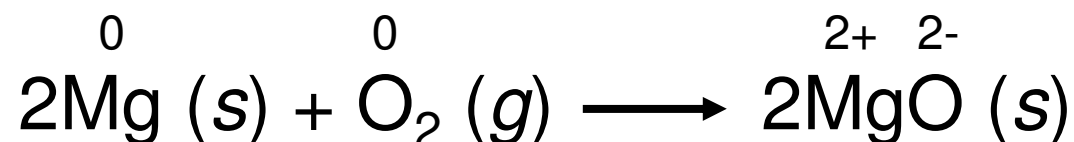


Electrochemistry

Chapter 19

Electrochemical processes are oxidation-reduction reactions in which:

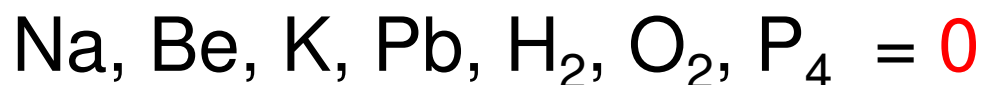
- the energy released by a spontaneous reaction is converted to electricity or
- electrical energy is used to cause a nonspontaneous reaction to occur



Oxidation number

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.

1. Free elements (uncombined state) have an oxidation number of zero.



2. In monatomic ions, the oxidation number is equal to the charge on the ion.



3. The oxidation number of oxygen is **usually** -2 . In H_2O_2 and O_2^{2-} it is -1 .

4. The oxidation number of hydrogen is $+1$ *except* when it is bonded to metals in binary compounds. In these cases, its oxidation number is -1 .
5. Group IA metals are $+1$, IIA metals are $+2$ and fluorine is always -1 .
6. The sum of the oxidation numbers of all the atoms in a molecule or ion is equal to the charge on the molecule or ion.

Identify the oxidation numbers of all the atoms in HCO_3^- ?



$$\text{O} = -2 \quad \text{H} = +1$$

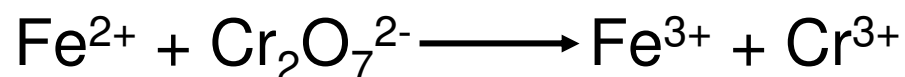
$$3 \times (-2) + 1 + ? = -1$$

$$\text{C} = +4$$

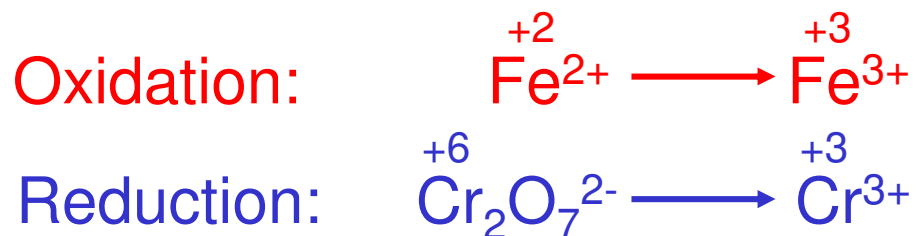
Balancing Redox Equations

The oxidation of Fe^{2+} to Fe^{3+} by $\text{Cr}_2\text{O}_7^{2-}$ in acid solution?

1. Write the unbalanced equation for the reaction in ionic form.



2. Separate the equation into two half-reactions.



3. Balance the atoms other than O and H in each half-reaction.

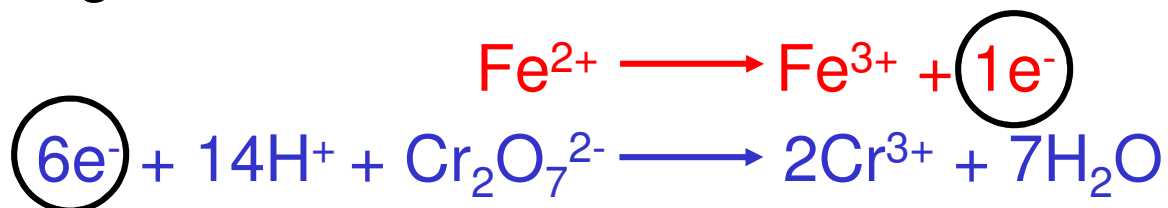


Balancing Redox Equations

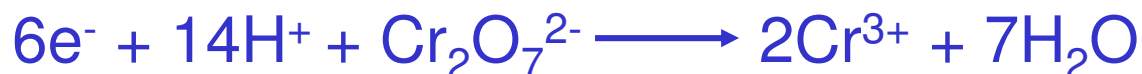
4. For reactions in acid, add H_2O to balance O atoms and H^+ to balance H atoms.



5. Add electrons to one side of each half-reaction to balance the charges on the half-reaction.

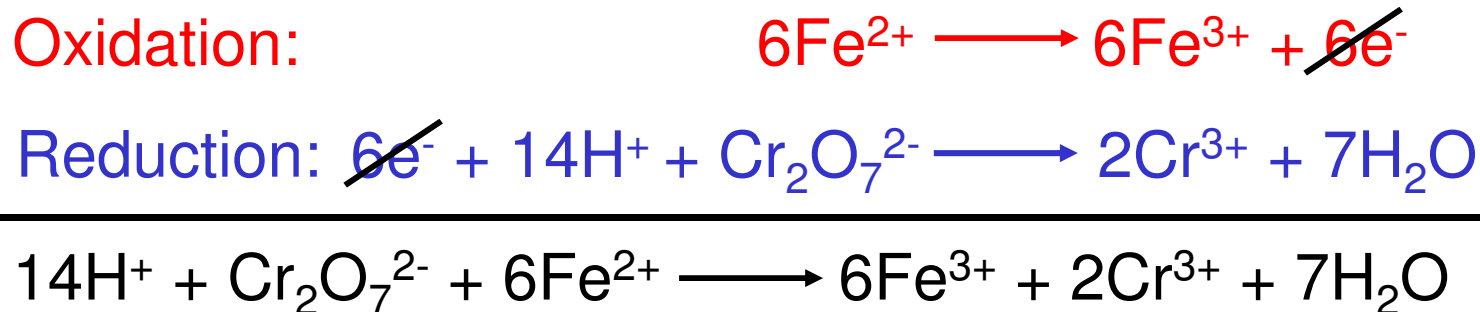


6. If necessary, equalize the number of electrons in the two half-reactions by multiplying the half-reactions by appropriate coefficients.



Balancing Redox Equations

7. Add the two half-reactions together and balance the final equation by inspection. **The number of electrons on both sides must cancel.**

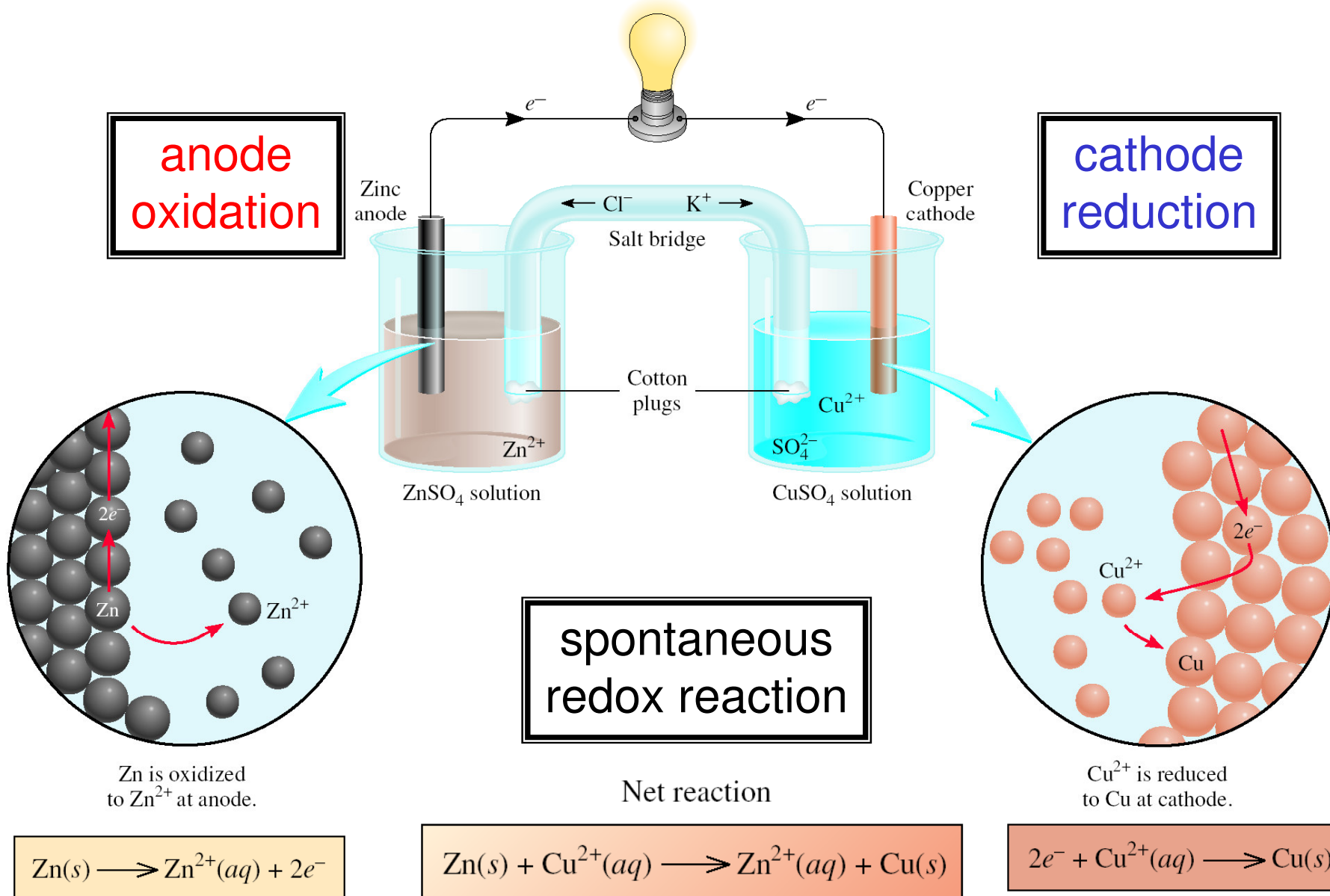


8. Verify that the number of atoms and the charges are balanced.

$$14 \times 1 - 2 + 6 \times 2 = 24 = 6 \times 3 + 2 \times 3$$

9. For reactions in basic solutions, add OH^- to **both sides** of the equation for every H^+ that appears in the final equation.

