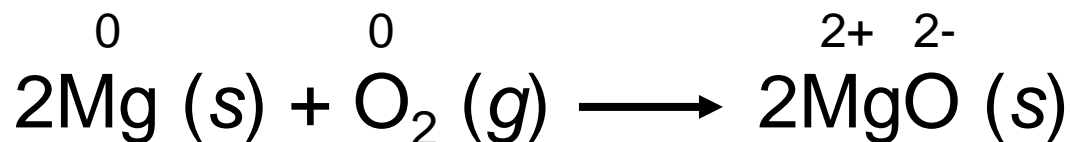# Electrochemistry

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

$$\overset{0}{2Mg}\ (s) + \overset{0}{O_2}\ (g) \longrightarrow \overset{2+\ \ 2-}{2MgO}\ (s)$$

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

$$O_2 + 4e^- \longrightarrow 2O^{2-}$$ ***Reduction*** half-reaction (gain e^-)

19.1

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.

$$Na, Be, K, Pb, H_2, O_2, P_4 = 0$$
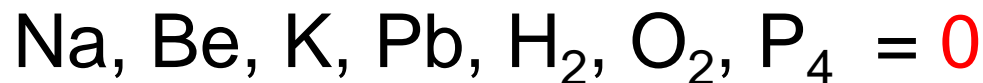
2. In monatomic ions, the oxidation number is equal to the charge on the ion.

$$Li^+, Li = +1; Fe^{3+}, Fe = +3; O^{2-}, O = -2$$

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

4.4

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.
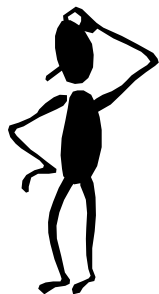
HCO_3^-

Oxidation numbers of all the atoms in HCO_3^- ?

$O = -2 \qquad H = +1$

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

$C = +4$
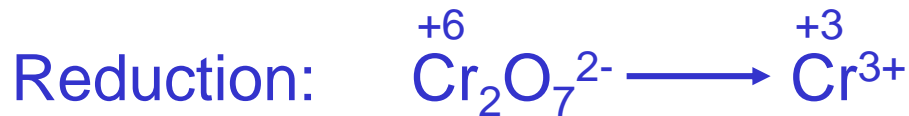
Balancing Redox Equations

The oxidation of Fe^{2+} to Fe^{3+} by $Cr_2O_7^{2-}$ in **acid solution**?

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

$$Fe^{2+} + Cr_2O_7^{2-} \longrightarrow Fe^{3+} + Cr^{3+}$$

2. Separate the equation into two half-reactions.

Oxidation: $\overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Fe^{3+}}$

Reduction: $\overset{+6}{Cr_2O_7^{2-}} \longrightarrow \overset{+3}{Cr^{3+}}$

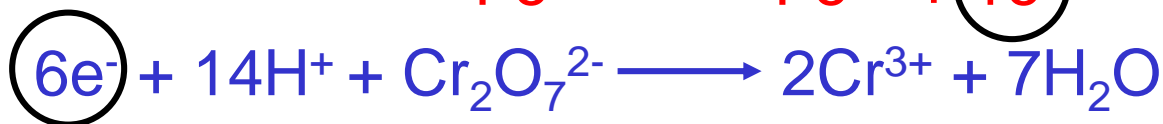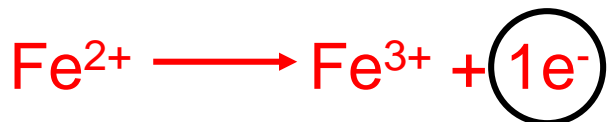3. Balance the atoms other than O and H in each half-reaction.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

Balancing Redox Equations

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

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

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

$$Fe^{2+} \longrightarrow Fe^{3+} + \boxed{1e^-}$$

$$\boxed{6e^-} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

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

$$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$$

$$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$
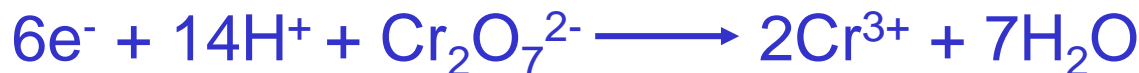
Balancing Redox Equations

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

Oxidation: $6Fe^{2+} \longrightarrow 6Fe^{3+} + \cancel{6e^-}$

Reduction: $\cancel{6e^-} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

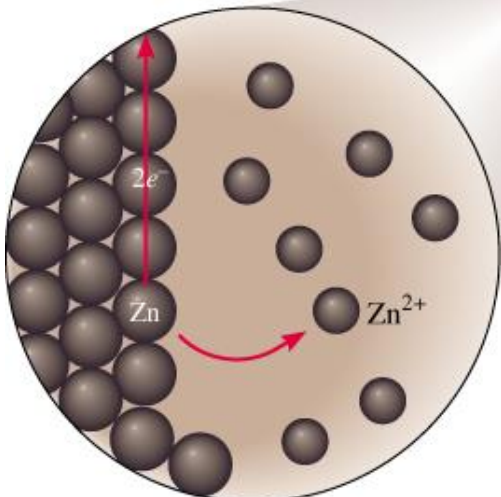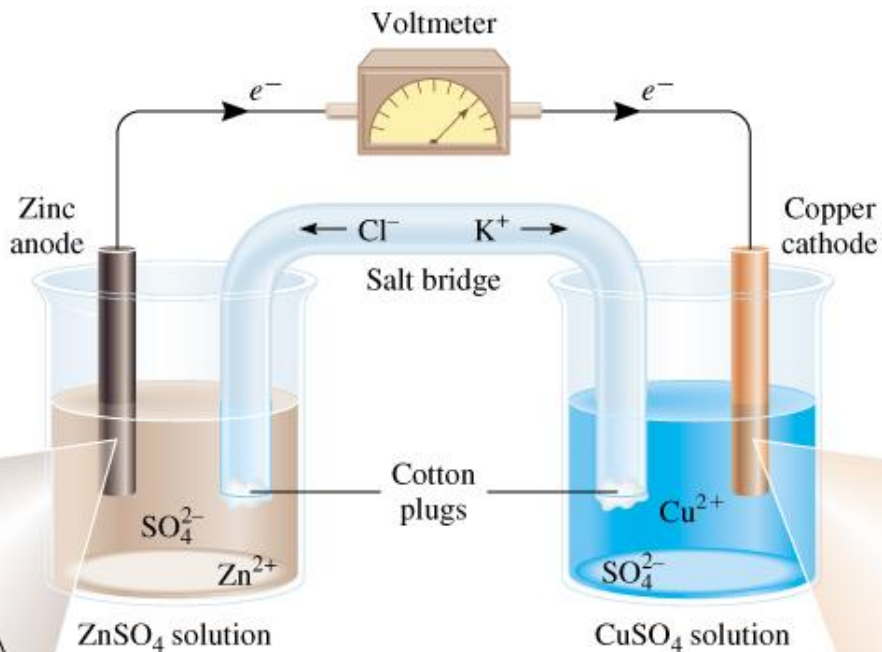8. Verify that the number of atoms and the charges are balanced.

