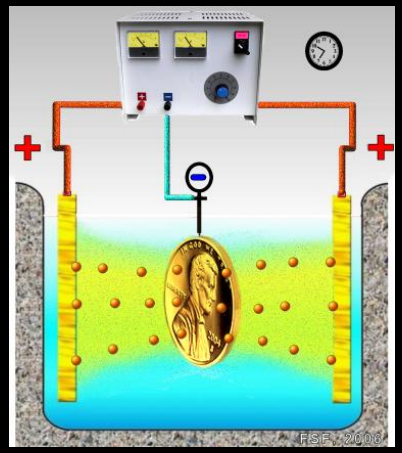
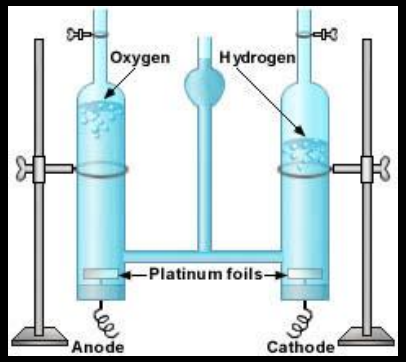
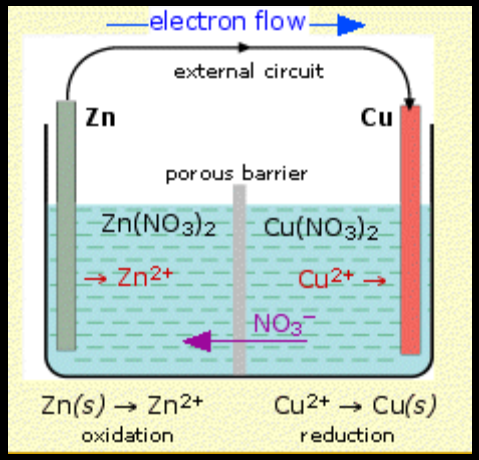
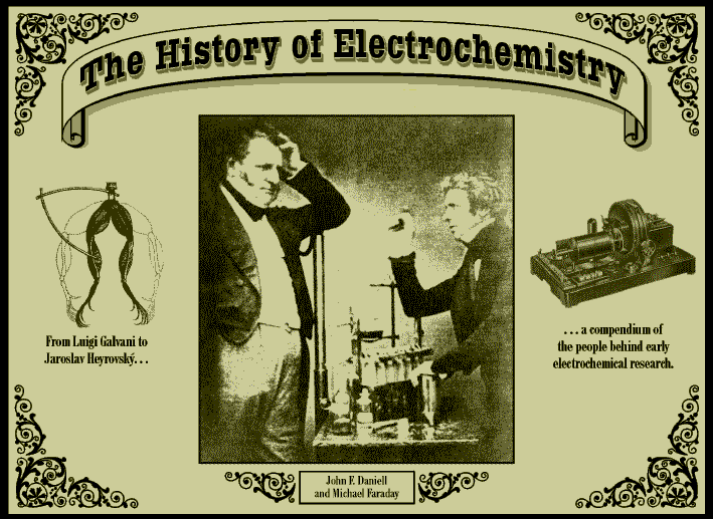






Electrochemistry



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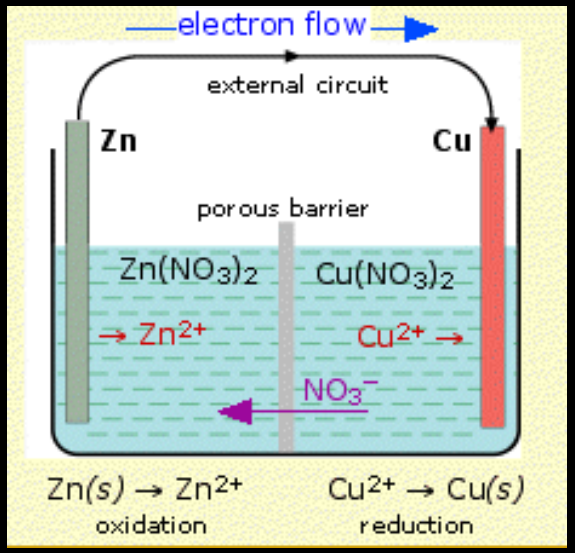
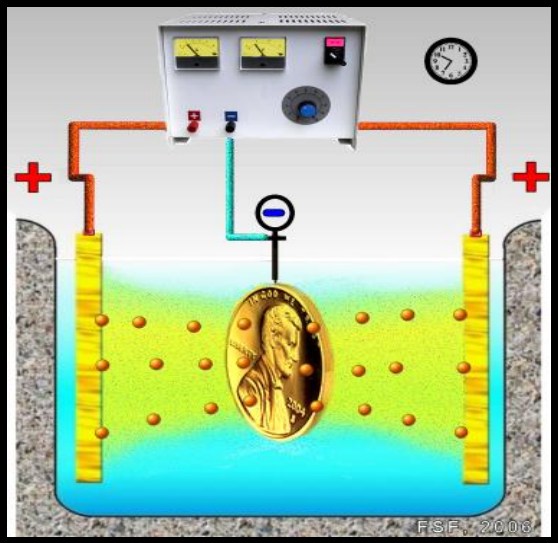
Electrochemistry

Interchange of *chemical* and *electrical* energy

Two Aspects:

- Producing current (electron flow → redox reactions)
- Using current to induce chemical change





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Common Electrical Terms

Electricity: presence and flow of electric charge

Electric Current: flow (movement) of electric charges

Proton is the unit of charge

Quantity	Definition	Measure or Unit
Electric charge	Charge on a proton	1.602×10^{-19} C
Electric current	The movement of charge	ampere = A = 1 C/s
Electric potential	The force trying to move the charge	volt = V = J/C
Electric field	The force acting upon other charges in the vicinity	

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Redox Revisited

Electrochemistry (movement of electrons): redox reactions

Best understood by the half-reaction scheme

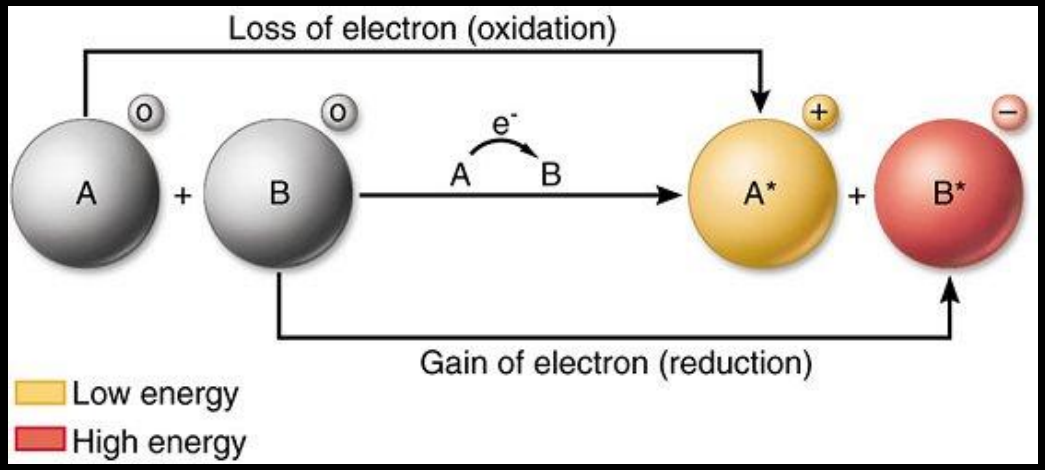
each half-reaction occurs at separate electrode

Electron transfer between atoms:

loss of electron = oxidation

gain of electron = reduction

simultaneous electron transfer = redox



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Electrochemistry: Producing Current

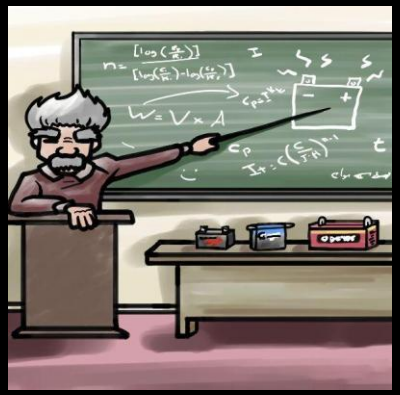
Production of current:

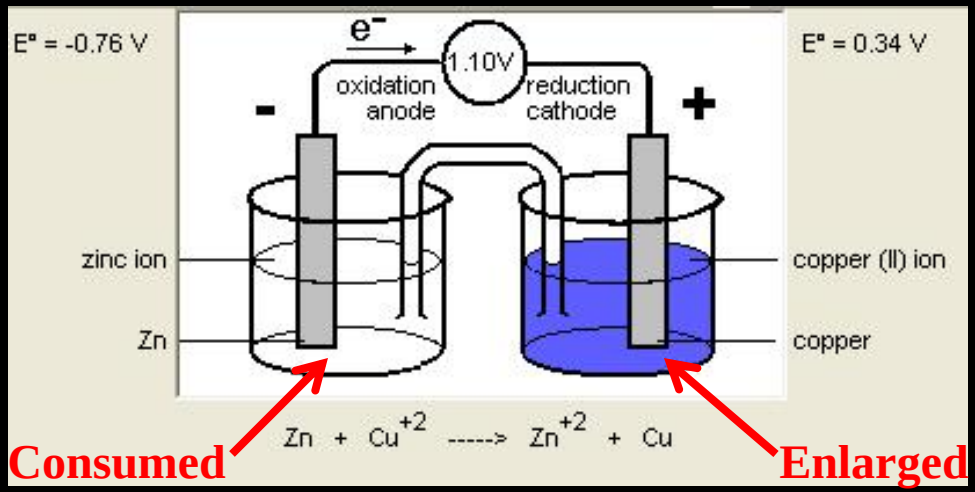
Batteries or galvanic cells

2 half-cells combine to produce a complete redox reaction

Half-cells connected via a salt bridge

Chemical Energy → Elecctrical Energy





Anode: Oxidation … lost electrons go to wire

Cathode: Reduction … electrons come from wire

Electrons move through an external wire & salt bridge

Current maintained until reactants consumed

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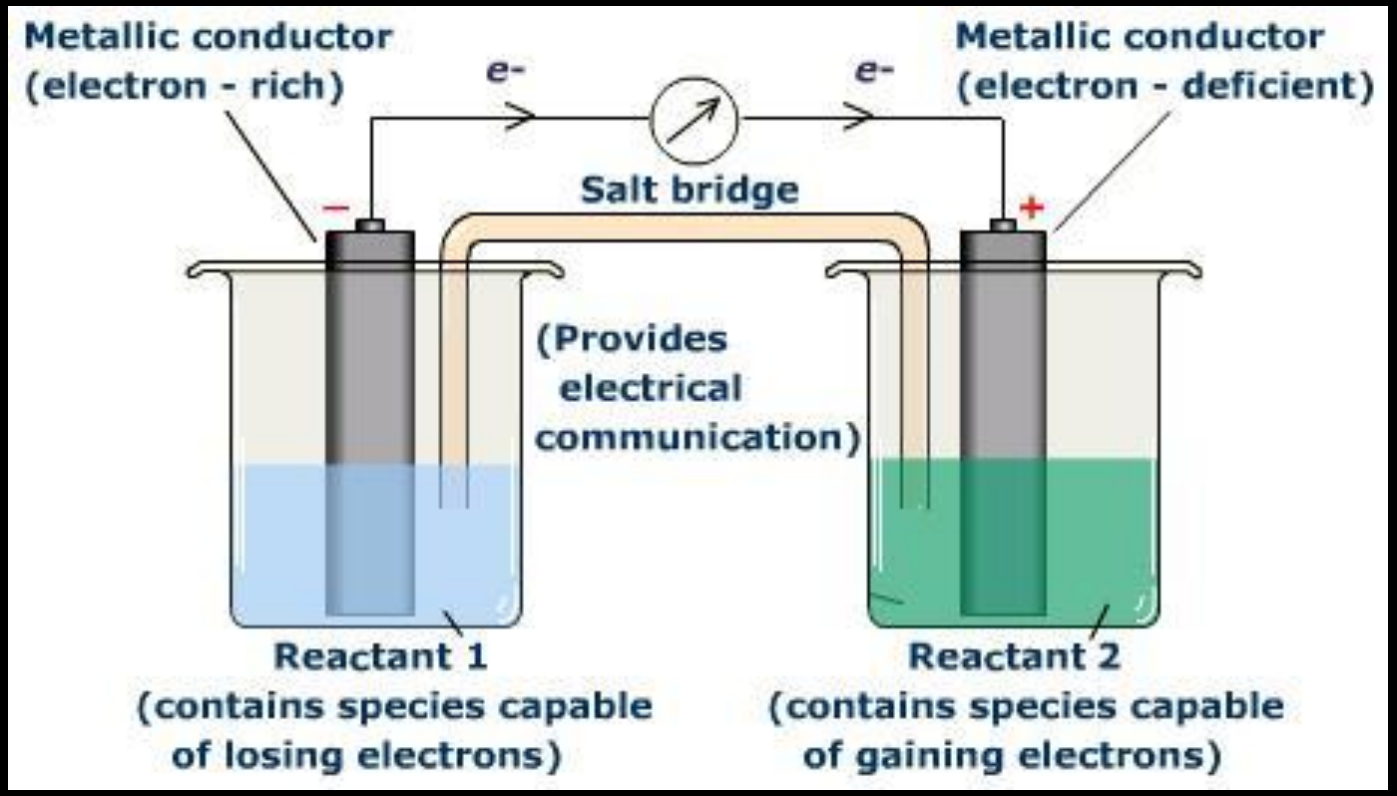
Galvanic (Voltaic) Cells

Devices using spontaneous redox reactions to create an electrical current

Half-reaction approach facilitates understanding

Each electrode: a half-cell

Current flows when half-cells are connected



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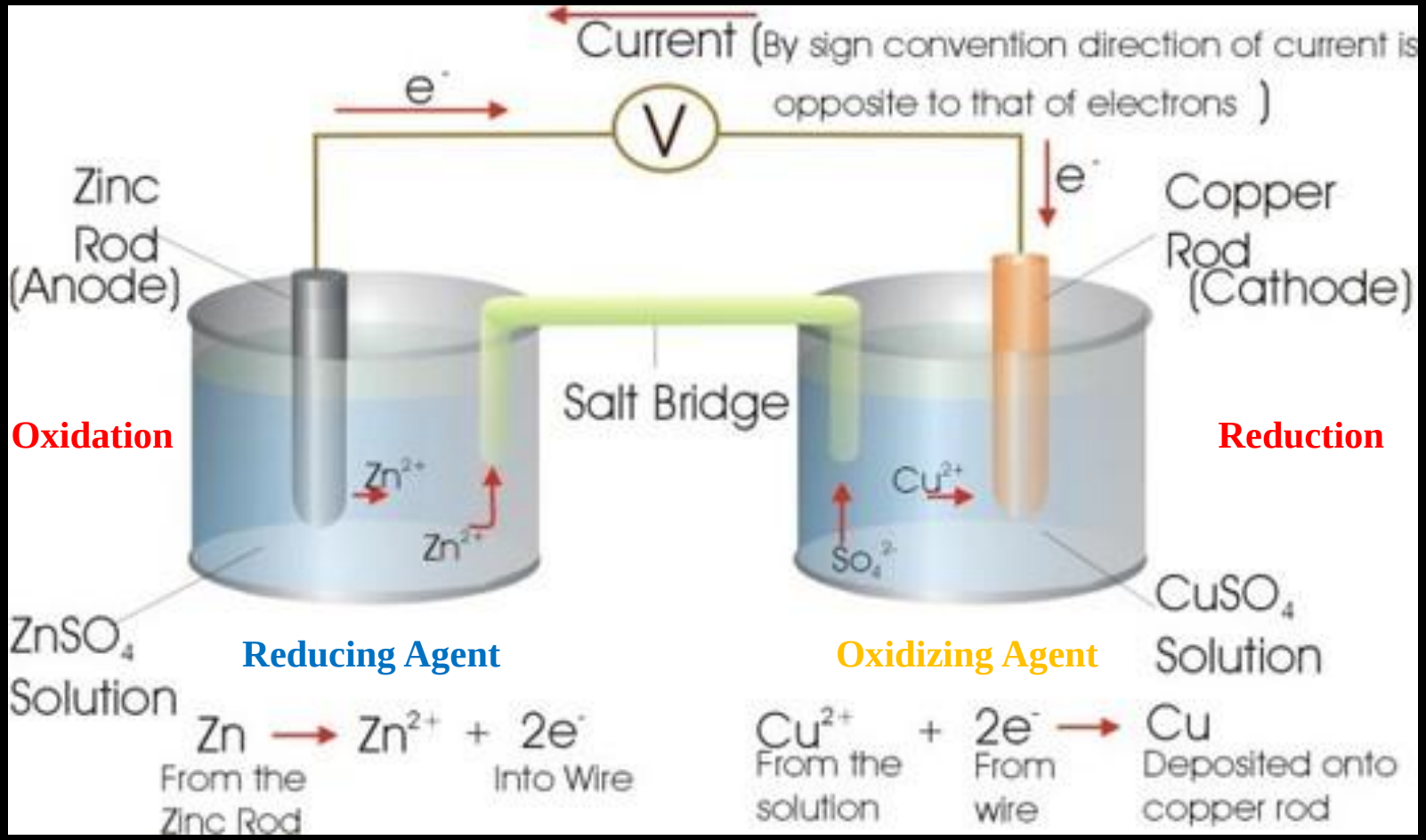
Galvanic Cell Terminology

