Electrochemistry 13.1

Current
Voltaic (Galvanic) Cells
Voltage
Standard Reduction Potentials
Standard Cell Potentials

Electric Current (I)

Electric Current

- the amount of charge that passes through the cross-sectional area of a medium per second.

$$I = \frac{q}{T}$$

I = Current [amperes (A)]
q = Charge [Coulombs (C)]
T = Time [seconds (s)]

F = Faraday's constant = 96,500 C/mol of electrons

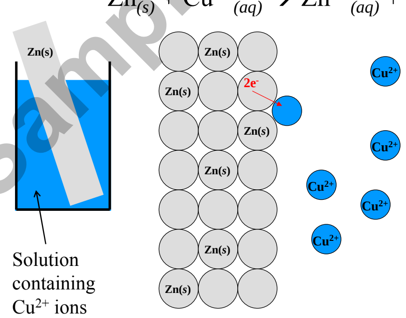
Ex) Electric Current (I)

a) How much charge passes through the cross-section of a wire that is carrying 0.987 A of current for 12.3 minutes?
b) How many moles of electrons passed through the cross-section?

Ex) Electric Current (I)

Spontaneous REDOX Reactions

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$



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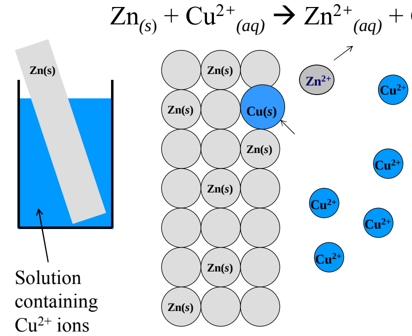


Ex) Spontaneous Redox Reaction

When you see a solid metal placed in a solution containing metal ions, it will always be this type of redox reaction.

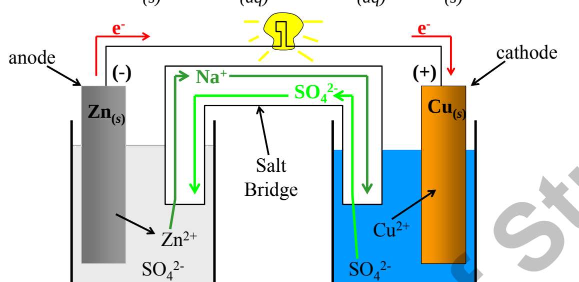
Ex) A copper penny is dropped into a solution of silver fluoride.

Voltaic (Galvanic) Cells

- A device that transfers electrons from one reactant to another through a pathway
  - As opposed to a direct transfer
- Always spontaneous
- Chemical energy is converted into electrical energy that moves electrons.

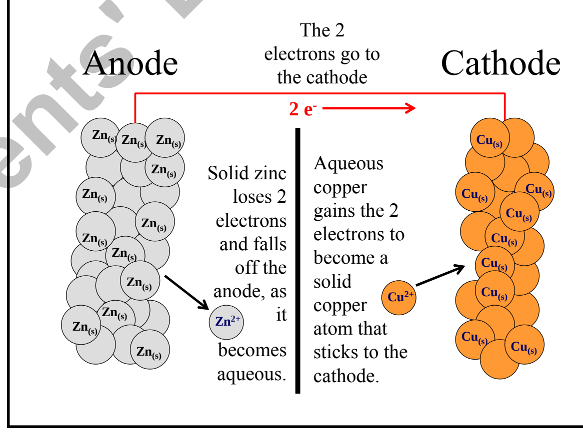
Voltaic (Galvanic) Cells

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$



$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$
Oxidation ½ reaction

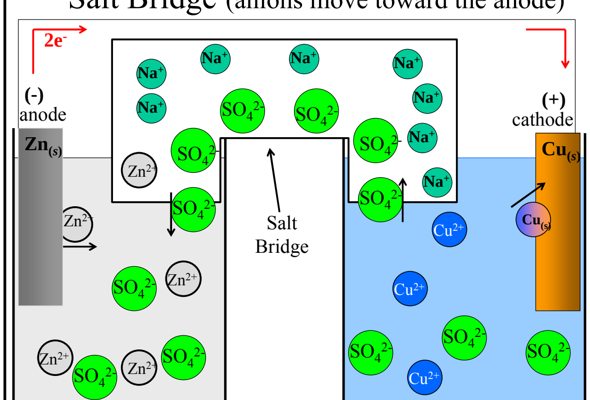
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$
Reduction ½ reaction