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

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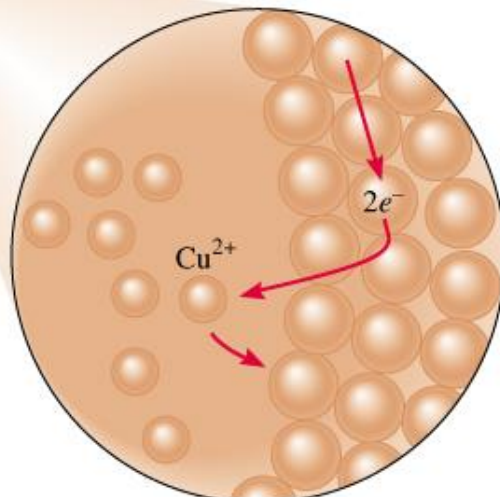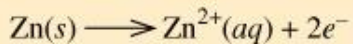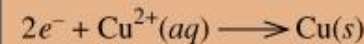
Galvanic Cells

Voltmeter

e^-

e^-

anode oxidation

Zinc anode

← Cl⁻   K⁺ →

Salt bridge

cathode reduction

Copper cathode

Cotton plugs

Cu^{2+}

SO_4^{2-}

SO_4^{2-}

Zn^{2+}

$ZnSO_4$ solution

$CuSO_4$ solution

$2e^-$

Zn

Zn^{2+}

$2e^-$

Cu^{2+}

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

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$
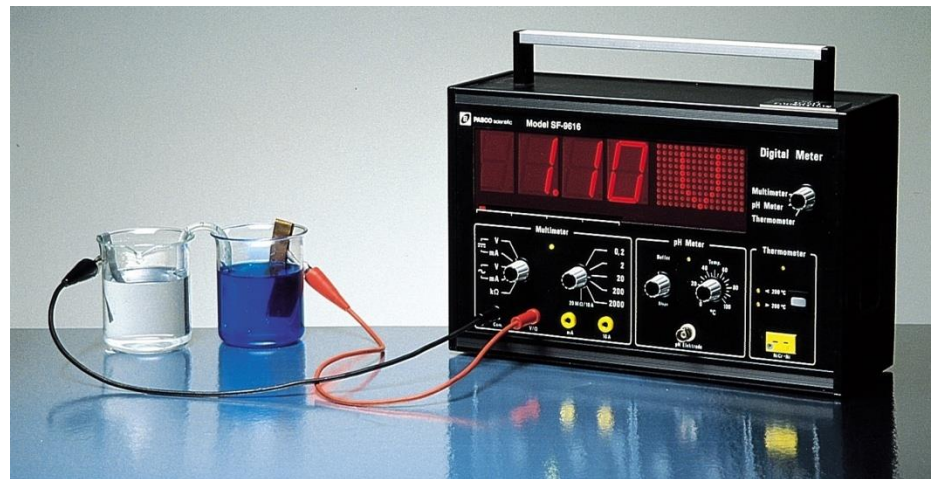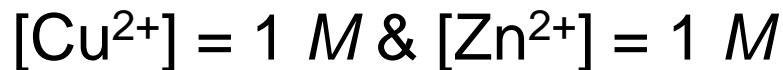
19.2
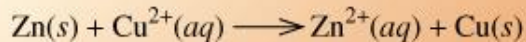
Galvanic Cells

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

- ***cell voltage***

- ***electromotive force (emf)***

- ***cell potential***

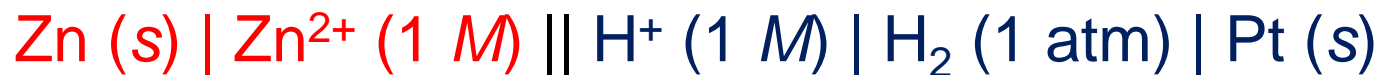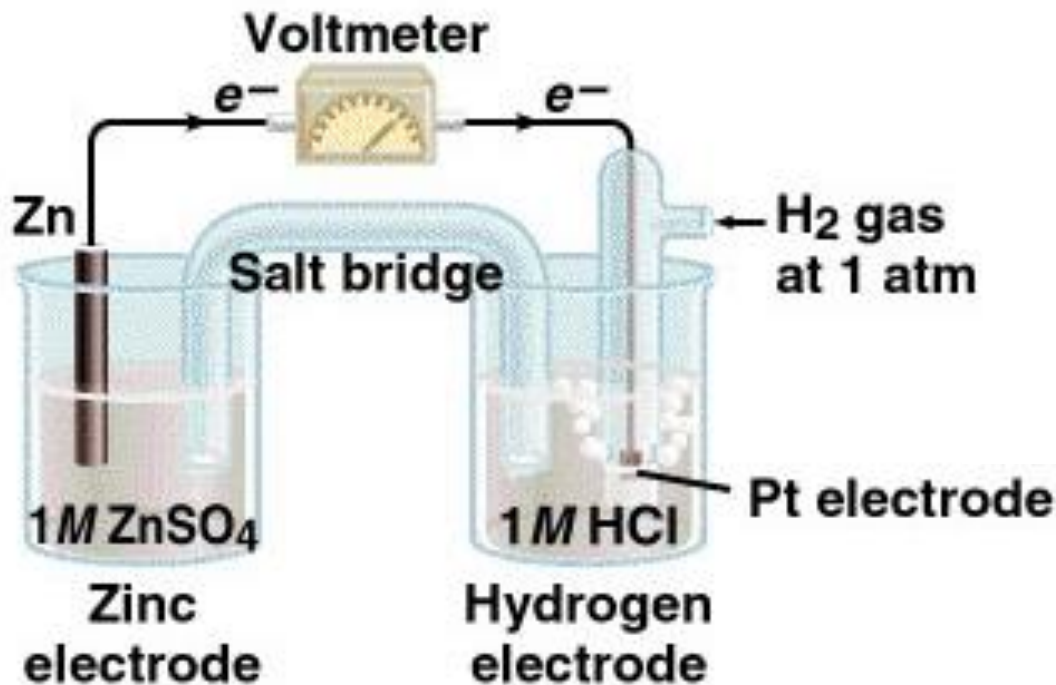## Cell Diagram

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

$$[Cu^{2+}] = 1\ M\ \&\ [Zn^{2+}] = 1\ M$$

$$Zn\ (s)\ |\ Zn^{2+}\ (1\ M)\ ||\ Cu^{2+}\ (1\ M)\ |\ Cu\ (s)$$

anode   cathode

Standard Electrode Potentials

Zn (s) | Zn^{2+} (1 M) || H$^+$ (1 M) | H$_2$ (1 atm) | Pt (s)

Anode (oxidation):   Zn (s) $\longrightarrow$ Zn^{2+} (1 M) + 2e$^-$

Cathode (reduction): 2e$^-$ + 2H$^+$ (1 M) $\longrightarrow$ H$_2$ (1 atm)

           Zn (s) + 2H$^+$ (1 M) $\longrightarrow$ Zn^{2+} + H$_2$ (1 atm)

