Electromotive Force (emf)

- The potential difference between the anode and cathode in a cell is called the electromotive force (emf).

- It is also called the cell potential, and is designated E_{cell}.

Standard Cell Potentials

The cell potential at standard conditions can be found through this equation:

$$E^{\circ}_{cell} = E^{\circ}_{red} \text{ (cathode)} - E^{\circ}_{red} \text{ (anode)}$$

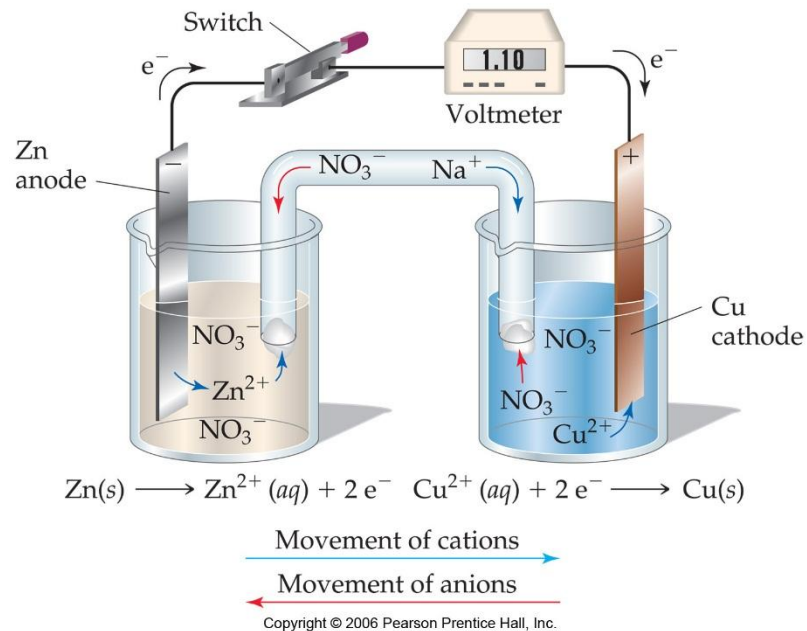Because cell potential is based on the potential energy per unit of charge, it is an intensive property.

Cell Potentials

Zn(s) ⟶ Zn²⁺ (aq) + 2 e⁻   Cu²⁺ (aq) + 2 e⁻ ⟶ Cu(s)

Movement of cations

Movement of anions

Copyright © 2006 Pearson Prentice Hall, Inc.

- For the oxidation in this cell,

$$E^{\circ}_{red} = -0.76 \text{ V}$$

- For the reduction,
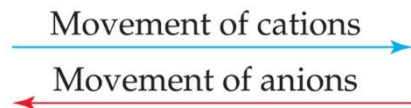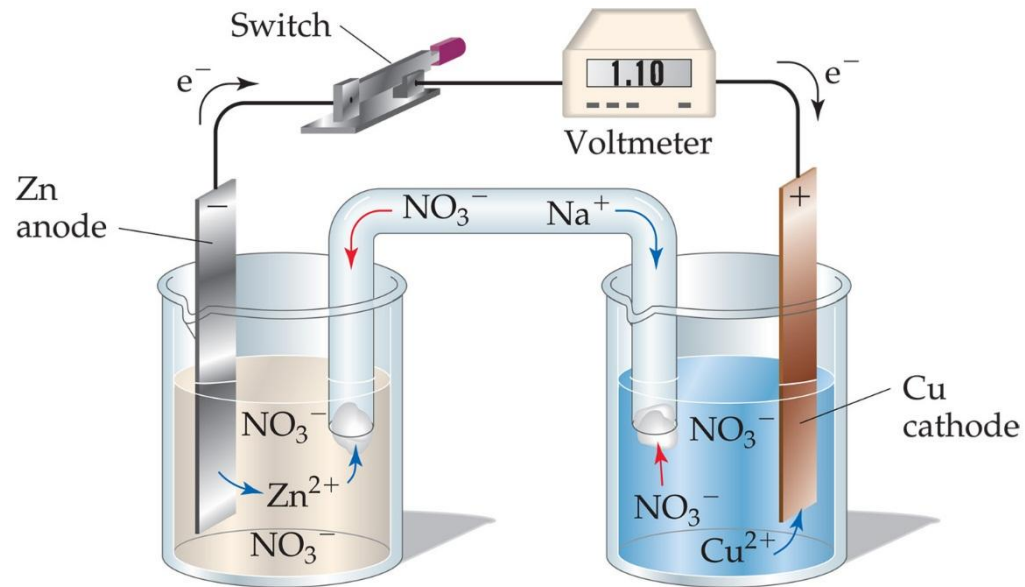
$$E^{\circ}_{red} = +0.34 \text{ V}$$