Object Losing Electrons:
is oxidized
is reducing agent

Object Gaining Electrons:
is reduced
is oxidizing agent



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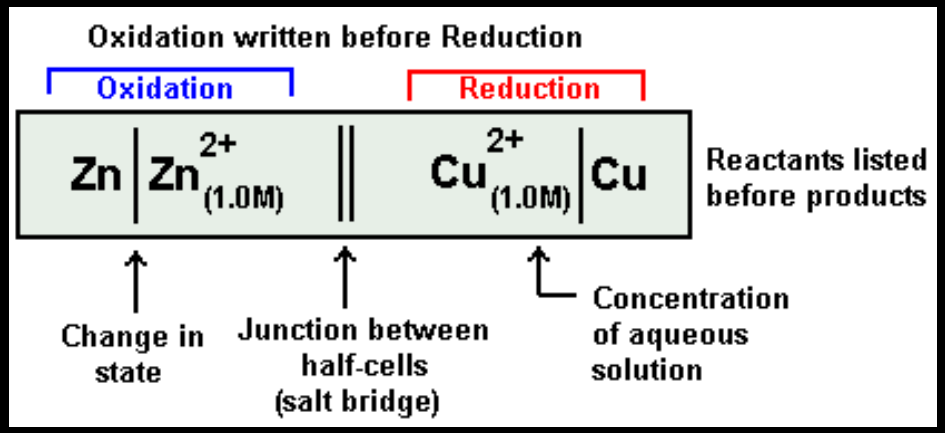
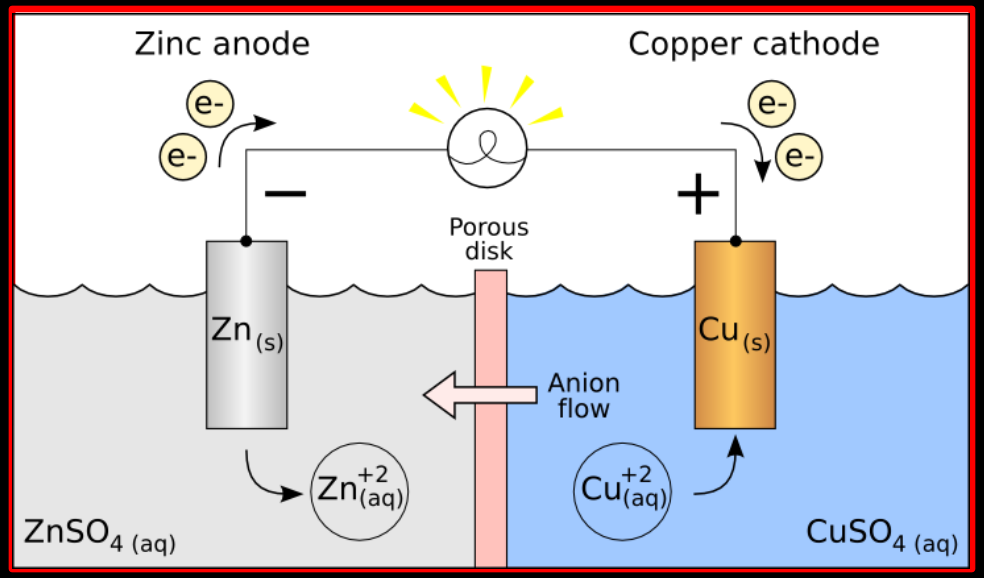
Cell Nomenclature





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Using Cell Notation

For;

magnesium undergoing oxidation at a magnesium anode
hydrogen undergoing reduction at a platinum cathode

Write the half-reactions:

Oxidation: $Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2\ e^-$

Reduction: $2\ H^+_{(aq)} + 2e^- \rightarrow H_{2\ (g)}$

Net: $Mg_{(s)} + 2\ H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2\ (g)}$

Write the cell notation with oxidation at the far left:

$Mg_{(s)} \mid Mg^{2+}_{(aq)} \parallel 2\ H^+_{(aq)} \mid H_{2\ (g)} \mid Pt_{(s)}$

↑ **Active electrode** ↑ **Inert electrode**

Inert electrode: does not participate in the chemical reaction
Active electrode: participates in the reaction

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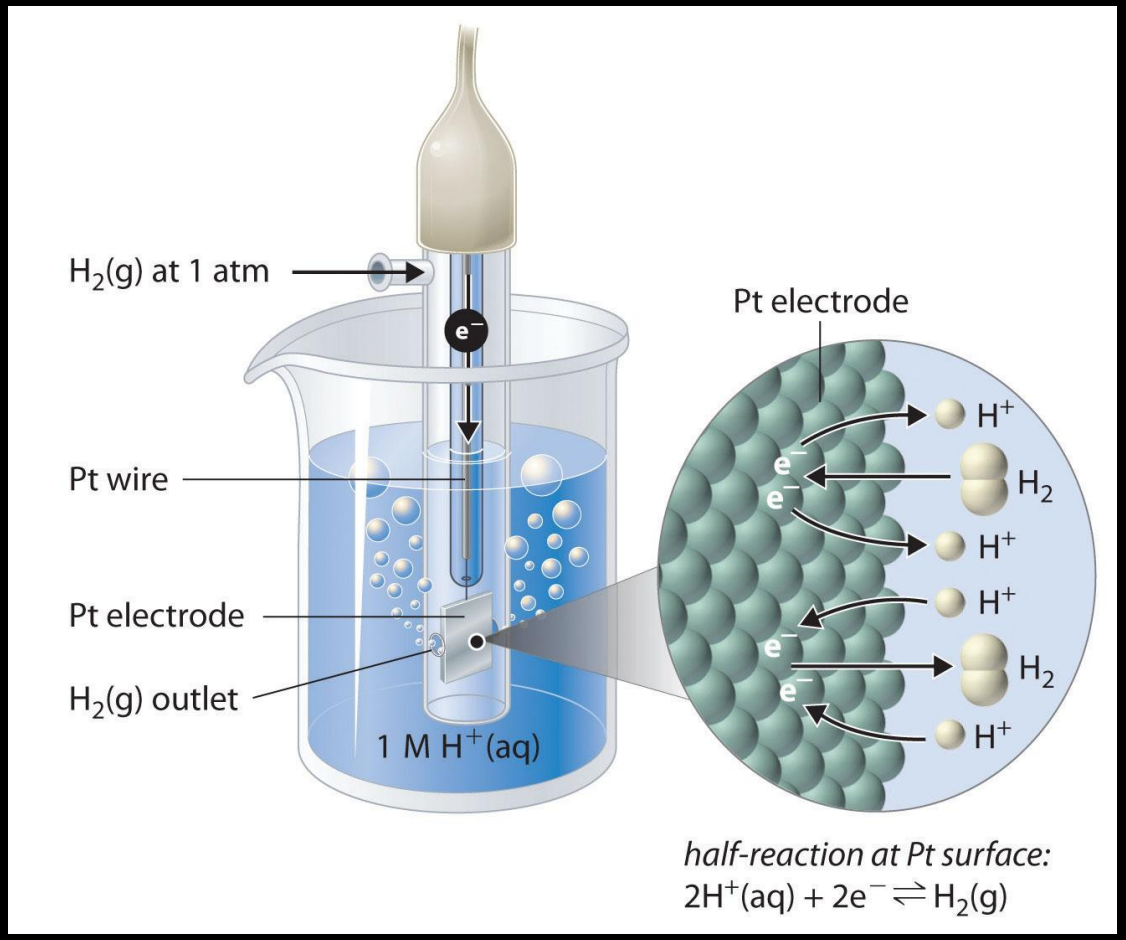
Standard Hydrogen Half-Cell

E= 0.00 V
1.0 Molar Solution
298 K
1 atm



$2H^+_{(aq,\ 1\ M)} + 2e^-$ **$H_{2\ (g,\ 1\ atm)}$** **$E^0 = 0.00$ V**

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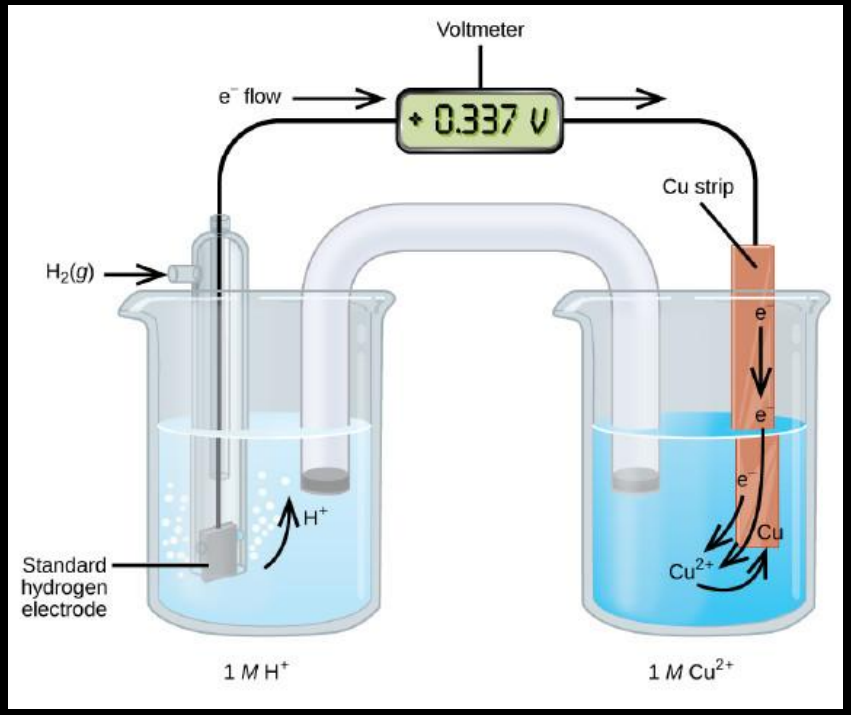
Establishing Reduction Potential

For: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ Half-reaction



Assemble Galvanic Cell
Use SHE as anode
Measure cell voltage

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$0.337\ V = E^0_{cathode} - 0.00\ V$$

$$E^0_{cathode} = 0.337\ V$$

Tables of half-reaction reduction potentials have been prepared
Oxidation (reverse of reduction) potential has opposite sign
Can be used to determine any cell potential

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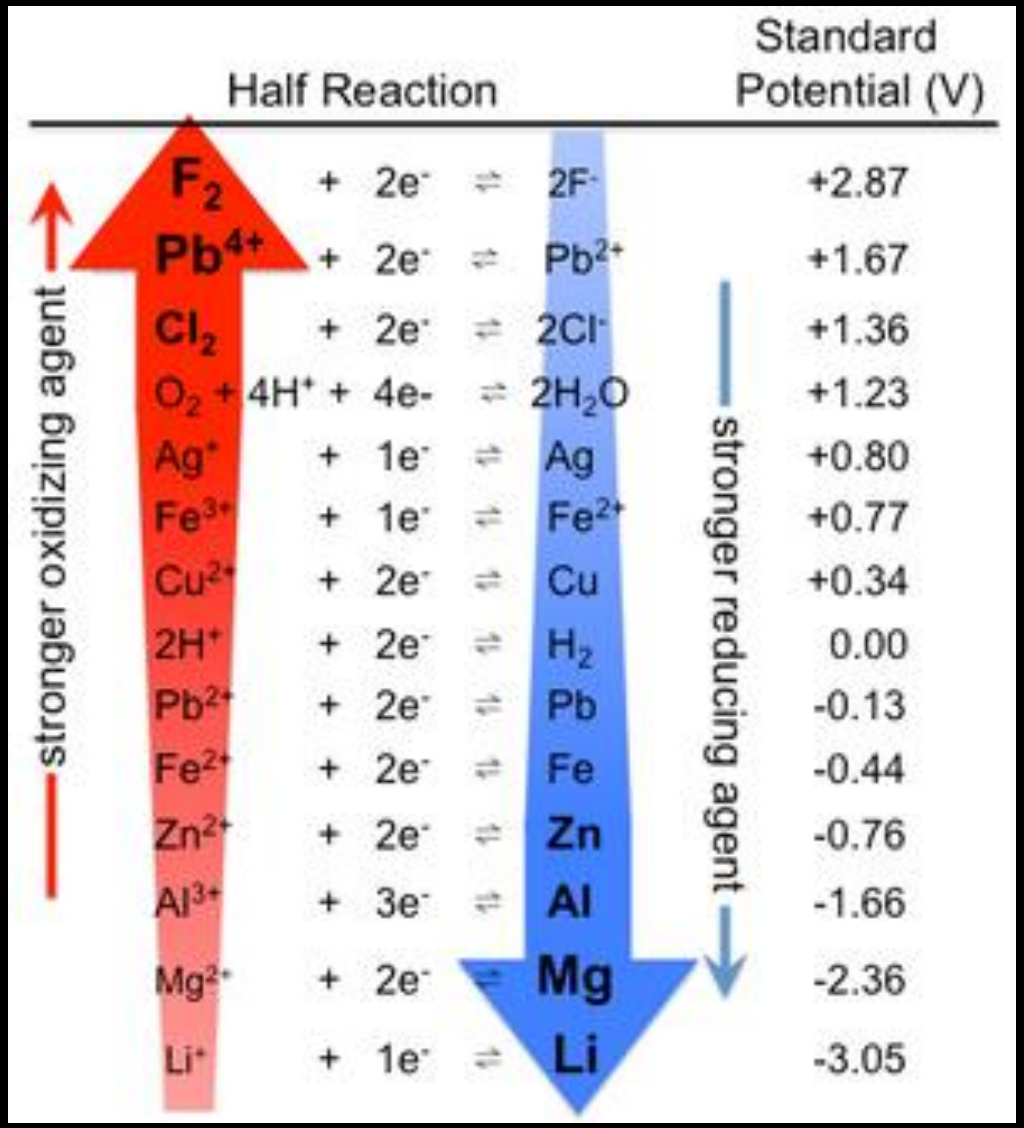
Electrochemical Series



