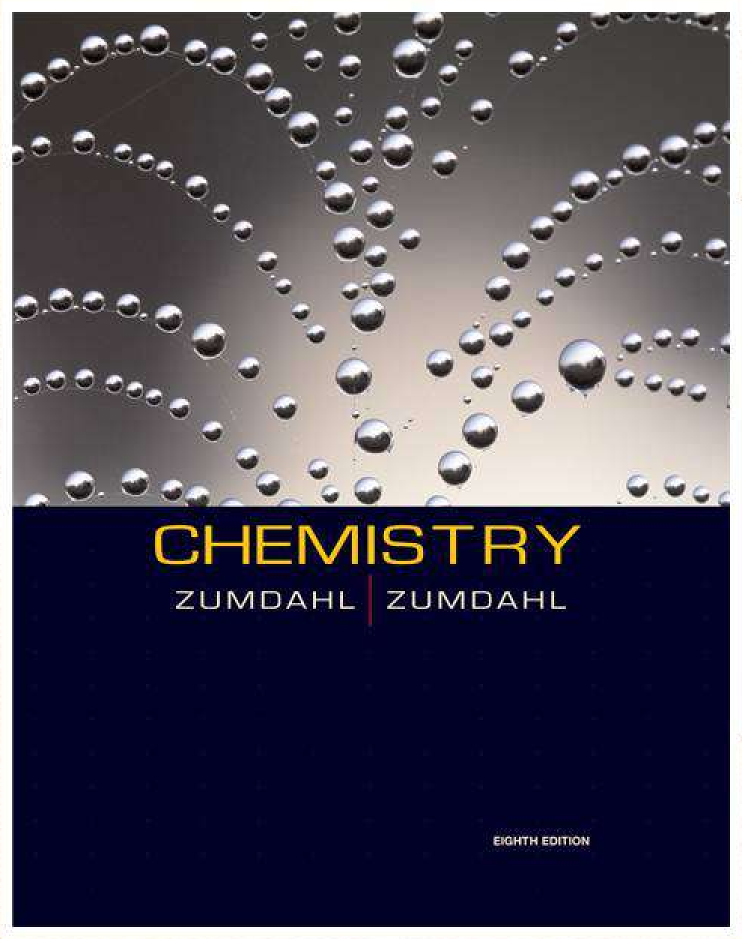

Chapter 18

Electrochemistry

Table of Contents

Electron Transfer Reactions

- Electron transfer reactions are **oxidation-reduction** or **redox** reactions.
- Results in the generation of an electric current (electricity) or be caused by imposing an electric current.
- Therefore, this field of chemistry is often called **ELECTROCHEMISTRY.**

Electrochemical processes are oxidation-reduction reactions in which:

- the energy released by a spontaneous reaction is converted to electricity or
- electrical energy is used to cause a nonspontaneous reaction to occur

$$2\overset{0}{\mathrm{Mg}}\,(s) + \overset{0}{\mathrm{O}_2}\,(g) \longrightarrow 2\overset{2+}{\mathrm{Mg}}\overset{2-}{\mathrm{O}}\,(s)$$

$2\mathrm{Mg} \longrightarrow 2\mathrm{Mg}^{2+} + 4e^-$ ***Oxidation*** half-reaction (lose e^-)

$\mathrm{O}_2 + 4e^- \longrightarrow 2\mathrm{O}^{2-}$ ***Reduction*** half-reaction (gain e^-)

Terminology for Redox Reactions

- **OXIDATION**—loss of electron(s) by a species; increase in oxidation number; increase in oxygen.
- **REDUCTION**—gain of electron(s); decrease in oxidation number; decrease in oxygen; increase in hydrogen.
- **OXIDIZING AGENT**—electron acceptor; species is reduced. (an agent facilitates something; ex. Travel agents don't travel, they facilitate travel)
- **REDUCING AGENT**—electron donor; species is oxidized.

Half–Reactions

- The overall reaction is split into two half–reactions, one involving oxidation and one reduction.

$8H^+ + MnO_4^- + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

Reduction: $8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Oxidation: $5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$

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The Half–Reaction Method for Balancing Equations for Oxidation–Reduction Reactions

1. Write separate equations for the oxidation and reduction half–reactions.
2. For each half–reaction:
   A. Balance all the elements except H and O.
   B. Balance O using H_2O.
   C. Balance H using H^+.
   D. Balance the charge using electrons.

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The Half–Reaction Method for Balancing Equations for Oxidation–Reduction Reactions

3. If necessary, multiply one or both balanced half–reactions by an integer to cancel out the electrons.
4. Add the half–reactions, and cancel identical species.
5. Check that the elements and charges are balanced.

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Balancing Oxidation–Reduction Equations

$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$

- How can we balance this equation?
- First Steps:
    - Separate into half-reactions.
    - Balance elements except H and O.

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Method of Half Reactions

- $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$
- $SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq)$
- Now, balance all elements except O and H.

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Method of Half Reactions (continued)

- $Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$
- $SO_3^{2-}(aq) \rightarrow + SO_4^{2-}(aq)$
- How can we balance the oxygen atoms?

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Method of Half Reactions (continued)

- $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq) + 7H_2O$
- $H_2O + SO_3^{2-}(aq) \rightarrow + SO_4^{2-}(aq)$
- How can we balance the hydrogen atoms?

Method of Half Reactions (continued)

- This reaction occurs in an acidic solution.
- $14H^{+} + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$
- $H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2H^{+}$
- How can we write the electrons?

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Method of Half Reactions (continued)

- This reaction occurs in an acidic solution.
- $6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$
- $H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2H^+ + 2e^-$
- How can we balance the electrons?

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Method of Half Reactions (continued)

- $14H^{+} + 6e^{-} + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$
- $3[H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2e^{-} + 2H^{+}]$

- Final Balanced Equation:

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^{+} \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

Return to TOC

Exercise

Balance the following oxidation–reduction reaction that occurs in acidic solution.

$$Br^{-}(aq) + MnO_4^{-}(aq) \rightarrow Br_2(l) + Mn^{2+}(aq)$$

$$10Br^{-}(aq) + 16H^{+}(aq) + 2MnO_4^{-}(aq) \rightarrow 5Br_2(l) + 2Mn^{2+}(aq) + 8H_2O(l)$$

Return to TOC

Exercise

Balance the following oxidation–reduction reaction.

$K_2Cr_2O_7 + SnCl_2 + HCl \rightarrow CrCl_3 + SnCl_4 + KCl + H_2O$

$K_2Cr_2O_7 + H_2O + S \rightarrow SO_2 + KOH + Cr_2O_3$

Return to TOC

The Half–Reaction Method for Balancing Equations for Oxidation–Reduction Reactions Occurring in Basic Solution

1. Use the half–reaction method as specified for acidic solutions to obtain the final balanced equation as *if H^+ ions were present*.
2. To both sides of the equation, add a number of OH^- ions that is equal to the number of H^+ ions. (We want to eliminate H^+ by forming H_2O.)

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The Half–Reaction Method for Balancing Equations for Oxidation–Reduction Reactions Occurring in Basic Solution

3. Form H_2O on the side containing both H^+ and OH^- ions, and eliminate the number of H_2O molecules that appear on both sides of the equation.
4. Check that elements and charges are balanced.

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Practice

Cr(OH)3 + ClO3- --> CrO42- + Cl- (basic)

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Galvanic Cell

- Device in which chemical energy is changed to electrical energy.
- Uses a spontaneous redox reaction to produce a current that can be used to do work.