Cell Potentials

$$E^\circ_{cell} = E^\circ_{red} \text{ (cathode)} - E^\circ_{red} \text{ (anode)}$$

$$= +0.34 \text{ V} - (-0.76 \text{ V})$$

$$= +1.10 \text{ V}$$

Voltaic Cells

Atoms in Zn strip

$2\,e^-$

Cu^{2+} ions in solution

Zn^{2+} ion

Cu atom

$Zn(s) + Cu^{2+}(aq)$

$Zn^{2+}(aq) + Cu(s)$
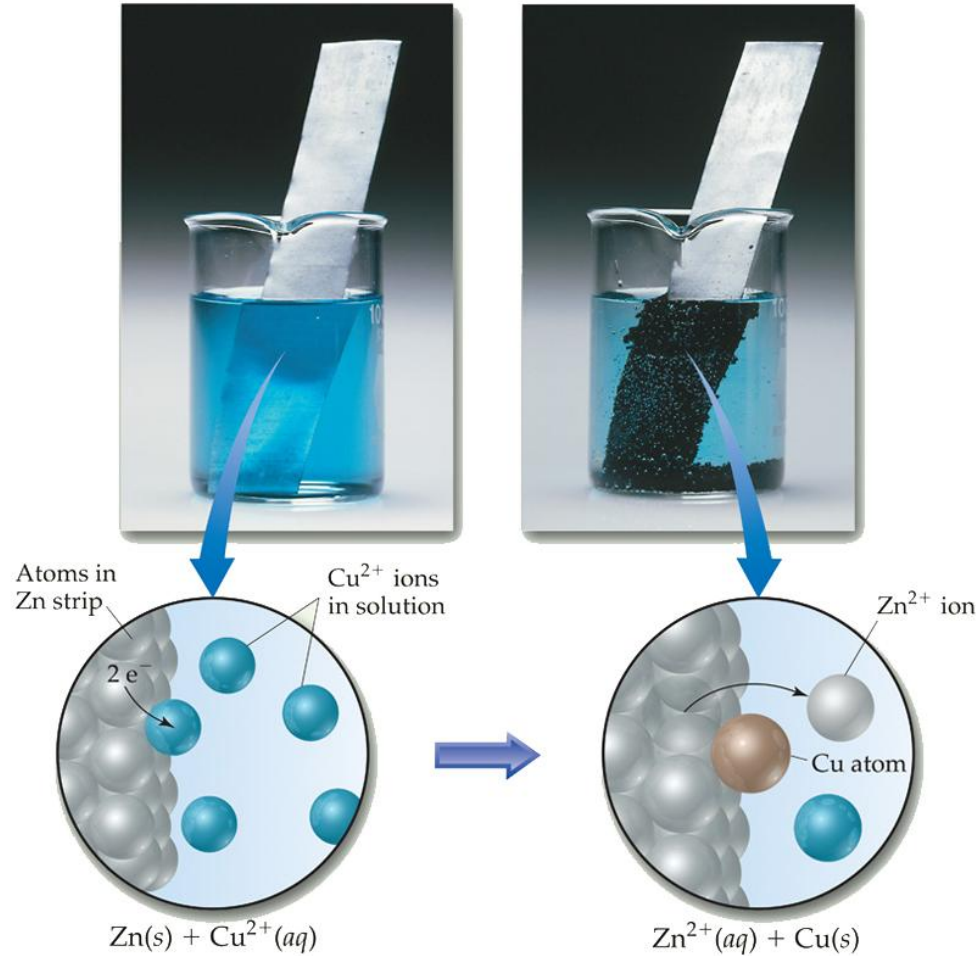
In spontaneous oxidation-reduction (redox) reactions, electrons are transferred and energy is released.