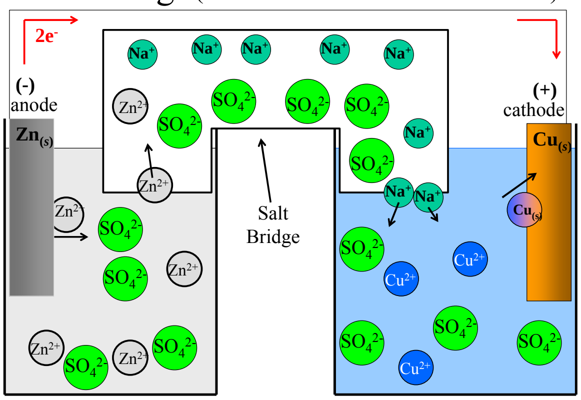
Salt Bridge

- U–shaped tube containing a solution of gel with soluble ions
  - Na^+, and SO_4^{2-} or NO_3^- are commonly used.
- These ions do not play a role in the redox reaction.
- Ions from the salt bridge must not react with ions in the electrolytic solutions to form a precipitate.
- Ions from the salt bridge keep the solutions in the half-cells neutral.
- If the solutions do not remain neutral, the reaction will stop.

Salt Bridge (anions move toward the anode)



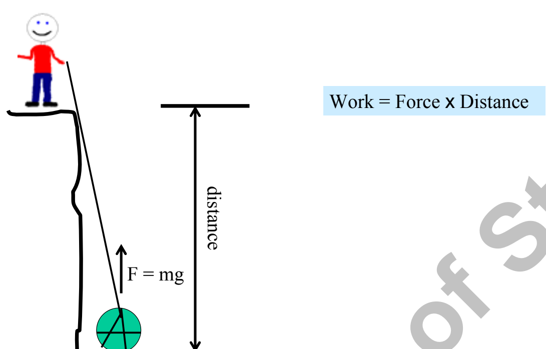
Salt Bridge (cations move toward the cathode)



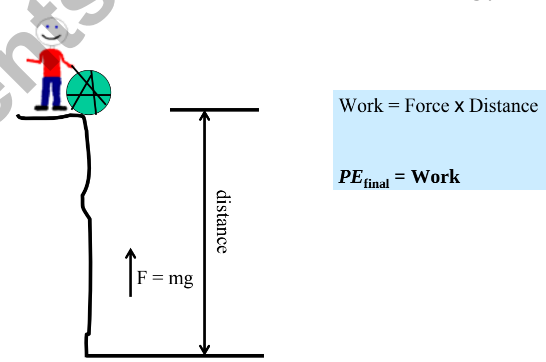
Why do Electrons Flow from the Anode to Cathode?

- The potential energy for electrons is higher at the anode than it is at the cathode.
- All things naturally move to achieve a state of lower potential energy.
  - A rock will naturally fall under the influence of gravity to obtain a lower gravitational potential energy.

Gravitational Potential Energy



Gravitational Potential Energy



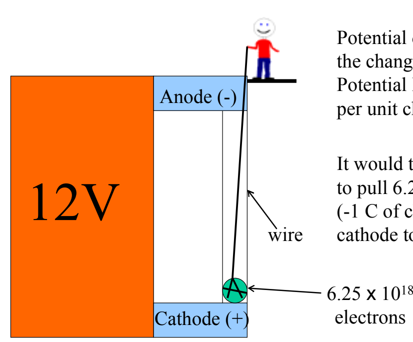
$PE_{electric}$ and Potential Difference (ΔV)

$$\Delta V \text{ (volts)} = \frac{\Delta PE \text{ (joules)}}{\text{Charge (Coulombs)}}$$

$1\ e^- = -1.60 \times 10^{-19}$ C

6.25×10^{18} electrons contain -1 C of charge.