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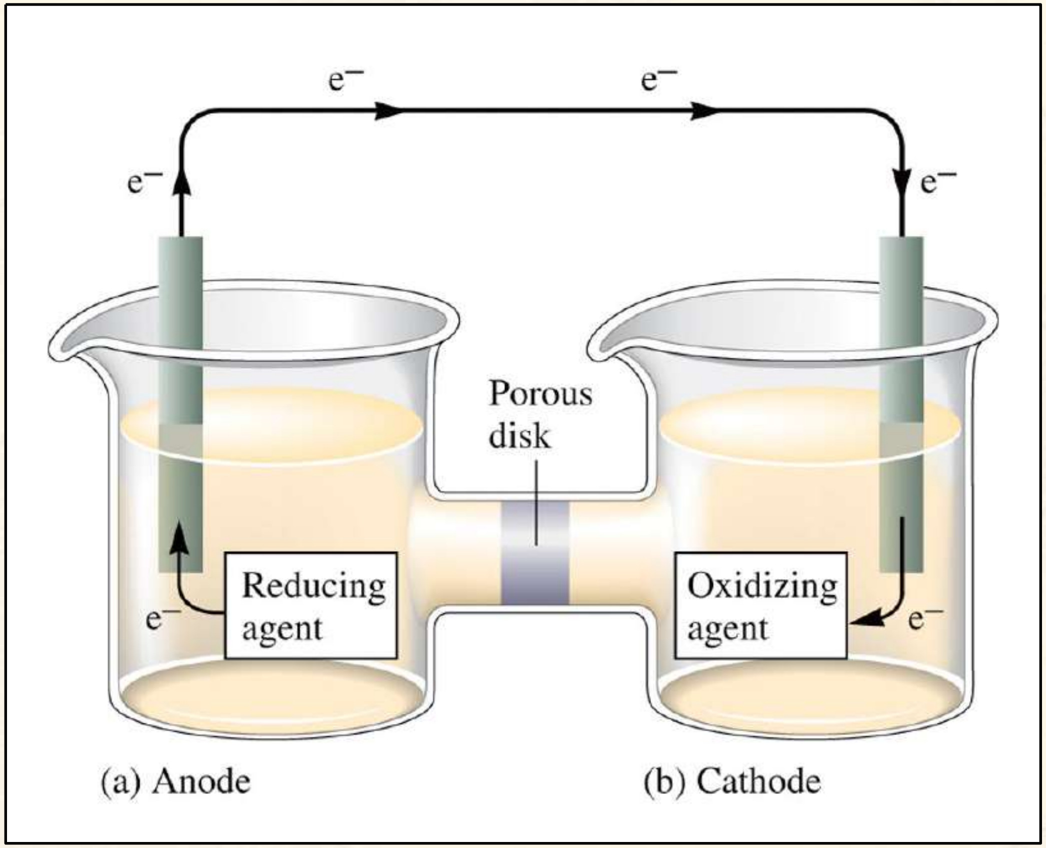
A Galvanic Cell



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Galvanic Cell

- Oxidation occurs at the anode.
- Reduction occurs at the cathode.
- Salt bridge or porous disk – devices that allow ions to flow without extensive mixing of the solutions.
  - Salt bridge – contains a strong electrolyte held in a Jello–like matrix.
  - Porous disk – contains tiny passages that allow hindered flow of ions.

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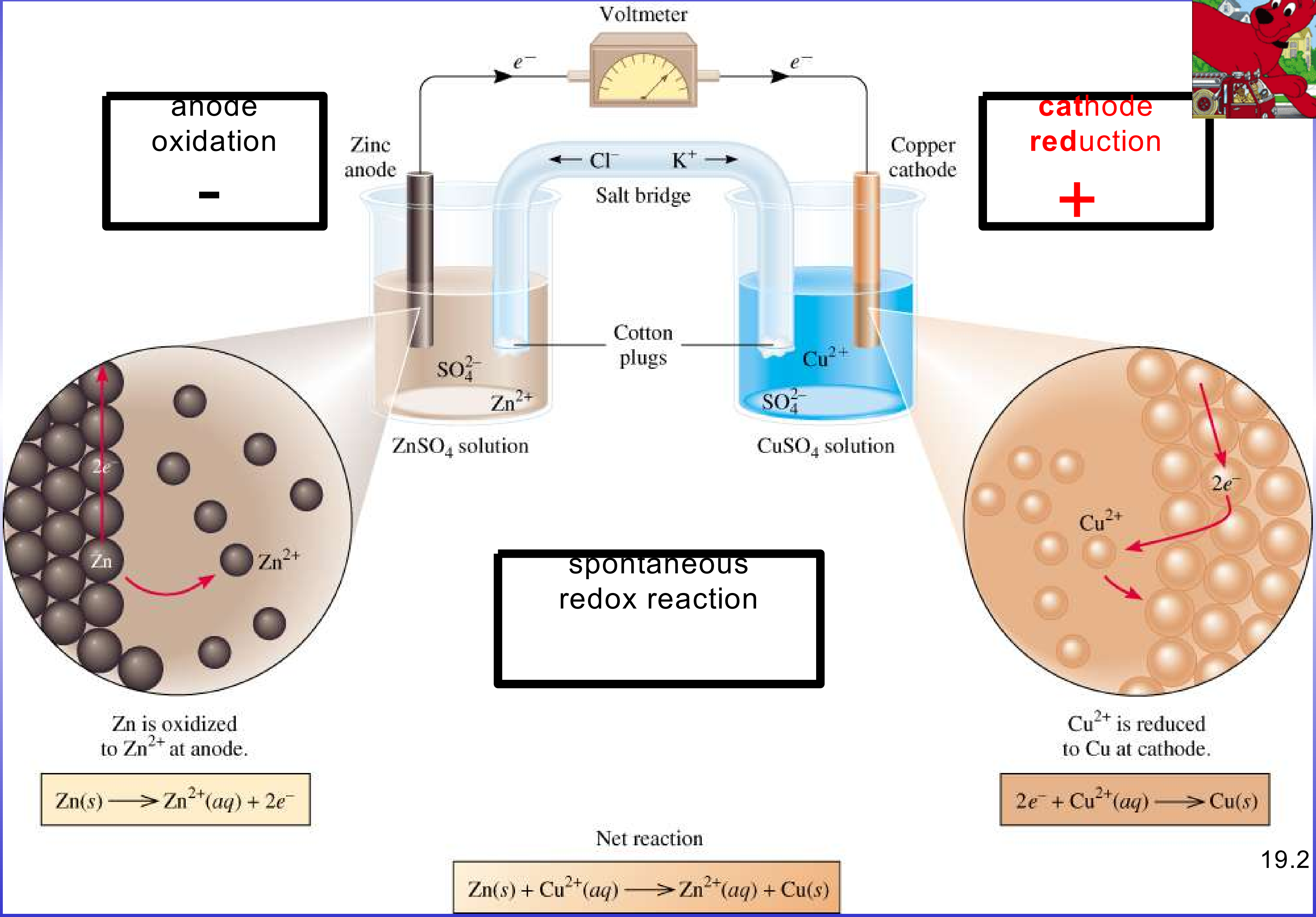
Galvanic Cells



anode
oxidation
-

cathode
reduction
+

spontaneous
redox reaction

Zn is oxidized to Zn^{2+} at anode.

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

Cu^{2+} is reduced to Cu at cathode.

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

Net reaction

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

Galvanic Cells

http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/galvan5.swf

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Cell Potential

- A galvanic cell consists of an oxidizing agent in one compartment that pulls electrons through a wire from a reducing agent in the other compartment.
- The “pull”, or driving force, on the electrons is called the cell potential ($\mathcal{E}_{\text{cell}}$), or the electromotive force (emf) of the cell.
  - Unit of electrical potential is the volt (V).
    - 1 joule of work per coulomb of charge transferred. (Joule = coulomb x volt)

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Galvanic Cell

- All half-reactions are given as reduction processes in standard tables.
  - Table 18.1 (or AP table!)
  - 1 *M*, 1 atm, 25°C
- When a half-reaction is reversed, the sign of E ° is reversed.
- When a half-reaction is multiplied by an integer, E ° **remains the same**.
- A galvanic cell runs spontaneously in the direction that gives a positive value for $E°_{\text{cell}}$.