Half-reactions ordered by E^0

> Negative > reducing agent

> Positive > oxidizing agent

Most negative: anode

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Determine Cell Voltage

Use tables to find Redox Potentials for each half-cell

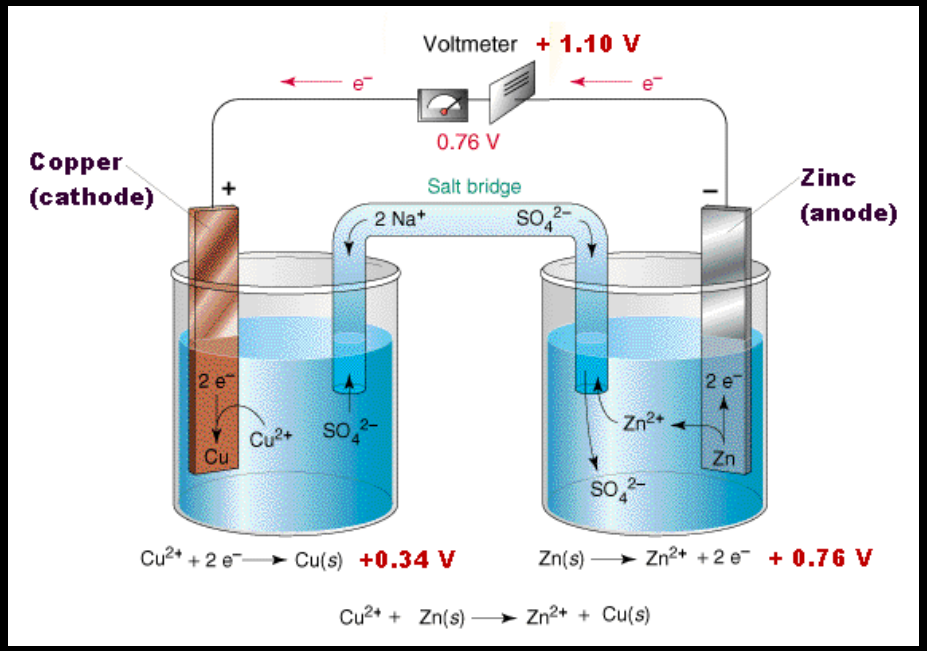
$Cu^{2+} + 2\ e^- \longrightarrow Cu_{(s)}$ + 0.34 V

$Zn^{2+} + 2\ e^- \longrightarrow Zn_{(s)}$ - 0.76 V (Zinc is anode)

Cu is reduced and Zn is oxidized

Using $E^0_{cell} = E^0_{reduced} - E^0_{Oxidized}$

$E^0_{cell} =$ 0.34 V - - 0.76 V = 1.10 V



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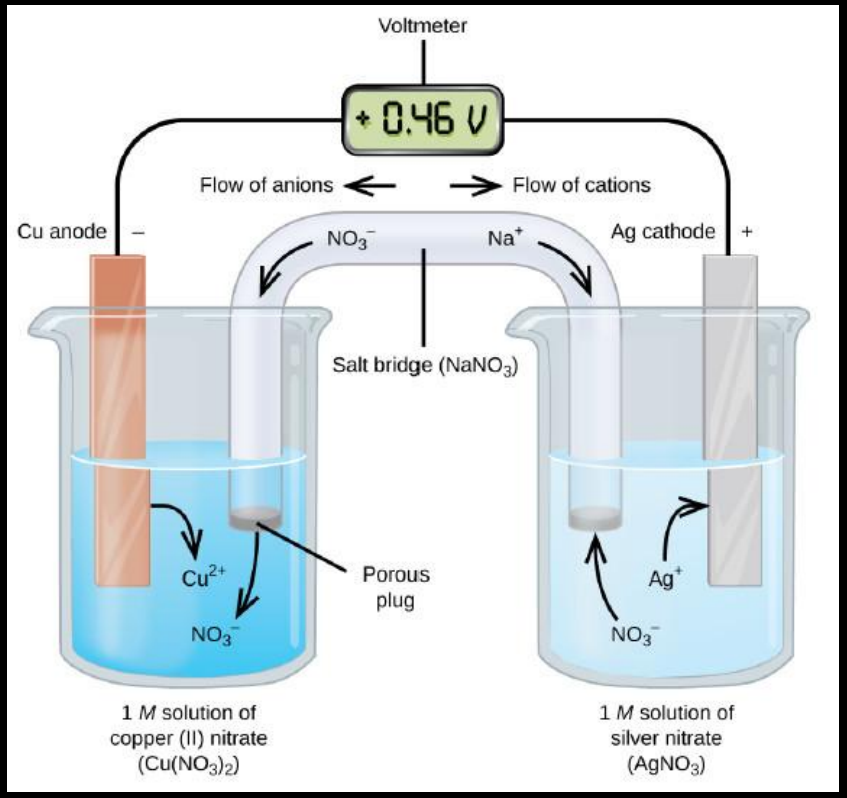
The Copper-Silver Cell



Anode: $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ **(0.34 V)**

Cathode: $2\,Ag^+_{(aq)} + 2e^- \rightarrow 2\,Ag_{(s)}$ **(0.80 V)**

Net: $Cu_{(s)} + 2\,Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2\,Ag_{(s)}$

$$Cu_{(s)}\,|Cu^{2+}_{(aq,\,1M)}\|Ag^+_{(aq,\,1M)}|Ag(s)$$

Using $E^0_{cell} = E^0_{reduced} - E^0_{Oxidized}$

Using $E^0_{cell} = E^0_{Cathode} - E^0_{Anode}$

$E^0_{cell} = 0.80\ V - 0.34\ V = 0.46\ V$

+ E: reaction spontaneously occurs

Electrons Flow: anode to cathode
Current Flow: cathode to anode

Anode: Copper Consumed
Cathode: Silver Deposited

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Calculate Cell Potential

What is the voltage of an electrochemical cell that consists of:
Mg electrode in 1 M $Mg(NO_3)_2$ solution and an Ag electrode in 1 M $AgNO_2$?

Determine the half-reactions:

$Mg^{2+}_{(aq)} + 2\ e^- \rightarrow Mg_{(s)}$ -2.372 V

$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$ 0.7996 V

Determine cell half-reactions:

Anode: $Mg^{2+}_{(aq)} + 2\ e^- \rightarrow Mg_{(s)}$

Cathode: $Ag_{(s)} \rightarrow Ag^+_{(aq)} + 1\ e^-$

Determine net cell reaction:

$Mg^{2+}_{(aq)} + 2\ Ag_{(s)} \rightarrow Mg_{(s)} + 2\ Ag^+_{(aq)}$

The Cell notation

$Mg^{2+}_{(aq)} \mid Mg_{(s)} \parallel Ag_{(s)} \mid Ag^+_{(aq)}$

Calculate cell voltage

$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$E^0_{cell} = 0.7996\ V - (-2.372\ V)$

$E^0_{cell} = 3.172\ V$

Reducing Agent: Mg^{2+}
Oxidizing Agent $Ag_{(s)}$

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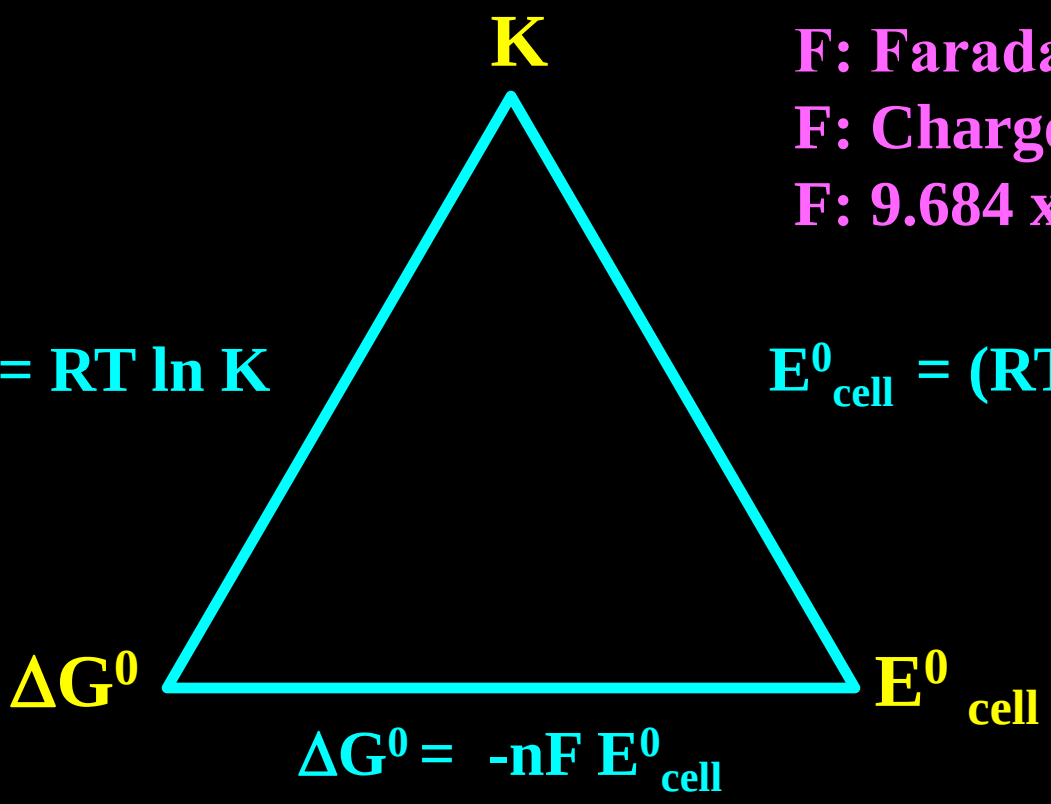
The Nernst Equation

Relates E^0 cell to:

ΔG^0 (Gibbs Free Energy) and / or K (Equilibrium) Constant

Electrochemical reactions related to thermodynamics (work)

Electrical Work = volts x charge (Coulombs) = Energy (Joules)



F: Faraday's Constant

F: Charge on 1 mole electrons

F: 9.684×10^4 J/Vmol

At standard temperature

$E^0_{cell} = (RT/nF) \ln K$

$E^0_{cell} = 0.0257 \text{ V} / n \ \ln K$

$E^0_{cell} = 0.0592 \text{ V} / n \ \log K$

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Using The Nernst Equation

What is the ΔG^0 and K_{eq} for the following at 25 °C?

$$2\ Ag^+_{(aq)} + Fe_{(s)} \rightleftarrows 2\ Ag_{(s)} + Fe^{2+}_{(aq)}$$

Write the reduction half-reactions; look up the E^0

$Ag^+_{(aq)} + 1\ e^- \rightarrow Ag_{(s)}$ 0.7996 V

$Fe^{2+}_{(aq)} + 2\ e^- \rightarrow Fe_{(s)}$ -0.447 V

The most negative value is the anode

Write the half-cell reactions and balance

Anode: $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2\ e^-$

Cathode: $2\ Ag^+_{(aq)} + 2\ e^- \rightarrow 2\ Ag_{(s)}$

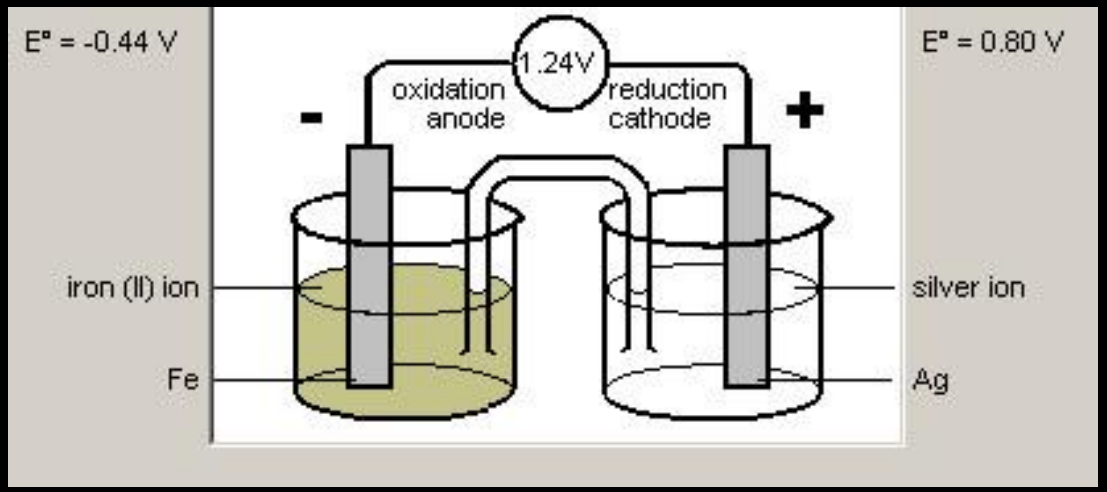
Net: $2\ Ag^+_{(aq)} + Fe_{(s)} \rightarrow 2\ Ag_{(s)} + Fe^{2+}_{(aq)}$

Determine E^0

$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$E^0_{cell} = 0.7996\ V - (-0.447)\ V$

$E^0_{cell} = 1.247\ V$



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Using The Nernst Equation

For n = 2, solve for K_{eq}

$E^0_{cell} = 0.0592\ V / 2 \log K_{eq}$

$E^0_{cell} = 0.0296\ V \log K_{eq}$

$1.247\ V = 0.0296\ V \log K_{eq}$

$\text{Log } K_{eq} = 42.2$

$K_{eq} = 1.34 \times 10^{42}$

Determine Standard Fee Energy

$\Delta G^0 = -nFE^0_{cell}$

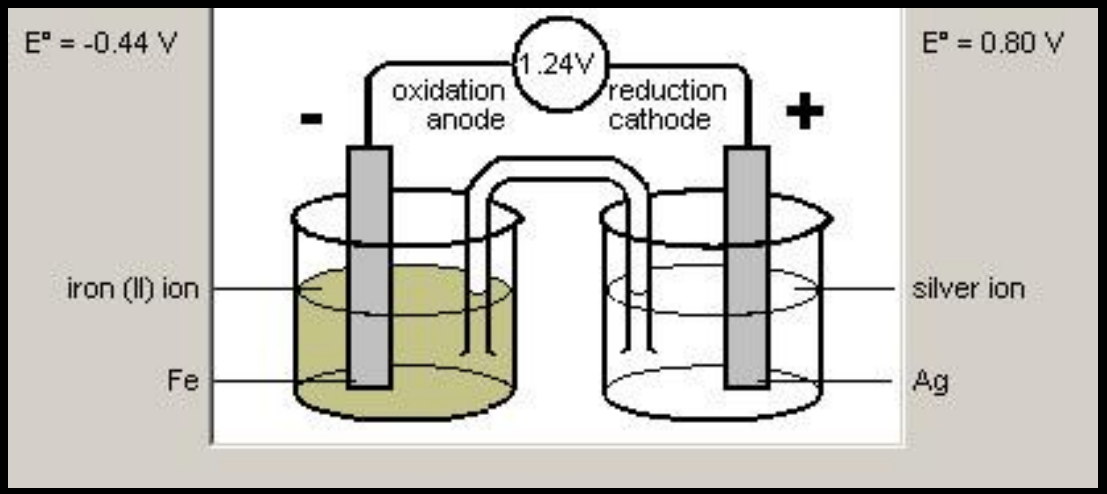
$\Delta G^0 = -2\ (96{,}485\ J/Vmol)\ 1.247\ V$

$\Delta G^0 = -240.6\ kJ/mol$

E^0 positive ➔ spontaneous

DG^0 negative ➔ spontaneous

$K_{eq} > 1$ ➔ spontaneous



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Nernst Equation Problem

What is the ΔG^0 and K_{eq} for the following at 25 °C?

