Topic 6L. Galvanic Cells

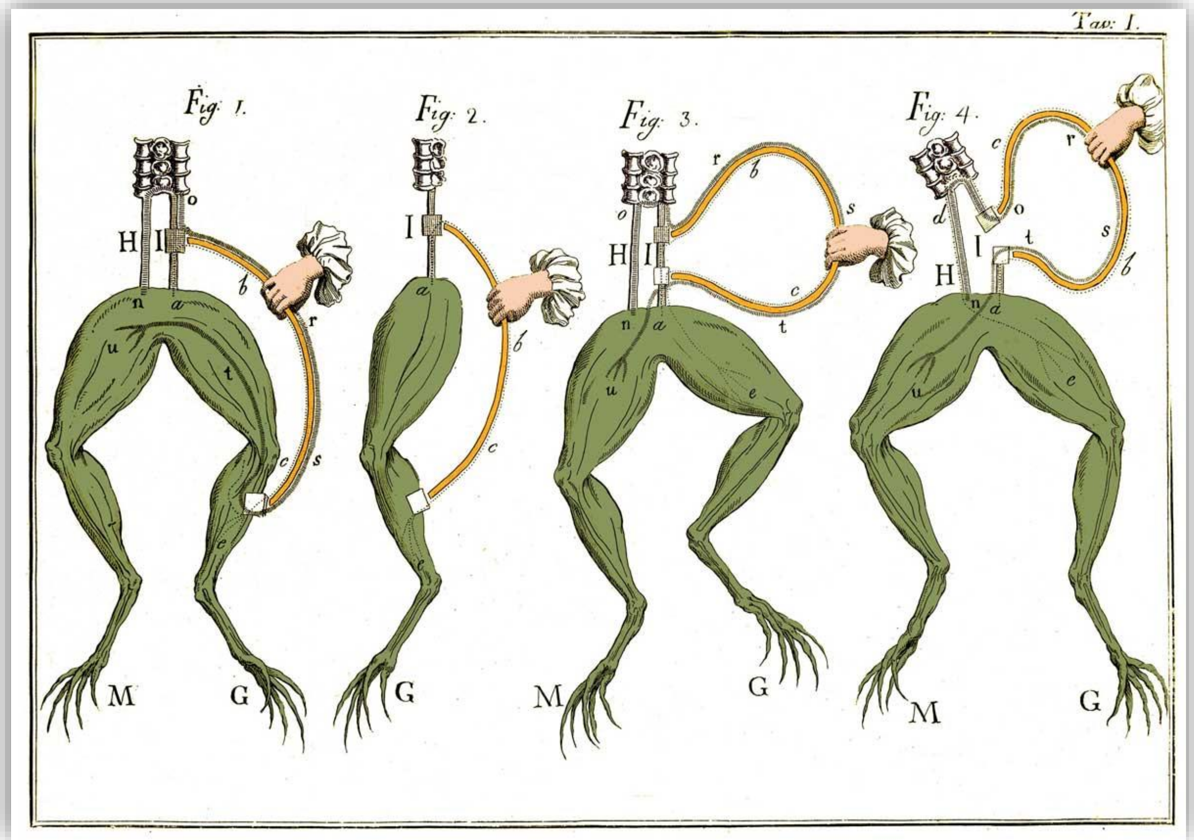
The Structure of Galvanic Cells

- Luigi Galvani vs. Alessandro Volta

https://www.chemi-in.com/540

The Structure of Galvanic Cells