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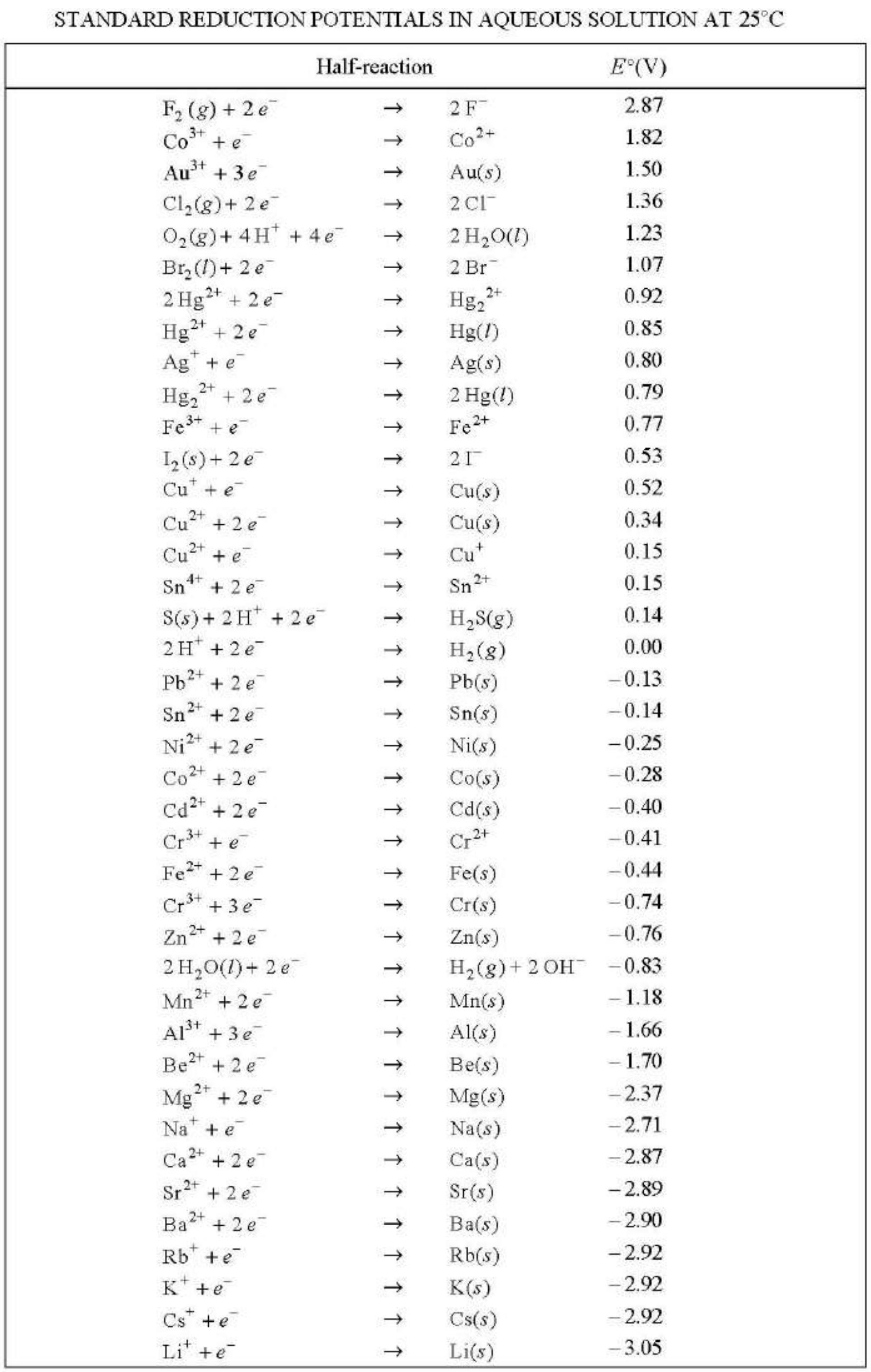

STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction			$E°$(V)
$F_2(g) + 2e^-$	→	$2F^-$	2.87
$Co^{3+} + e^-$	→	Co^{2+}	1.82
$Au^{3+} + 3e^-$	→	$Au(s)$	1.50
$Cl_2(g) + 2e^-$	→	$2Cl^-$	1.36
$O_2(g) + 4H^+ + 4e^-$	→	$2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	→	$2Br^-$	1.07
$2Hg^{2+} + 2e^-$	→	Hg_2^{2+}	0.92
$Hg^{2+} + 2e^-$	→	$Hg(l)$	0.85
$Ag^+ + e^-$	→	$Ag(s)$	0.80
$Hg_2^{2+} + 2e^-$	→	$2Hg(l)$	0.79
$Fe^{3+} + e^-$	→	Fe^{2+}	0.77
$I_2(s) + 2e^-$	→	$2I^-$	0.53
$Cu^+ + e^-$	→	$Cu(s)$	0.52
$Cu^{2+} + 2e^-$	→	$Cu(s)$	0.34
$Cu^{2+} + e^-$	→	Cu^+	0.15
$Sn^{4+} + 2e^-$	→	Sn^{2+}	0.15
$S(s) + 2H^+ + 2e^-$	→	$H_2S(g)$	0.14
$2H^+ + 2e^-$	→	$H_2(g)$	0.00
$Pb^{2+} + 2e^-$	→	$Pb(s)$	–0.13
$Sn^{2+} + 2e^-$	→	$Sn(s)$	–0.14
$Ni^{2+} + 2e^-$	→	$Ni(s)$	–0.25
$Co^{2+} + 2e^-$	→	$Co(s)$	–0.28
$Cd^{2+} + 2e^-$	→	$Cd(s)$	–0.40
$Cr^{3+} + e^-$	→	Cr^{2+}	–0.41
$Fe^{2+} + 2e^-$	→	$Fe(s)$	–0.44
$Cr^{3+} + 3e^-$	→	$Cr(s)$	–0.74
$Zn^{2+} + 2e^-$	→	$Zn(s)$	–0.76
$2H_2O(l) + 2e^-$	→	$H_2(g) + 2OH^-$	–0.83
$Mn^{2+} + 2e^-$	→	$Mn(s)$	–1.18
$Al^{3+} + 3e^-$	→	$Al(s)$	–1.66
$Be^{2+} + 2e^-$	→	$Be(s)$	–1.70
$Mg^{2+} + 2e^-$	→	$Mg(s)$	–2.37
$Na^+ + e^-$	→	$Na(s)$	–2.71
$Ca^{2+} + 2e^-$	→	$Ca(s)$	–2.87
$Sr^{2+} + 2e^-$	→	$Sr(s)$	–2.89
$Ba^{2+} + 2e^-$	→	$Ba(s)$	–2.90
$Rb^+ + e^-$	→	$Rb(s)$	–2.92
$K^+ + e^-$	→	$K(s)$	–2.92
$Cs^+ + e^-$	→	$Cs(s)$	–2.92
$Li^+ + e^-$	→	$Li(s)$	–3.05

Official AP Reduction Table

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Standard Reduction Potentials

Example: $Fe^{3+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + Fe^{2+}(aq)$

- Half-Reactions:
  - $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$ $E° = 0.77$ V
  - $Cu^{2+} + 2e^{-} \rightarrow Cu$ $E° = 0.34$ V
- To calculate the cell potential, we must reverse reaction 2.
  - $Cu \rightarrow Cu^{2+} + 2e^{-}$ $-E° = -0.34$ V

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Overall Balanced Cell Reaction

$2Fe^{3+} + 2e^{-} \rightarrow 2Fe^{2+}$ $E° = 0.77\ V$ (cathode)

$Cu \rightarrow Cu^{2+} + 2e^{-}$ $-E° = -0.34\ V$ (anode)

- Cell Potential:

$E°_{cell} = E°(\text{cathode}) - E°(\text{anode})$

****not on formula sheet!**

***** the – in the equation *automatically flips* the anode**

$E°_{cell} = 0.77\ V - 0.34\ V = 0.43\ V$

Return to TOC

Charging a Battery

When you charge a battery, you are forcing the electrons backwards (from the + to the -). To do this, you will need a higher voltage backwards than forwards. This is why the ammeter in your car often goes slightly higher while your battery is charging, and then returns to normal.