Standard Electrode 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.
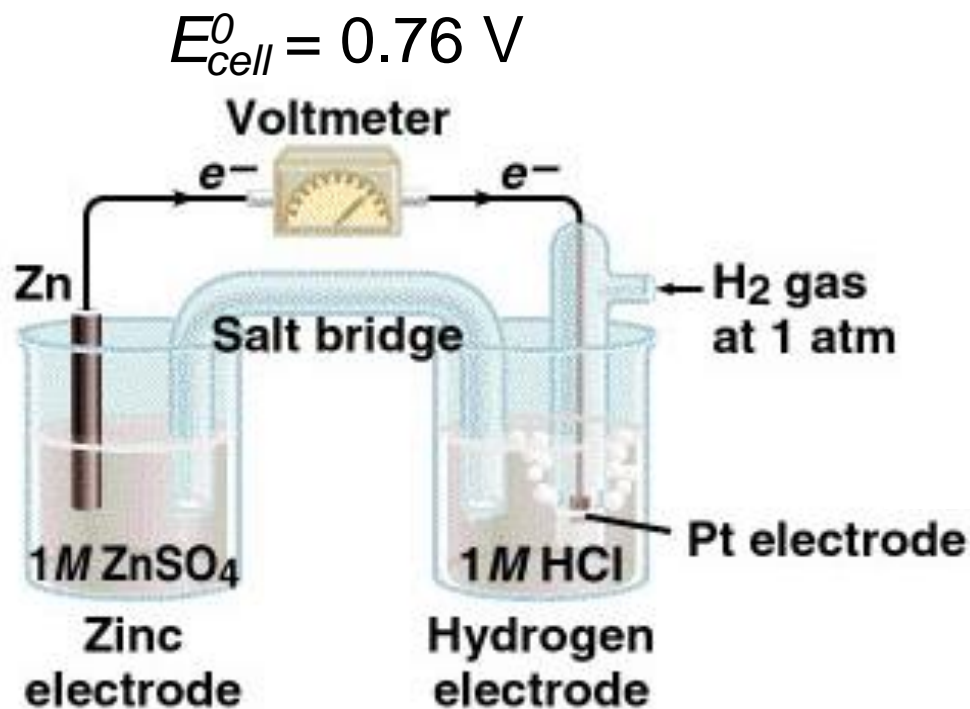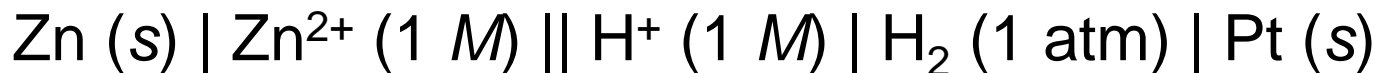
H$_2$ gas at 1 atm

Pt electrode

1M HCl

Reduction Reaction

$2e^- + 2H^+ (1\ M) \longrightarrow H_2\ (1\ atm)$
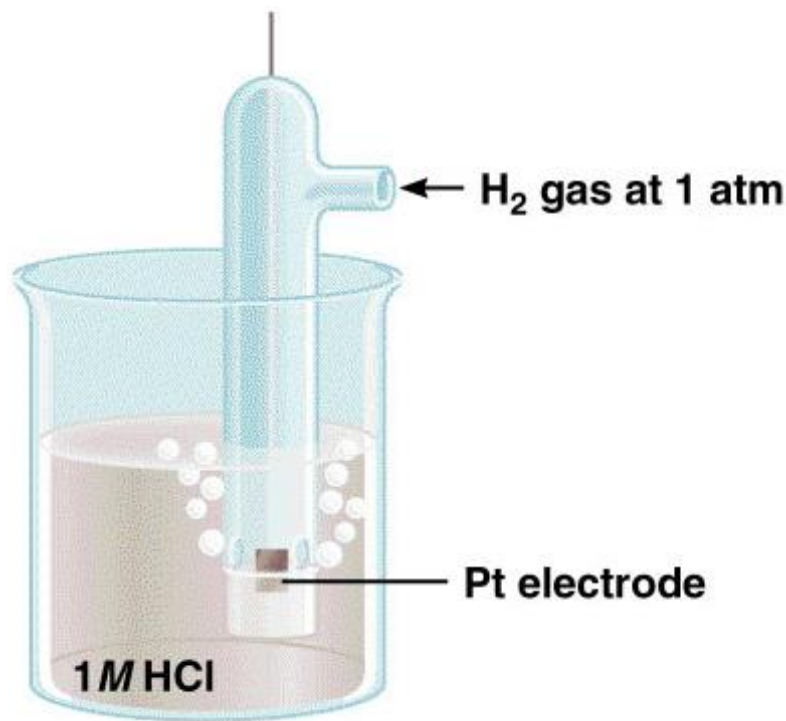
$E^0 = 0$ V

Standard hydrogen electrode (SHE)

Standard Electrode Potentials

E^0_{cell} = 0.76 V

Standard emf (E^0_{cell})

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

Zn (*s*) | Zn²⁺ (1 *M*) || H⁺ (1 *M*) | H₂ (1 atm) | Pt (*s*)

$$E^0_{cell} = E^0_{H^+/H_2} - E^0_{Zn^{2+}/Zn}$$

0.76 V = 0 - $E^0_{Zn^{2+}/Zn}$

$E^0_{Zn^{2+}/Zn}$ = -0.76 V

Zn^{2+} (1 *M*) + 2e⁻ ⟶ Zn E^0 = -0.76 V

Standard Electrode Potentials

$E^0_{cell} = 0.34$ V

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

$E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{H^+/H_2}$

$0.34 = E^0_{Cu^{2+}/Cu} - 0$

$E^0_{Cu^{2+}/Cu} = 0.34$ V

Pt (s) | H$_2$ (1 *atm*) | H$^+$ (1 *M*) || Cu^{2+} (1 *M*) | Cu (s)

Anode (oxidation): H$_2$ (1 *atm*) $\longrightarrow$ 2H$^+$ (1 *M*) + 2e$^-$

Cathode (reduction): 2e$^-$ + Cu^{2+} (1 *M*) $\longrightarrow$ Cu (s)

H$_2$ (1 *atm*) + Cu^{2+} (1 *M*) $\longrightarrow$ Cu (s) + 2H$^+$ (1 *M*)

