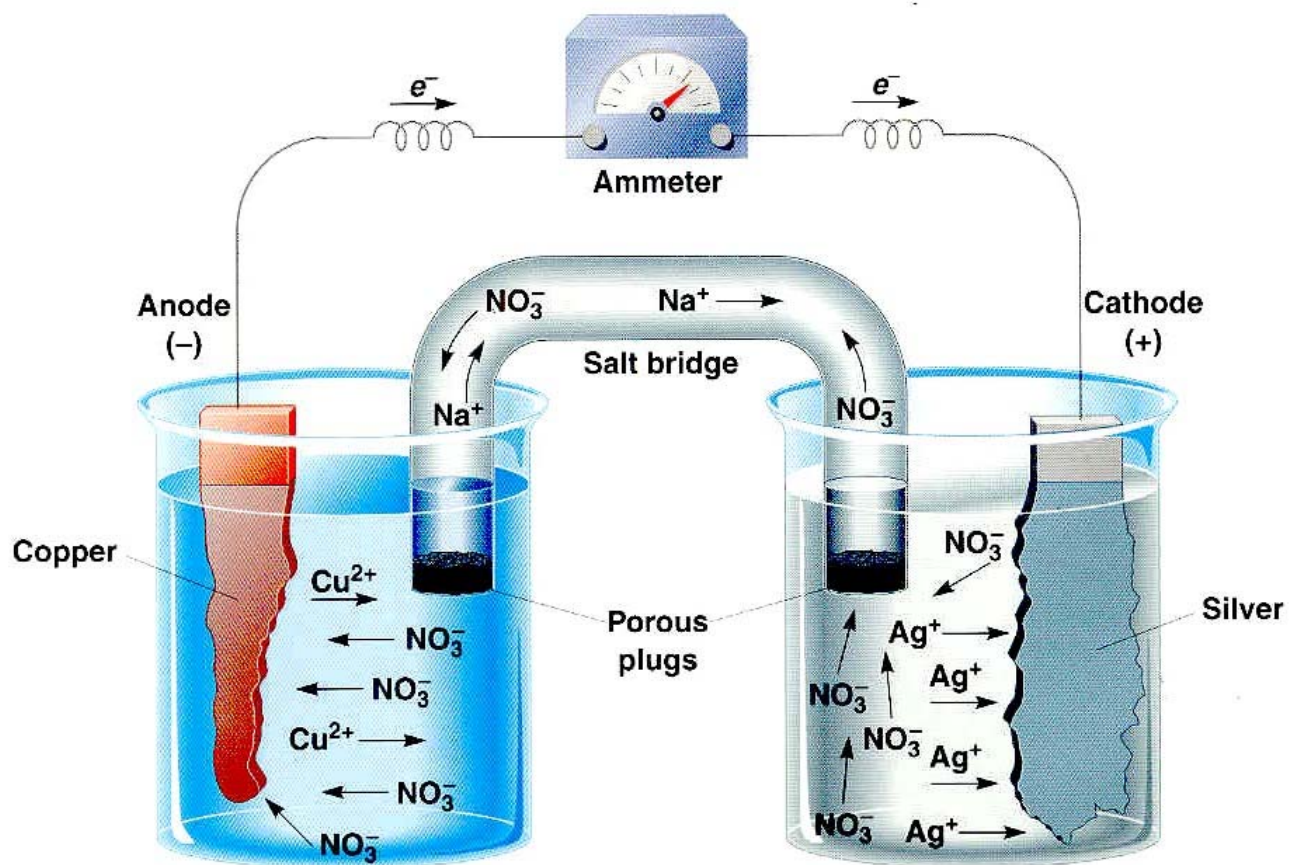
Direct contact of reactants ($w_{\text{elec}} = 0$)