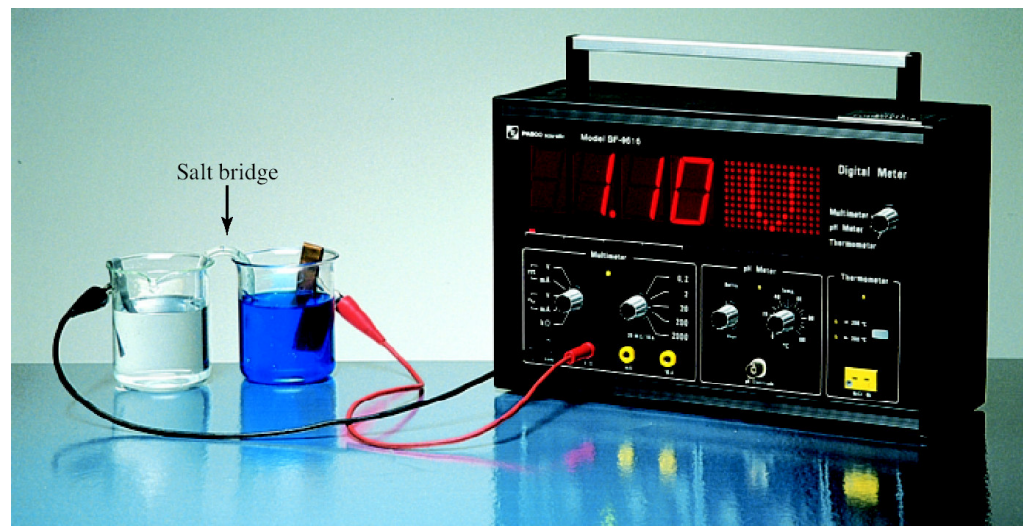
Galvanic Cells



Galvanic Cells

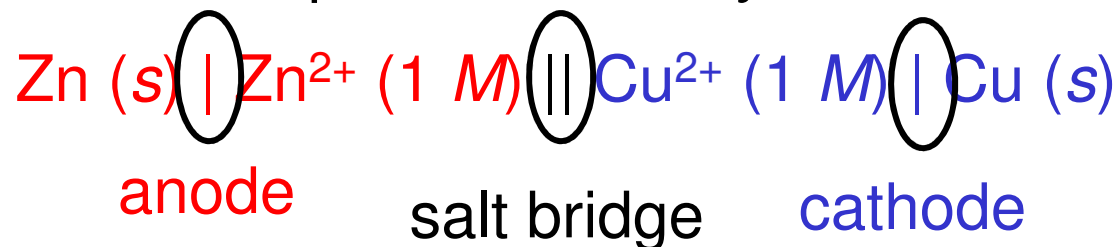
The difference in electrical potential between the anode and cathode is called:

- ***cell voltage***
- ***electromotive force (emf)***
- ***cell potential***

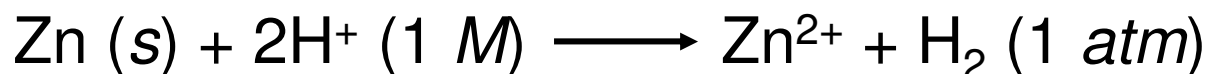
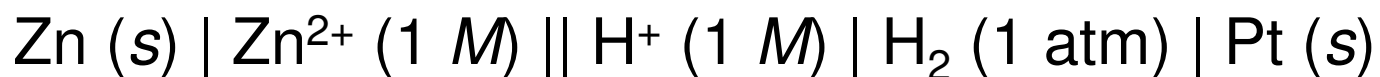
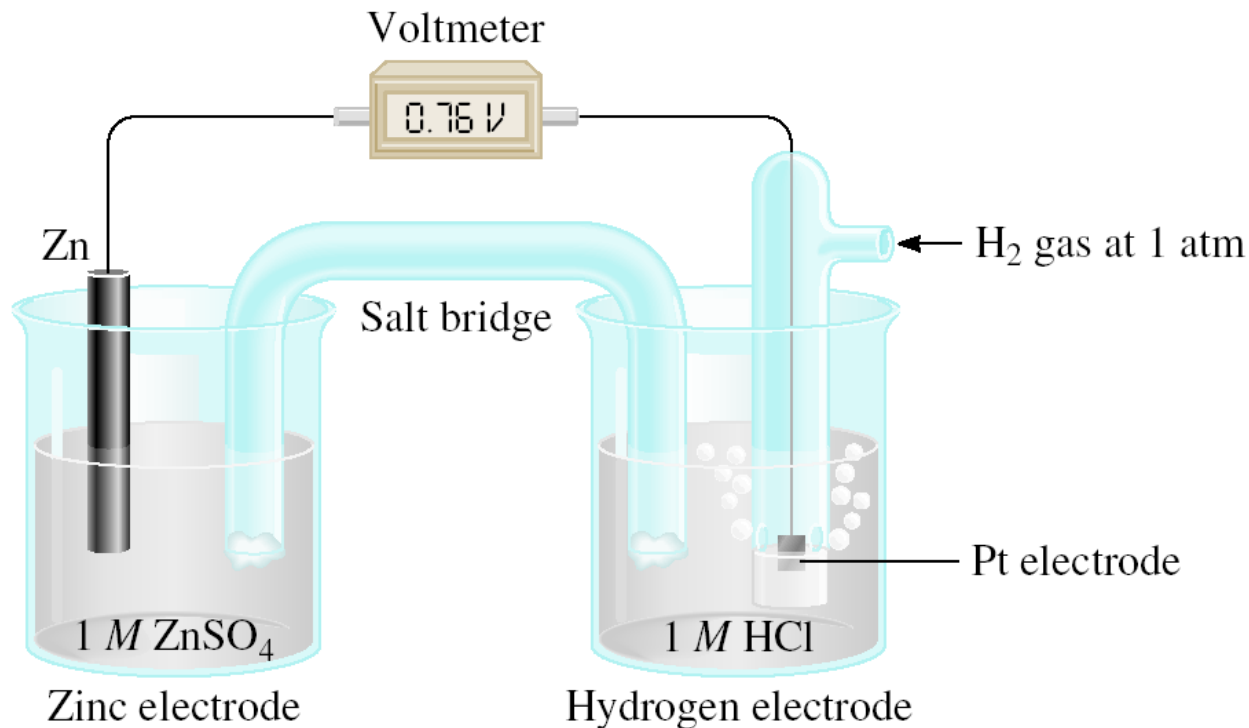


Cell Diagram

phase boundary

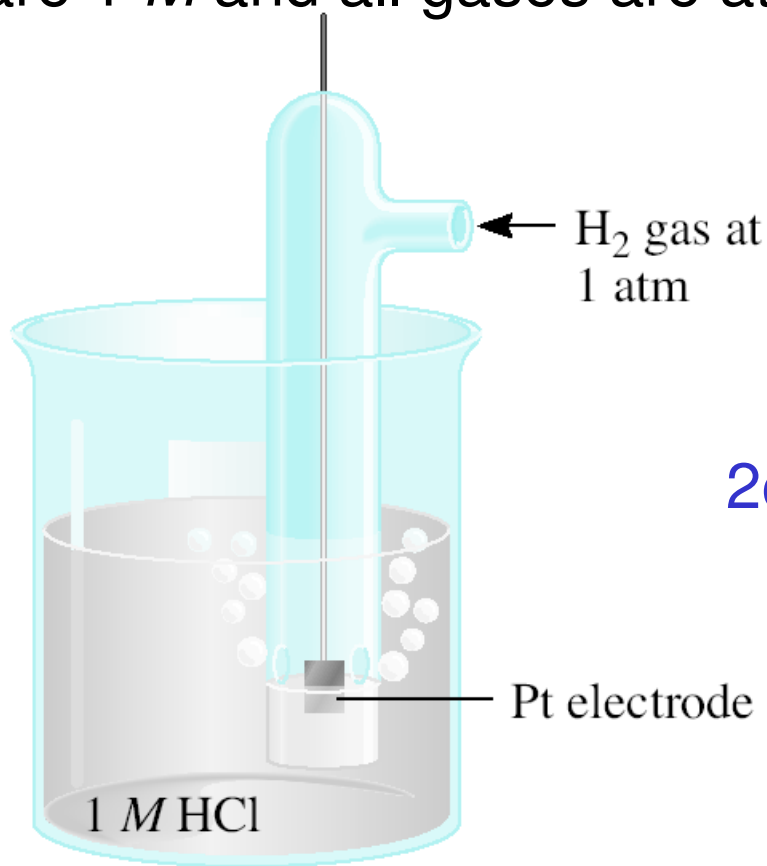


Standard Reduction Potentials



Standard Reduction Potentials

Standard reduction potential (E^0) is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 *M* and all gases are at 1 atm.