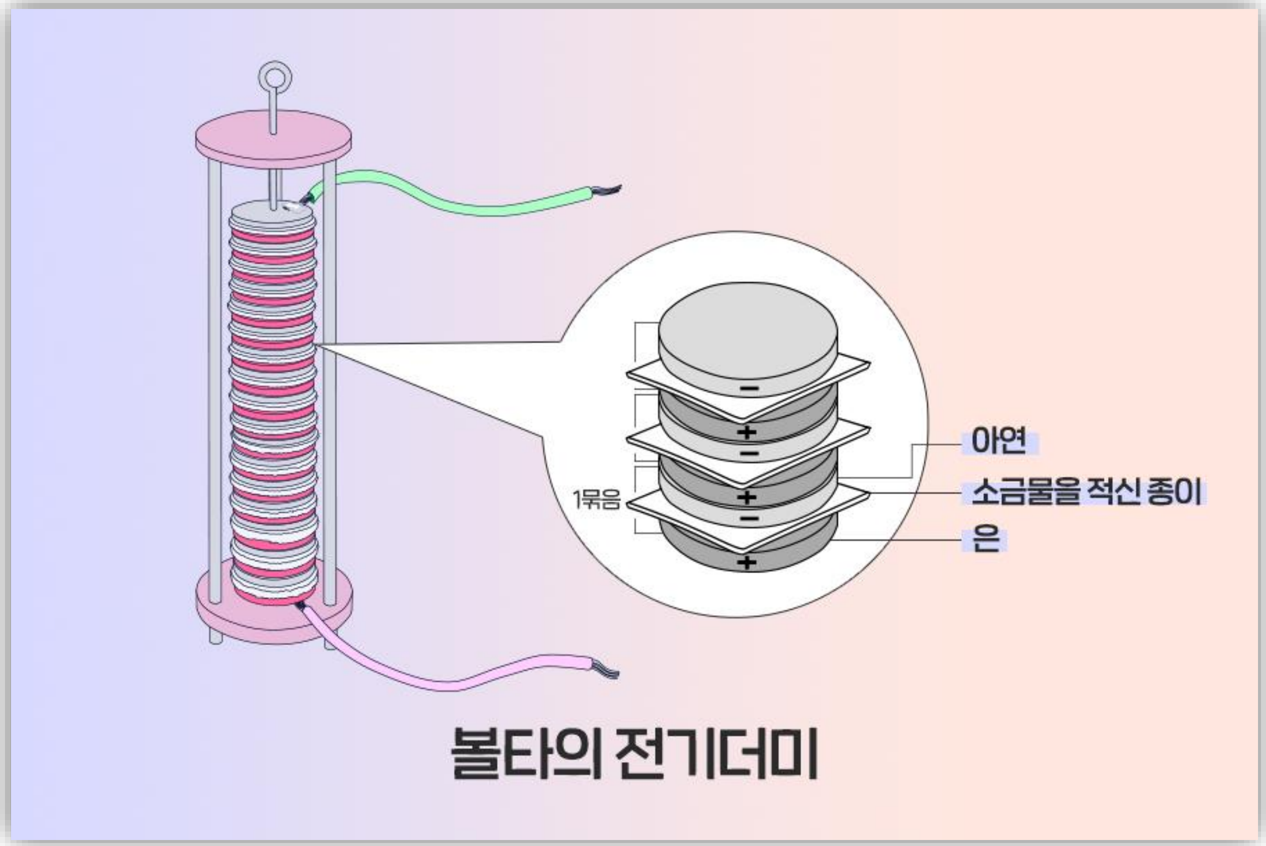
- Luigi Galvani: "Animal electricity"



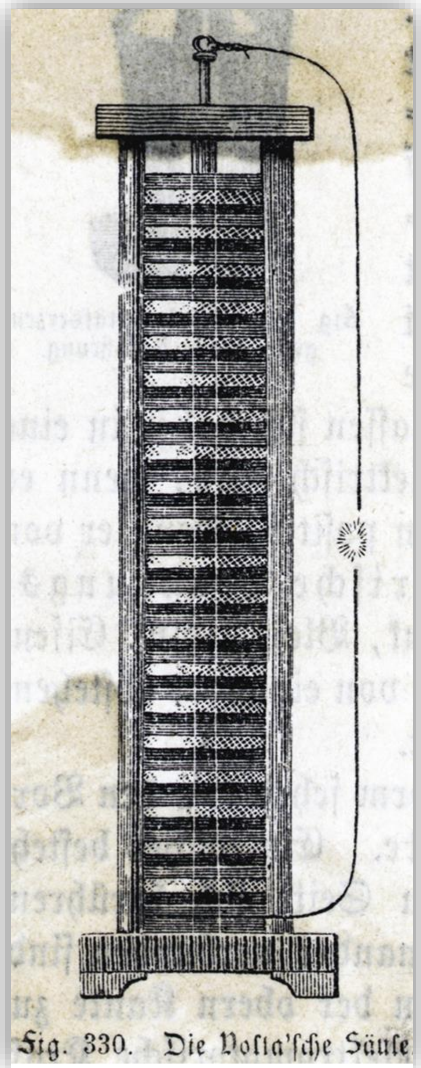
https://www.historytoday.com/archive/months-past/galvani-discovers-animal-electricity