$$2\ Cu^{2+}_{(aq)} + Sn_{(s)} \rightleftarrows Sn^{2+}_{(aq)} + Cu^{+}_{(aq)}$$

Write the reduction half-reactions; look up the E^0

$Cu^{2+}_{(aq)} + 1\ e^- \rightarrow Cu^{+}_{(aq)}$ 0.153 V

$Sn^{2+}_{(aq)} + 2\ e^- \rightarrow Sn_{(s)}$ - 0.1375 V

The most negative value is the anode

Write the half-cell reactions and balance

Anode: $Sn^{2+}_{(aq)} + 2\ e^- \rightarrow Sn_{(s)}$

Cathode: $2\ Cu^{+}_{(aq)} \rightarrow 2\ Cu^{2+}_{(aq)} + 2\ e^-$

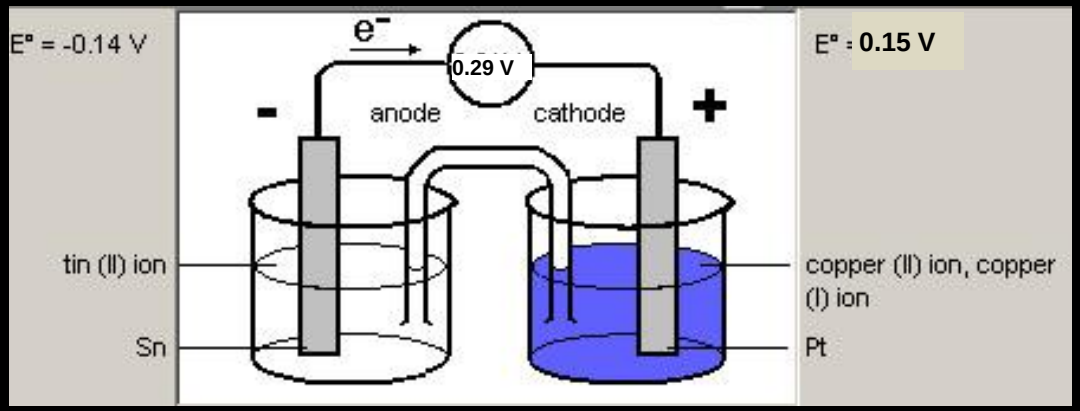
Net: $Sn^{2+}_{(aq)} + 2\ Cu^{+}_{(aq)} \rightarrow Sn_{(s)} + 2\ Cu^{2+}_{(aq)}$

Determine E^0

$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$E^0_{cell} = 0.153\ V - (-0.1375)\ V$

$E^0_{cell} = 0.291\ V$



Nernst Equation Problem

For n = 2, solve for K_{eq}

$E^0_{cell} = 0.0592\ V / 2 \log K_{eq}$

$E^0_{cell} = 0.0296\ V \log K_{eq}$

$0.291\ V = 0.0296\ V \log K_{eq}$

$\text{Log } K_{eq} = 9.836$

$K_{eq} = 6.78 \times 10^9$

Determine Standard Fee Energy

$\Delta G^0 = -nFE^0_{cell}$

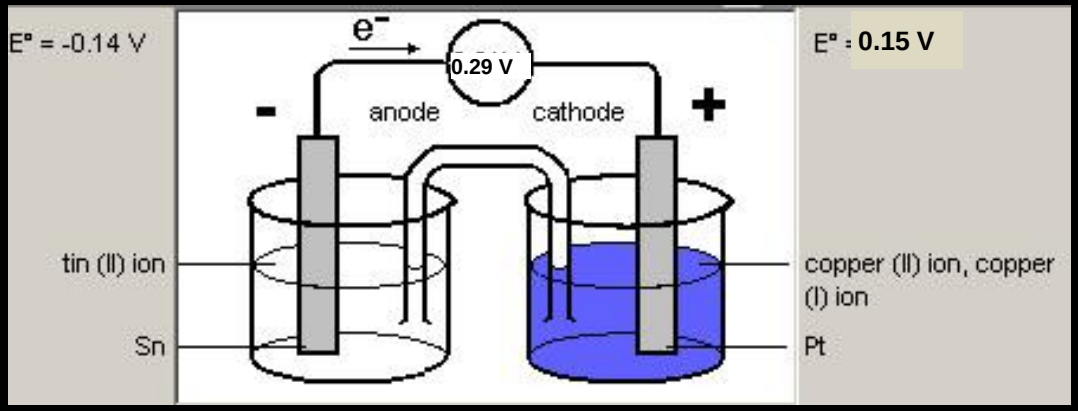
$\Delta G^0 = -2\ (96{,}485\ J/Vmol)\ 0.291\ V$

$\Delta G^0 = -\ 56.2\ kJ\ /mol$

E^0 positive ➔ spontaneous

DG^0 negative ➔ spontaneous

$K_{eq} > 1$ ➔ spontaneous



Correlating Cell Potential to Reaction Quotient (Q)

For the reaction: $mA + nB \rightleftharpoons xC + yD$

$$Q = \frac{[C]^x[D]^y}{[A]^m[B]^n}$$

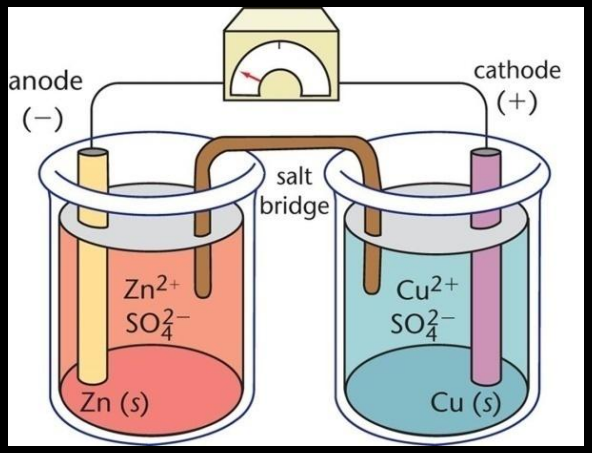
Where Q will have values changing from 0 to K_{eq} as reaction proceeds

Relating cell potential to changes over time gives the Nernst Equation:

$$E_{cell} = E^0_{cell} - RT/nF \ln Q$$

At standard temperature (298.15 K):

$$E_{cell} = E^0_{cell} - 0.0257\ V/n \ln Q \quad \text{or} \quad E_{cell} = E^0_{cell} - 0.0592\ V/n \log Q$$



At temperatures different from standard, expression must be reevaluated

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Correlating Cell Potential to Reaction Quotient (Q)

At room temperature, is the following spontaneous:

$$Co_{(s)} + Fe^{2+}_{(aq,\ 1.96\ M)} \rightarrow Co^{2+}_{(aq,\ 0.15\ M)} + Fe_{(s)}$$

At standard temperature and conditions, can simply look at reduction potentials:

$Co_{(s)} \rightarrow Co_{(aq)} + 2e^-$ $\quad E^0 =$ 0.28 V (oxidation: anode)

$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$ $\quad E^0 =$ - 0.447 V (reduction: cathode)

As written Co is the anode

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = -0.447\ V - (-0.28)\ V$$

$E^0_{cell} = -0.17$ V Negative E^0 → reaction as written is not spontaneous

At concentrations given; use Nernst Equation to get E_{cell}:

$Q = 0.15\ M / 1.94\ M = 0.077$

$$E_{cell} = E^0_{cell} - 0.0592\ V / 2 \log Q$$

$$E_{cell} = -0.17\ V - 0.0592\ V / 2 \log 0.077$$

$$E_{cell} = -0.17\ V - 0.0592\ V / 2 \ (-1.11)$$

$$E_{cell} = -0.17\ V + 0.033\ V$$

$E_{cell} = -0.014$ V Negative E_{cell} → reaction as written is not spontaneous

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Correlating Cell Potential to Reaction Quotient (Q)

What is the standard temperature cell potential for:

$$Al_{(s)} \mid Al^{3+}_{(aq,\ 0.15\ M)} \parallel Cu^{2+}_{(aq,\ 0.025\ M)} \mid Cu_{(s)}$$

At standard temperature and conditions, can simply look at reduction potentials:

$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-$ $\quad E^0 = -1.662$ V (oxidation: anode)

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ $\quad E^0 = 0.34$ V (reduction: cathode)

As written Al is the anode

Net: $3\ Cu^{2+}_{(aq)} + 2\ Al_{(s)} \rightarrow 2\ Al^{3+}_{(aq)} + 2\ Cu_{(s)}$

$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$E^0_{cell} = 0.34\ V - (-1.662)\ V$

$E^0_{cell} = 2.00$ V Positive $E^0 \rightarrow$ reaction as written is spontaneous

At concentrations given; use Nernst Equation to get E_{cell}:

$Q = (0.15)^2 / (0.025)^3 = 1{,}440$

$E_{cell} = E^0_{cell} - 0.0592\ V / 2 \quad \log Q$

$E_{cell} = 2.00\ V - 0.0592\ V / 6 \quad \log 1440$

$E_{cell} = 2.00\ V - 0.0592\ V / 6 \quad (3.15)$

$E_{cell} = 2.00\ V - 0.031\ V$

$E_{cell} = 1.97\ V$ Positive $E_{cell} \rightarrow$ reaction as written is spontaneous

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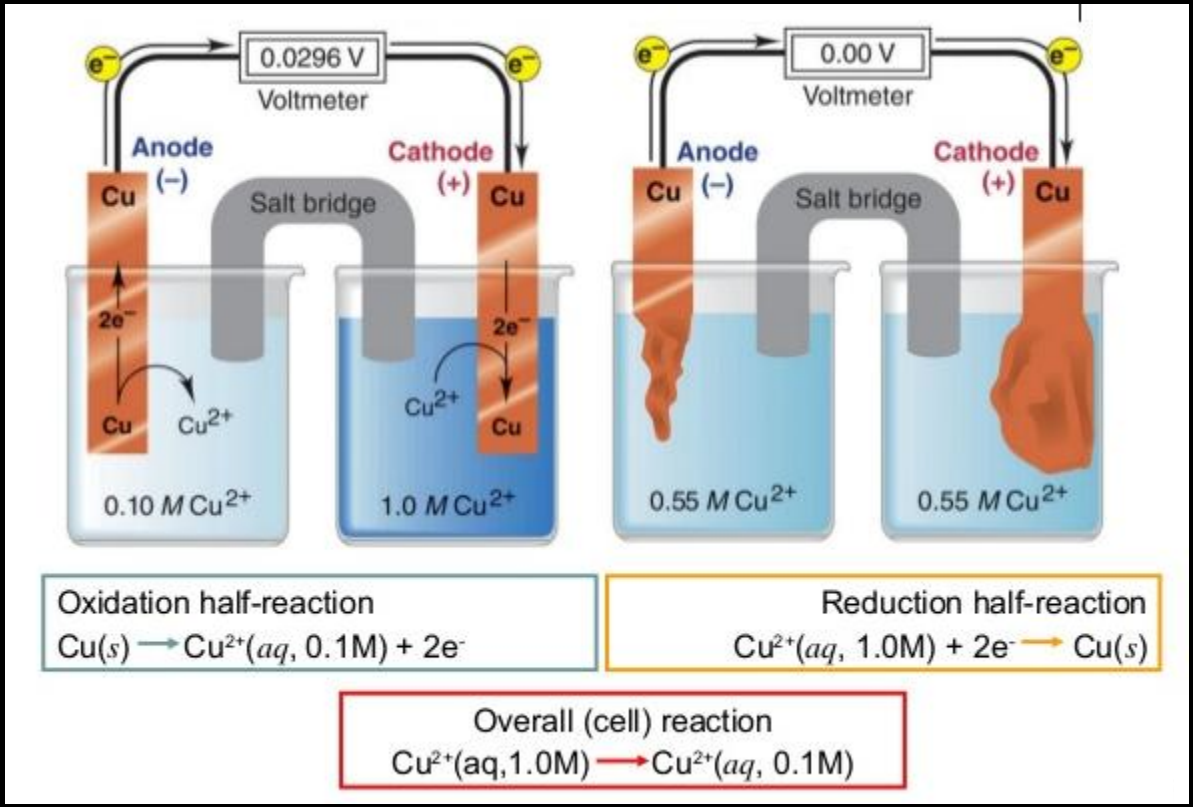
Concentration Cells

Two identical chemical half-cells (same metal / ion components)

Different concentrations of dissolved ionic component

Electrons flow from lower to higher concentration

Electrons flow until ion concentrations are equal across salt bridge



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Concentration Cell

Both sides the same electrodes; cells differ by concentration. For:

$$Zn_{(s)} \mid Zn^{2+}_{(aq,\ 0.10\ M)} \parallel Zn_{(s)} \mid Zn^{2+}_{(aq,\ 0.50\ M)}$$

Since both cells use the same half-reaction, E^0_{cell} is 0.00 V

At concentrations given; use Nernst Equation to get E_{cell}:

$Q = (0.10) / (0.50) = 0.20$

$E_{cell} = E^0_{cell} - 0.0592\ V / 2 \quad \log Q$

$E_{cell} = 0.00\ V - 0.0592\ V / 2 \quad \log 0.20$

$E_{cell} = 0.00\ V - 0.0592\ V / 2 \quad (-0.69)$

$E_{cell} = 0.00\ V - (-0.021\ V)$

$E_{cell} = 0.021\ V$ Positive E_{cell} ➔ reaction as written is spontaneous

For a concentration cell to be spontaneous, Q must be < 1

Anode is the least concentrated solution

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Concentration Cell Problem

What must Q be for the cell below to result in a E_{cell} of 0.10 V?
What would the anode concentration be for the same cathode concentration?

$$Zn_{(s)} \mid Zn^{2+}_{(aq,\ 0.10\ M)} \parallel Zn_{(s)} \mid Zn^{2+}_{(aq,\ 0.50\ M)}$$

Use Nernst Equation to get Q:

$$E_{cell} = E^0_{cell} - 0.0592\ V / 2 \ \log Q$$
$$0.10\ V = 0.00\ V - 0.0592\ V / 2 \ \log Q$$
$$0.10\ V = 0.00\ V - 0.0296\ V \ Log\ Q$$
$$0.10\ V = -\ 0.\ 0296\ V \log Q$$
$$\log Q = -\ 3.37$$
$$Q = 0.00042$$

$$Q = [0.50] / [Zn^{2+}]$$
$$0.00042 = [Zn^{2+}] / [0.50]$$
$$Zn^{2+} = 2.1 \times 10^{-4}\ M$$

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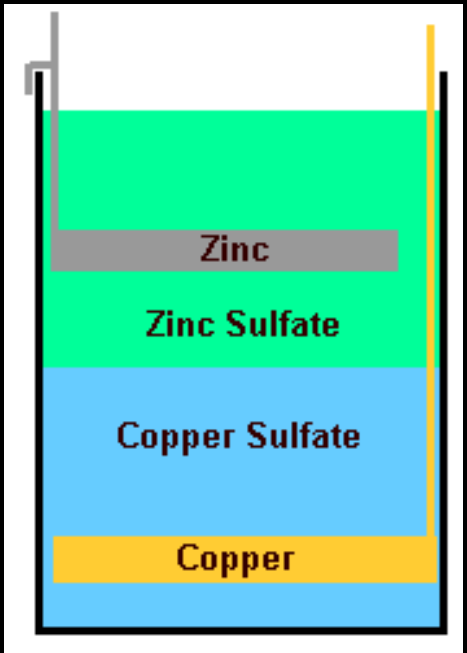
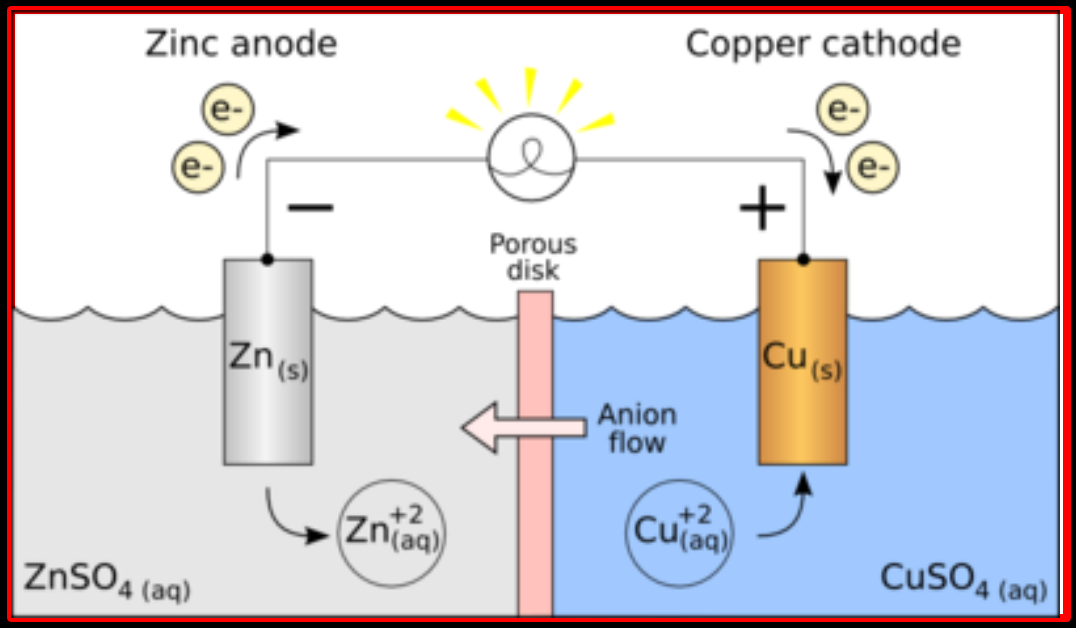
Configurations Without A Salt Bridge