Reduction Reaction

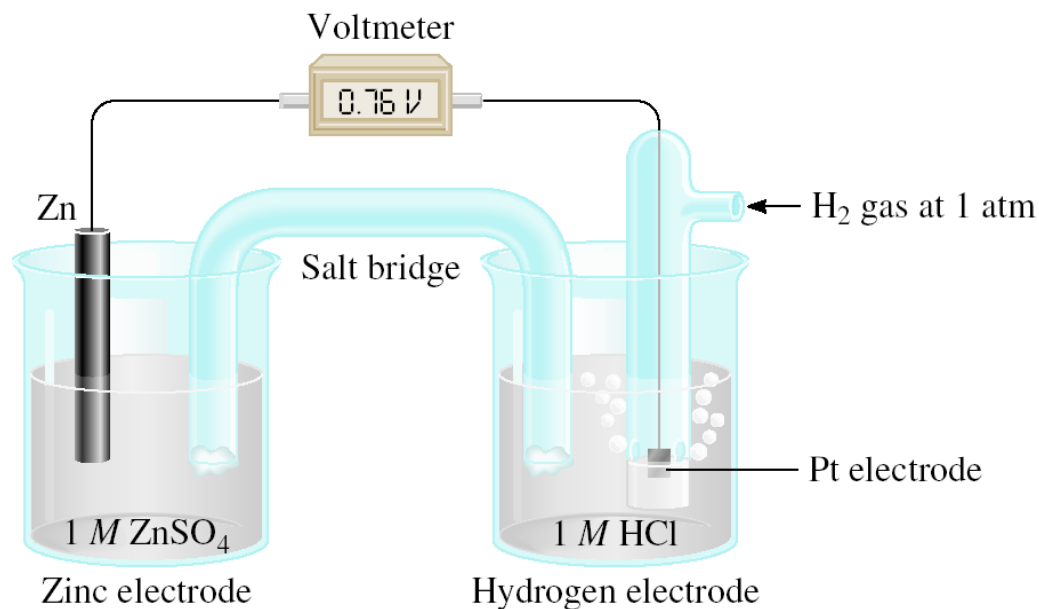


$$E^0 = 0\ V$$

Standard hydrogen electrode (SHE)

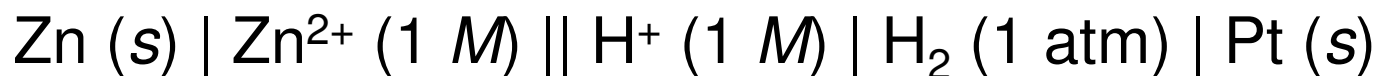
Standard Reduction Potentials

$$E_{\text{cell}}^0 = 0.76 \text{ V}$$



Standard emf (E_{cell}^0)

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$



$$E_{\text{cell}}^0 = E_{\text{H}^+/\text{H}_2}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0$$

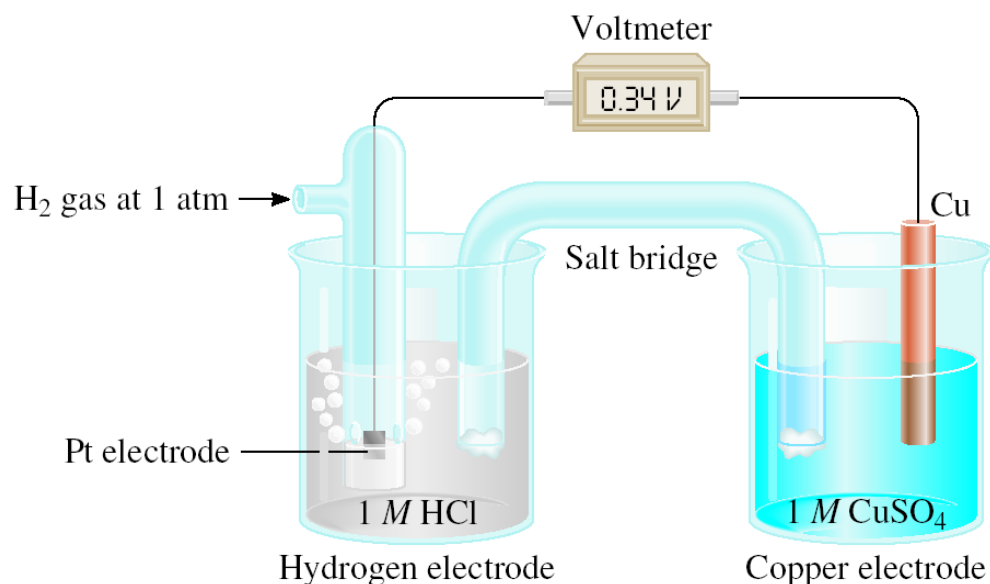
$$0.76 \text{ V} = 0 - E_{\text{Zn}^{2+}/\text{Zn}}^0$$

$$E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ V}$$



Standard Reduction Potentials

$$E_{\text{cell}}^0 = 0.34 \text{ V}$$



$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

$$E_{\text{cell}}^0 = E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{H}^+/\text{H}_2}^0$$

$$0.34 = E_{\text{Cu}^{2+}/\text{Cu}}^0 - 0$$

$$E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34 \text{ V}$$

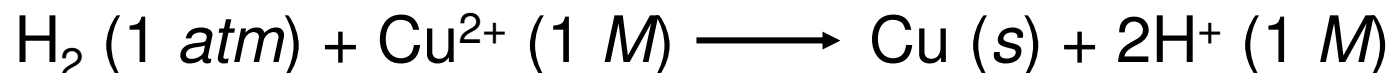
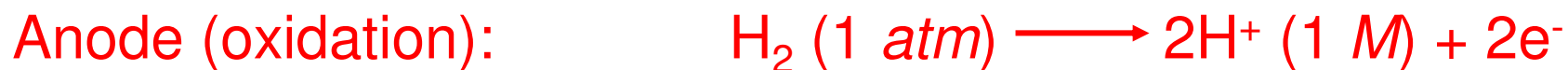
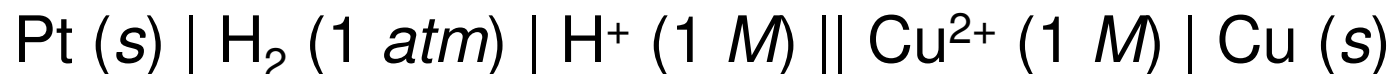


TABLE 19.1 Standard Reduction Potentials at 25°C*

Half-Reaction	$E^0(\text{V})$
$\text{F}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{F}^-(\text{aq})$	+2.87
$\text{O}_3(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}$	+2.07
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Co}^{2+}(\text{aq})$	+1.82
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+1.77
$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \longrightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$	+1.70
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \longrightarrow \text{Ce}^{3+}(\text{aq})$	+1.61
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$	+1.51
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Au}(\text{s})$	+1.50
$\text{Cl}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$	+1.33
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	+1.23
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Br}_2(\text{l}) + 2\text{e}^- \longrightarrow 2\text{Br}^-(\text{aq})$	+1.07
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \longrightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}$	+0.96
$2\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Hg}_2^{2+}(\text{aq})$	+0.92
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Hg}(\text{l})$	+0.85
$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$	+0.68
$\text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O} + 3\text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$	+0.59
$\text{I}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{I}^-(\text{aq})$	+0.53
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^-(\text{aq})$	+0.40
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$	+0.34
$\text{AgCl}(\text{s}) + \text{e}^- \longrightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22
$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}$	+0.20
$\text{Cu}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Cu}(\text{s})$	+0.15
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	+0.13
$2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$	0.00
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ni}(\text{s})$	-0.25
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Co}(\text{s})$	-0.28
$\text{PbSO}_4(\text{s}) + 2\text{e}^- \longrightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.31
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cd}(\text{s})$	-0.40
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Cr}(\text{s})$	-0.74
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Mn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Al}(\text{s})$	-1.66
$\text{Be}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Be}(\text{s})$	-1.85
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ca}(\text{s})$	-2.87
$\text{Sr}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sr}(\text{s})$	-2.89
$\text{Ba}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ba}(\text{s})$	-2.90
$\text{K}^+(\text{aq}) + \text{e}^- \longrightarrow \text{K}(\text{s})$	-2.93
$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	-3.05