In your car, the battery charger is called an alternator. If you have a dead battery, it could be the battery needs to be replaced OR the alternator is not charging the battery properly.

Line Notation

- Used to describe electrochemical cells.
- Anode components are listed on the left.
- Cathode components are listed on the right.
- Separated by double vertical lines.
- The concentration of aqueous solutions should be specified in the notation when known.
- Example: $\mathrm{Mg}(s)|\mathrm{Mg}^{2+}(aq)||\mathrm{Al}^{3+}(aq)|\mathrm{Al}(s)$
  - $\mathrm{Mg} \rightarrow \mathrm{Mg}^{2+} + 2e^{-}$(anode)
  - $\mathrm{Al}^{3+} + 3e^{-} \rightarrow \mathrm{Al}$(cathode)

Return to TOC

Work

- Work is never the maximum possible if any current is flowing.
- In any real, spontaneous process some energy is always wasted – the actual work realized is always less than the calculated maximum.

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Maximum Cell Potential

- Directly related to the free energy difference between the reactants and the products in the cell.
  - $\Delta G° = -nFE°$
    - F = 96,485 C/mol e^-

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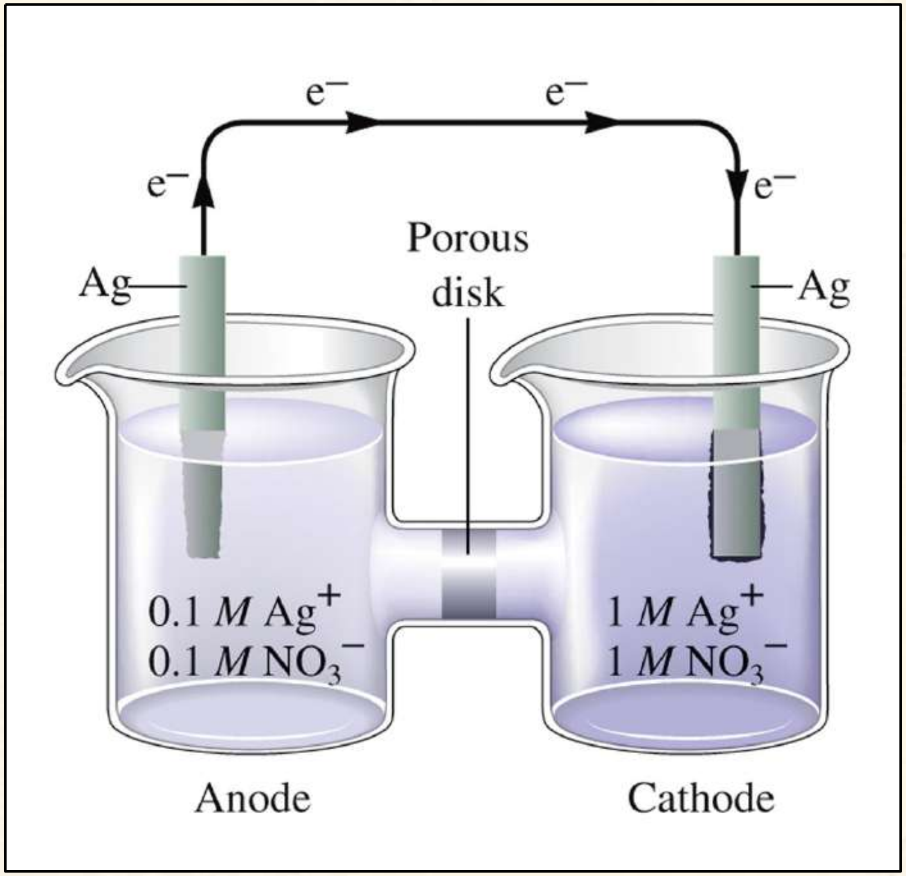
A Concentration Cell



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Nernst Equation

- At 25°C: n = number of moles of e-

$$\mathscr{E} = \mathscr{E}^\circ - \frac{0.0591}{n}\log(Q)$$

or

$$\mathscr{E}^\circ = \frac{0.0591}{n}\log(K)$$

(at equilibrium)

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Nernst Equation

- At ANY temp: n = number of moles of e-

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF}\ln Q$$

Concept Check

Explain the difference between E and E °.

When is E equal to zero?

When the cell is in equilibrium ("dead" battery).

Spontaneity of Redox Reactions

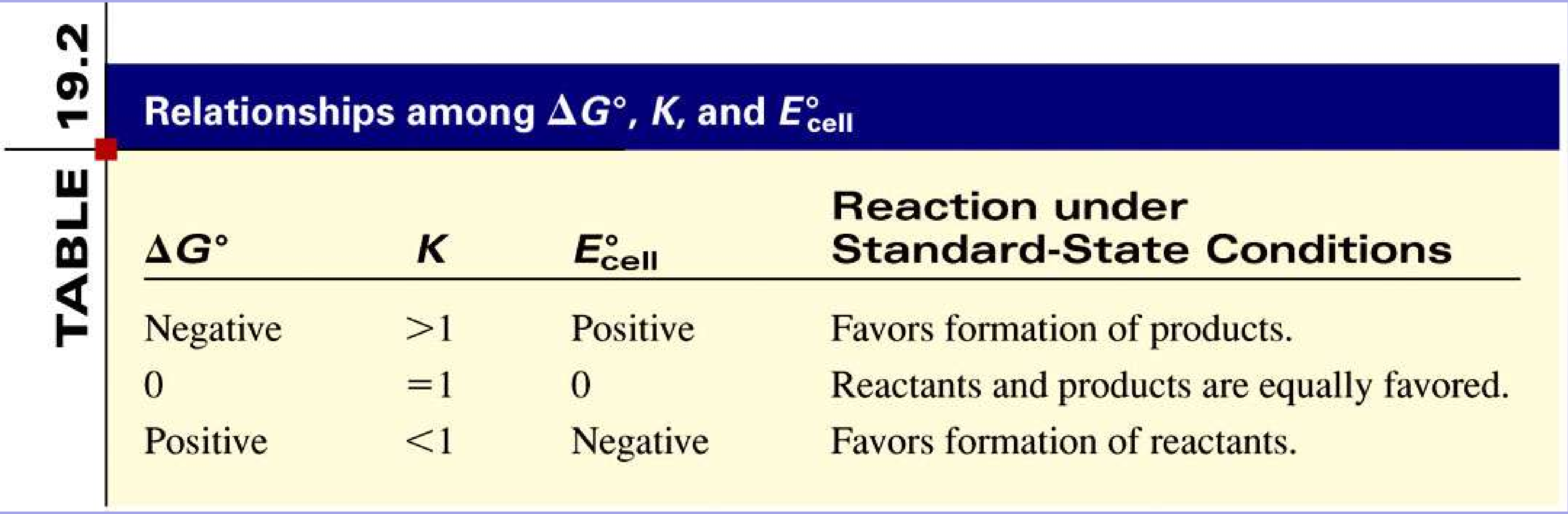

TABLE 19.2 **Relationships among ΔG°, K, and E°_{cell}**

ΔG°	K	E°_{cell}	Reaction under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	$=1$	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.