Gravity Cell
Density separates cells



Porous Membrane
Ceramic desk separates cells



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Batteries

Battery: electrochemical cell (or cells) that produces an electric current

Primary: cannot be recharged

Secondary: can be recharged

All batteries are compromise with respect to:

- **mass**
- **volume**
- **current capacity**
- **environmental use**
- **cost**
- **reliability**

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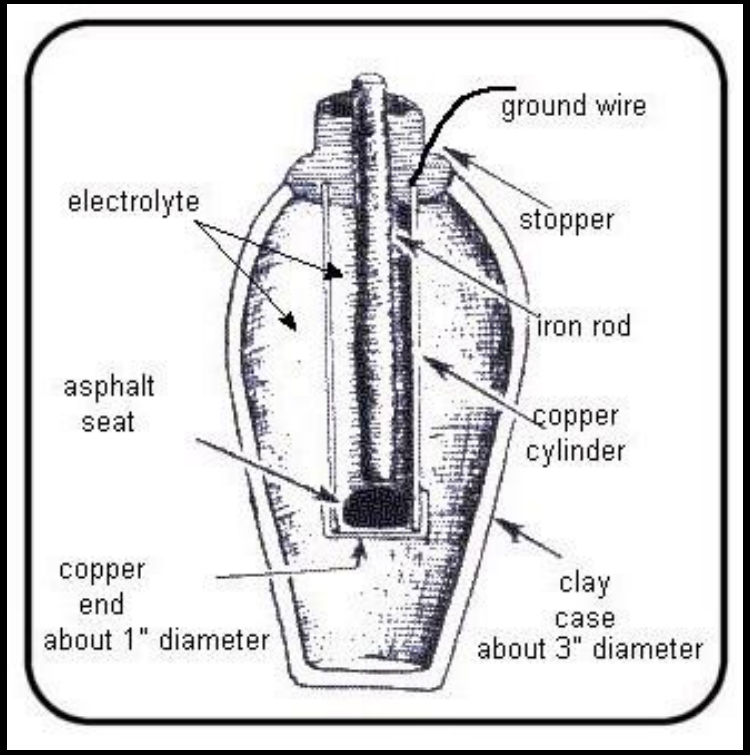
Baghdad Battery



~ 100 AD

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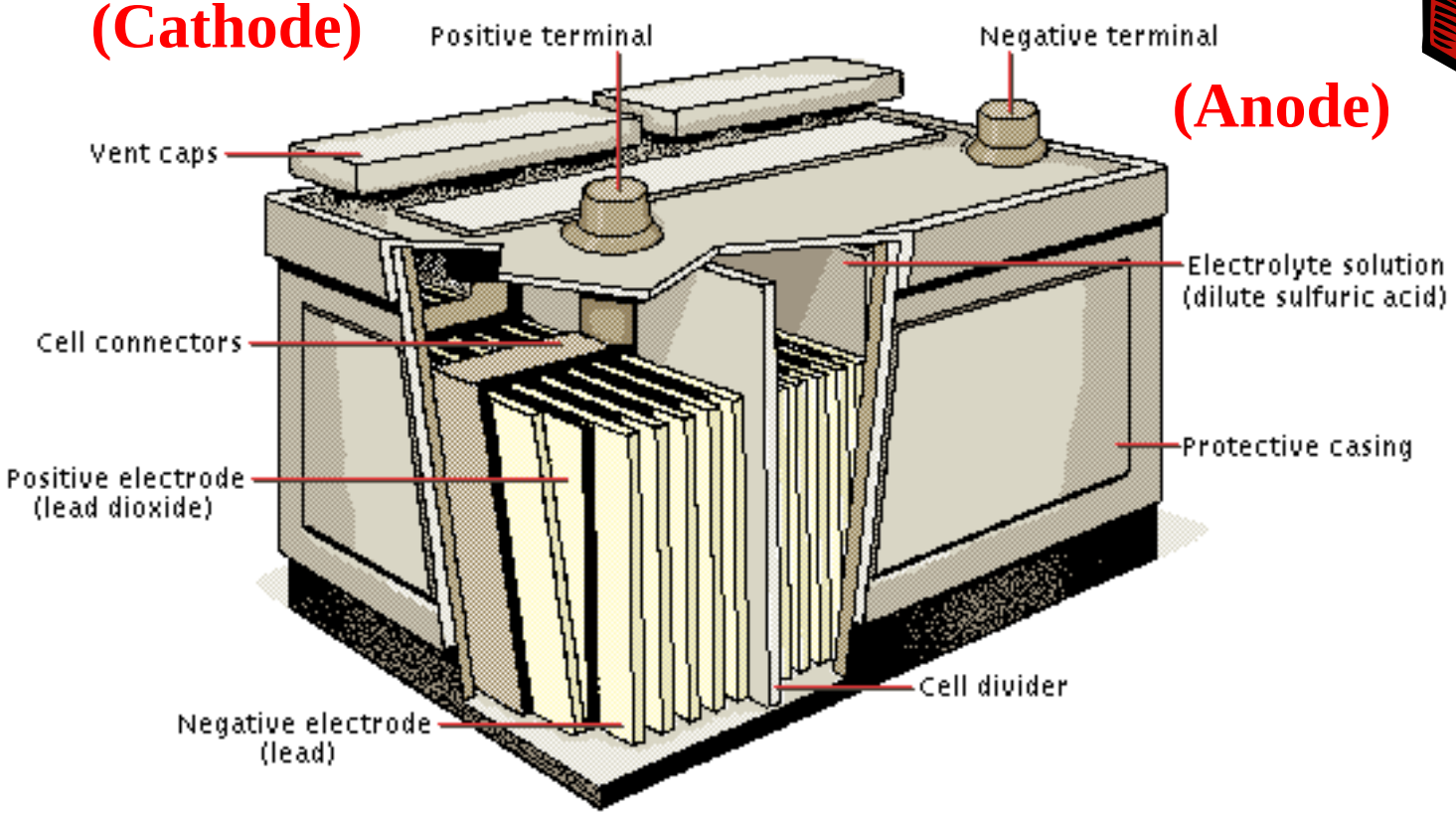
Lead Acid Battery



Anode: $Pb_{(s)} + HSO_4^-{}_{(aq)} \rightarrow PbSO_{4(s)} + H^+{}_{(aq)} + 2e^-$

Cathode: $PbO_{2(s)} + 3H^+{}_{(aq)} + HSO_4^-{}_{(aq)} + 2e^- \rightarrow PbSO_{4\,(s)} + 2\,H_2O$

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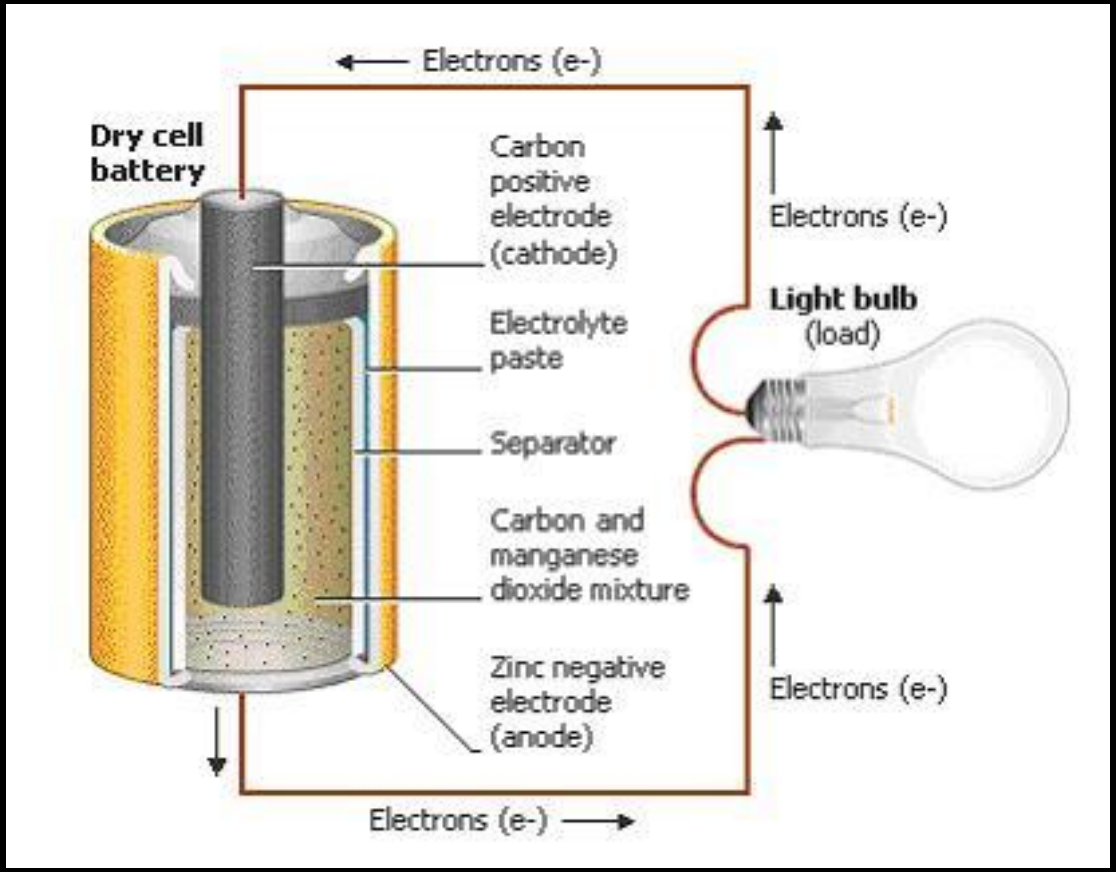
Dry Cell Battery



Anode: $Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$

Cathode: $2\ NH_4^+{}_{(aq)} + 2\ MnO_{2\,(s)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2\ NH_{3(aq)} + H_2O$

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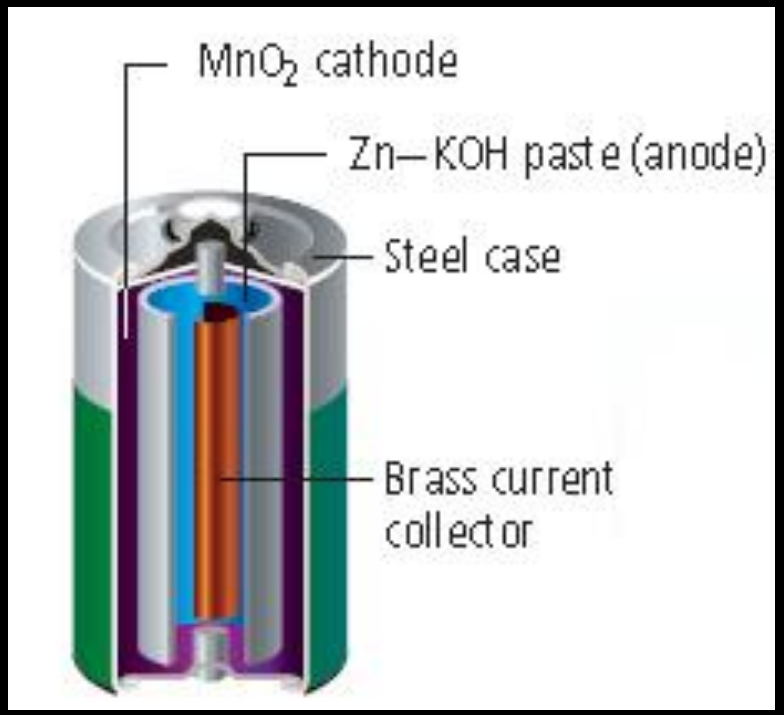
Alkaline Cell Battery



Zinc more stable in basic environment

Anode: $Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$

Cathode: $2MnO_{2(s)} + H_2O_{(l)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)}$

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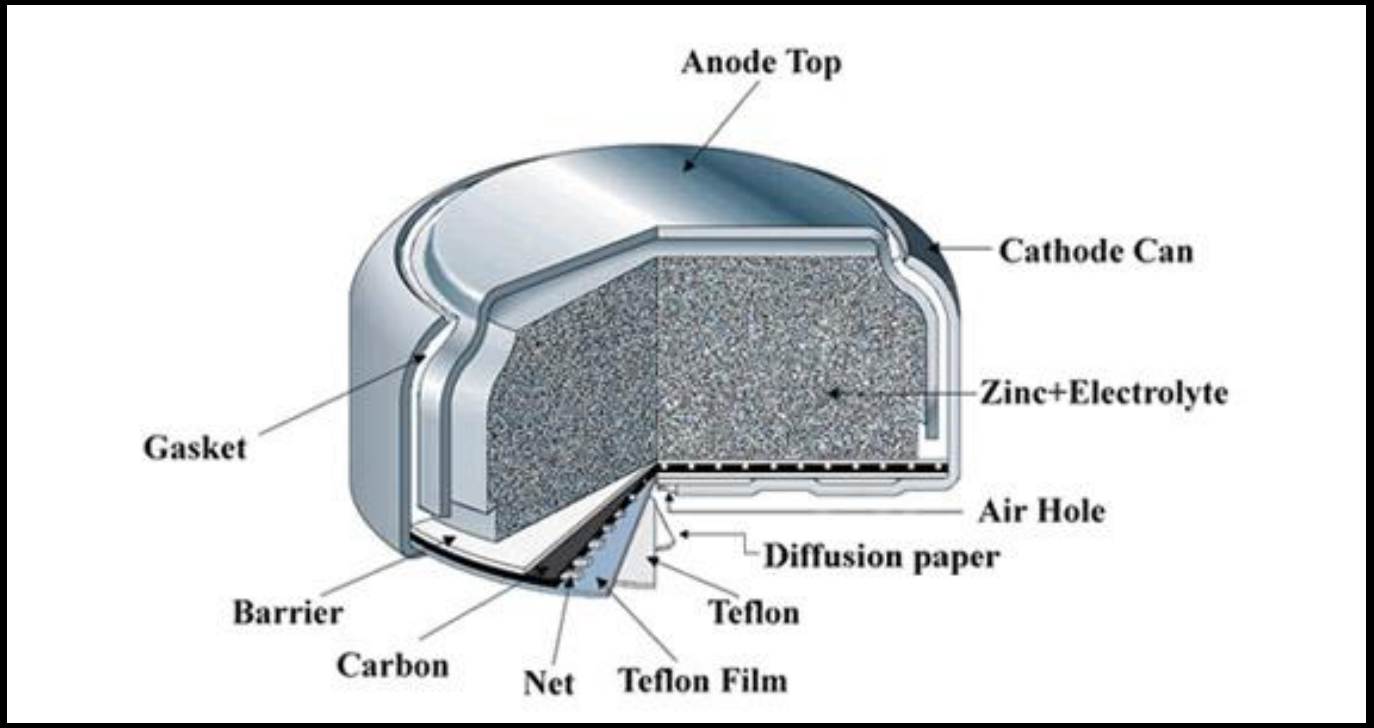
Micro Silver Cell Battery



Anode: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

Cathode: $Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \rightarrow 2\,Ag_{(s)} + 2\,OH^-_{(aq)}$