TABLE 19.1

Standard Reduction Potentials at 25°C*
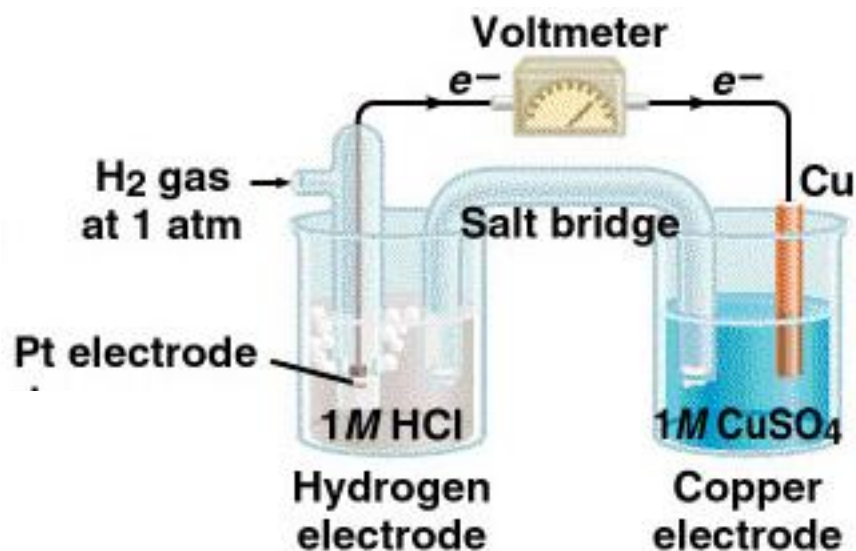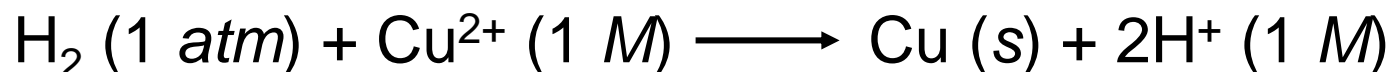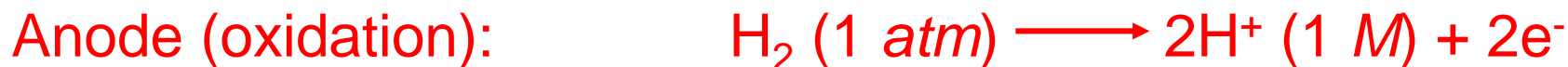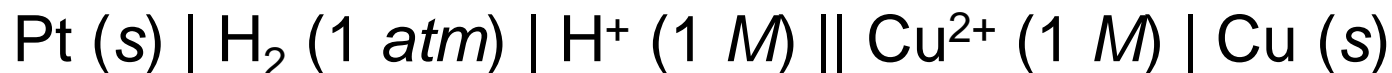
+ve

Oxidizing agent

reducing agent

Increasing strength as oxidizing agent

Increasing strength as reducing agent

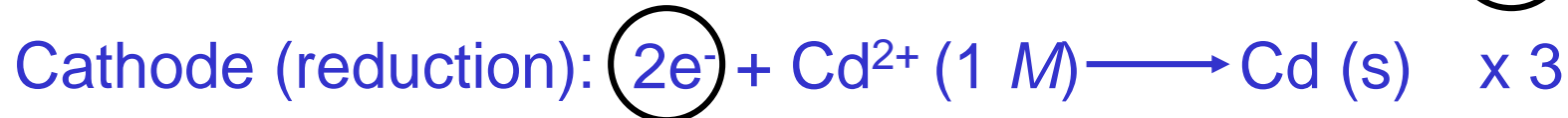| Half-Reaction	$E°(V)$
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

-ve

*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.

- 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

- Changing the stoichiometric coefficients of a half-cell reaction *does not* change the value of E^0

19.3

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

Cd^{2+} (aq) + 2e$^-$ ⟶ Cd (s) E^0 = -0.40 V   Cd is the stronger oxidizer

Cr^{3+} (aq) + 3e$^-$ ⟶ Cr (s) E^0 = -0.74 V   Cd will oxidize Cr

Anode (oxidation):   Cr (s) ⟶ Cr^{3+} (1 M) + 3e$^-$ x 2

Cathode (reduction): 2e$^-$ + Cd^{2+} (1 M) ⟶ Cd (s)   x 3

──

2Cr (s) + 3Cd^{2+} (1 M) ⟶ 3Cd (s) + 2Cr^{3+} (1 M)

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

E^0_{cell} = -0.40 − (-0.74)

E^0_{cell} = 0.34 V

19.3
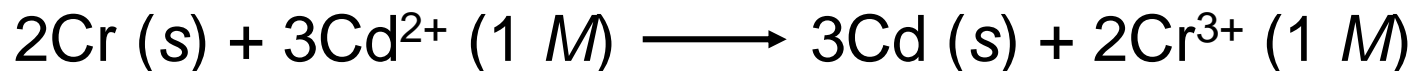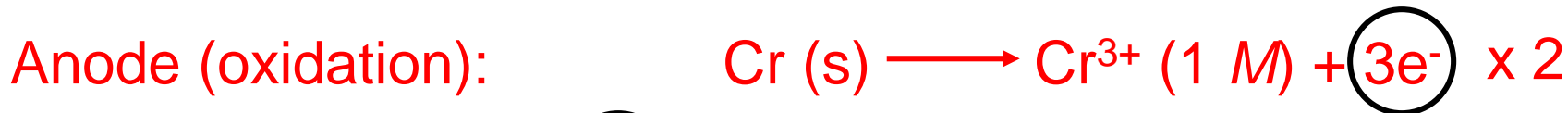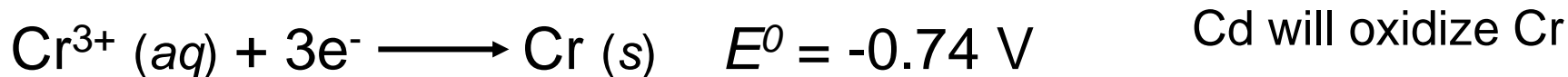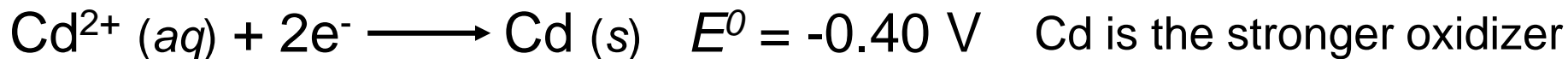
Spontaneity of Redox Reactions

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

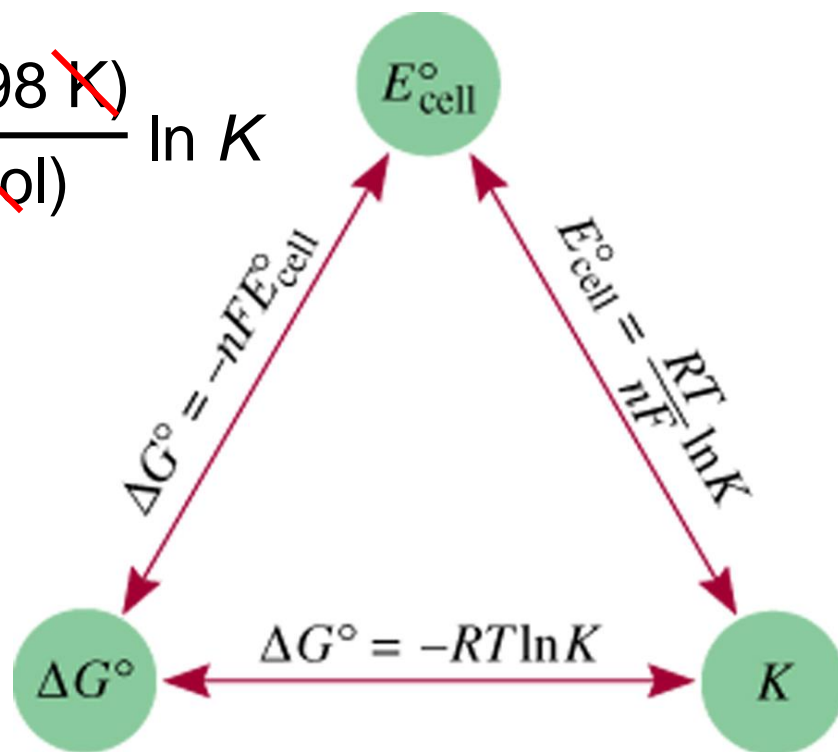$$\Delta G^0 = -nFE_{cell}^0 \qquad F = 96{,}500 \; \frac{J}{V \cdot mol} = 96{,}500 \; C/mol$$