The Structure of Galvanic Cells

- Alessandro Volta: "Voltaic pile"

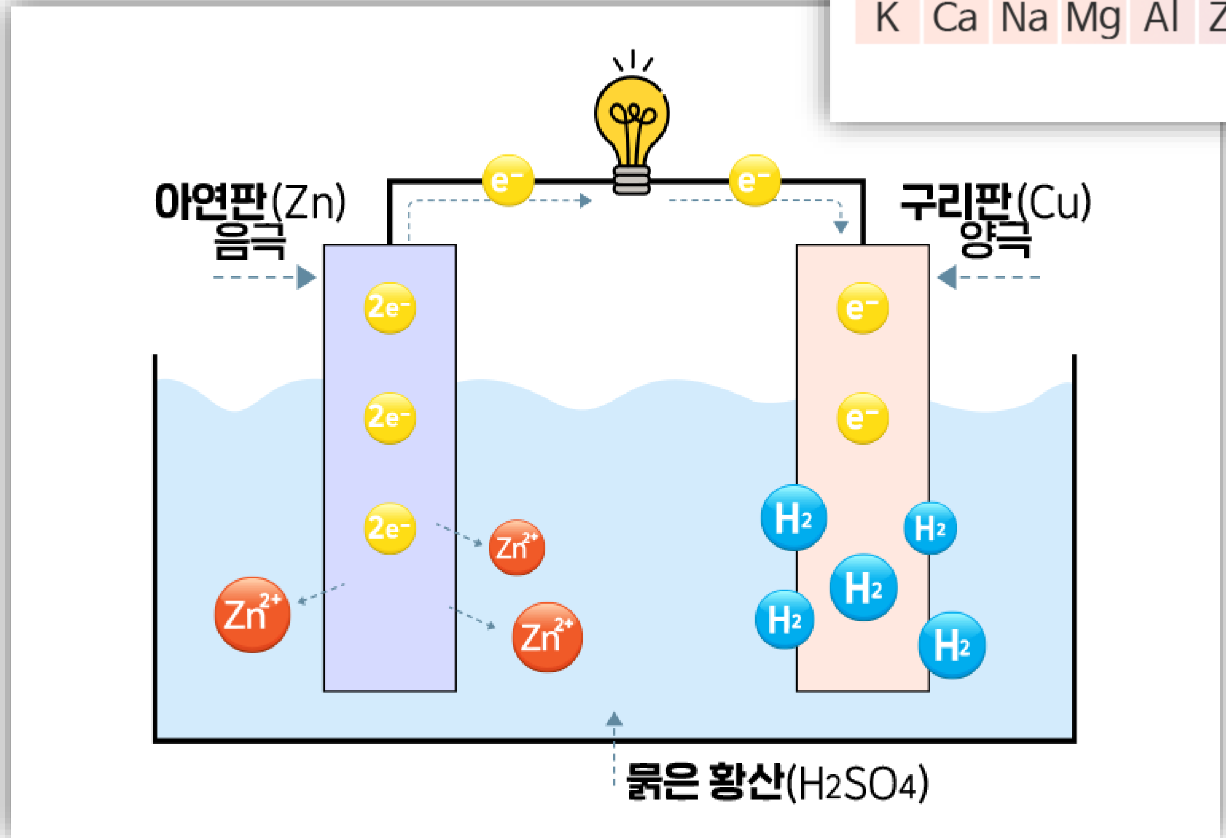


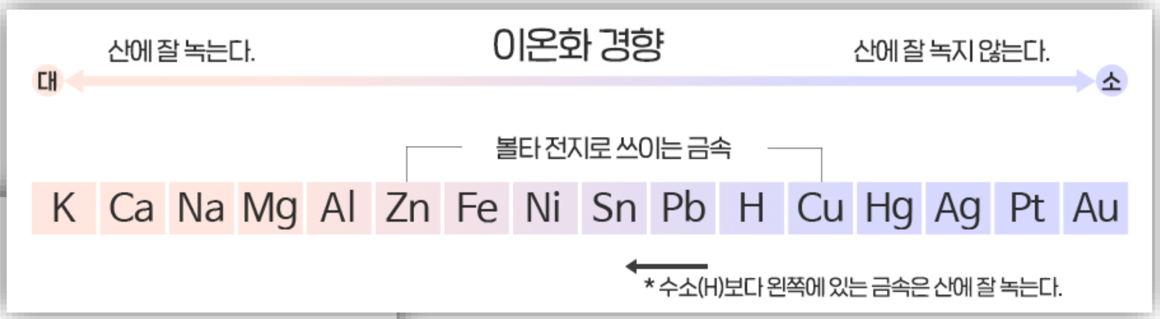
https://www.chemi-in.com/540



The Structure of Galvanic Cells

- Voltaic cell



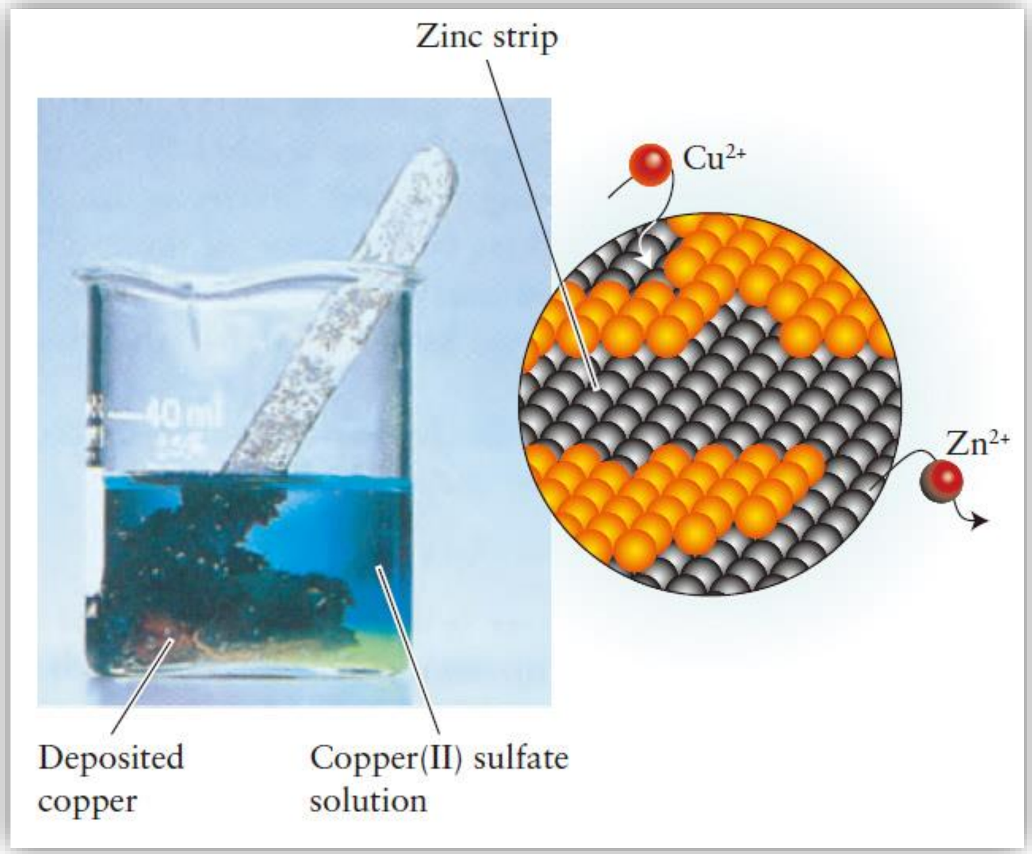


The Structure of Galvanic Cells

- Electrochemical cell: a device in which an electric current—a flow of electrons through a circuit—is either produced by a spontaneous chemical reaction or used to bring about a nonspontaneous reaction.
- Galvanic cell: an electrochemical cell in which a spontaneous chemical reaction is used to generate an electric current.
  - Battery is a collection of galvanic cells connected in series.
- Electrolytic cell: an electrochemical cell in which an electric current is used to bring about a nonspontaneous reaction.