Exercise

A concentration cell is constructed using two nickel electrodes with Ni^{2+} concentrations of 1.0 *M* and 1.00 x 10^{-4} *M* in the two half-cells.

Calculate the potential of this cell at 25°C.

0.118 V

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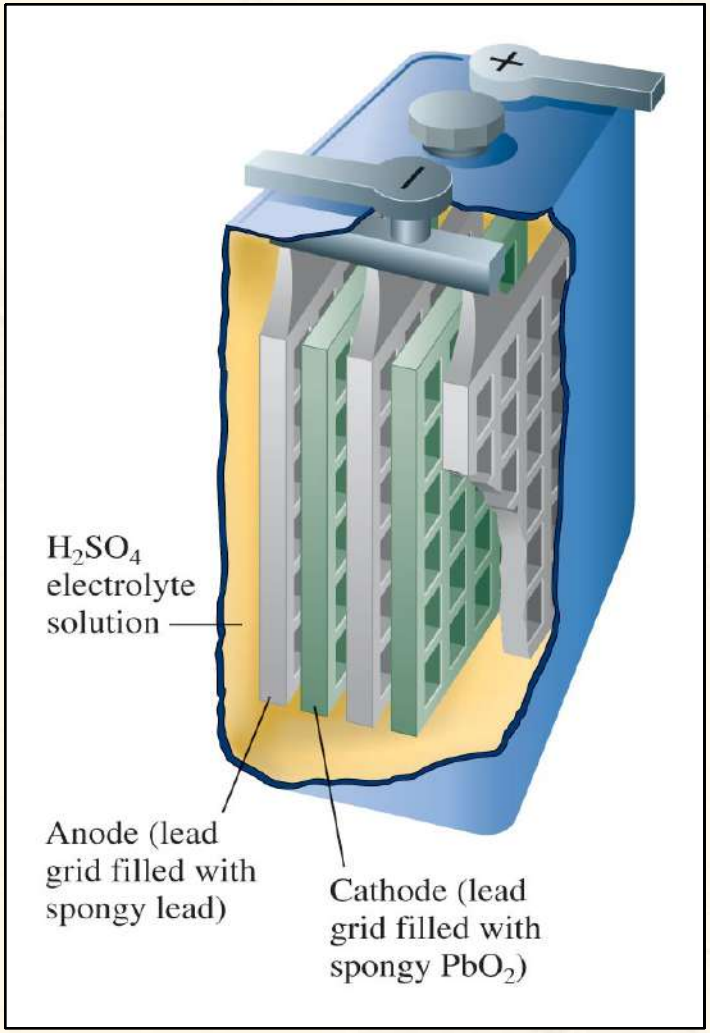
One of the Six Cells in a 12–V Lead Storage Battery



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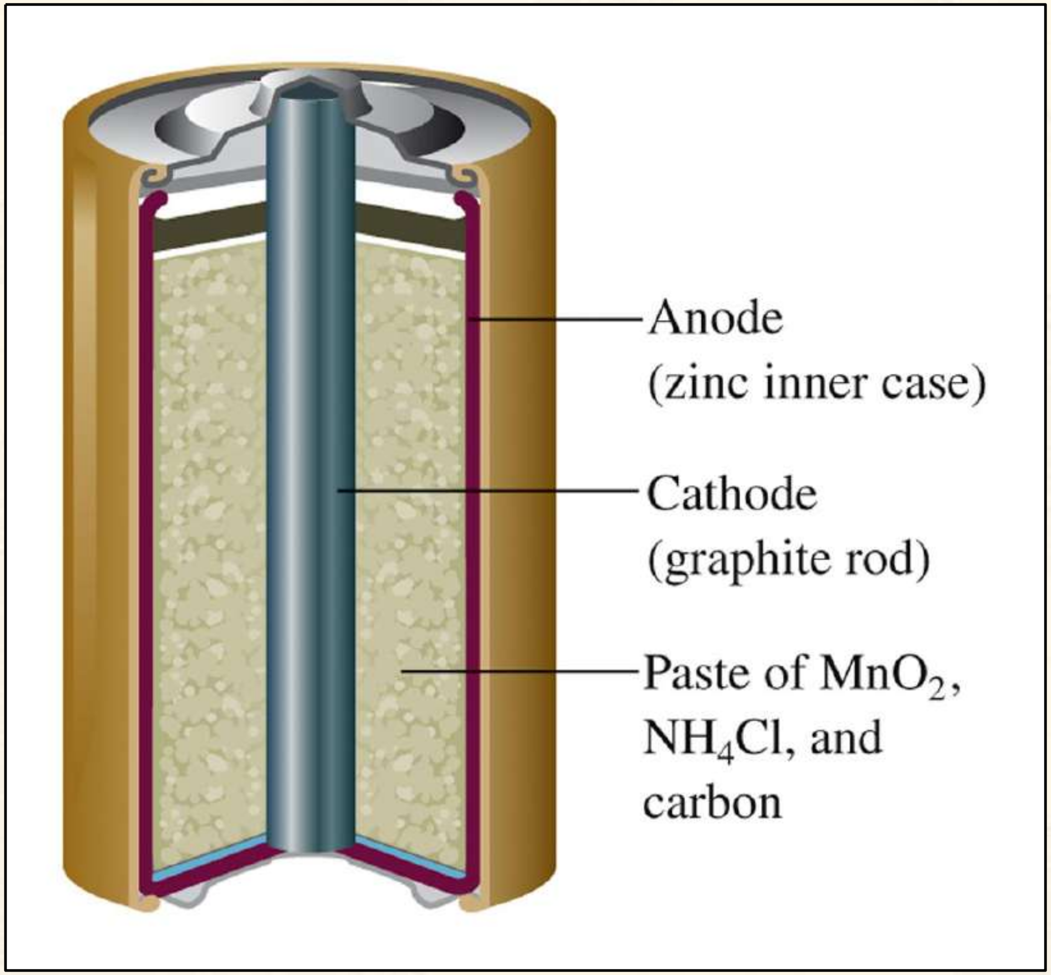
A Common Dry Cell Battery



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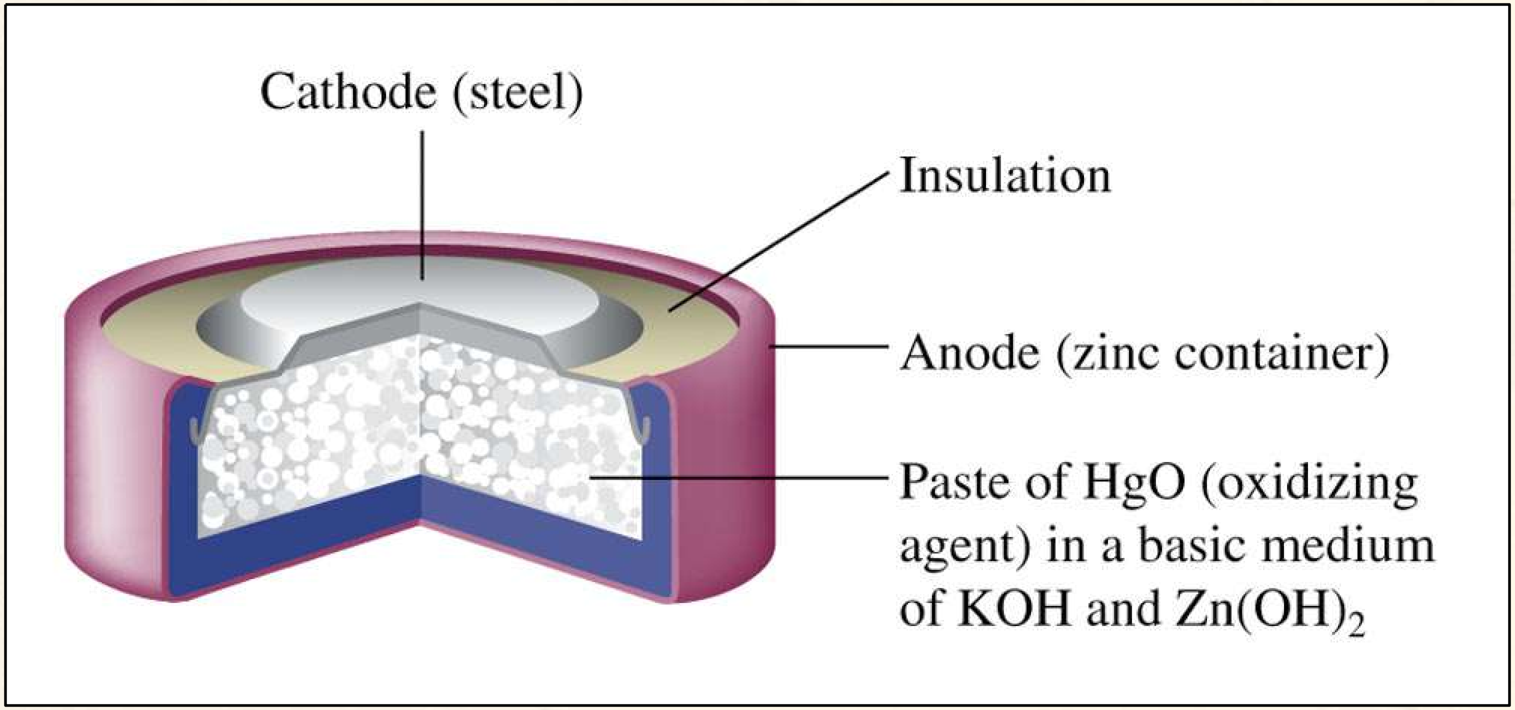
A Mercury Battery