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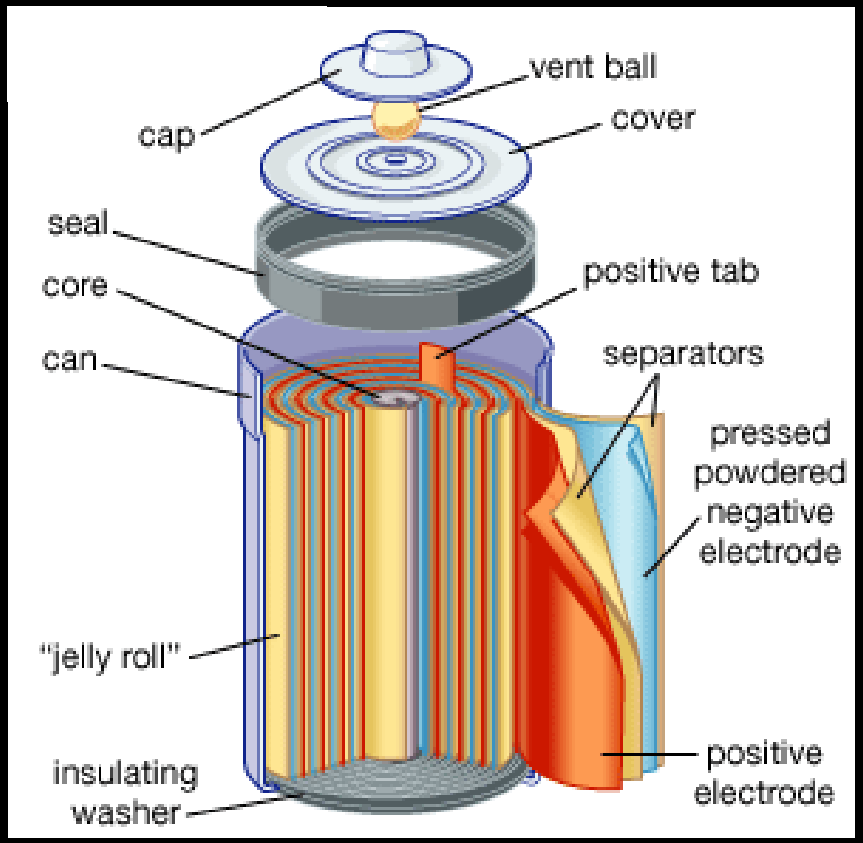
Nickel-Cadmium Battery



Anode: $Cd + 2\ OH^- \rightarrow Cd(OH)_2 + 2\ e^-$

Cathode: $2\ NiO(OH) + 2\ H_2O + 2e^- \rightarrow Ni(OH)_2 + OH^-$

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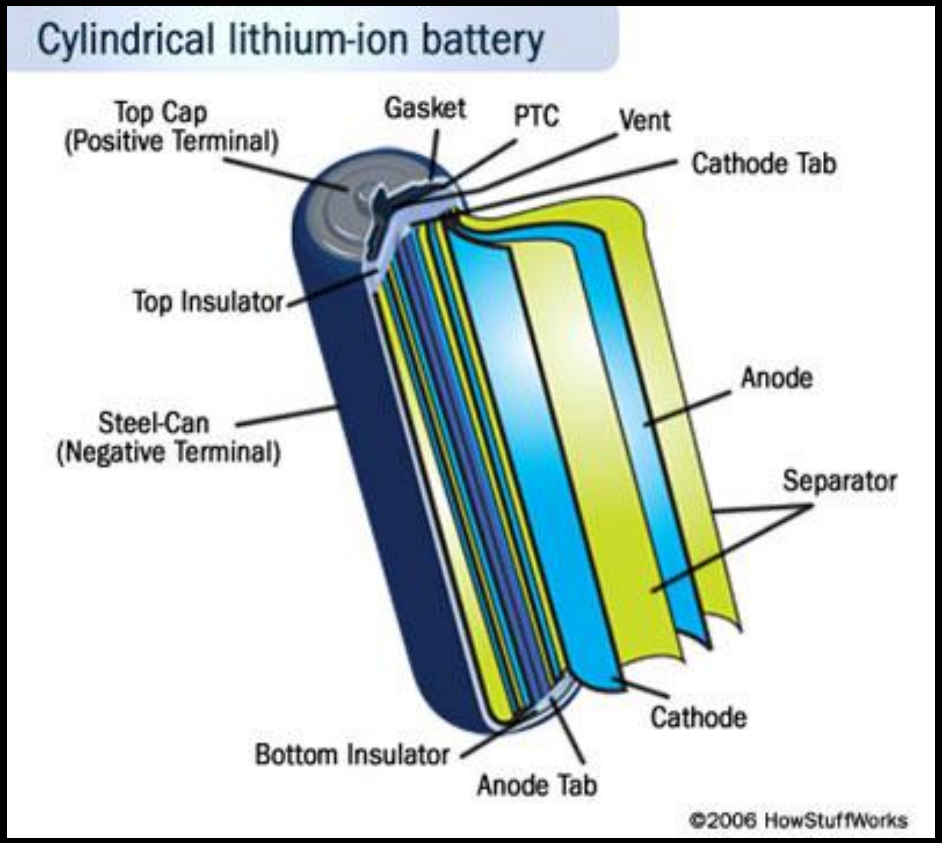
Lithium Battery



Anode: $xLi^+ + C + xe^- \rightarrow Li_yC$

Cathode: $LiCoO_2 \rightarrow Li_{1-x}CoO_2 + x\,Li^+ + xe^-$

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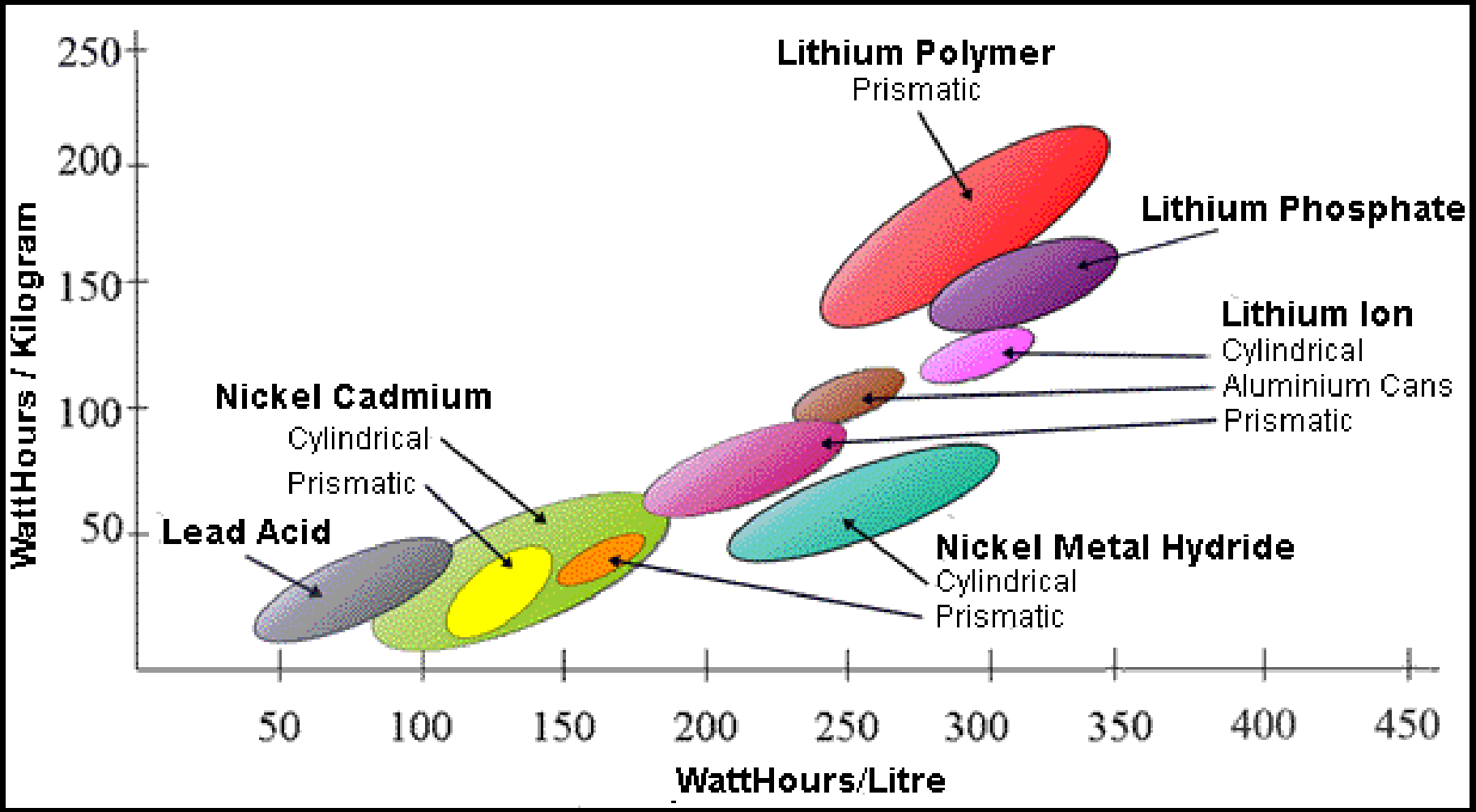
Battery Engergy Comparisons



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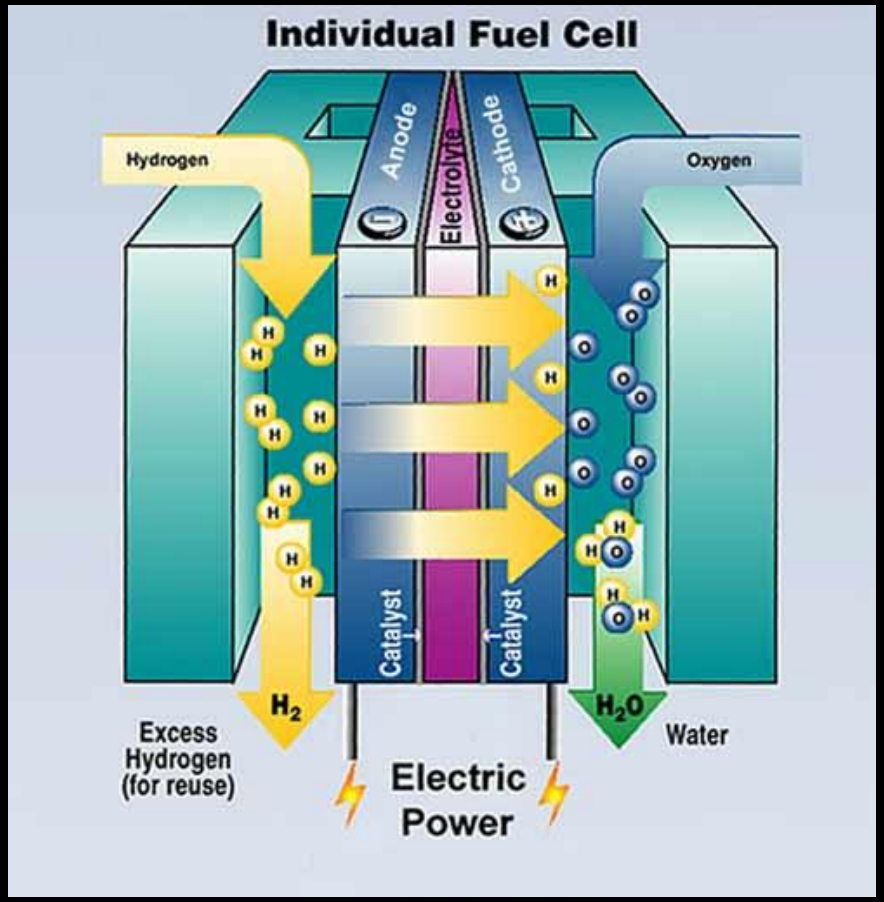
Fuel Cell



Anode: $2\ H_2 \rightarrow 4\ H^+ + 4e^-$

Cathode: $4\ H^+ + O_2 + 4\ e^- \rightarrow 2\ H_2O$

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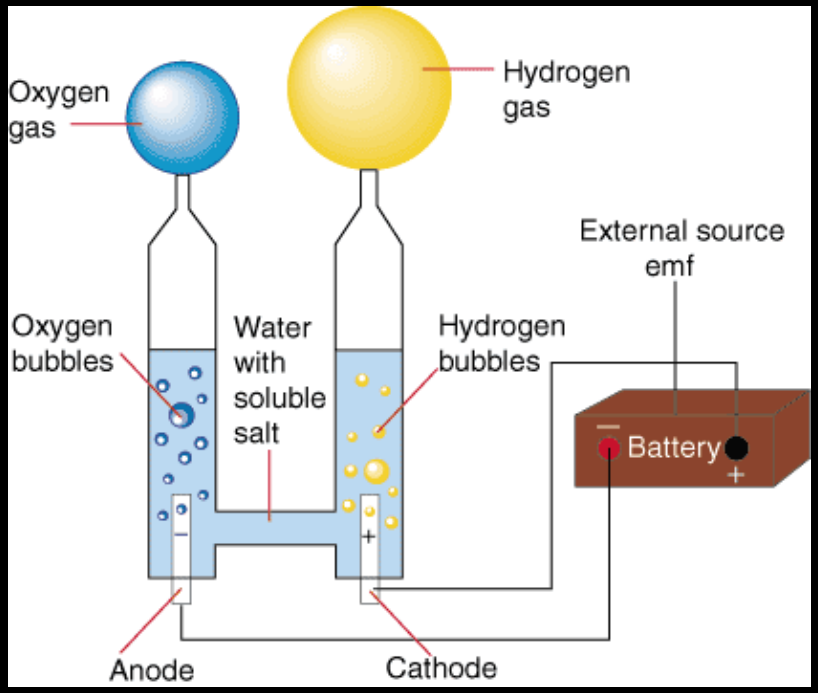
Electrolytic Cell: Electrolysis of Water
Chemical Conversion via Current

lysis means "split apart"



Anode: $2\ H_2O_{(l)} \rightarrow O_{2(g)} + 4\ H^+_{(aq)} + 4\ e^-$

Cathode: $2\ H^+ + 2e^- \rightarrow H_{2(g)}$

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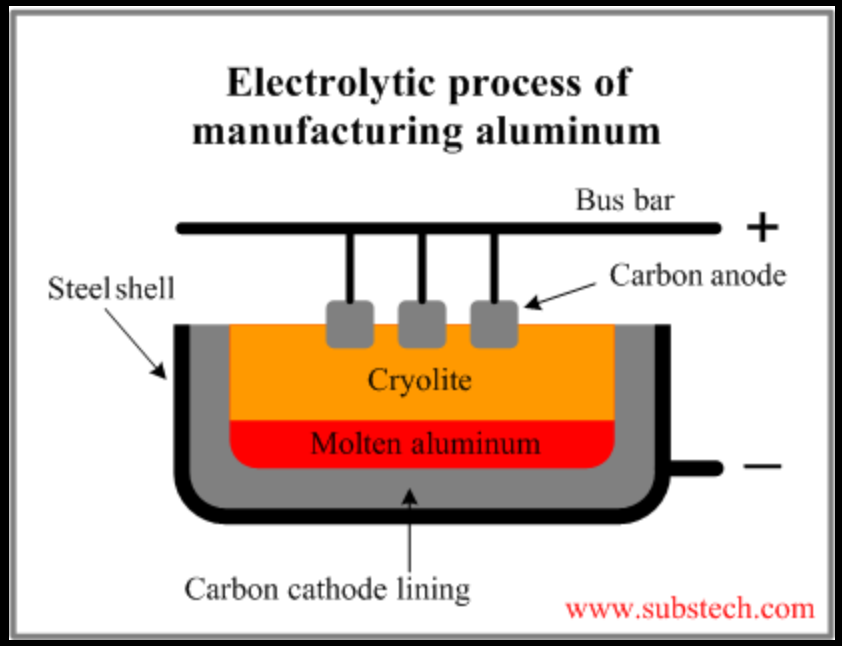
Electrolytic Cell: Hall Process
Conversion of Bauxite (Al_2O_3) to Al