Voltaic Cells

Switch

e⁻

1.10

Voltmeter

e⁻

Zn anode

NO₃⁻   Na⁺

+

NO₃⁻

Zn²⁺

NO₃⁻

Cu cathode

NO₃⁻

NO₃⁻

Cu²⁺

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^- \quad Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$

Movement of cations

Movement of anions

- A typical cell looks like this.
- The oxidation occurs at the anode.
- The reduction occurs at the cathode.
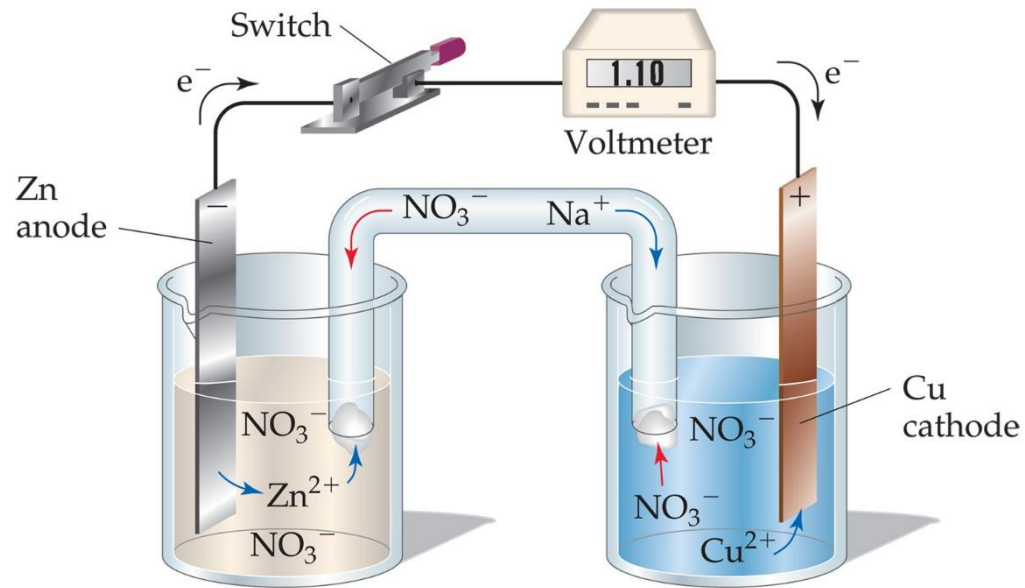
Voltaic Cells

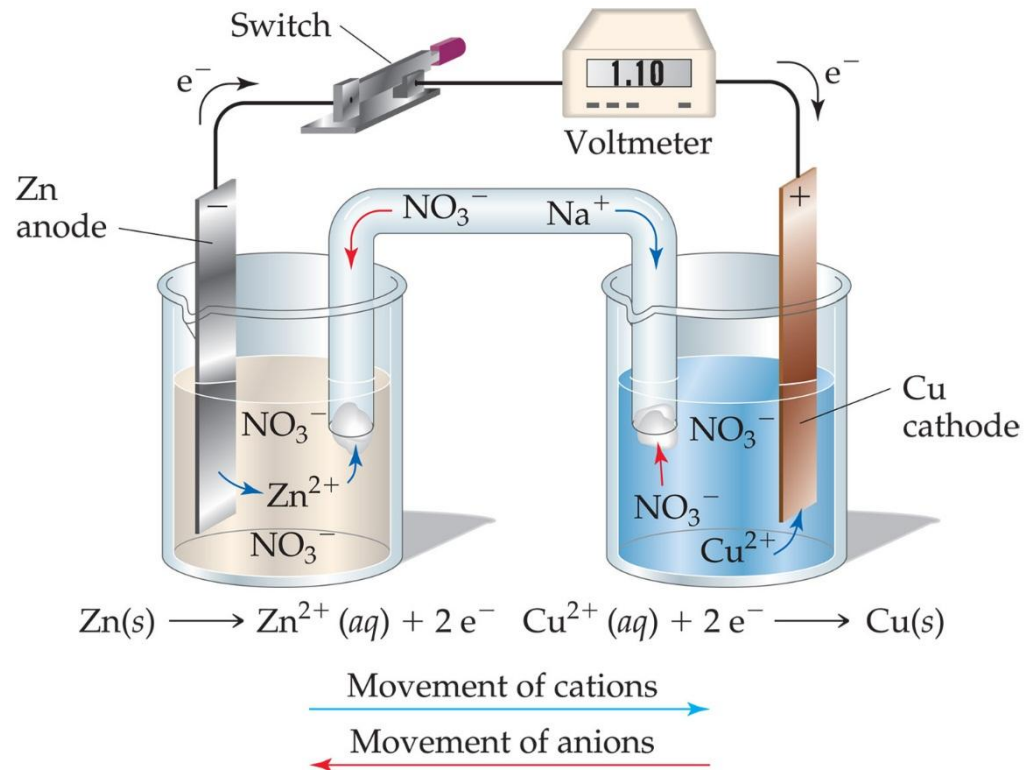Once even one electron flows from the anode to the cathode, the charges in each beaker would not be balanced and the flow of electrons would stop.
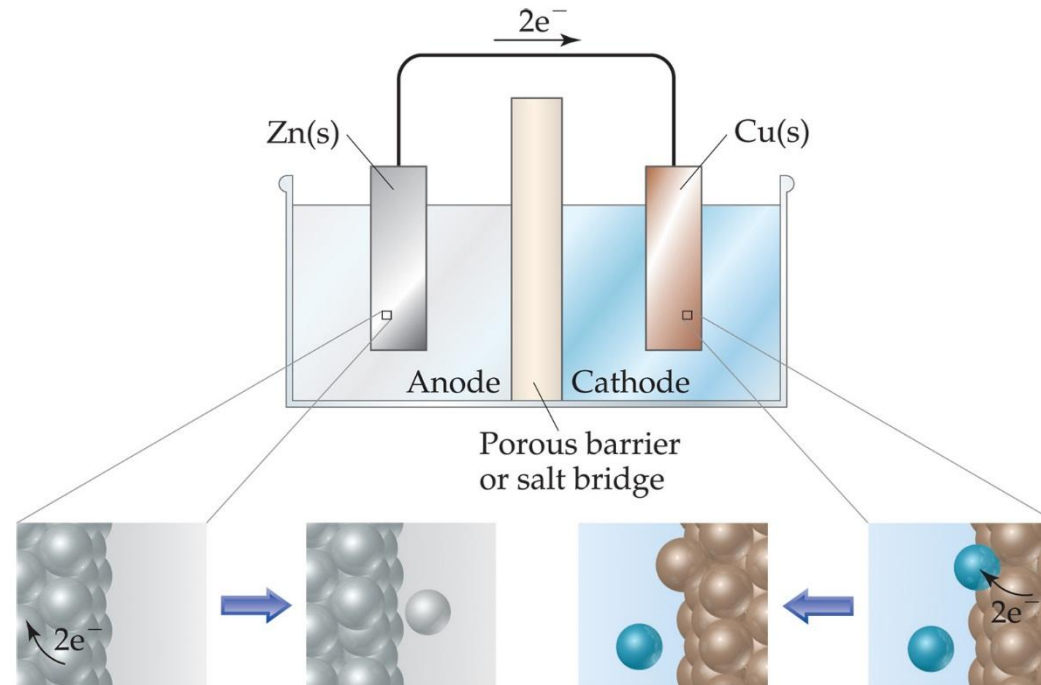
Voltaic Cells