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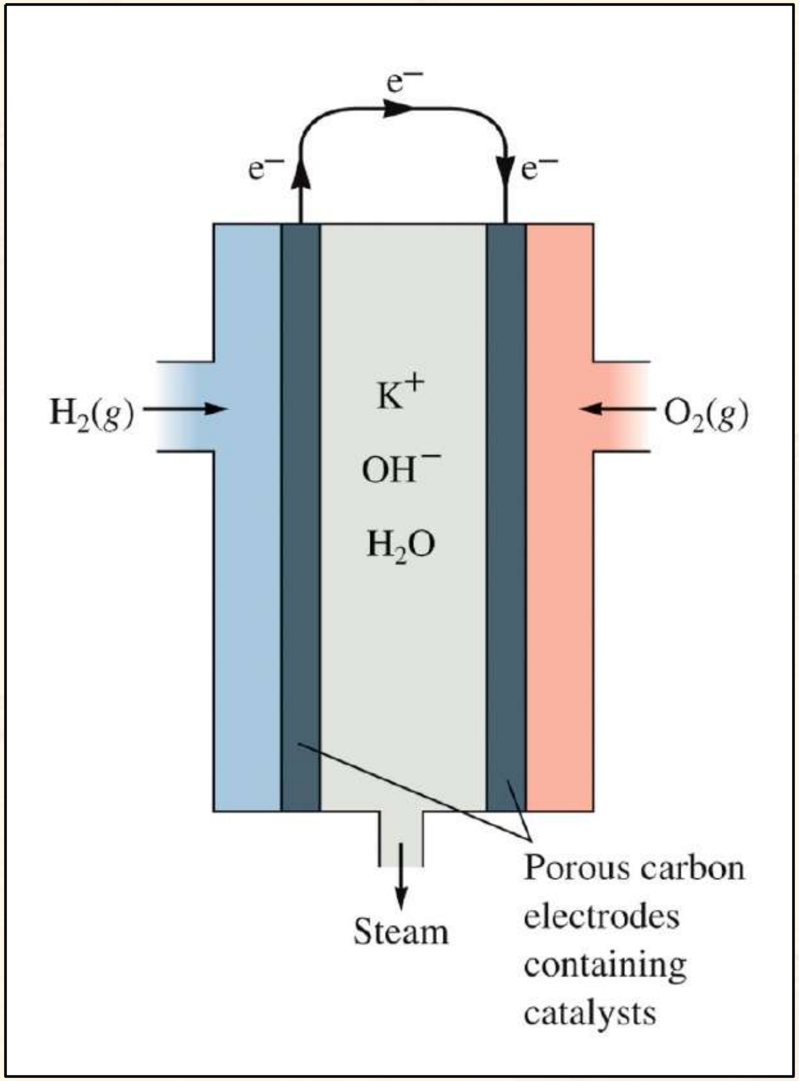
Schematic of the Hydrogen-Oxygen Fuel Cell



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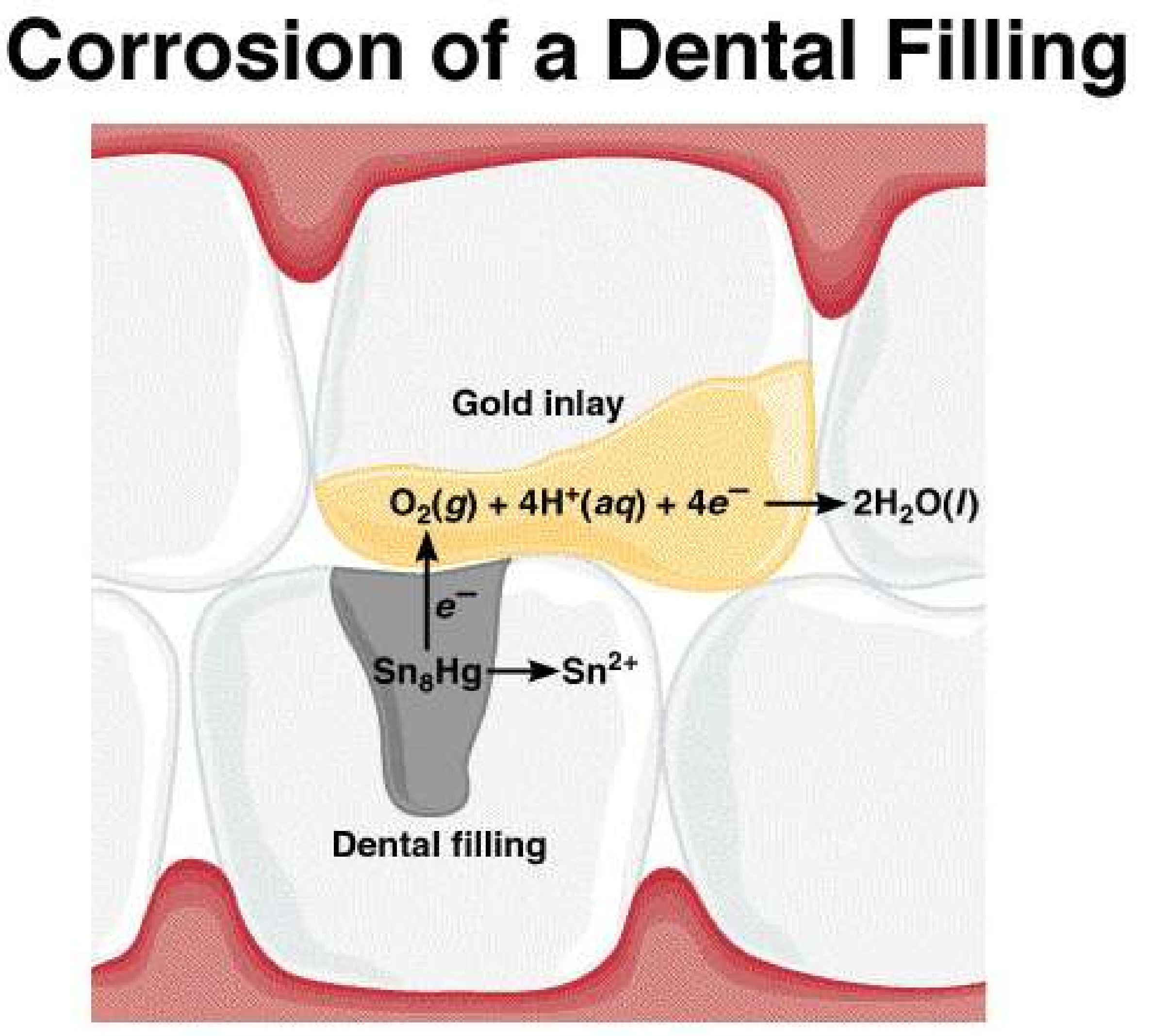
Chemistry In Action: Dental Filling Discomfort