Before Hall process, pure Aluminum was one of world's most expensive metals



Anode: $2\ O^{2-} \rightarrow O_2 + 4\ e^-$

Cathode: $Al^{3+} + 3\ e^- \rightarrow Al$

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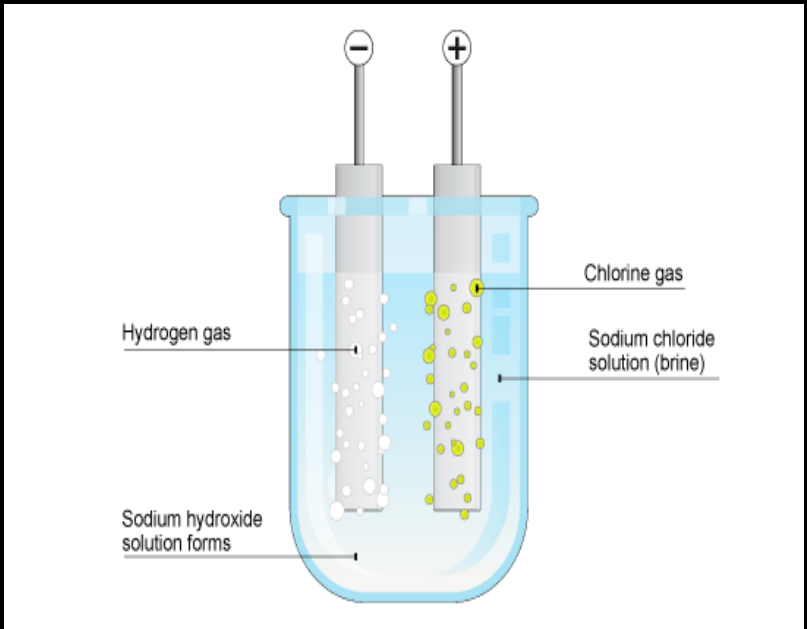
Electrolytic Cell: Chlorine Production

Electrolysis of Sea water



Anode: $2\ Cl^-_{(aq)} \rightarrow Cl_{2\ (g)} + 2\ e^-$

Cathode: $2\ H^+_{(aq)} + 2\ e^- \rightarrow H_{2\ (g)}$

Cell Reaction: $H^+ + 2\ Cl^- \longrightarrow H_2 + Cl_2$

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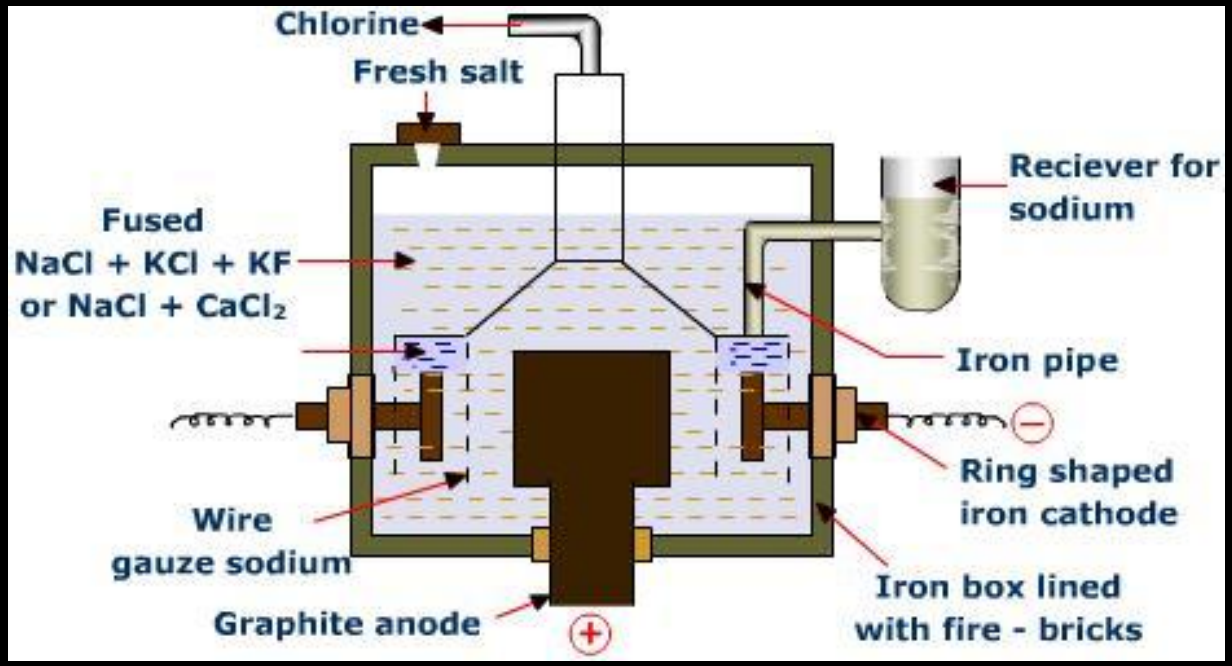
Electrolytic Cell: Down Cell For Chlorine Production

Electrolysis of Fused NaCl



Anode: $2\ Cl^-_{(aq)} \rightarrow Cl_{2\ (g)} + 2\ e^-$

Cathode: $2\ Na^+_{(aq)} + 2\ e^- \rightarrow 2\ Na_{(s)}$

Cell Reaction: $2\ NaCl \longrightarrow 2Na + Cl_2$

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Down Cell Calculations

Anode: $2\ Cl^-_{(aq)} \rightarrow Cl_{2\ (g)} + 2\ e^-$ **- 1.36 V**

Cathode: $2\ Na^+_{(aq)} + 2\ e^- \rightarrow 2\ Na_{(s)}$ **- 2.71 V**

Using $E^0_{cell} = E^0_{Cathode} - E^0_{Anode}$

$E^0 = 2.71\ v - (-1.36\ v) = 4.07\ v$ **Reaction is spontaneous**

If cell runs 1 hour at 20,0 amps, how many moles Cl_2 are produced?

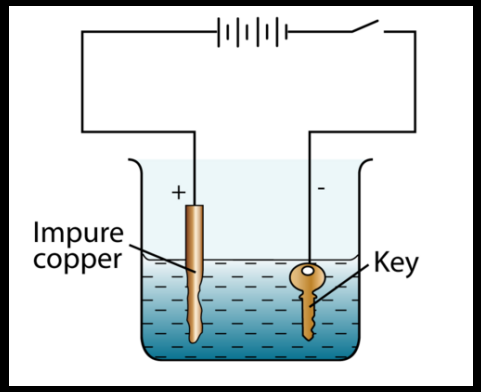
Q charge in Coulombs = amp x seconds

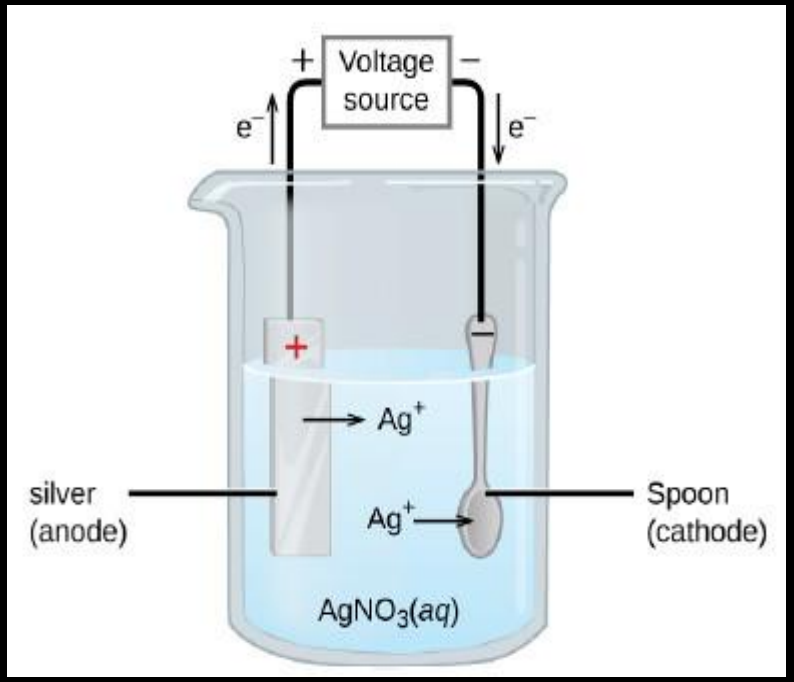
Moles produced = Q / 96500 x valence change

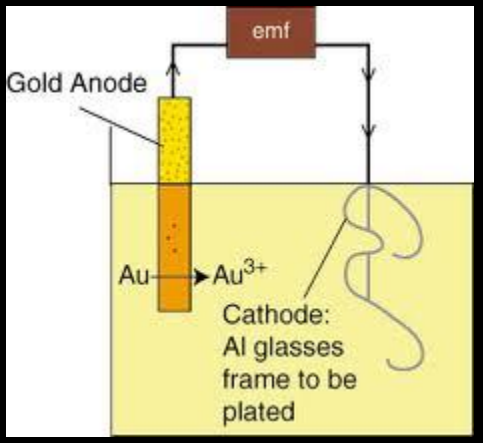
$$\text{Moles} = \frac{20{,}0\ \text{amps} \times 1\ \text{hr} \times 60\ \text{min / hr} \times 60\ \text{sec / min}}{96{,}500\ \text{Q / mole } e^- \times 2\ \text{moles } e^-}$$

Moles = 0.373

Electrolytic Cell: Electroplating







Anode: Metal to be deposited

Cathode: Object to be plated

Commonly electroplated: Cd, Cr, Cu, Au, Ni, Ag and Sn

Quality determined by thickness of the plated metal

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Quantitative Electroplating

Amount of current related to number of moles of electrons moving
Moles of electrons depend on reaction stoichiometry

A current of 10.23 A passes thru a silver plating cell for 1 hour. How many moles of electrons passed thru the cell? What mass of silver was deposited on the cathode from a silver nitrate solution?

Determine moles of electrons based on charge (Q) using the current (A):

$$N = \frac{Q}{F} = \frac{10.23\ C/s \times 60\ s/min \times 60\ min/hr \times 1\ hr}{96{,}485\ C/mol\ e^-} = \frac{36{,}830\ C}{96{,}485\ C/mole\ e^-} = 0.3817\ mol$$

Determine mass of deposited silver at the cathode:

Cathode reaction: $Ag_{(aq)} + e^- \rightarrow Ag_{(s)}$

$$0.3817\ mol\ e^- \times \frac{1\ mol\ Ag}{1\ mol\ e^-} \times \frac{107{,}9\ g}{1\ mol\ Ag} = 41.19\ g\ Ag$$

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Quantitative Electroplating Problem

Aluminum can be made by electrolysis. What is the cathode half-reaction? What mass of Al will be deposited if a current of 2.50×10^3 A passes through the plating solution for 15.0 minutes?

Determine moles of electrons based on charge (Q) using the current (A):

$$N = \frac{Q}{F} = \frac{2500\ C/s \times 60\ s/min \times 15.0\ min}{96{,}485\ C/mol\ e^-} = 23.31\ mol$$

Determine mass of deposited silver at the cathode:

Cathode reaction: $Al^{3+}_{(aq)} + 3\ e^- \rightarrow 3\ Al_{(s)}$

$$23.31\ mol\ e^- \times \frac{1\ mol\ Ag}{3\ mol\ e^-} \times \frac{26.98\ g}{1\ mol\ Al} = 210\ g\ Al$$

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Time Required For Deposition

Using a current of 33.46 A, how long will it take to deposit a layer of Chromium ($d = 7.19\ g/cm^3$) that is 0.010 mm thick over a surface area of 3.3 m^2 from a solution of Chromium (III) ions?

Determine volume of Cr needed:

$$V = (0.010\ mm \times \frac{1\ cm}{10\ mm}) \times [\ 3.3\ m^2 \times (\frac{10{,}000\ cm^2}{1\ m^2})\ ] = 33\ cm^3$$

Using density and atomic mass, determine the moles of Cr needed:

$$33\ cm^3 \times \frac{7.19\ g}{cm^3} \times \frac{1\ mole\ Cr}{52.00\ g} = 4.56\ mole$$

Determine total charge needed:

Cathode half-reaction: $Cr^{3+}_{(aq)} + 3\ e^- \rightarrow Cr_{(s)}$

$$4.56\ mol\ Cr \times \frac{3\ mole\ e^-}{1\ mole\ Cr} \times \frac{96{,}485\ C}{mole\ e^-} = 1.32 \times 10^6\ C$$

Time required:

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6\ C}{33.46\ C/s} = 3.95 \times 10^4\ sec\ [\ \frac{1\ min}{60\ sec} \times \frac{1\ hour}{60\ min} = 11.0\ hr$$

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Time Required For Deposition

Using a current of 25.5 A, how long will it take to deposit a layer of zinc ($d = 7.140\ g/cm^3$) that is 0.100 mm thick over a of 3.00 m x 5.50 m iron sheet from a solution of zinc nitrate? What mass of Zn is deposited?

Determine volume of Zn needed:

$$V = (0.100\ mm \times \frac{1\ cm}{10\ mm}) \times [\ 3.0\ m \times 5.50\ m \times (\frac{10{,}000\ cm^2}{1\ m^2})\ ] = 1650\ cm^3$$

Using density and atomic mass, determine the moles of Zn needed:

$$1650\ cm^3 \times \frac{7.140\ g}{cm^3} = 11700\ g \times \frac{1\ mole\ Zn}{65.41\ g} = 179\ mole$$

Determine total charge needed:

Cathode half-reaction: $Zn^{2+}_{(aq)} + 2\ e^- \rightarrow Zn_{(s)}$

$$179\ mol\ Zn \times \frac{2\ mole\ e^-}{1\ mole\ Zn} \times \frac{96{,}485\ C}{mole\ e^-} = 3.45 \times 10^7\ C$$

Time required:

$$t = \frac{Q}{I} = \frac{3.45 \times 10^7\ C}{25.5\ C/s} = 1.35 \times 10^6\ sec\ [\ \frac{1\ min}{60\ sec} \times \frac{1\ hour}{60\ min}\ ] = 376\ hr$$

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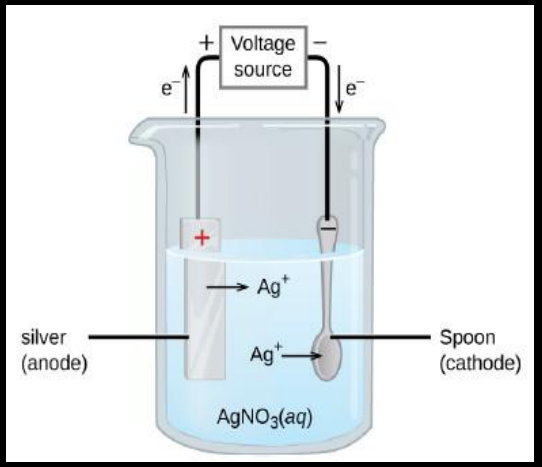
Summary: Galvanic vs. Electrolytic Cells

Galvanic Cell	Electrolytic Cell
Spontaneous Redox Reactions	Non-Spontaneous Reactions
Chemical Energy ➔ Electrical Energy	External Current ➔ Chemical Reaction
Cathode + Anode -	Anode + Cathode -
Anode Oxidation Cathode Reduction	Anode Oxidation Cathode Reduction
Half-Cells Connected via Salt Bridge	Electrodes in same container
Batteries	Hall Process and Electroplating



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Corrosion

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Corrosion

Corrosion: Electrochemical (redox) degradation of metals

example: copper patina

Original (painting) | Modern photo

Original Copper Sheeting:

$4\ Cu_{(s)} + O_{2(g)} \rightarrow 2\ Cu_2O_{(s)}$ (red)

$2\ Cu_2O_{(s)} + O_{2(g)} \rightarrow 4\ CuO_{(aq)}$ (black)

Burned Coal Pollutants:

$2\ CuO_{(s)} + CO_{2(g)} + H_2O_{(l)} \rightarrow Cu_2CO_3(OH)_{2(s)}$ (green)

$3\ CuO_{(s)} + 2\ CO_{2(g)} + H_2O_{(l)} \rightarrow Cu_2(CO_3)_2(OH)_{2(s)}$ (blue)