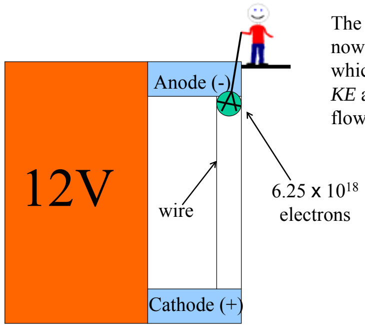
$PE_{electric}$ and Potential Difference (ΔV)



Potential difference, ΔV, is the change in Electrical Potential Energy, $\Delta PE_{electric}$, per unit charge.

It would take 12 J of energy to pull 6.25×10^{18} electrons (-1 C of charge) from the cathode to the anode.

$PE_{electric}$ and Potential Difference (ΔV)



The 6.25×10^{18} electrons now possess 12 J of *PE*, which will be converted into *KE* as they spontaneously flow back to the cathode.

Summary: $PE_{electric}$ and ΔV

Voltage: Energy per unit charge

- The energy here is the difference in potential energy between the anode and the cathode.
- The charges are the electrons, each carrying -1.60×10^{-19} C.
- It takes 6.25×10^{18} electrons to add up to -1 C of charge.
- In a 12 V battery, the difference in potential energy between the anode and the cathode is 12 J per C of charge.
- If we were to take 6.25×10^{18} electrons at the cathode and drag them back to the anode, it would require 12 J of work.
- 12 J of potential energy is converted into kinetic energy that moves 6.25×10^{18} electrons from the anode to the cathode in a 12 V battery.

Other Words for Potential Difference

Potential Difference is also known as:

- **emf** (electromotive force → force that causes electrons to move)
- **Standard emf** (electromotive force under standard conditions → 25°C and 1 *M* concentrations or 1 atm partial pressures of reactants and products)
- E_{cell} (cell potential)
- E^o_{cell} (standard cell potential → 25°C and 1 *M* concentrations or 1 atm partial pressures of reactants and products)
- **Cell Voltage**

The unit for all the above is the volt (V).

Standard Conditions for all Cells

	Reactants	Products
Concentration	1.0 *M*	1.0 *M*
Pressure	1 atm	1 atm
Temperature	25°C	25°C

Standard Reduction Potentials (E^o_{red})

The standard potentials for half-cell reactions are used to calculate the standard cell potential, E^o_{cell}, for the overall reaction.

By convention, all standard half-cell potentials are given as reduction potentials, E^o_{red}.

e.g. $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ $\quad E^o_{red} = +0.34$ V

Some E^o_{red} values at 25°C

Reduction half reaction	E^o_{red}
$Ag^+ + e^- \rightarrow Ag_{(s)}$	+ 0.80 V
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+ 0.77 V
$I_{2(s)} + 2e^- \rightarrow 2\ I^-$	+ 0.53 V
$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$	+ 0.34 V
$2\ H^+ + 2e^- \rightarrow H_{2(g)}$	0.00 V
$Ni^{2+} + 2e^- \rightarrow Ni_{(s)}$	- 0.25 V
$Fe^{2+} + 2e^- \rightarrow Fe_{(s)}$	- 0.44 V
$Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$	- 0.76 V
$Al^{3+} + 3e^- \rightarrow Al_{(s)}$	- 1.66 V

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$I_{2(s)} + 2e^- \rightarrow 2\ I^-$	+ 0.53 V
$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$	+ 0.34 V
$2\ H^+ + 2e^- \rightarrow H_{2(g)}$	0.00 V
$Ni^{2+} + 2e^- \rightarrow Ni_{(s)}$	- 0.25 V
$Fe^{2+} + 2e^- \rightarrow Fe_{(s)}$	- 0.44 V
$Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$	- 0.76 V
$Al^{3+} + 3e^- \rightarrow Al_{(s)}$	- 1.66 V

Increasing strength of oxidizing agent (↑)

Increasing strength of reducing agent (↓)

Standard Reduction (half-cell) Potentials (E^o_{red})

Which species will be reduced?