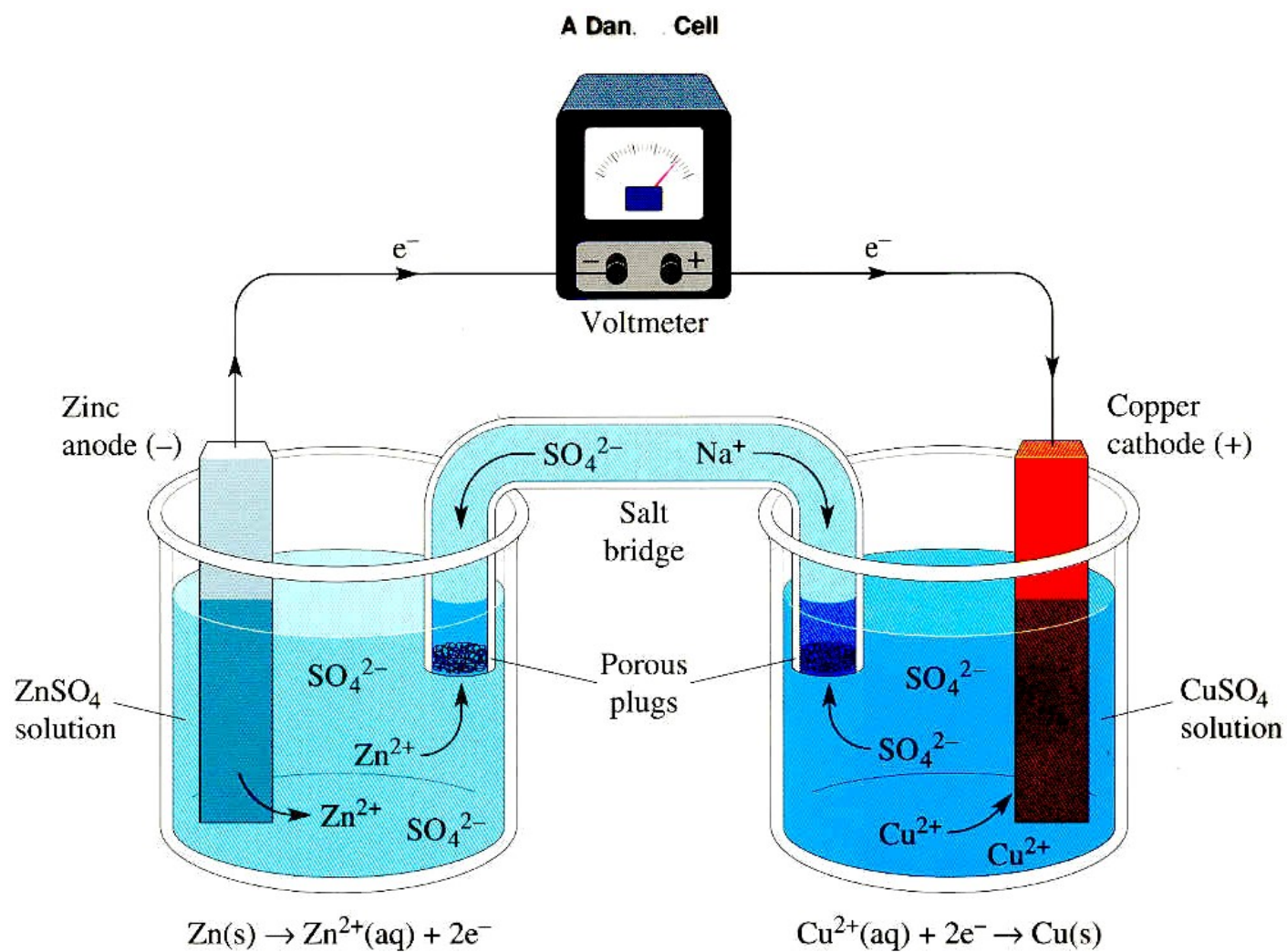
Separated half-cells ($w_{\text{elec}} > 0$)