$4\ CuO_{(s)} + SO_{3(g)} + 3\ H_2O_{(l)} \rightarrow Cu_4SO_4(OH)_{6(s)}$ (green)

Patina forms protective coat that prevents further degradation

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Any time 2 Dissimilar Metals Touch
Electrons will flow from most active metal

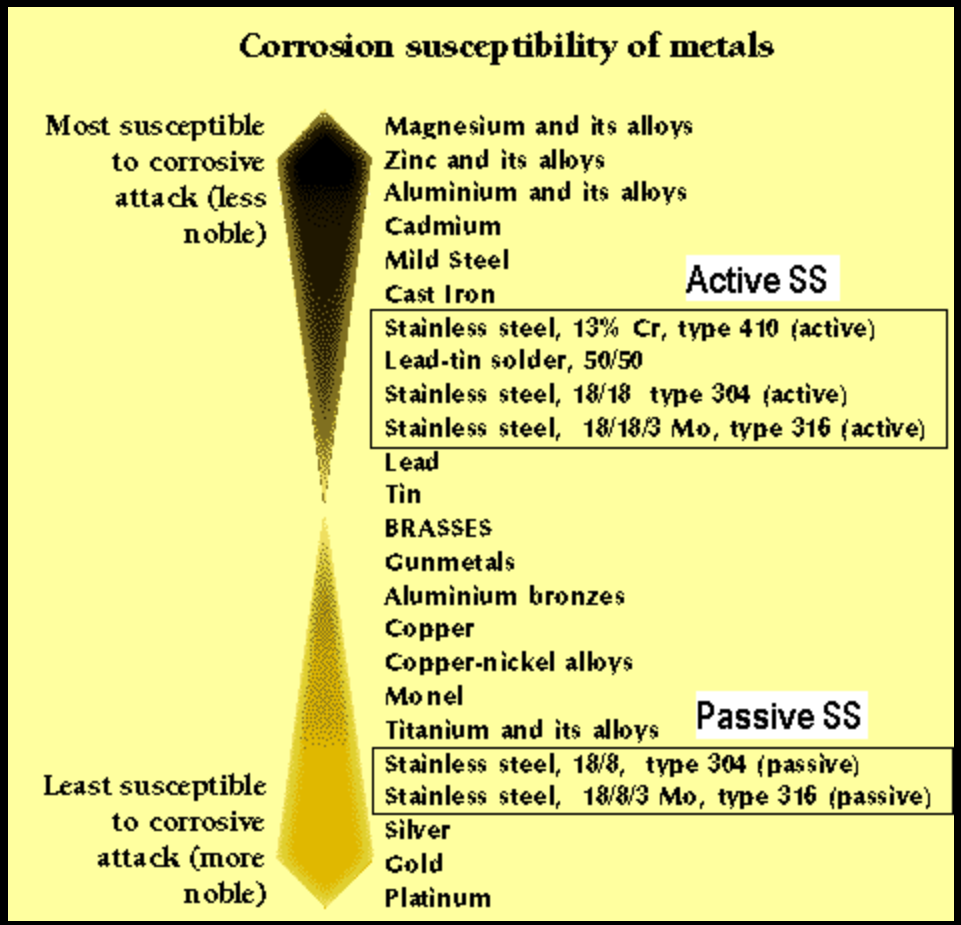
Simple galvanic corrosive table

The farther apart on the chart, the more dissimlar the metals are, and the higher the levet of corrosion of the anode.

Active (Anode)

Magnesium
Zinc
Aluminum
Steel or Iron
Nickel
Brass
Copper
Bronze
Stainless Steel (304)
Silver
Graphite
Titanium
Gold

Noble (Cathode)



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Corrosion: Rust

Iron rapidly oxides with atmospheric oxygen

Anode: $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2\ e^-$

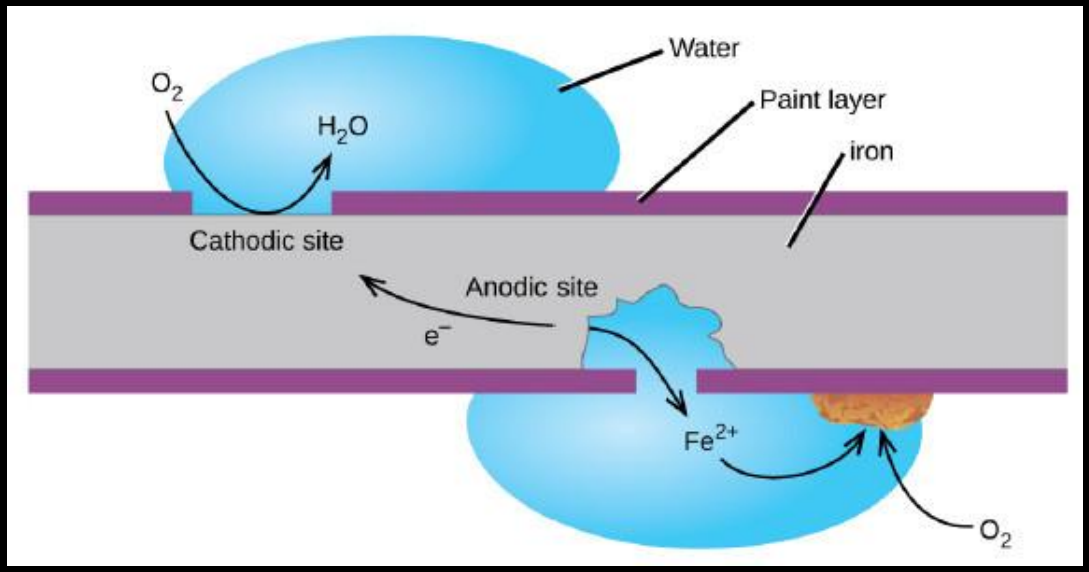
Oxygen reduced in acidic solutions

Cathode: $O_{2(g)} + 2\ H^+_{(aq)} + 4\ e^- \rightarrow 2\ H_2O_{(l)}$

Net: $2\ Fe_{(s} + O_{2(g)} + 2\ H^+_{(aq)} \rightarrow Fe^{2+}_{(aq)} + 2\ H_2O_{(l)}$

The iron 2^+ reacts with O_2 to form rust:

$Fe^{2+}_{(aq)} + O_{2(g)} + (4 + 2x)\ H_2O_{(l)} \rightarrow 2\ Fe_2O_3 \cdot H_2O_{(s)} + 8\ H^+_{(aq)}$



Rust is NOT protective, corrosion rapidly degrades the metal

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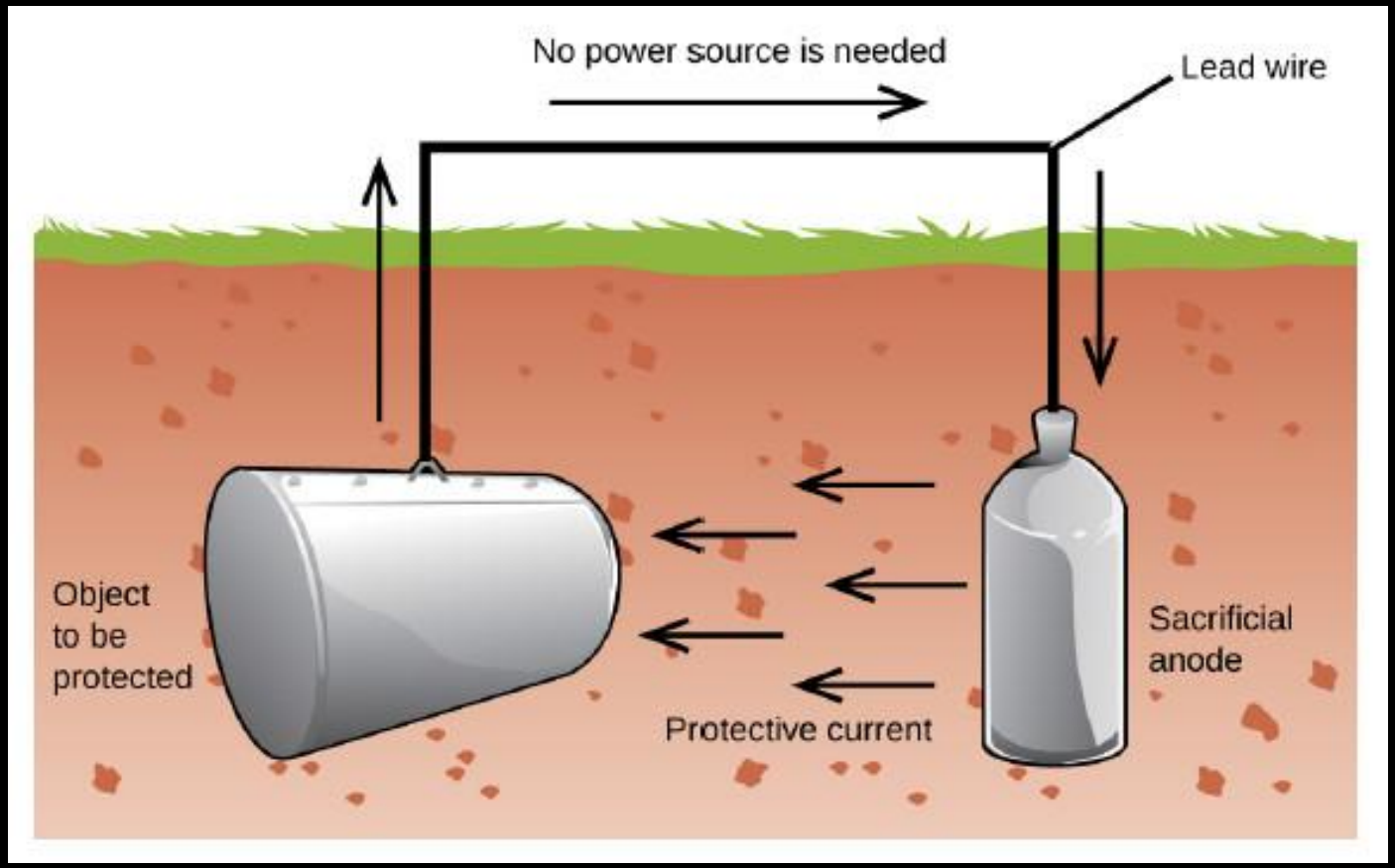
Passive Cathode Corrosion Protection



Use active metal (Zn or Mg) as a "sacrificial" anode:
Metal degrades (redox reaction) protecting the connected object (cathode)
No power supply needed

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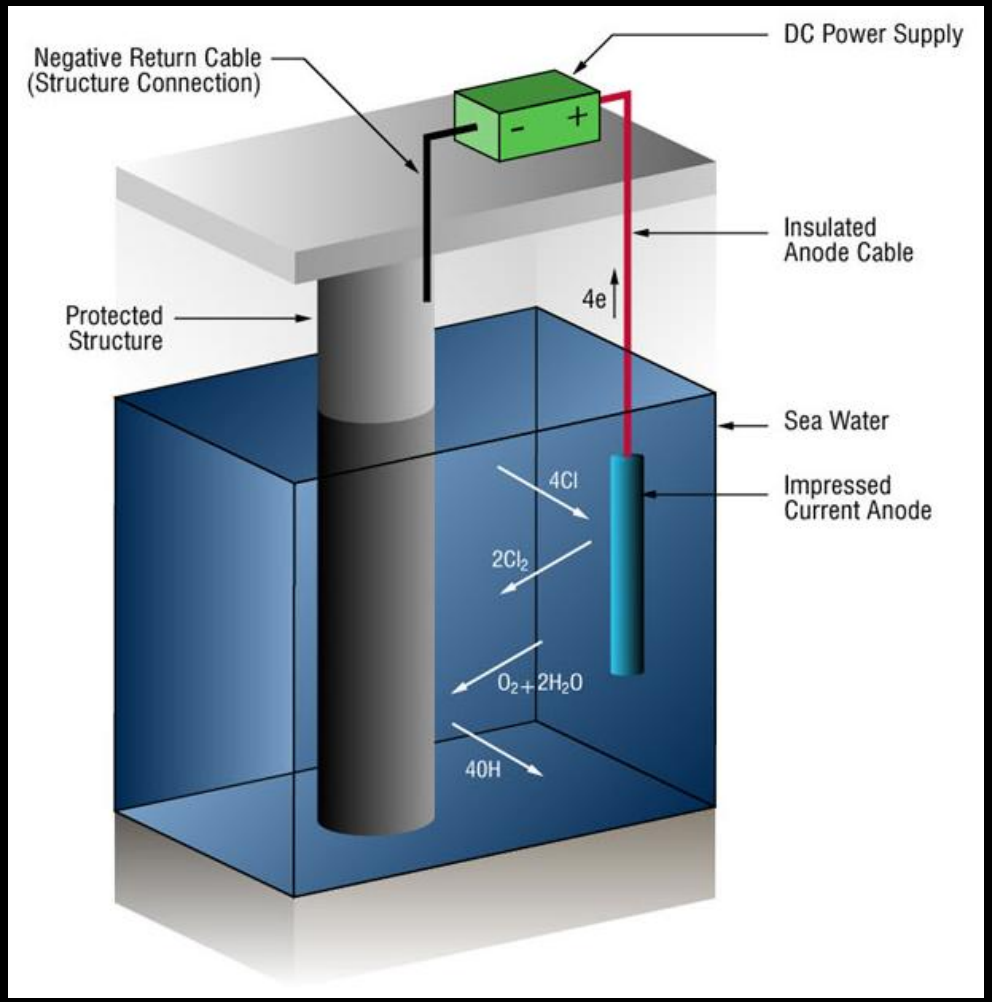
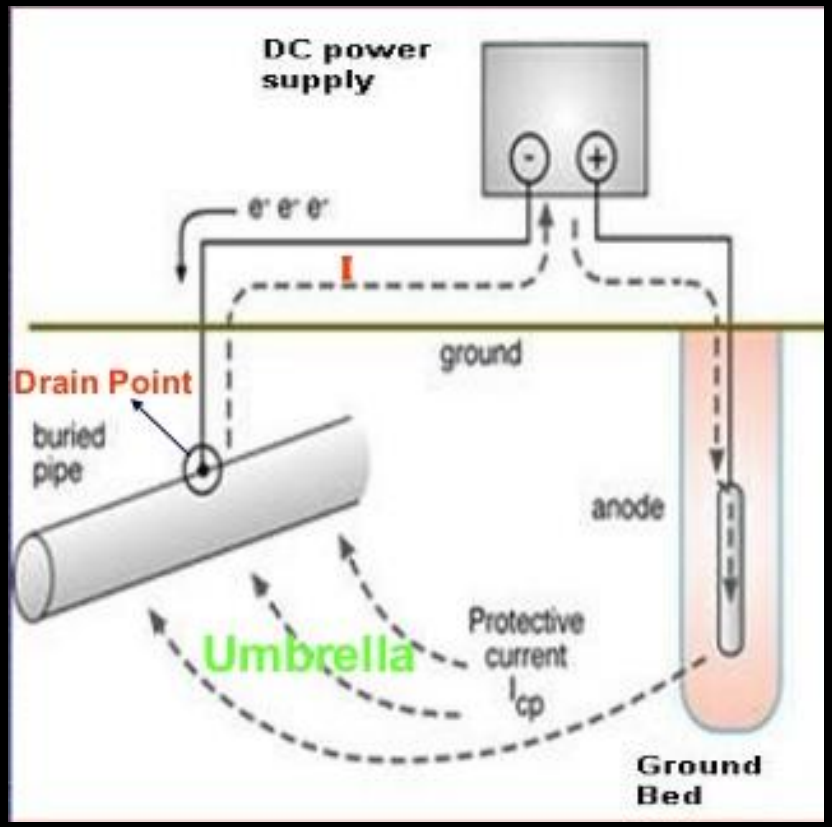
Active Cathode Corrosion Protection

Uses an "Impressed Current" to protect metal structures

Used on underground pipes and ocean going vessels





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Everything
and
Everywhere
Chemistry is