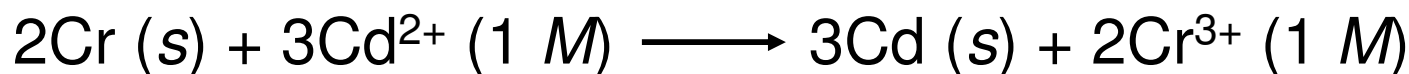
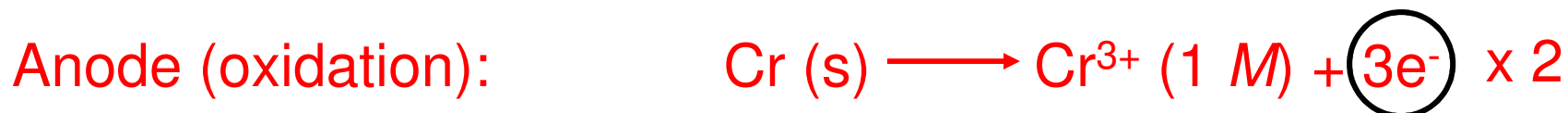
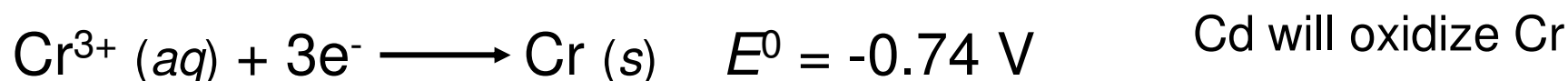
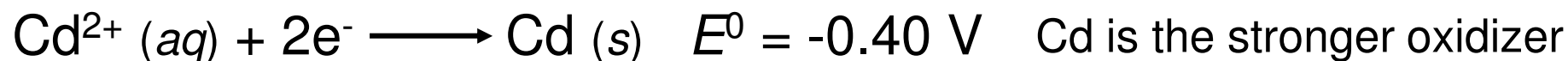
Increasing strength as oxidizing agent

Increasing strength as reducing agent

- E^0 is for the reaction as written
- The more positive E^0 the greater the tendency for the substance to be reduced
- The half-cell reactions are reversible
- The sign of E^0 changes when the reaction is reversed
- Changing the stoichiometric coefficients of a half-cell reaction **does not** change the value of E^0

*For all half-reactions the concentration is 1 M for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

What is the standard emf of an electrochemical cell made of a Cd electrode in a 1.0 M $\text{Cd}(\text{NO}_3)_2$ solution and a Cr electrode in a 1.0 M $\text{Cr}(\text{NO}_3)_3$ solution?



$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

$$E_{\text{cell}}^0 = -0.40 - (-0.74)$$

$$E_{\text{cell}}^0 = 0.34 \text{ V}$$

Spontaneity of Redox Reactions

$$\Delta G = -nFE_{\text{cell}} \quad n = \text{number of moles of electrons in reaction}$$

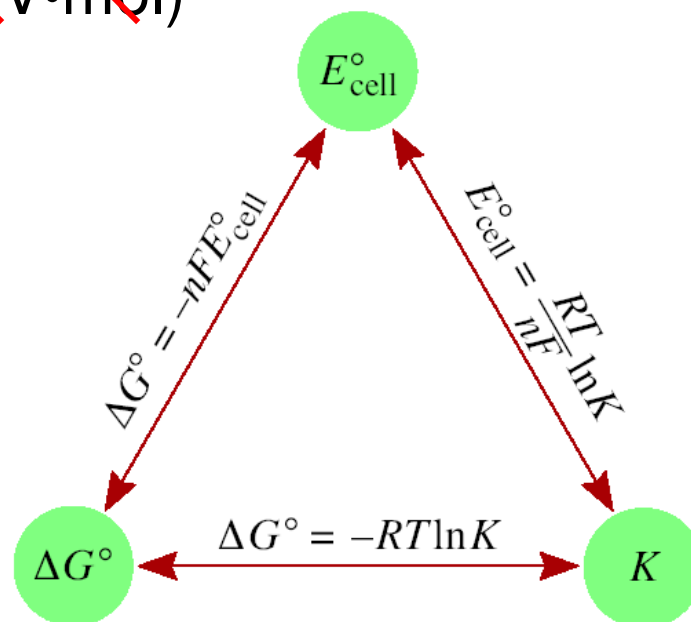
$$\Delta G^0 = -nFE_{\text{cell}}^0 \quad F = 96,500 \frac{\text{J}}{\text{V} \cdot \text{mol}} = 96,500 \text{ C/mol}$$

$$\Delta G^0 = -RT \ln K = -nFE_{\text{cell}}^0$$

$$E_{\text{cell}}^0 = \frac{RT}{nF} \ln K = \frac{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{n (96,500 \text{ J/V} \cdot \text{mol})} \ln K$$

$$E_{\text{cell}}^0 = \frac{0.0257 \text{ V}}{n} \ln K$$

$$E_{\text{cell}}^0 = \frac{0.0592 \text{ V}}{n} \log K$$



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.

$$\Delta G^\circ = -RT \ln K = -nFE^\circ_{\text{cell}}$$

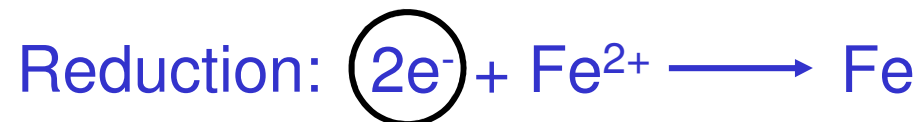
What is the equilibrium constant for the following reaction at 25°C?

$$\text{Fe}^{2+} (\text{aq}) + 2\text{Ag} (\text{s}) \rightleftharpoons \text{Fe} (\text{s}) + 2\text{Ag}^+ (\text{aq})$$

$$E_{\text{cell}}^0 = \frac{0.0257 \text{ V}}{n} \ln K$$



$$n = 2$$



$$E^0 = E_{\text{Fe}^{2+}/\text{Fe}}^0 - E_{\text{Ag}^+/\text{Ag}}^0$$

$$E^0 = -0.44 - (0.80)$$

$$E^0 = -1.24 \text{ V}$$

$$K = e^{\left[\frac{E_{\text{cell}}^0 \times n}{0.0257 \text{ V}} \right]} = e^{\left[\frac{-1.24 \text{ V} \times 2}{0.0257 \text{ V}} \right]}$$

$$K = 1.23 \times 10^{-42}$$

The Effect of Concentration on Cell Emf

$$\Delta G = \Delta G^0 + RT \ln Q \quad \Delta G = -nFE \quad \Delta G^0 = -nFE^0$$

$$-nFE = -nFE^0 + RT \ln Q$$

Nernst equation

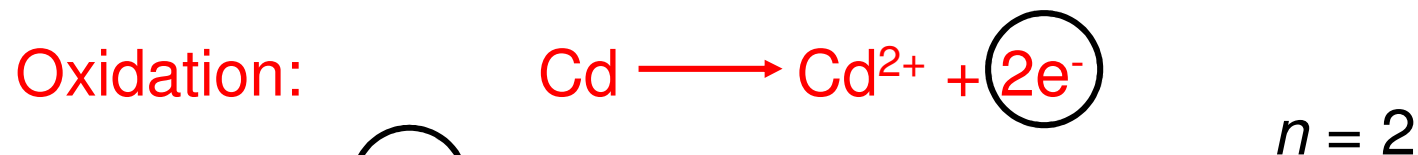
$$E = E^0 - \frac{RT}{nF} \ln Q$$

At 298 K

$$E = E^0 - \frac{0.0257 \text{ V}}{n} \ln Q$$

$$E = E^0 - \frac{0.0592 \text{ V}}{n} \log Q$$

Will the following reaction occur spontaneously at 25°C if $[\text{Fe}^{2+}] = 0.60 \text{ M}$ and $[\text{Cd}^{2+}] = 0.010 \text{ M}$?



$$E^0 = E_{\text{Fe}^{2+}/\text{Fe}}^0 - E_{\text{Cd}^{2+}/\text{Cd}}^0$$

$$E^0 = -0.44 - (-0.40)$$

$$E^0 = -0.04 \text{ V}$$

$$E = E^0 - \frac{0.0257 \text{ V}}{n} \ln Q$$

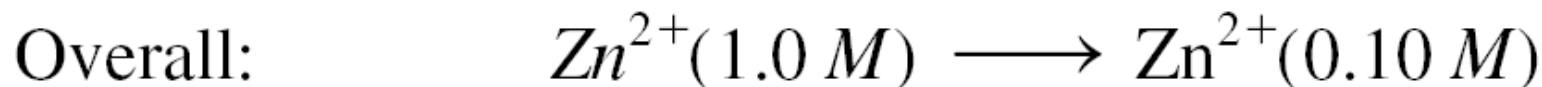
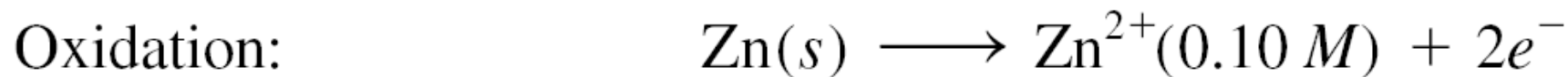
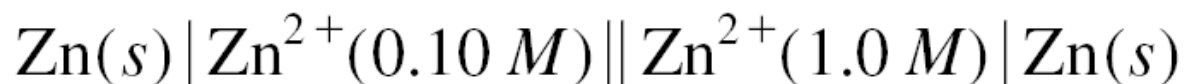
$$E = -0.04 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.010}{0.60}$$

$$E = 0.013$$

$E > 0$ Spontaneous

Concentration Cells

Galvanic cell from two half-cells composed of the *same* material but differing in ion concentrations.