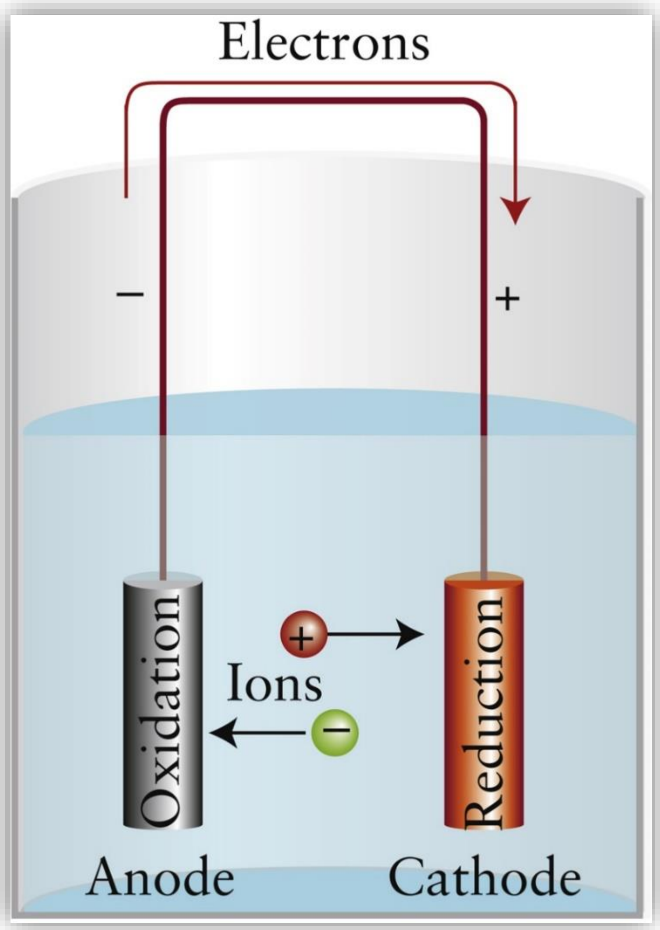
The Structure of Galvanic Cells

- Spontaneous redox reaction
  $Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$



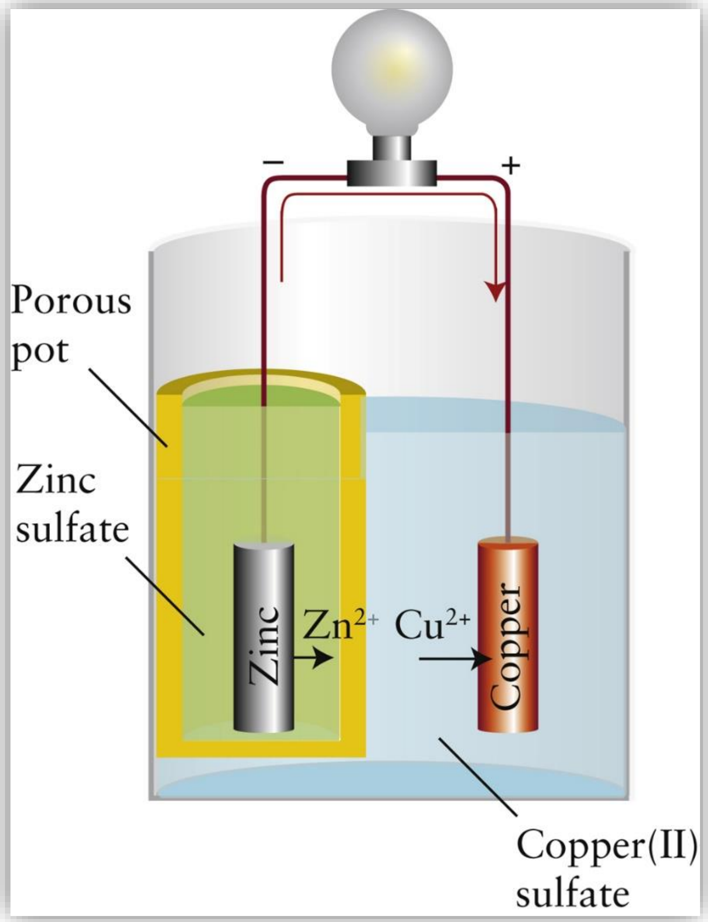
The Structure of Galvanic Cells

- Electrode
  - Anode: an electrode at which oxidation takes place
  - Cathode: an electrode at which reduction takes place
- Electrolyte: an ionically conducting medium inside the cell