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

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

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

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

E_{cell}°

$\Delta G^\circ = -nFE_{cell}^\circ$

$E_{cell}^\circ = \dfrac{RT}{nF}\ln K$

ΔG°

$\Delta G^\circ = -RT \ln K$

K

19.4

Spontaneity of Redox Reactions

TABLE 19.2

Relationships among $\Delta G°$, K, and $E°_{cell}$

$\Delta G°$	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.

19.4

What is the equilibrium constant for the following reaction at 25^{0}C? Fe^{2+} (aq) + 2Ag (s) $\rightleftharpoons$ Fe (s) + 2Ag$^+$ (aq)

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

Oxidation: 2Ag $\longrightarrow$ 2Ag$^+$ + 2e$^-$

Reduction: 2e$^-$ + Fe^{2+} $\longrightarrow$ Fe

$n = 2$

$E^0 = E^0_{Fe^{2+}/Fe} - E^0_{Ag^+/Ag}$

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

$E^0 = -1.24$ V

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

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

19.4

The Effect of Concentration on Cell emf

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

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

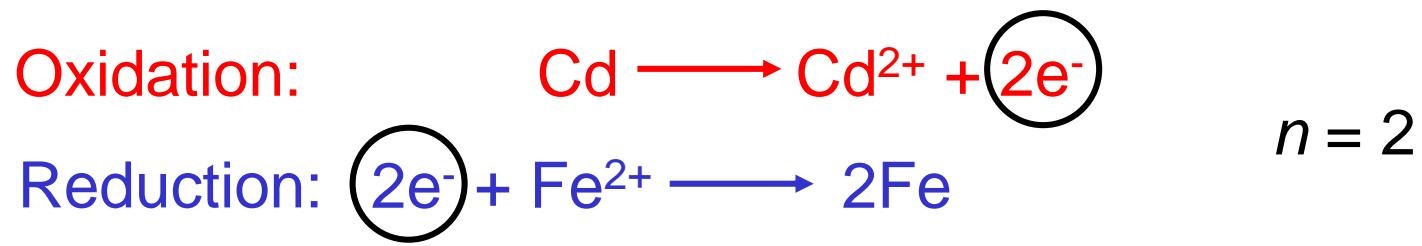## *Nernst equation*

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

At 298

$$E = E^0 - \frac{0.0257 \text{ V}}{n} \ln Q \qquad\qquad E = E^0 - \frac{0.0592 \text{ V}}{n} \log Q$$

19.5

Will the following reaction occur spontaneously at 25^0C if $[Fe^{2+}] = 0.60\ M$ and $[Cd^{2+}] = 0.010\ M$?

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

Oxidation: $Cd \longrightarrow Cd^{2+} + 2e^-$

Reduction: $2e^- + Fe^{2+} \longrightarrow 2Fe$ $n = 2$

$E^0 = E^0_{Fe^{2+}/Fe} - E^0_{Cd^{2+}/Cd}$

$E^0 = -0.44 - (-0.40)$
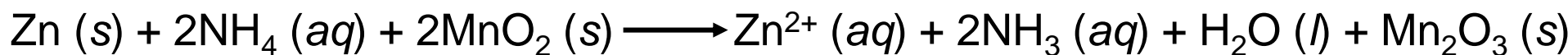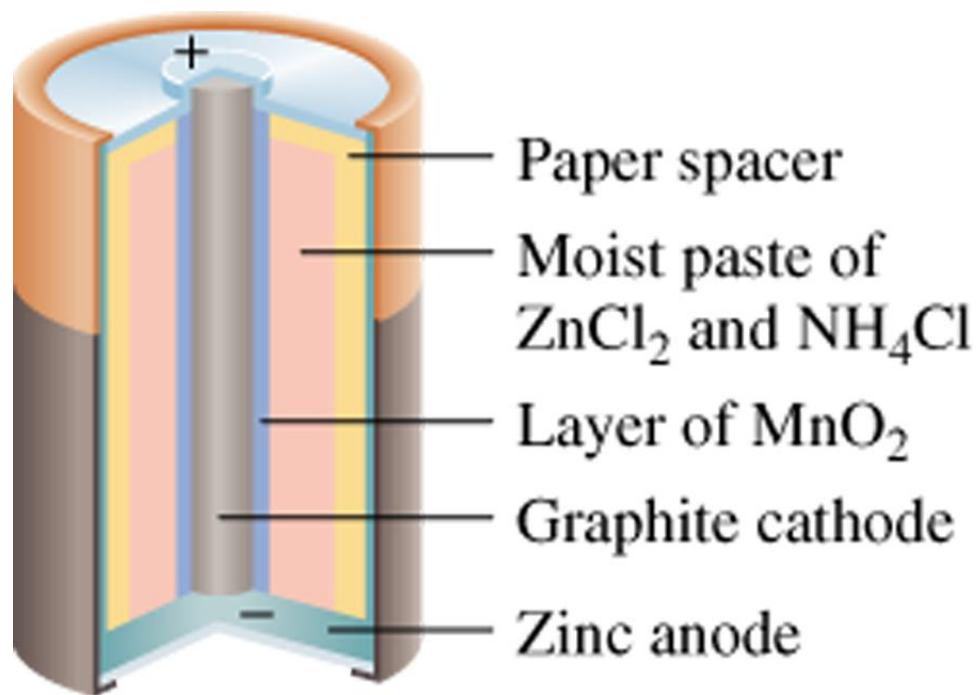
$E^0 = -0.04\ V$

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

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

$E = 0.013$

$E > 0$ Spontaneous

Batteries

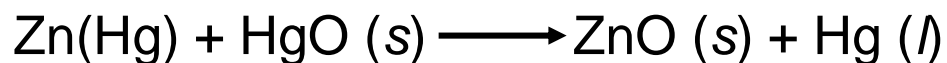### Dry cell

Leclanché cell

Paper spacer

Moist paste of $ZnCl_2$ and NH_4Cl

Layer of MnO_2

Graphite cathode

Zinc anode

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

Cathode: $2NH_4^+\ (aq) + 2MnO_2\ (s) + 2e^- \longrightarrow Mn_2O_3\ (s) + 2NH_3\ (aq) + H_2O\ (l)$