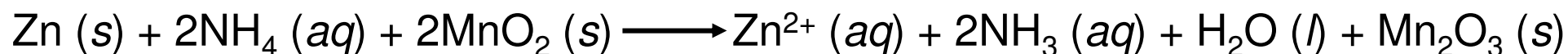
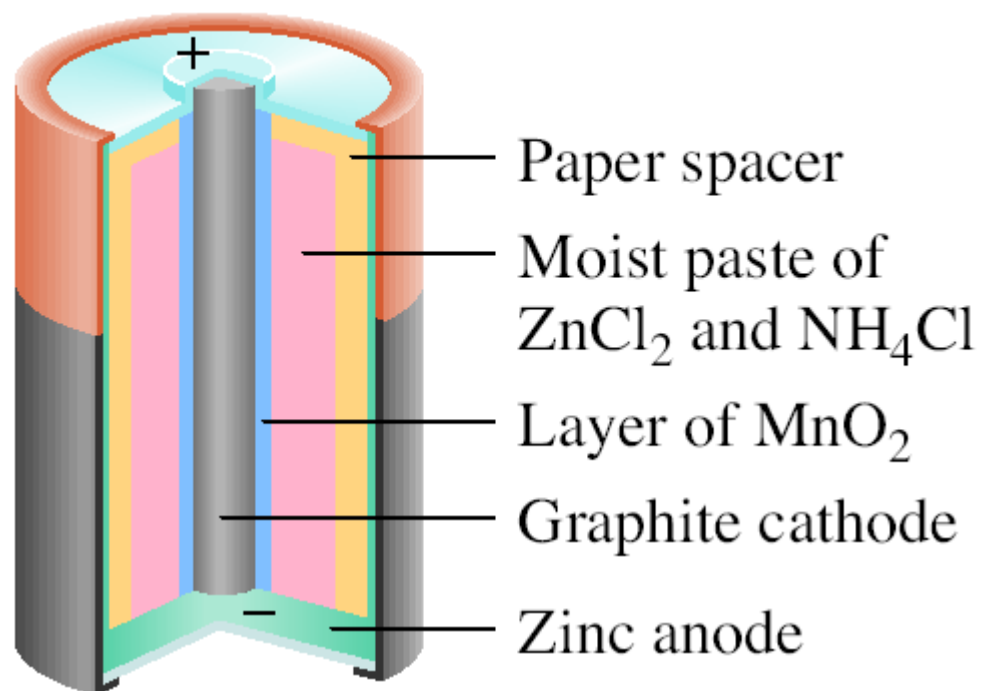


$$E = E^{\circ} - \frac{0.0257\text{ V}}{2} \ln \frac{[\text{Zn}^{2+}]_{\text{dil}}}{[\text{Zn}^{2+}]_{\text{conc}}}$$