- Therefore, we use a salt bridge, usually a U-shaped tube that contains a salt solution, to keep the charges balanced.
  - Cations move toward the cathode.
 - Anions move toward the anode.

Voltaic Cells

- In the cell, then, electrons leave the anode and flow through the wire to the cathode.

- As the electrons leave the anode, the cations formed dissolve into the solution in the anode compartment.

Voltaic Cells

- As the electrons reach the cathode, cations in the cathode are attracted to the now negative cathode.

- The electrons are taken by the cation, and the neutral metal is deposited on the cathode.
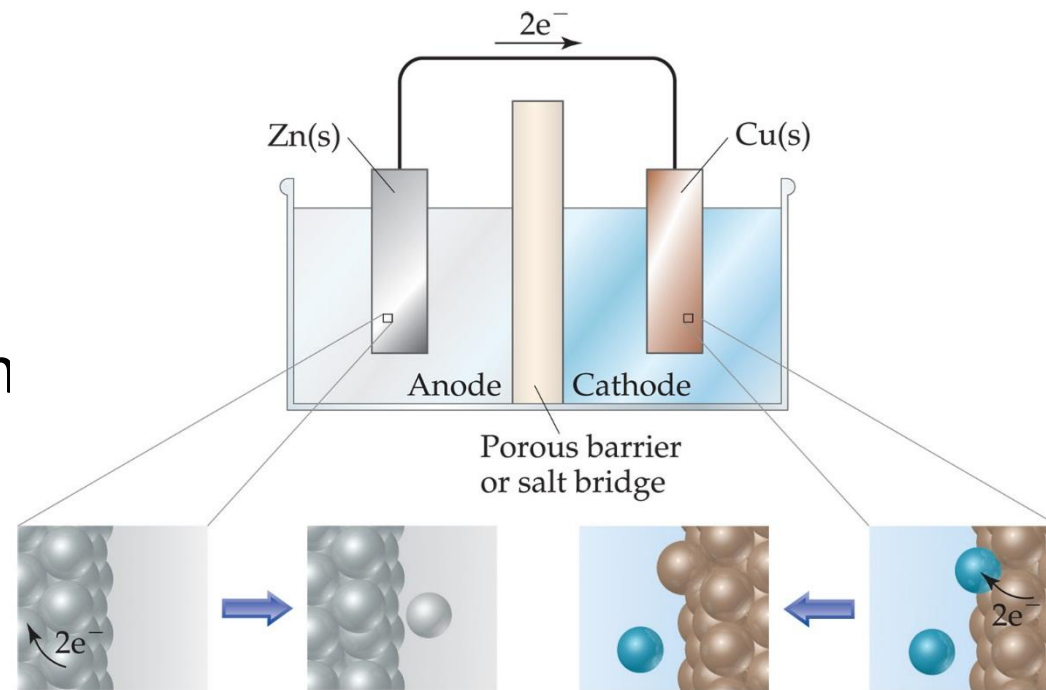
Nernst's equation