$Zn\ (s) + 2NH_4\ (aq) + 2MnO_2\ (s) \longrightarrow Zn^{2+}\ (aq) + 2NH_3\ (aq) + H_2O\ (l) + Mn_2O_3\ (s)$

19.6

Batteries

Mercury Battery

Insulation Cathode (steel) Anode (Zn can)

Electrolyte solution containing KOH
and paste of $Zn(OH)_2$ and HgO

Anode: $Zn(Hg) + 2OH^- (aq) \longrightarrow ZnO (s) + H_2O (l) + 2e^-$

Cathode: $HgO (s) + H_2O (l) + 2e^- \longrightarrow Hg (l) + 2OH^- (aq)$

$Zn(Hg) + HgO (s) \longrightarrow ZnO (s) + Hg (l)$

19.6
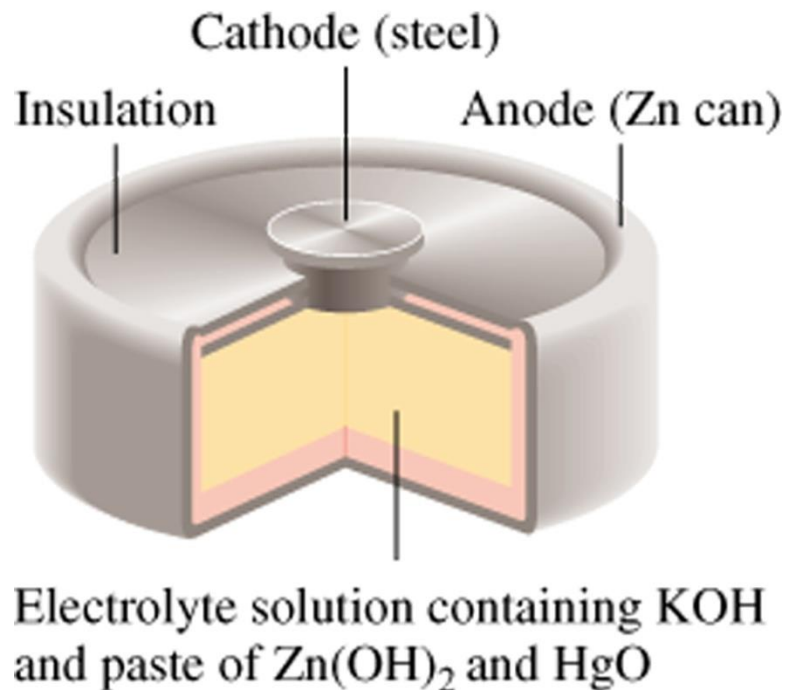
Batteries

Lead storage battery

Anode ─ Removable cap ─ Cathode

H_2SO_4 electrolyte

Negative plates (lead grills filled with spongy lead)

Positive plates (lead grills filled with PbO_2)

Anode: $\quad Pb\ (s) + SO_4^{2-}\ (aq) \longrightarrow PbSO_4\ (s) + 2e^-$

Cathode: $\quad PbO_2\ (s) + 4H^+\ (aq) + SO_4^{2-}\ (aq) + 2e^- \longrightarrow PbSO_4\ (s) + 2H_2O\ (l)$

$$Pb\ (s) + PbO_2\ (s) + 4H^+\ (aq) + 2SO_4^{2-}\ (aq) \longrightarrow 2PbSO_4\ (s) + 2H_2O\ (l)$$