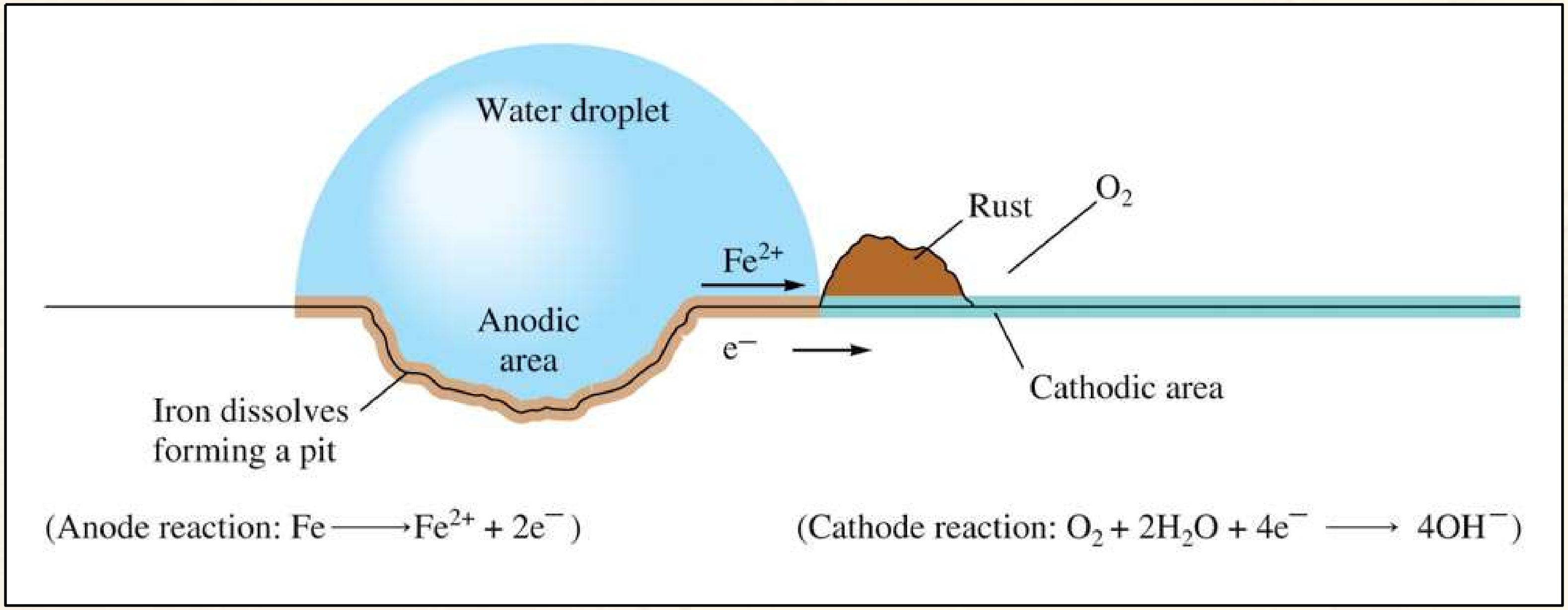
$\mathrm{Hg2}^{2+}/\mathrm{Ag2Hg3}$ 0.85 V

$\mathrm{Sn}^{2+}/\mathrm{Ag3Sn}$ -0.05 V

$\mathrm{Sn}^{2+}/\mathrm{Ag3Sn}$ -0.05 V



The Electrochemical Corrosion of Iron



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Corrosion

- Process of returning metals to their natural state – the ores from which they were originally obtained.
- Involves oxidation of the metal.

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Corrosion Prevention

- Application of a coating (like paint or metal plating)
  - Galvanizing
- Alloying
- Cathodic Protection
  - Protects steel in buried fuel tanks and pipelines.

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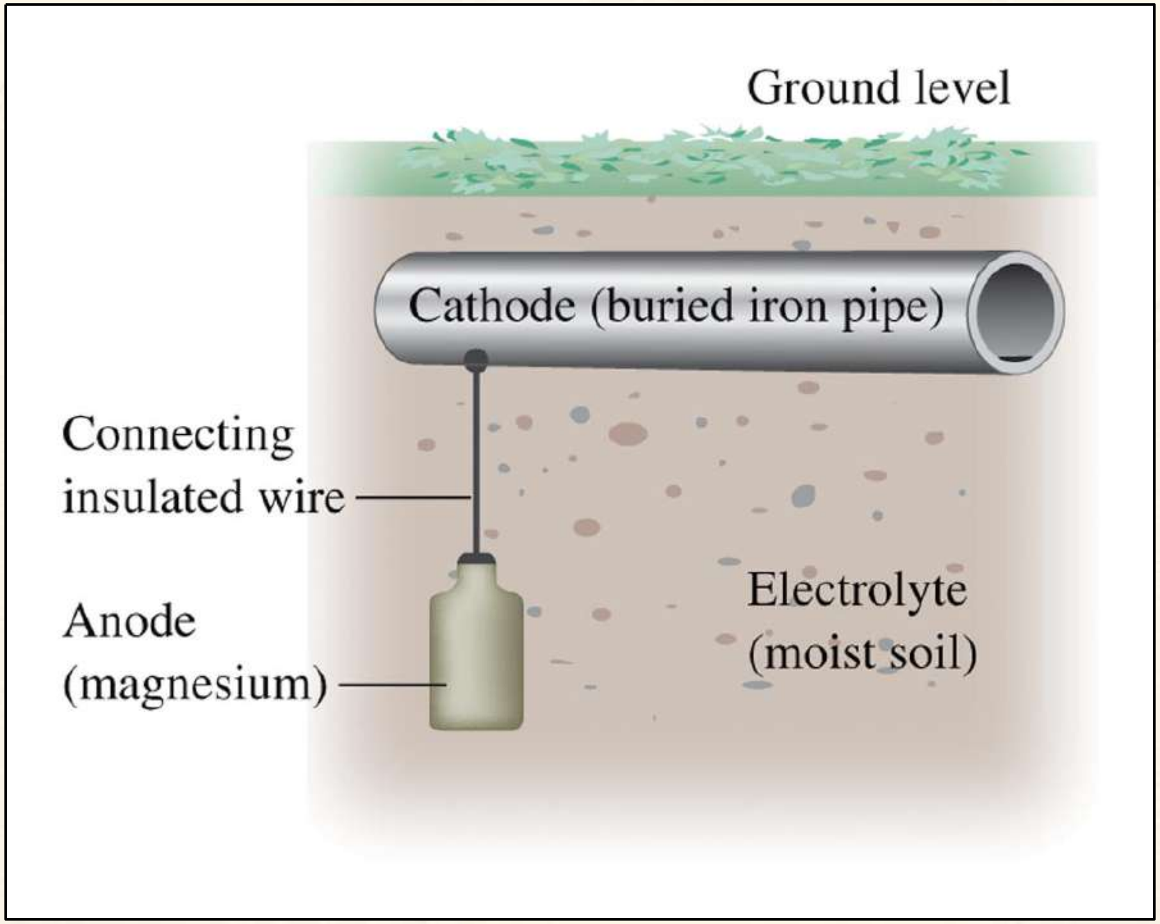
Cathodic Protection



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Electrolysis

- Forcing a current through a cell to produce a chemical change for which the cell potential is negative.