- The species with the most positive, least negative, E^o_{red} value will be reduced, as it has the greatest ability to attract electrons.
- An electron can only decrease its *PE* by moving to the species with the most positive, least negative, E^o_{red} value.

Standard Cell Potentials

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

- E^o_{cell}: The standard cell potential. The overall difference in *PE*/charge between the anode and the cathode.
- E^o_{red}(cathode): **This is where the reduction takes place.** **Most positive, least negative E^o_{red} value.** **Greater driving force to attract electrons.**
- E^o_{red}(anode): **This is where the oxidation takes place.** $E^o_{oxidation} = -E^o_{red}$ **If you flip the reaction you change the sign.**

Ex1) Standard Cell Potentials

Ex1) What is the cell potential for a voltaic cell that has nickel at one electrode and copper at the other? The cells are kept at 25°C and all ions in solution have 1.0 *M* concentrations.

From the table of reduction potentials:

$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ $E^o_{red} = +\ 0.34$ V

$Ni^{2+} + 2e^- \rightarrow Ni_{(s)}$ $E^o_{red} = -\ 0.25$ V

Ex1) Standard Cell Potentials (cont.)

$$E^o_{cell} = E^o_{red}(\text{cathode}) - E^o_{red}(\text{anode})$$
$$E^o_{cell} = E^o_{red}(\text{cathode}) + E^o_{oxidation}(\text{anode})$$

A positive value for E^o_{cell} means that the reaction is spontaneous.

Ex2) Standard Cell Potentials

Ex 2) Determine the value of the standard cell potential for a voltaic cell operating on a reaction between $AgNO_3$ and solid nickel.

Taken from the table of reduction potentials

$Ag^+ + e^- \rightarrow Ag_{(s)}$ $E^o_{red} = +\ 0.80$ V

$Ni^{2+} + 2e^- \rightarrow Ni_{(s)}$ $E^o_{red} = -\ 0.25$ V

Silver is reduced as it has a more positive reduction potential.

Ex2) Standard Cell Potentials (cont.)

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

$E^o_{cell} = E^o_{red}(\text{cathode}) + E^o_{oxidation}(\text{anode})$

Ex2) Standard Cell Potentials (cont.)

OR

$Ag^+ + e^- \rightarrow Ag_{(s)}$ $E^o_{red} = +0.80$ V

$Ni^{2+} + 2e^- \rightarrow Ni_{(s)}$ $E^o_{red} = -0.25$ V

You do not double the voltage when you multiply the equation by two. If you double the number of electrons you also double the energy (V = J/C).

$2Ag^+ + 2e^- \rightarrow 2Ag_{(s)}$ $E^o_{red} = +0.80$ V

$Ni_{(s)} \rightarrow Ni^{2+} + 2e^-$ $E^o_{oxidation} = +0.25$ V

$2Ag^+ + Ni_{(s)} \rightarrow 2Ag_{(s)} + Ni^{2+}$ $\mathbf{E^o_{red} = +1.05}$ **V**

Ex3) Standard Cell Potentials

Ex3) In a galvanic cell aqueous silver is reduced by an unknown metal. The standard cell potential is found to be 0.47 V. What is the reduction potential of the unknown metal?

$Ag^+ + e^- \rightarrow Ag_{(s)}$ $E^o_{red} = +0.80$ V

Ex3) Standard Cell Potentials (cont.)

The question is asking for the reduction potential of the unknown metal, even though that metal is being oxidized.

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