$$E = 0 - \frac{0.0257\text{ V}}{2} \ln \frac{0.10}{1.0} = 0.0296\text{ V}$$

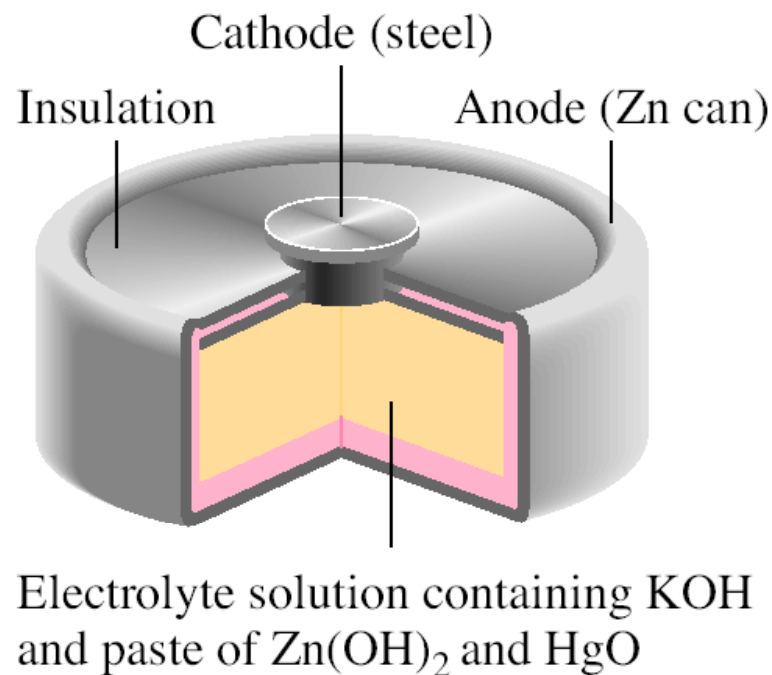
Batteries

Dry cell
Leclanché cell



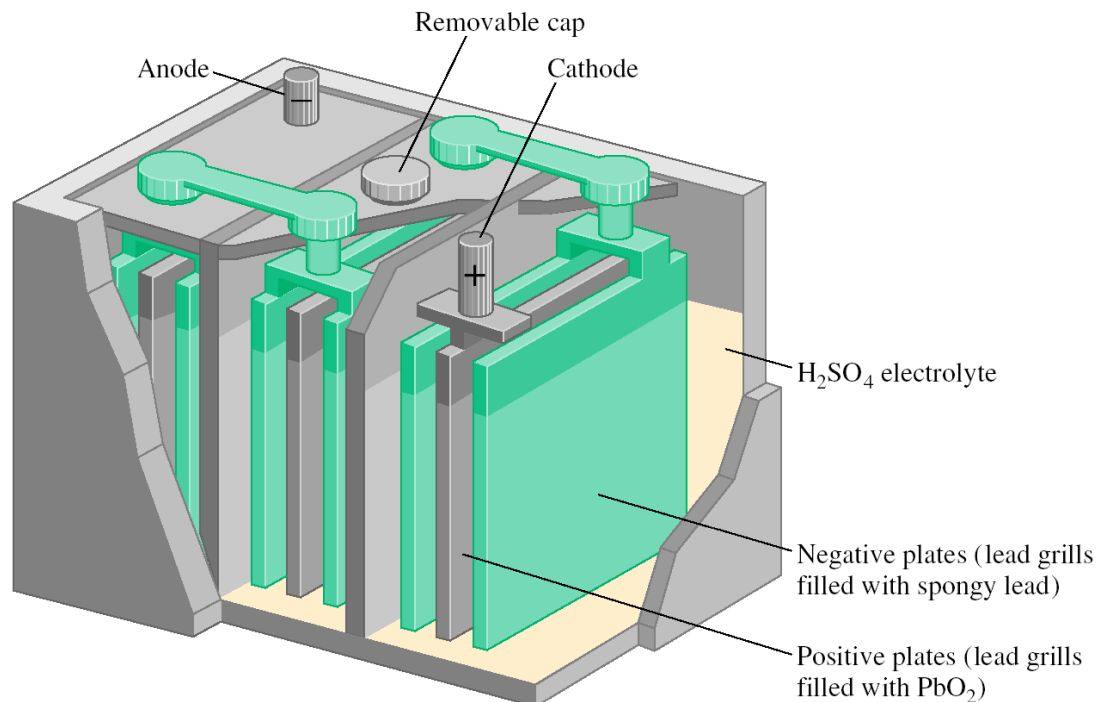
Batteries

Mercury Battery

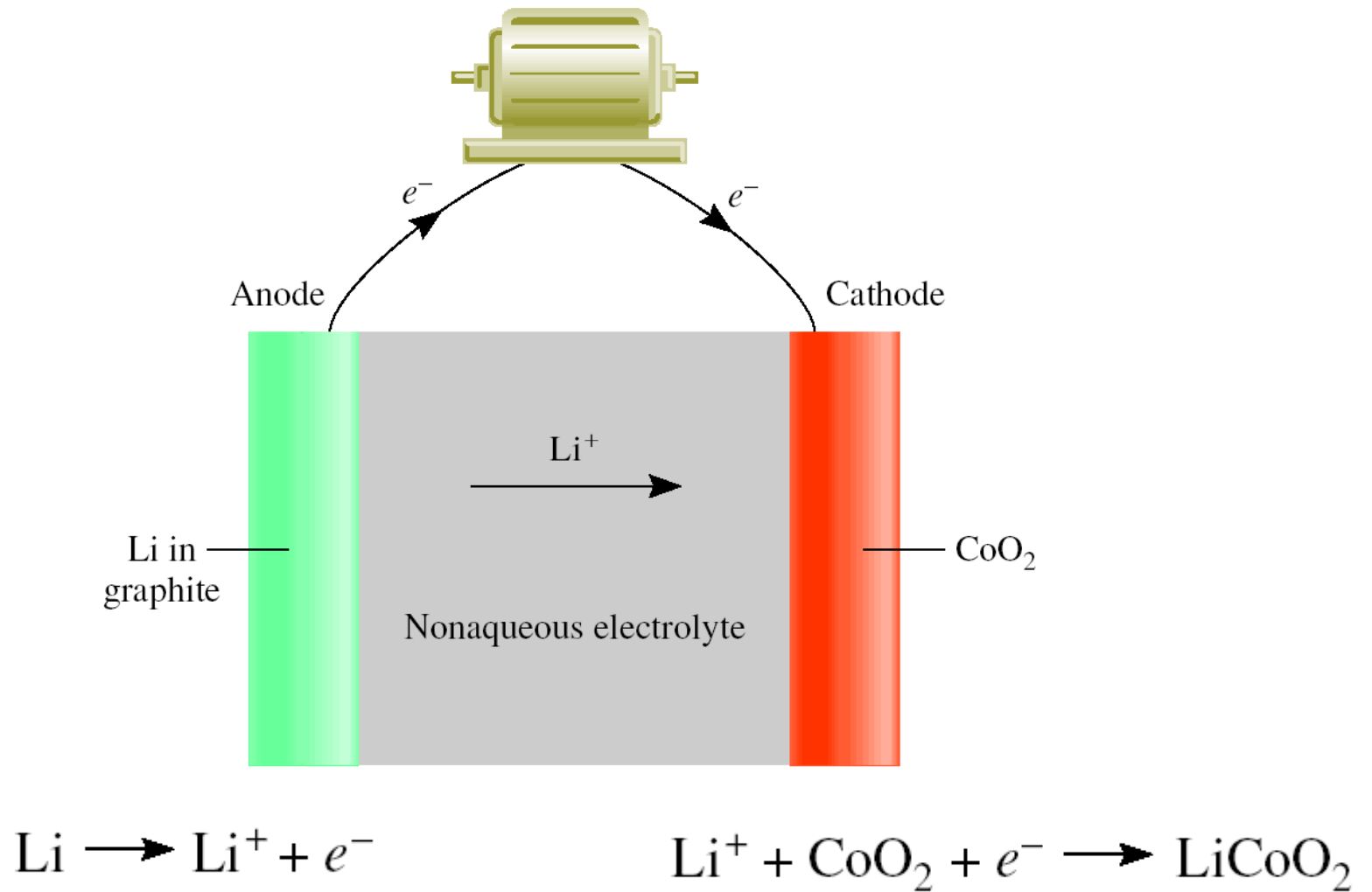


Batteries

Lead storage battery

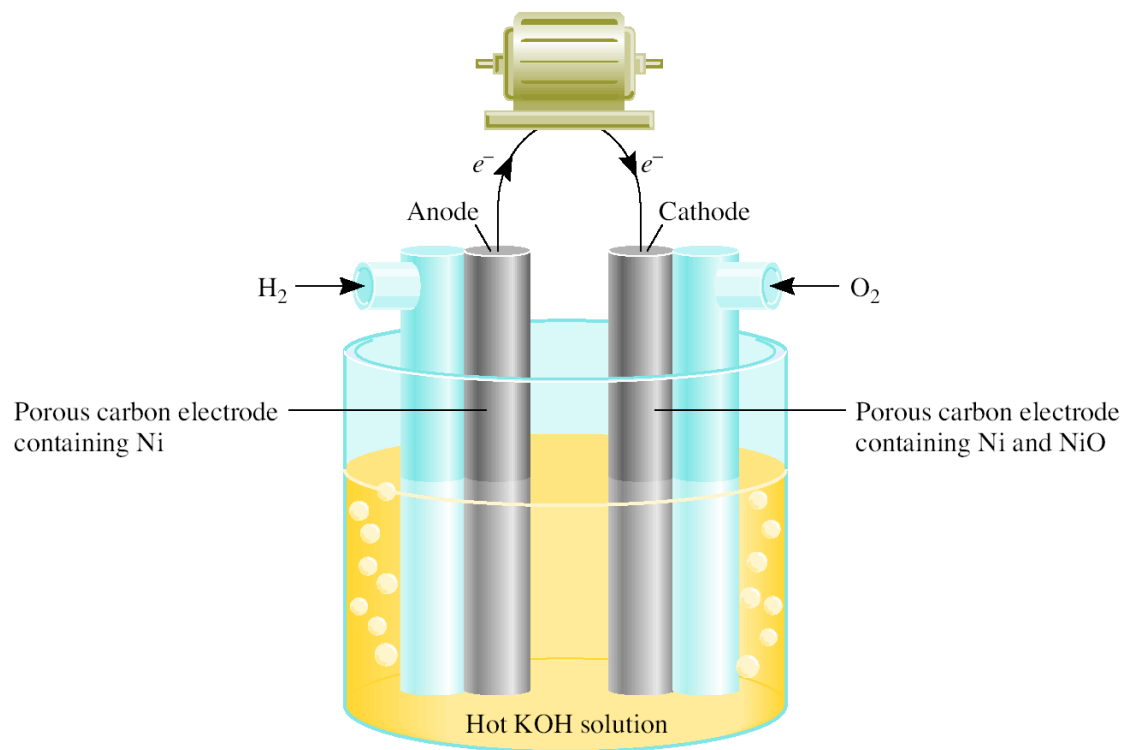


Batteries

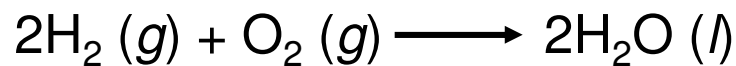


Solid State Lithium Battery

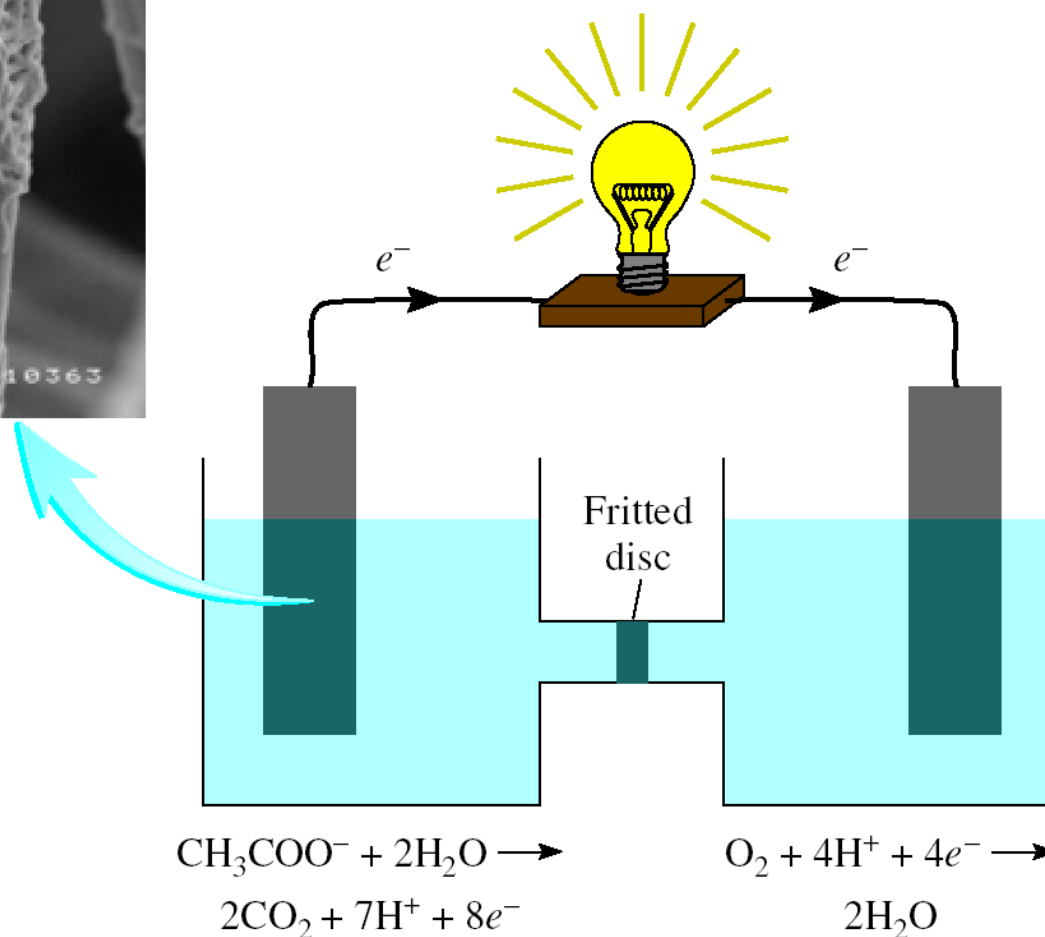
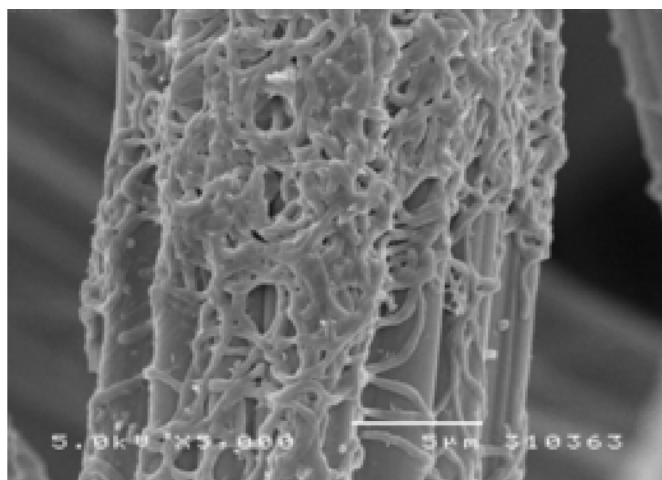
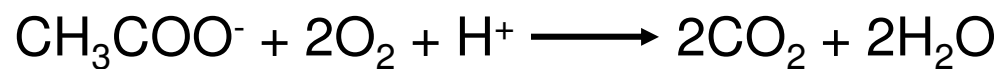
Batteries



A ***fuel cell*** is an electrochemical cell that requires a continuous supply of reactants to keep functioning