The Structure of Galvanic Cells

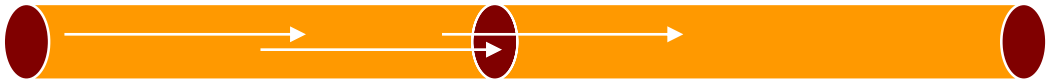
- Daniel cell
  - Anode: $Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$
  - Cathode: $Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$



Cell Potential and Reaction Gibbs Free Energy

- Charge (Q)
  - Unit: Coulomb (C)
  - Charge of one electron: 1.6×10^{-19} C
  - Number of electrons for 1 C: 6.25×10^{18}
  - Total charge for 1 mol of electrons
    $(6.02 \times 10^{23}) \times (1.6 \times 10^{-19})$ = 96,485 C = Faraday constant
  - $Q = I \times t$
  - 1 C = 1 A · s

$$Q = It$$



$$I = Q / t$$

Charge flow per second

Cell Potential and Reaction Gibbs Free Energy

- Electric potential (difference)
  - Potential difference → Causes charges to flow
  - Charge flow → Existence of potential difference
  - Electrical potential is analogous to gravitational potential
  - Electrical work is a type of nonexpansion work because it involves moving electrons rather than changing the volume of the system.
  - $1\ C \cdot V = 1\ J$

Cell Potential and Reaction Gibbs Free Energy

- Electric potential difference calculation

  $\Delta G = w_{e,max}$ at const. pressure and temperature (Topic 4J)

  w_e = total charge x potential difference = $(-neN_A) \times \Delta V$

  F = Faraday constant = 96485 $C \cdot mol^{-1}$

  $w_e = -nF\Delta V$

  $\Delta G = -nF\Delta V_{rev} = -nFE_{cell}$

  for $E > 0$, $\Delta G < 0$ → Spontaneous reaction

Cell Potential and Reaction Gibbs Free Energy

- Standard cell potential

  $\Delta G^\circ = -nFE_{cell}^\circ$

  (gases at 1 bar, solutes in unit activity, liquids and solids are pure)

- ΔG vs. E

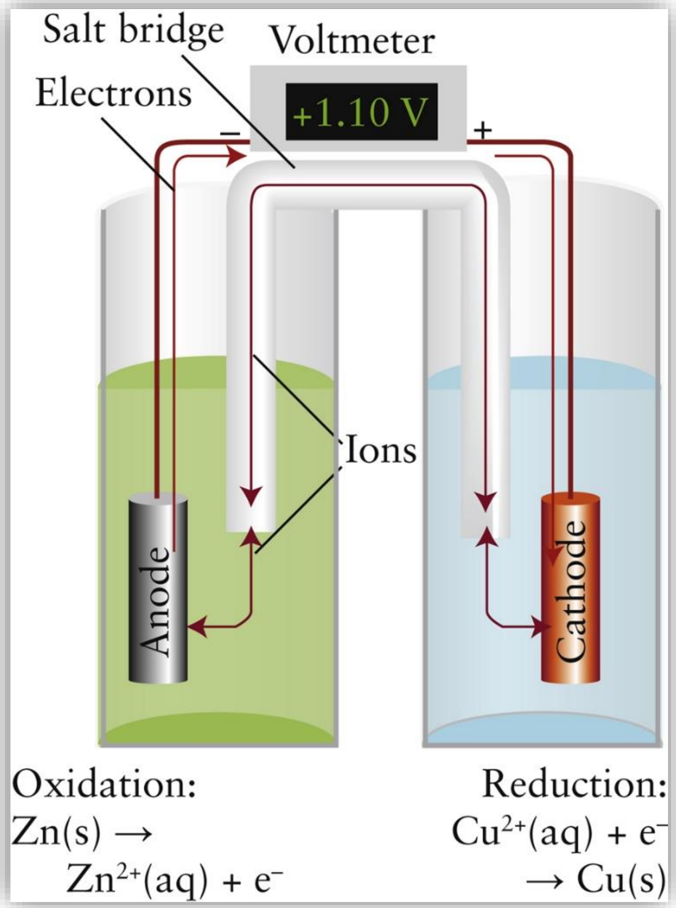
	ΔG°	E_{cell}°
$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$	-212 kJ	$+1.10$ V
$2\,Zn(s) + 2\,Cu^{2+}(aq) \longrightarrow 2\,Zn^{2+}(aq) + 2\,Cu(s)$	-424 kJ	$+1.10$ V

$E_{cell}^\circ = -\,\Delta G^\circ / nF$

The cell potential is independent of the size of the cell.