Maintenance of electrical neutrality

Salt bridge

Potential difference vs. current





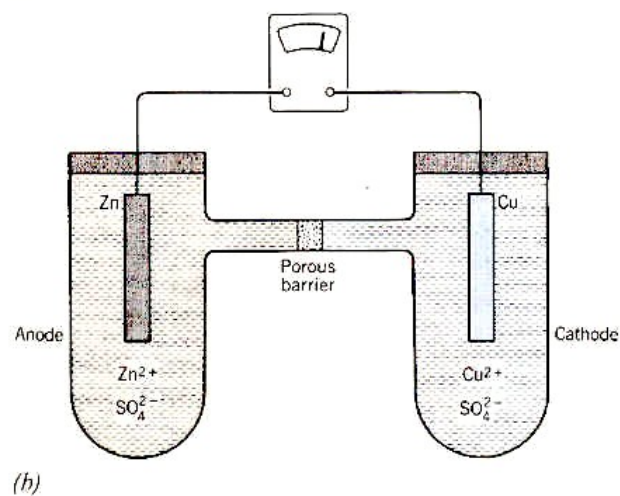
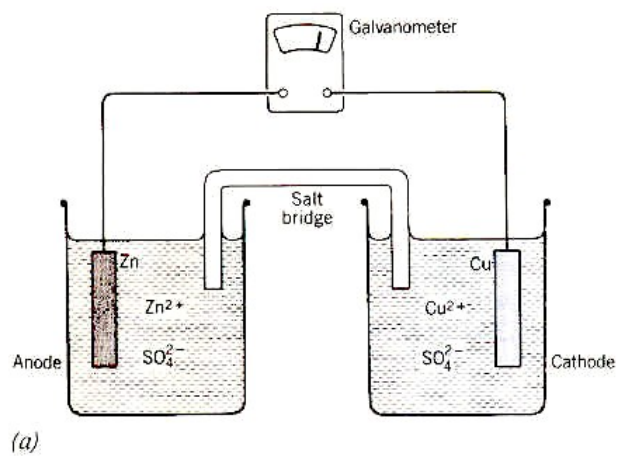
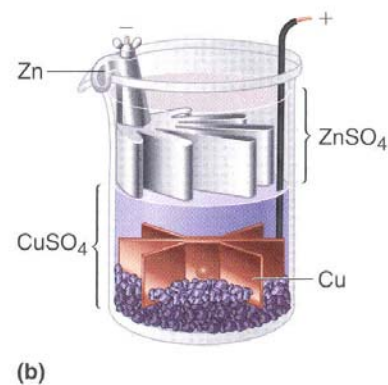
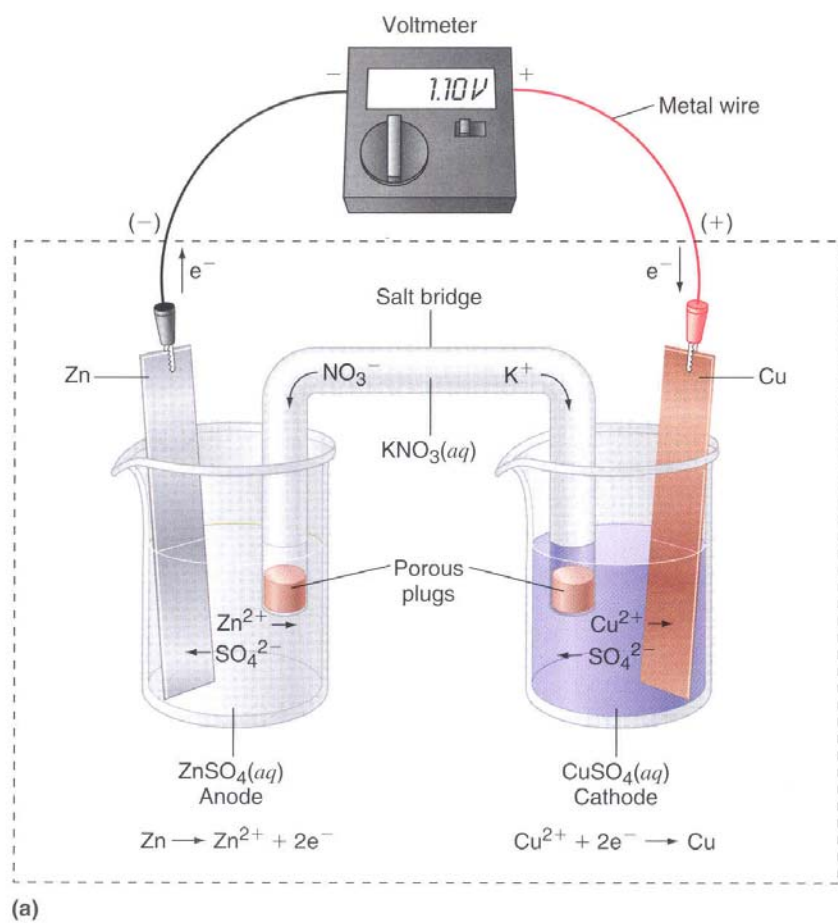


Fig. 18.3. Two ways of designing a Daniell cell, (a) using a salt bridge, and (b) using a porous barrier to separate the two solutions. The cathode reaction is $\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}$, and the anode reaction is $\text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2e^-$.