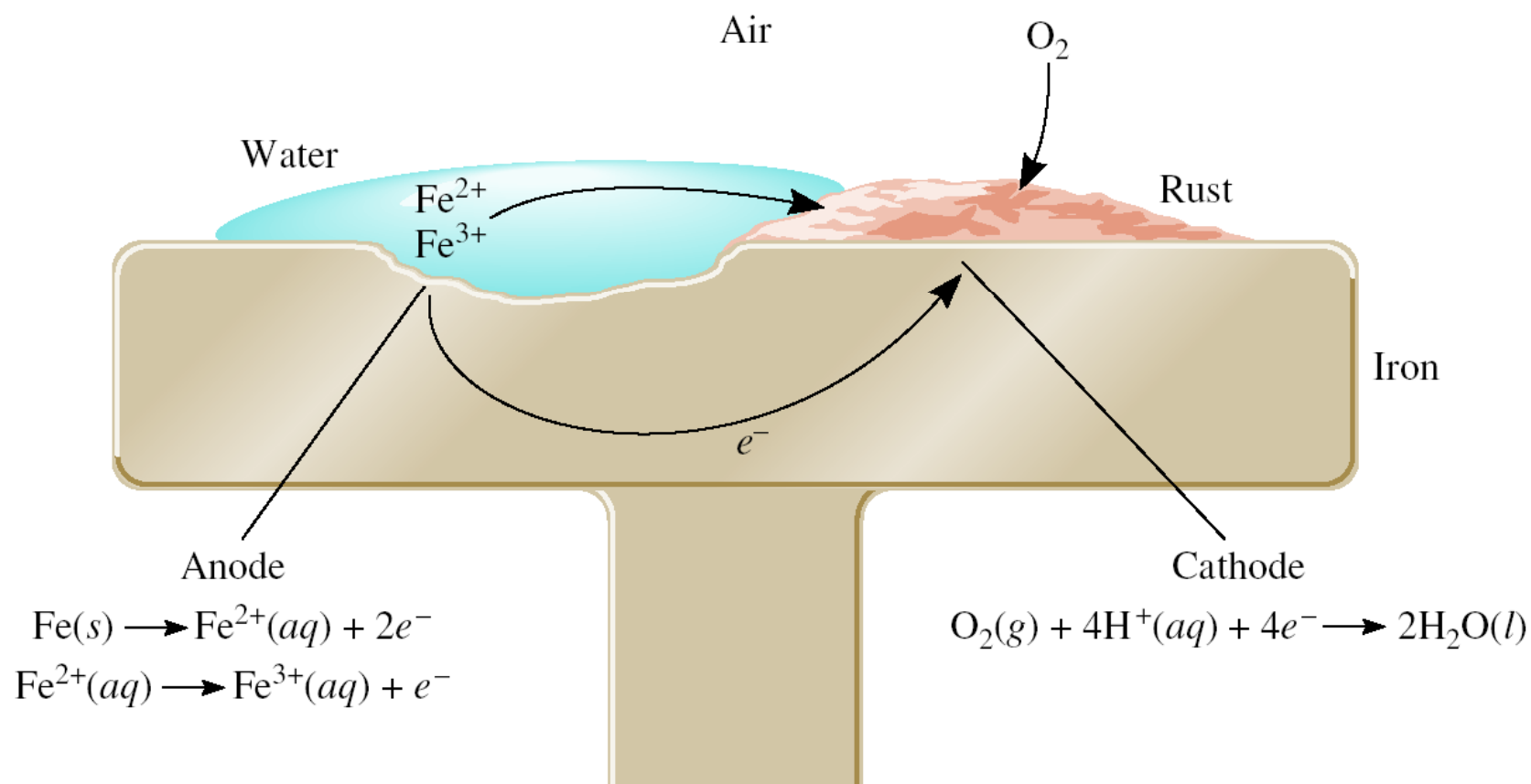


Chemistry In Action: Bacteria Power

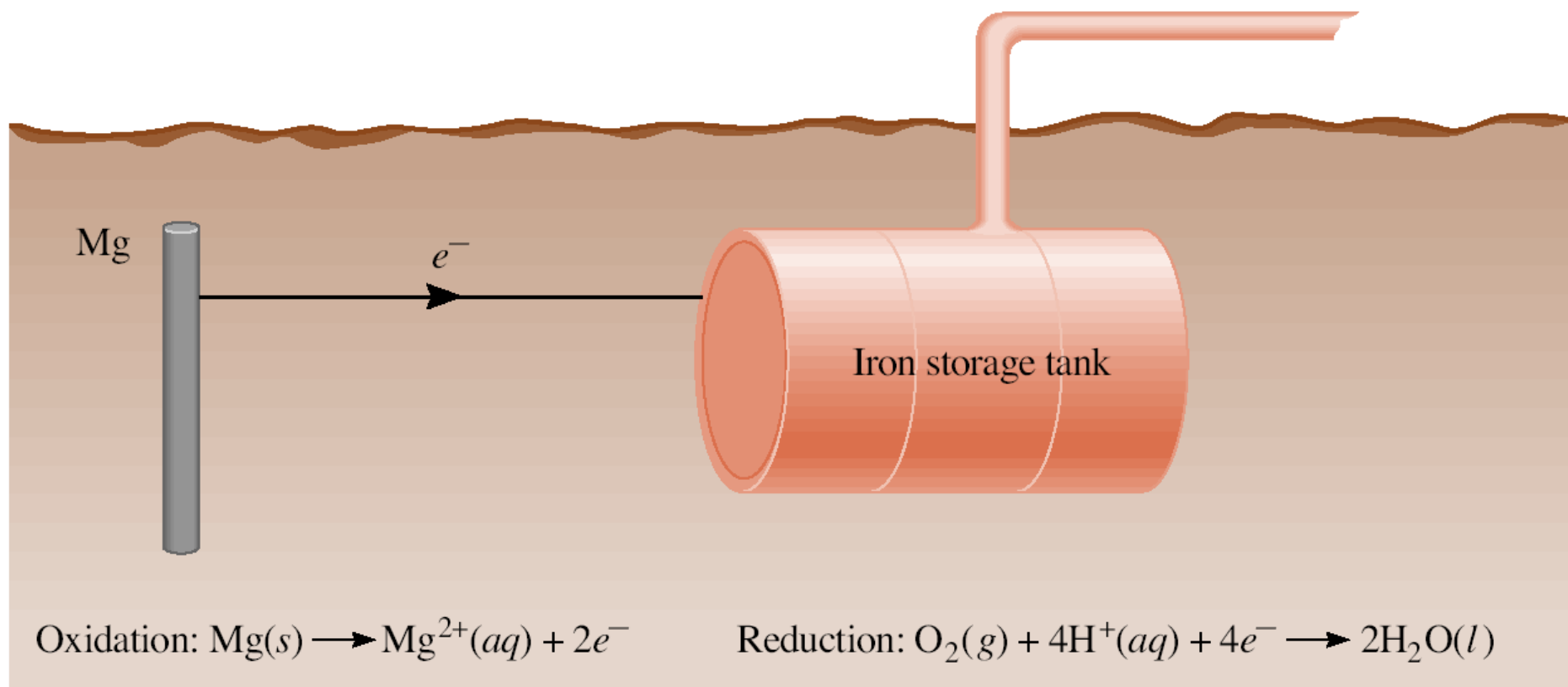


Corrosion

Corrosion is the term usually applied to *the deterioration of metals by an electrochemical process.*

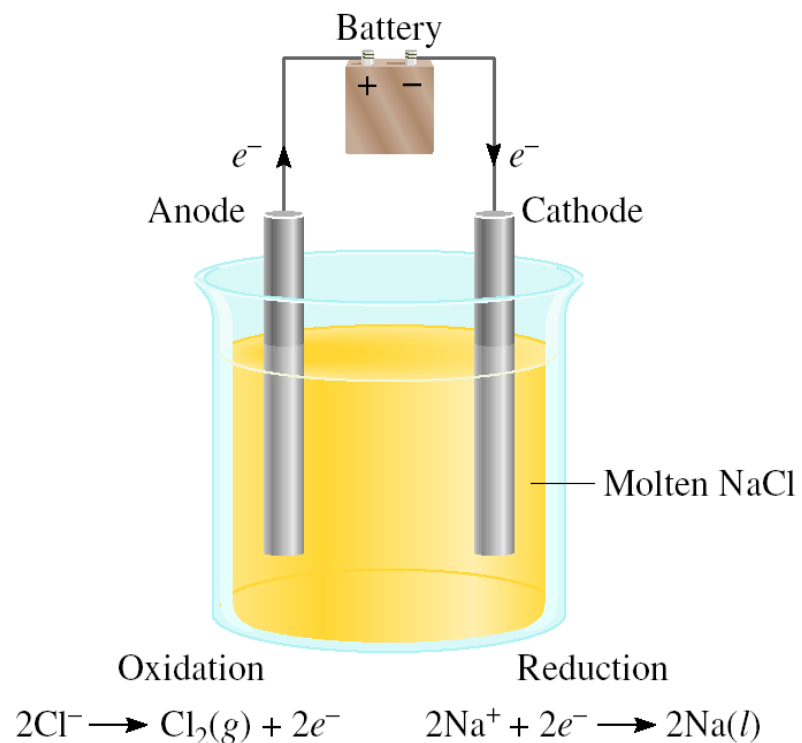
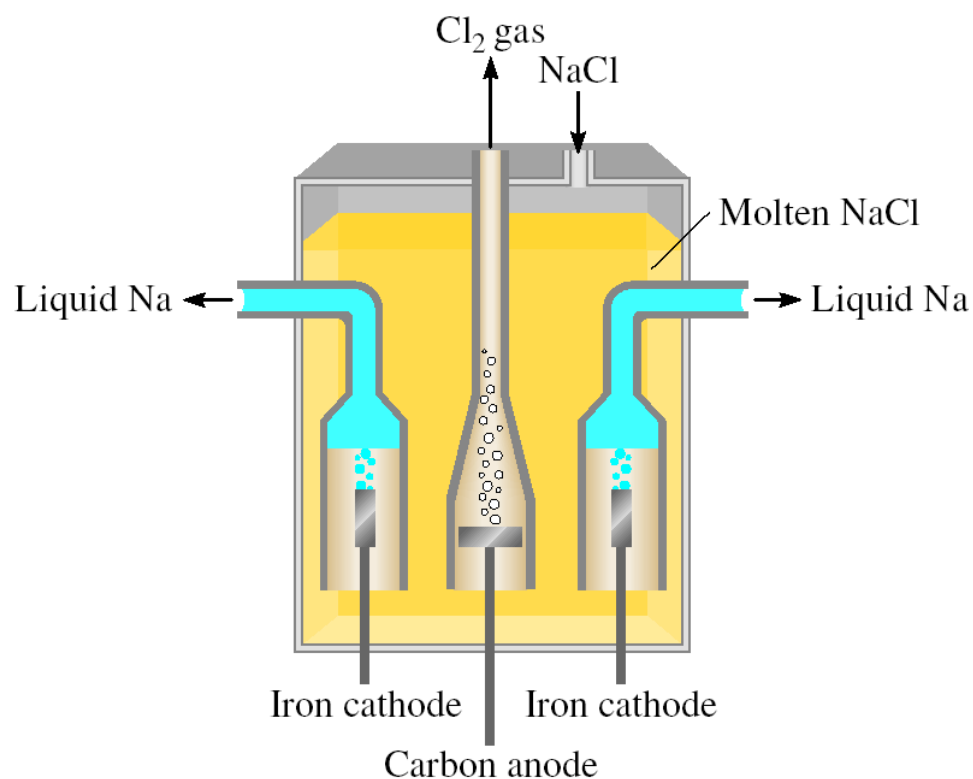