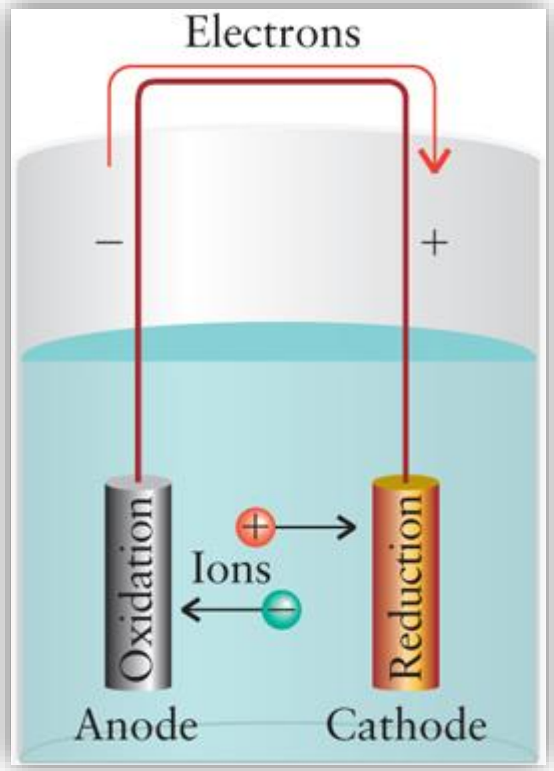
The Notation for Cells

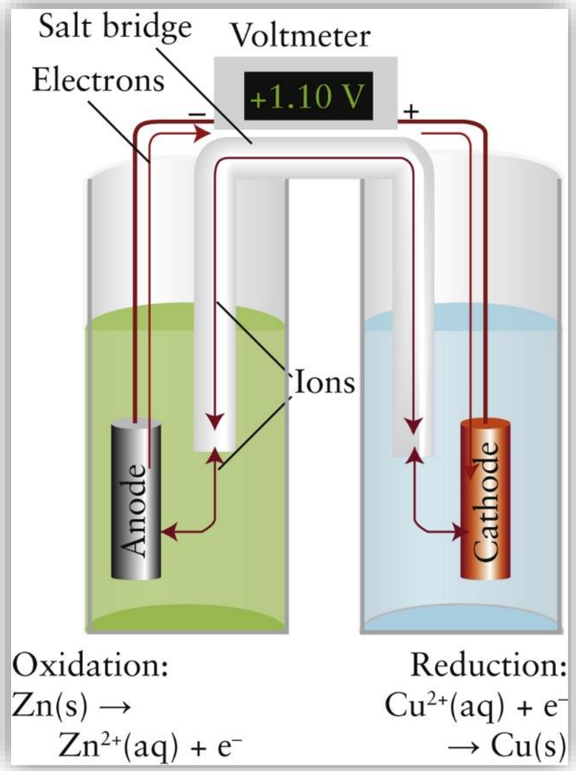
- Cell diagram
  For Daniel cell
  $Zn(s)|Zn^{2+}(aq)|Cu^{2+}(aq)|Cu(s)$
- With salt bridge
  $Zn(s)|Zn^{2+}(aq)\|Cu^{2+}(aq)|Cu(s)$
- With inert metallic electrode
  $H^+(aq)|H_2(g)|Pt(s)$, $Pt(s)|H_2(g)|H^+(aq)$



The Notation for Cells

- Salt bridge
  - Two separate beakers without salt bridge
    → The reaction will stop after a short period of time.
  - One beaker:
    → mixture of Zn^{2+} and Cu^{2+} leads to ill-defined potential.





The Notation for Cells

- Electronic voltmeter

The Notation for Cells

- Notation convention

Left (L)	**Right (R)**
$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$ (oxidation)	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$ (reduction)
Overall (R + L): $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$	$E_{cell} = +1V$

Left (L)	**Right (R)**
$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$ (oxidation)	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$ (reduction)
Overall (L + R): $Cu(s) + Zn^{2+}(aq) \longrightarrow Cu^{2+}(aq) + Zn(s)$	$E_{cell} = -1V$