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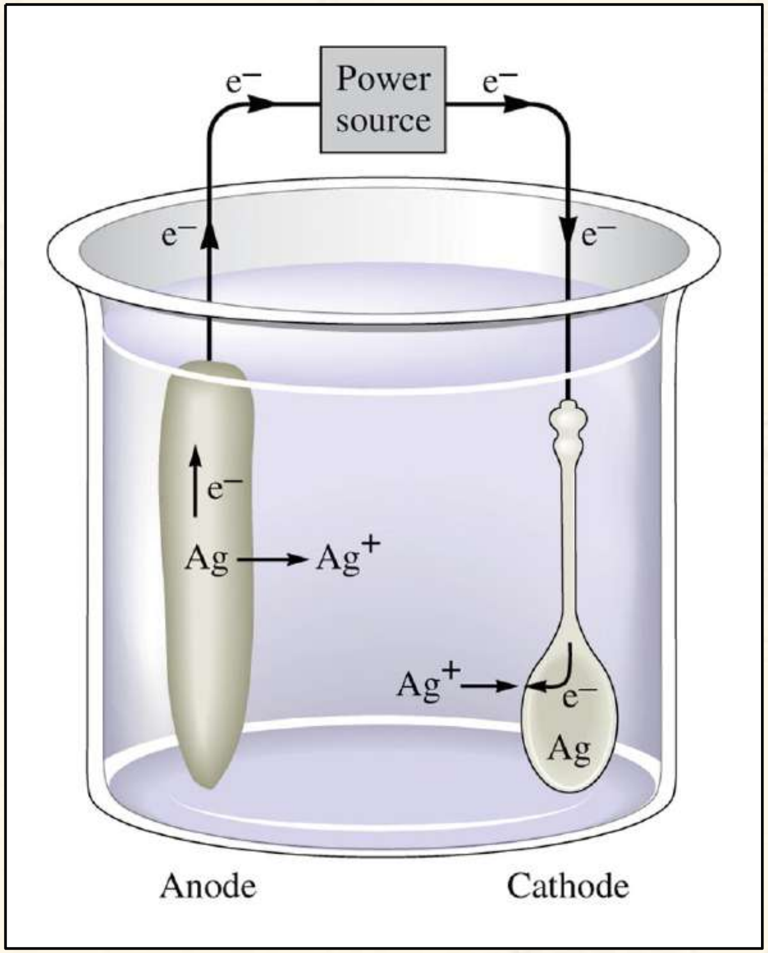
Electroplating a Spoon



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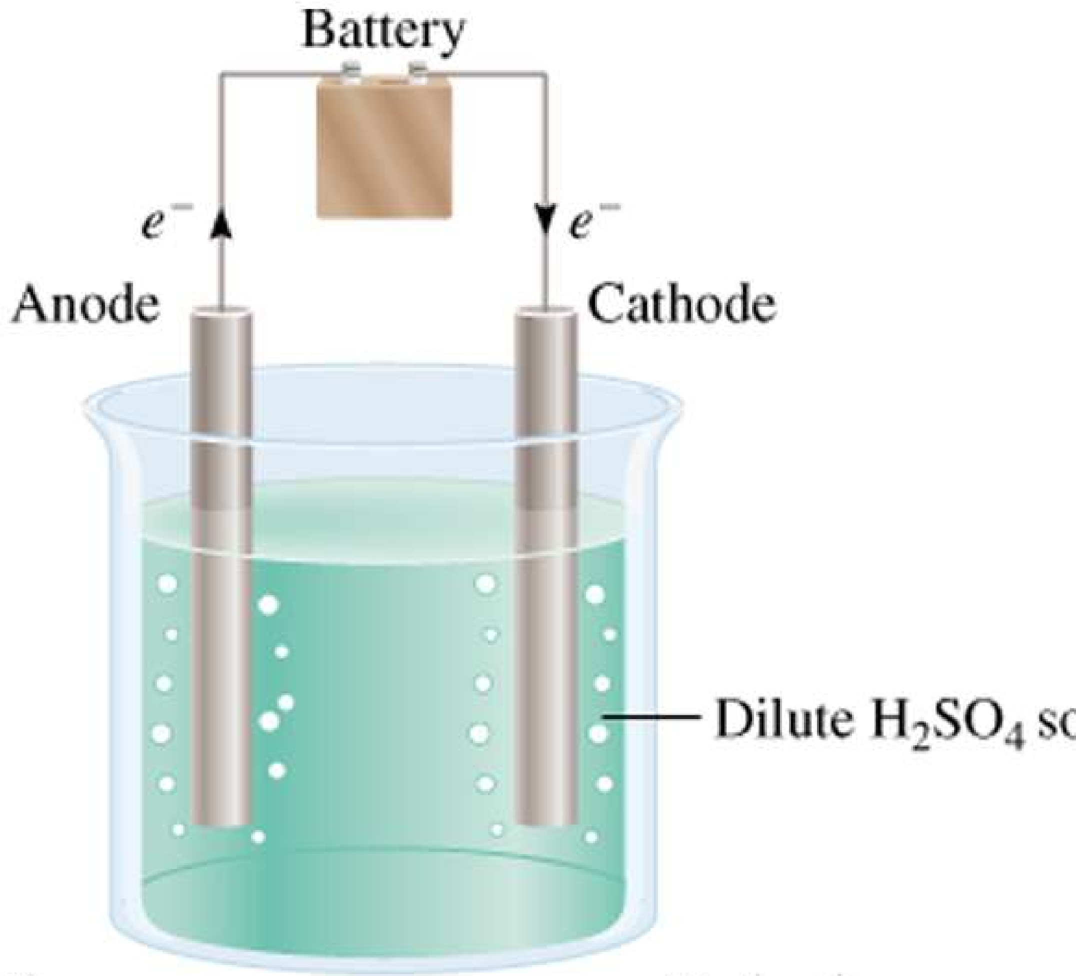
Electrolysis of Water



Oxidation

$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Reduction

$4H^+(aq) + 4e^- \longrightarrow 2H_2(g)$

Stoichiometry of Electrolysis

- How much chemical change occurs with the flow of a given current for a specified time?

current and time → quantity of charge →
moles of electrons → moles of analyte →
grams of analyte

Stoichiometry of Electrolysis

- current and time → quantity of charge

  1 ampere = 1 coulomb per second

  1 mole of e- = 96,485 coulombs

  Coulombs of charge = amps (C/s) × seconds (s)

- quantity of charge → moles of electrons

$$\text{mol } e^{-} = \text{Coulombs of charge} \times \frac{1 \text{ mol } e^{-}}{96,485\ \text{C}}$$

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How much Ca will be produced in an electrolytic cell of molten $CaCl_2$ if a current of 0.452 A is passed through the cell for 1.5 hours?

Anode: $2Cl^- (l) \rightarrow Cl_2 (g) + 2e^-$

Cathode: $Ca^{2+} (l) + 2e^- \rightarrow Ca (s)$

$Ca^{2+} (l) + 2Cl^- (l) \rightarrow Ca (s) + Cl_2 (g)$

2 mole e- = 1 mole Ca

$$\text{mol Ca} = 0.452 \frac{\cancel{C}}{\cancel{s}} \times 1.5\ \text{hr} \times \cancel{3}600 \frac{\cancel{s}}{\cancel{hr}} \times \frac{1\ \cancel{\text{mol e}^-}}{96{,}500\ \cancel{C}} \times \frac{1\ \text{mol Ca}}{2\ \cancel{\text{mol e}^-}}$$

= 0.0126 mol Ca

= 0.50 g Ca