19.6

Batteries

Anode

Cathode

Li — $\quad$ — TiS_2

Li^+ →

Solid electrolyte
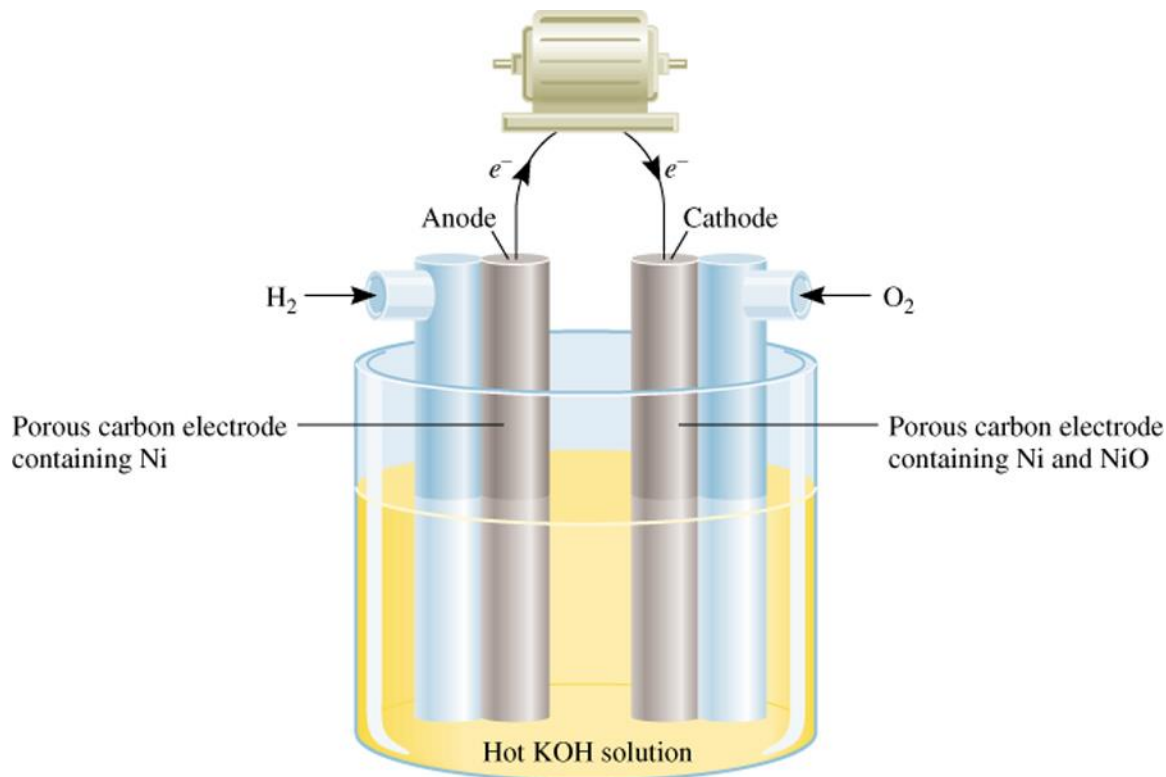
$Li \longrightarrow Li^+ + e^-$
$\qquad$
$TiS_2 + e^- \longrightarrow TiS_2^-$
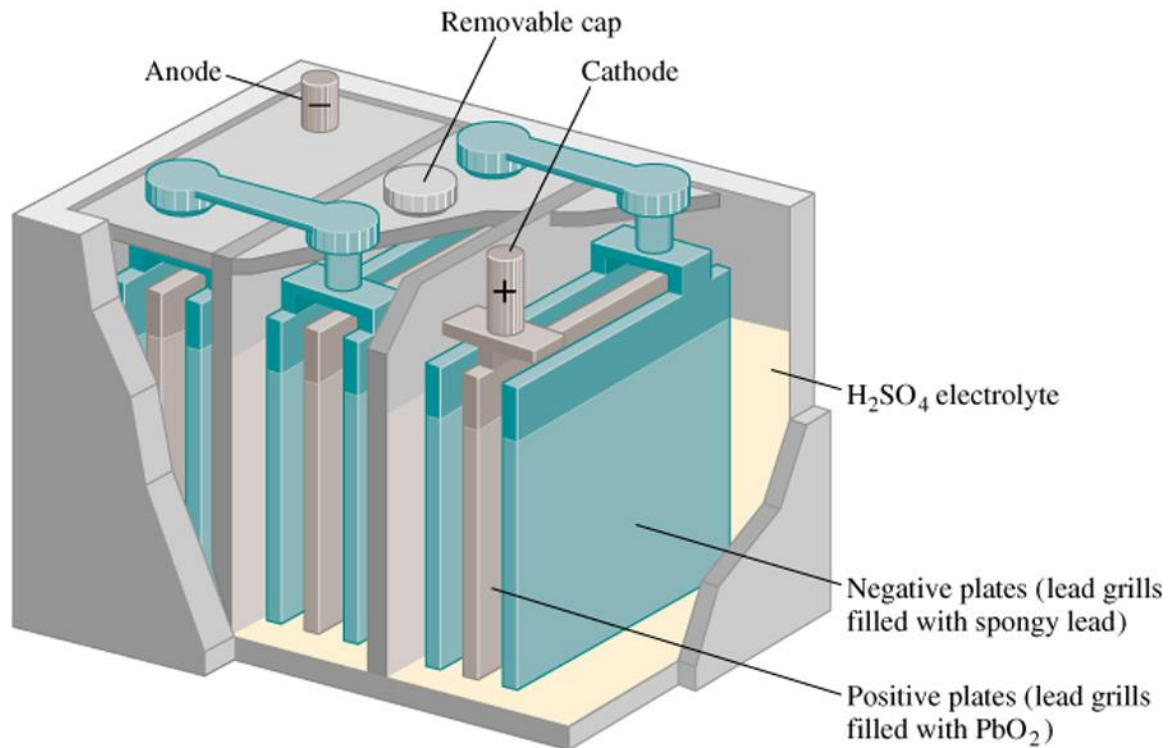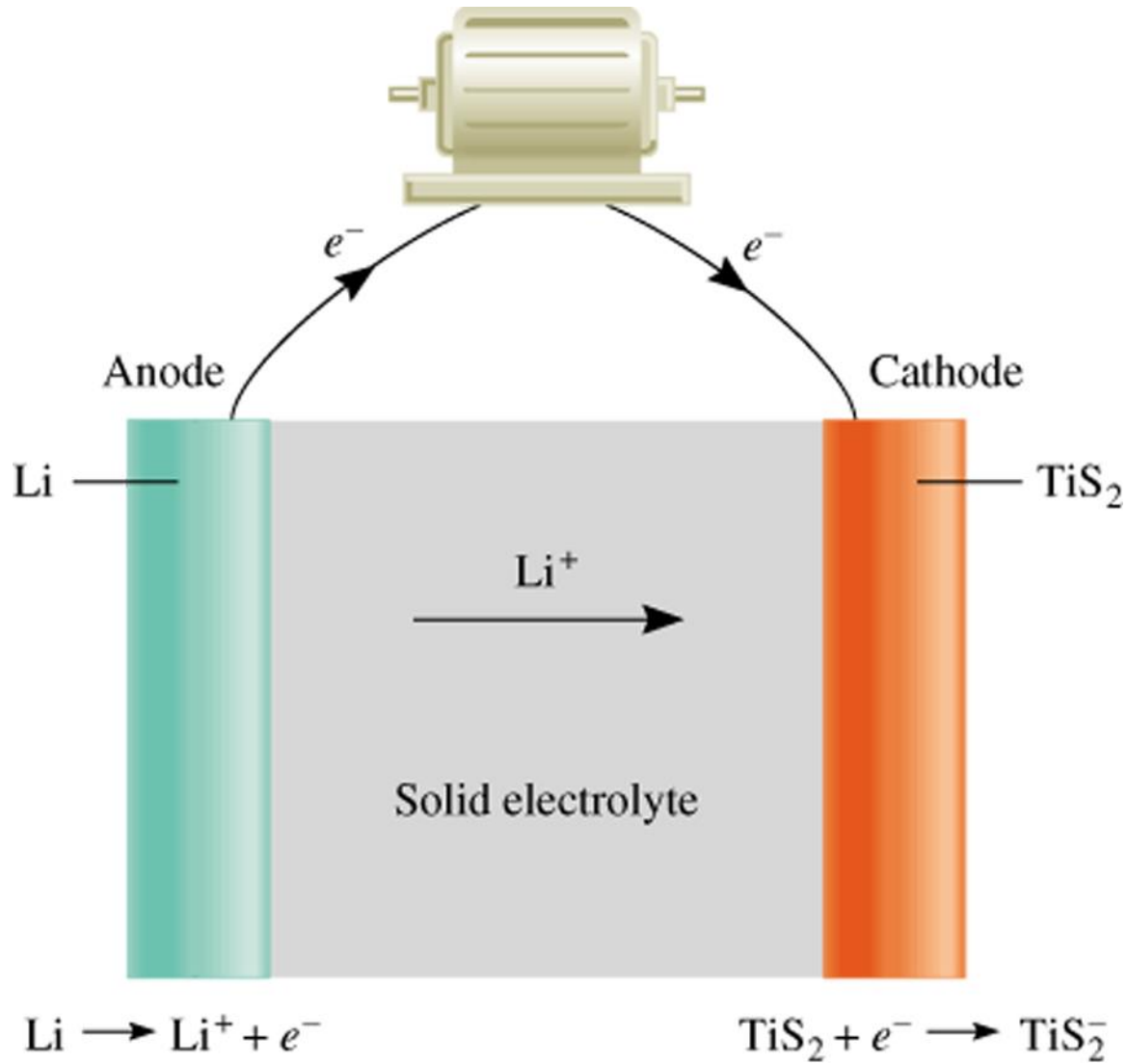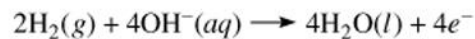
Solid State Lithium Battery

19.6

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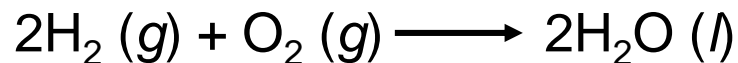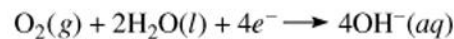
A ***fuel cell*** is an electrochemical cell that requires a continuous supply of reactants to keep functioning