Cathodic Protection of an Iron Storage Tank

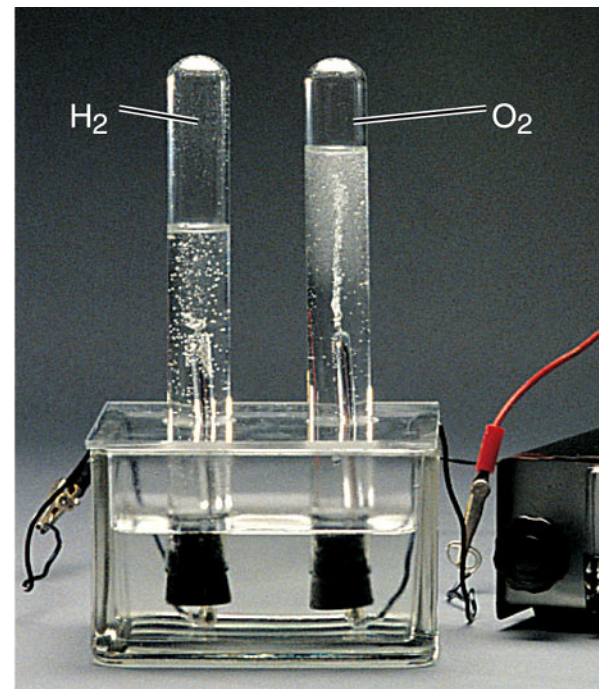
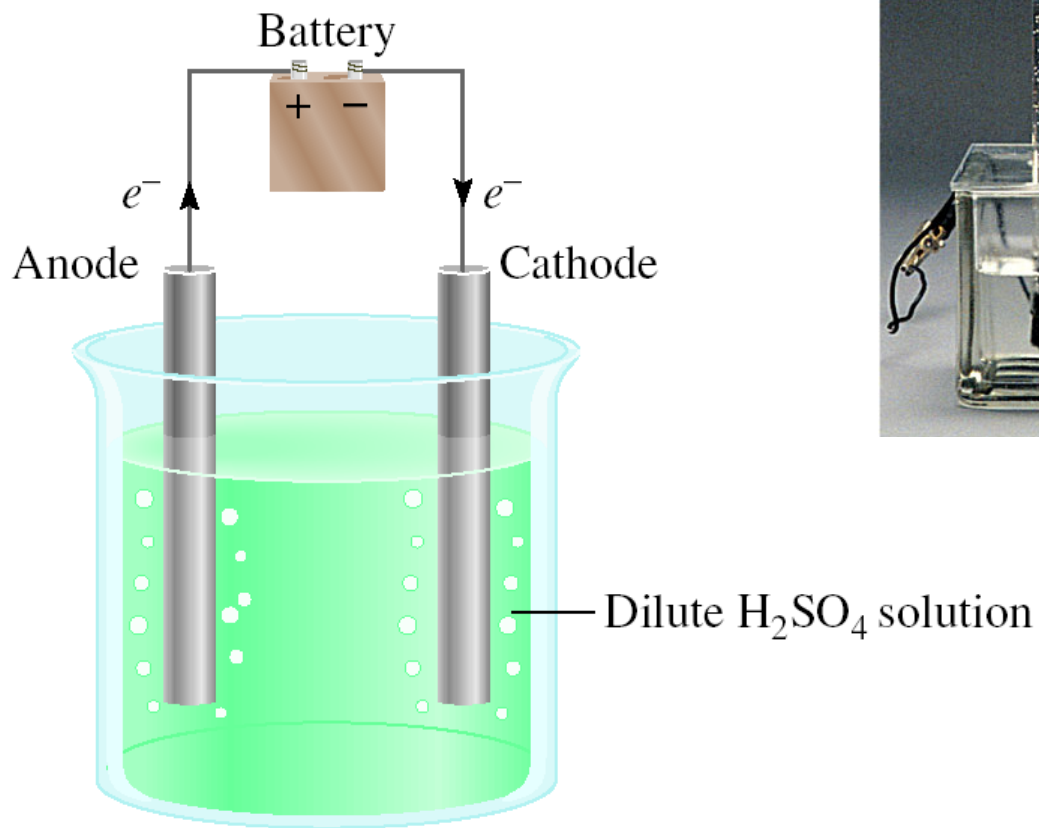


Electrolysis is the process in which electrical energy is used to cause a **nonspontaneous** chemical reaction to occur.

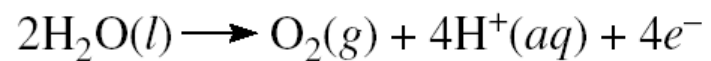
Electrolysis of molten NaCl



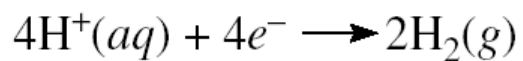
Electrolysis of Water

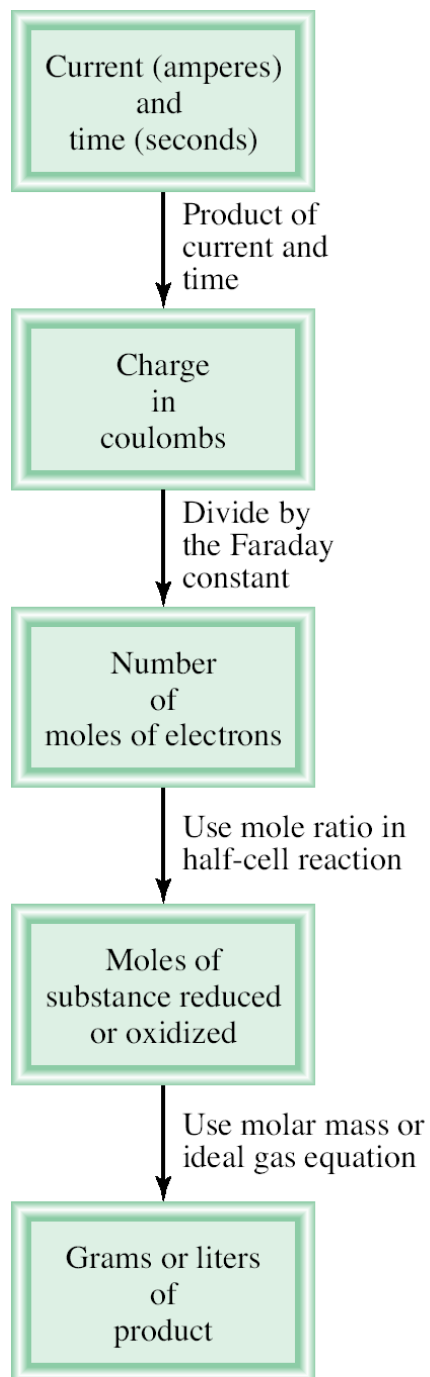


Oxidation



Reduction



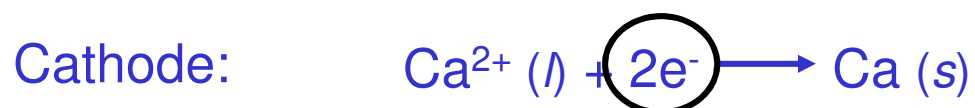


Electrolysis and Mass Changes

$$\text{charge (C)} = \text{current (A)} \times \text{time (s)}$$

$$1 \text{ mol e}^- = 96,500 \text{ C}$$

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?



2 mole e^- = 1 mole Ca

$$\text{mol Ca} = 0.452 \frac{\cancel{\text{C}}}{\cancel{\text{s}}} \times 1.5 \cancel{\text{hr}} \times 3600 \frac{\cancel{\text{s}}}{\cancel{\text{hr}}} \times \frac{1 \cancel{\text{mol } e^-}}{96,500 \cancel{\text{C}}} \times \frac{1 \cancel{\text{mol Ca}}}{2 \cancel{\text{mol } e^-}}$$

$$= 0.0126 \text{ mol Ca}$$

$$= 0.50 \text{ g Ca}$$

Chemistry In Action: Dental Filling Discomfort