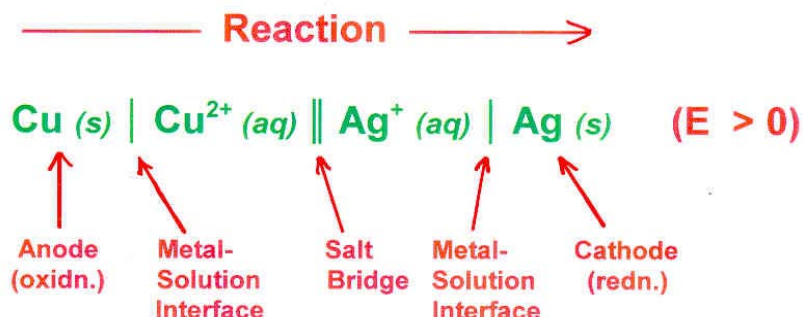
Figure 13.2: Two Versions of the Daniell Cell

Electrochemical Cell Terminology

Anode: Electrode at which oxidation occurs
(e^- 's released; O.N. increases)

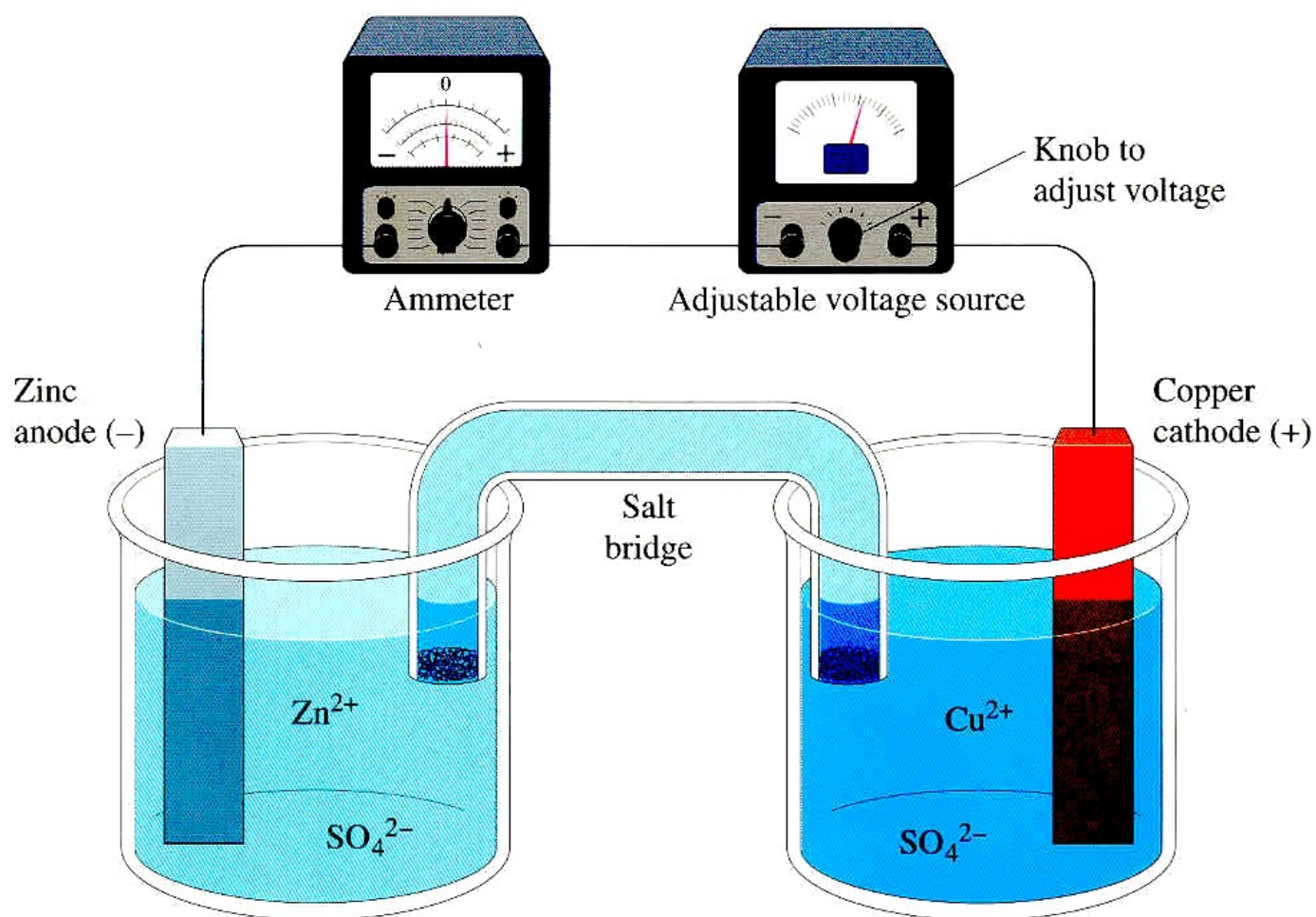
Cathode: Electrode at which reduction occurs
(e^- 's consumed; O.N. decreases)

Electrochemical Cell Notation



True cell potential can only be determined at zero load ($I = 0$). Thus, external variable voltage source can be used to exactly oppose intrinsic voltage of cell to measure E .