- We have assumed in the previous section that the concentration of all the species involved in the electrode reaction is unity. This need not be always true. Nernst showed that for the electrode reaction:

- $M^{n+}(aq) + ne^- \rightarrow M(s)$

Nernst equation

$$E_{(M^{n+}|M)} = E^0_{(M^{n+}|M)} - \frac{RT}{nF}\ln\frac{M}{[M^{n+}]}$$

But solid M concentrate constant

$$E_{(M^{n+}|M)} = E^0_{(M^{n+}|M)} - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]}$$

Example of Daniel cell

For cathode : $E_{(Cu^{2+}|Cu)} = E^0_{(Cu^{2+}|Cu)} - \frac{RT}{2F}\ln\frac{1}{[Cu^{2+}]}$

For anode : $E_{(Zn^{2+}|Zn)} = E^0_{(Zn^{2+}|Zn)} - \frac{RT}{2F}\ln\frac{1}{[Zn^{2+}]}$

Cell Potential : $E_{cell} = : E_{(Cu^{2+}|Cu)} - E_{(Zn^{2+}|Zn)}$

$$= E^0_{(Cu^{2+}|Cu)} - \frac{RT}{2F}\ln\frac{1}{[Cu^{2+}]} - E^0_{(Zn^{2+}|Zn)} - \frac{RT}{2F}\ln\frac{1}{[Zn^{2+}]}$$

$$= E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

- It can be seen that $E_{(cell)}$ depends on the concentration of both Cu^{2+} and Zn^{2+} ions. It increases with increase in the concentration of Cu^{2+} ions and decrease in the concentration of Zn^{2+} ions.

- By converting the natural logarithm to the base 10 and substituting the values of R, F and T = 298 K, it reduces to

$$E^0_{(cell)} = E^0_{(cell)} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

For a general electrochemical Nernst's equation

- $a\,A + b\,B \rightarrow c\,C + d\,D$ (on passing it with ne^-)

$$E^0_{(cell)} = E^0_{(cell)} - \frac{RT}{nF} \ln Q$$

$$E^0_{(cell)} = E^0_{(cell)} - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Equilbirum constant from Nernst's equation

- If the circuit in Daniell celis closed then we note that the reaction

- $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ takes place and as time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu^{2+} keeps on decreasing.

- At the same time voltage of the cell as read on the voltmeter keeps on decreasing. After some time, we shall note that there is no change in the concentration of Cu^{2+} and Zn^{2+} ions and at the same time, voltmeter gives zero reading. This indicates that equilibrium has been attained. In this situation the Nernst equation may be written as:

$$E^0_{(cell)} = 0 = E^0_{(cell)} - \frac{2.303 \ RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Therefore,

$$E^0_{(cell)} = \frac{2.303 \ RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium,

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = K_c$$

and at T = 298K the above equation can be written as

$$E^0_{(cell)} = \frac{0.059V}{2} \log K_c = 1.1V$$

Therefore , $\log K_c = \frac{1.1V \times 2}{0.059} = 37.288$

Therefore Kc $= 2 \times 10^{37}$ at 298K.
In general,

$$E^0_{(cell)} = \frac{2.303RT}{nF} \log K_c$$

- Thus, the above equation gives a relationship between equilibrium constant of the reaction and standard potential of the cell in which that reaction takes place. Thus, equilibrium constants of the reaction, difficult to measure otherwise, can be calculated from the corresponding $E^{\ominus}$ value of the cell.