If external voltage is increased above intrinsic cell voltage, then direction of reaction is reversed, and spontaneous **Galvanic** cell becomes non-spontaneous **Electrolytic** cell.

Measuring EMF with a Potentiometer

Cell Potential and Free Energy

Just as ΔG° is a measure of the spontaneity of a chemical reaction (at constant T and P), so also is the electrochemical cell potential, E:

$$E \propto \Delta G_r \quad \text{and} \quad E^\circ \propto \Delta G_r^\circ \quad (1 \text{ V} \cdot \text{C} = 1 \text{ J})$$

At equilibrium, $E = 0$ (since $\Delta G_r = 0$)

When all chemical components are in their standard states, then $E = E^\circ$ and $\Delta G_r = \Delta G_r^\circ$.

Recall that ΔG_r represents the maximum amount of non-expansion work that is available in a system (at constant T and P):

$$\Delta G = w_{\text{elec}} = -nN_a E = -nFE \quad \begin{array}{l} F = \text{Faraday Const.} \\ = 96,485 \text{ C/mol} \end{array}$$

Thus, if $E > 0$, then $\Delta G < 0$, and the reaction is spontaneous in the direction written. If $E < 0$, then $\Delta G > 0$, and the reaction is spontaneous in the opposite direction from that written.

$w_{\text{elec}} = w_{\text{elec, max}}$ only if the cell operates reversibly (i.e., $I = 0$). Under these conditions, $E = \text{emf}$. If $I > 0$, then $E < \text{emf}$.

When all chemical components are in their standard states, then

$$\Delta G_r^\circ = -nFE^\circ$$

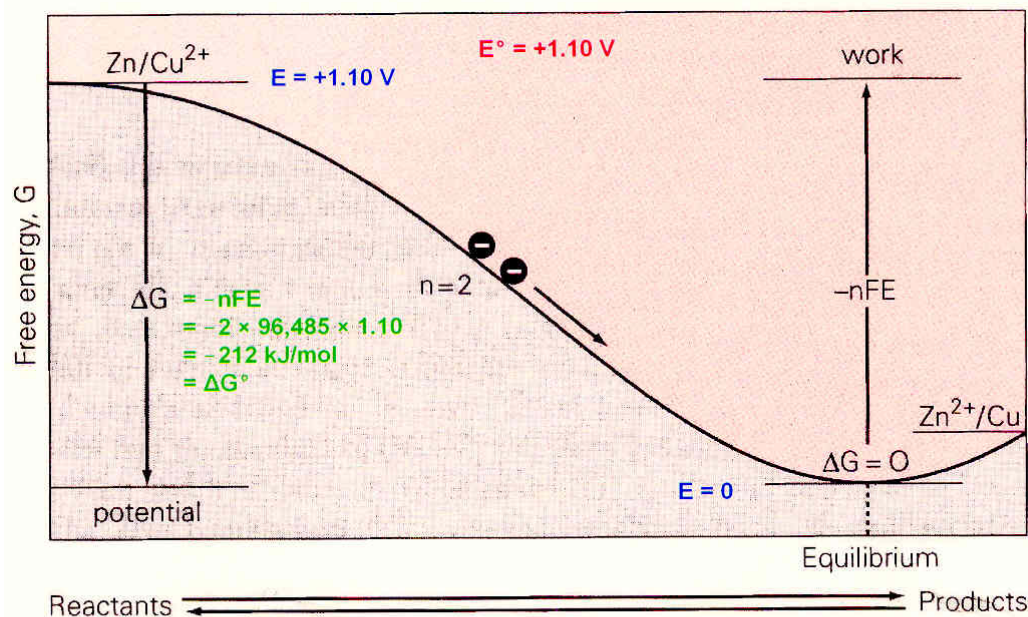


FIGURE 17-4. The goal is to use the free energy of a redox reaction to drive electrons around a circuit. As long as the reacting mixture remains out of equilibrium, its residual chemical energy (ΔG) furnishes the electrical work ($-n\mathcal{F}\mathcal{E}$) to move n moles of electrons across a voltage \mathcal{E} . The Faraday constant, \mathcal{F} , denotes the charge carried by one mole, and the value $-n\mathcal{F}\mathcal{E}$ represents the maximum amount of work available under idealized conditions—when the transformation occurs reversibly, inching forward in a series of infinitesimally small steps.