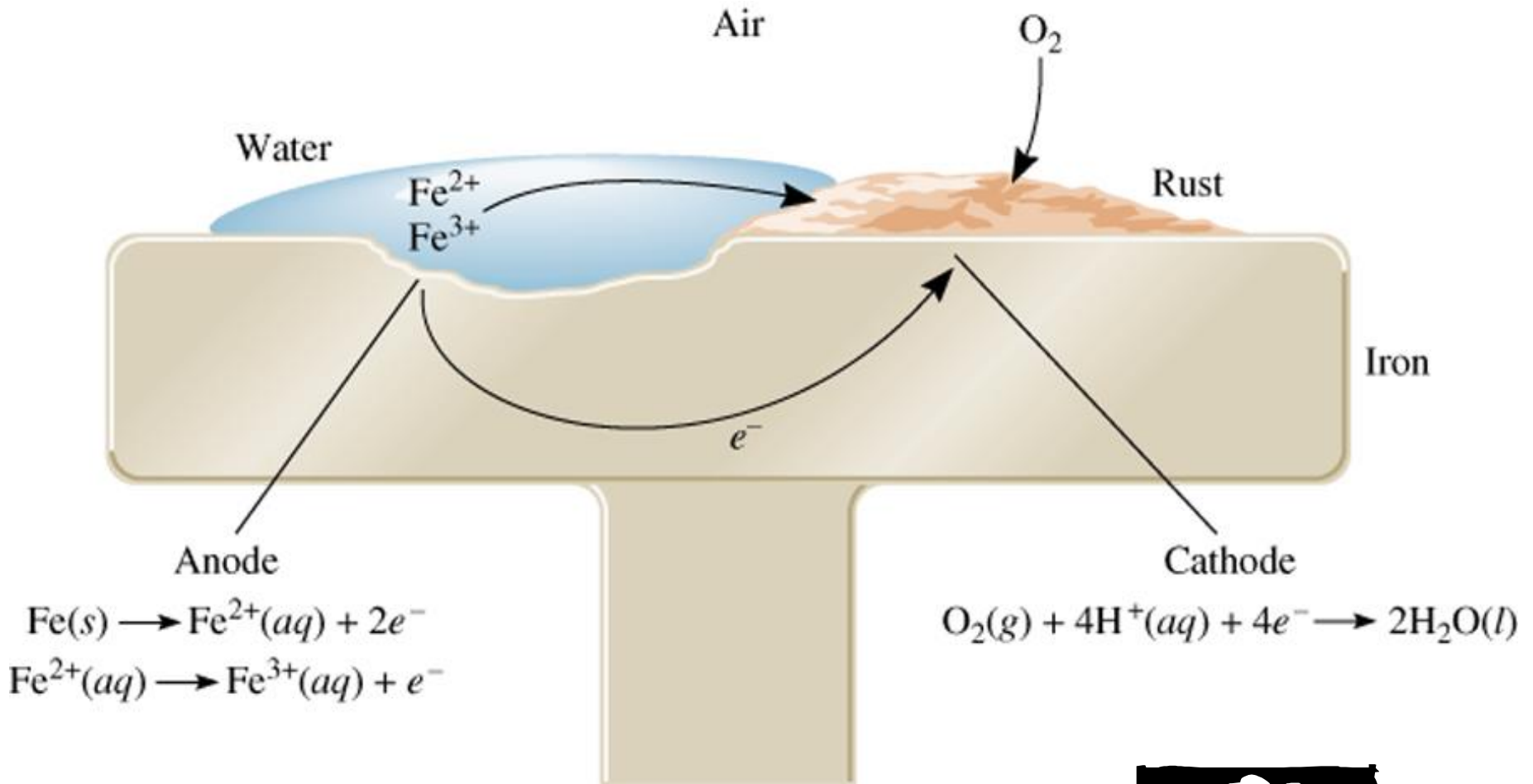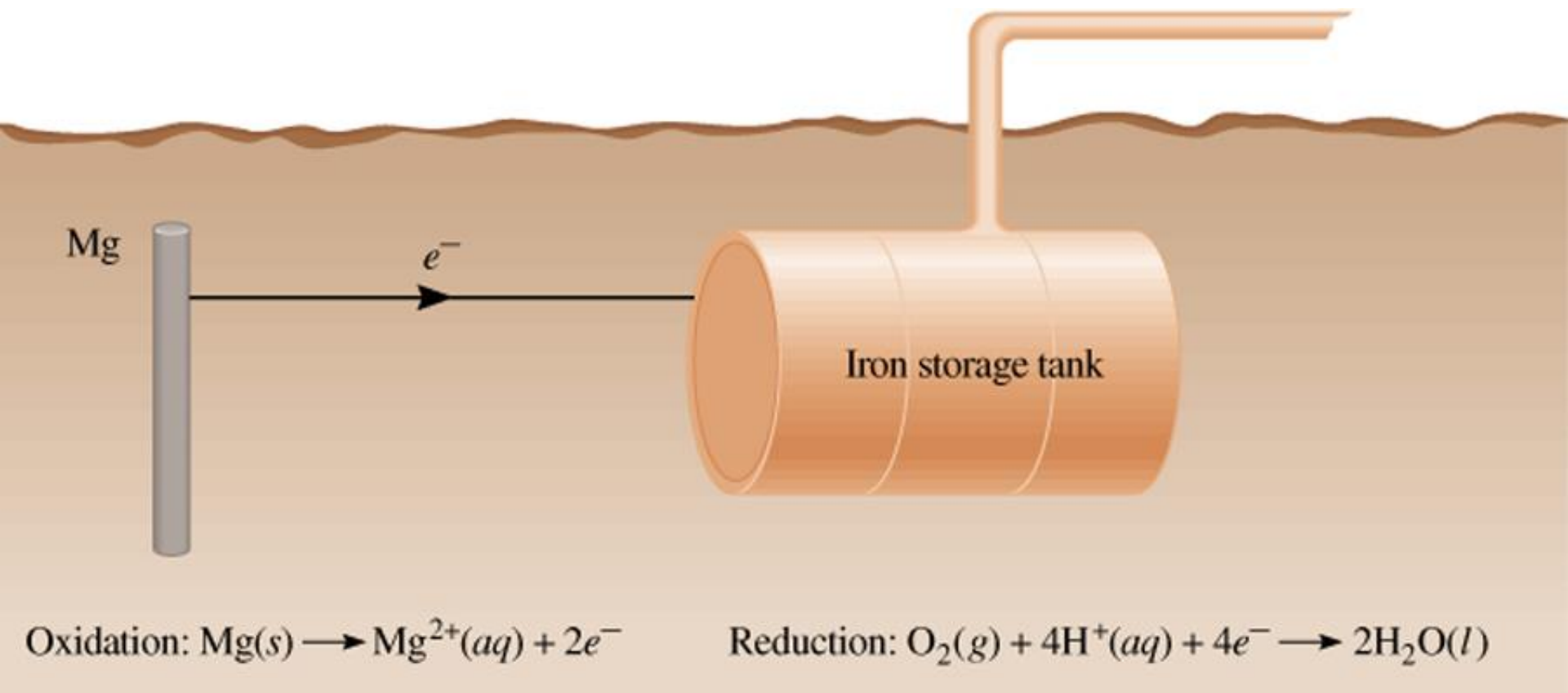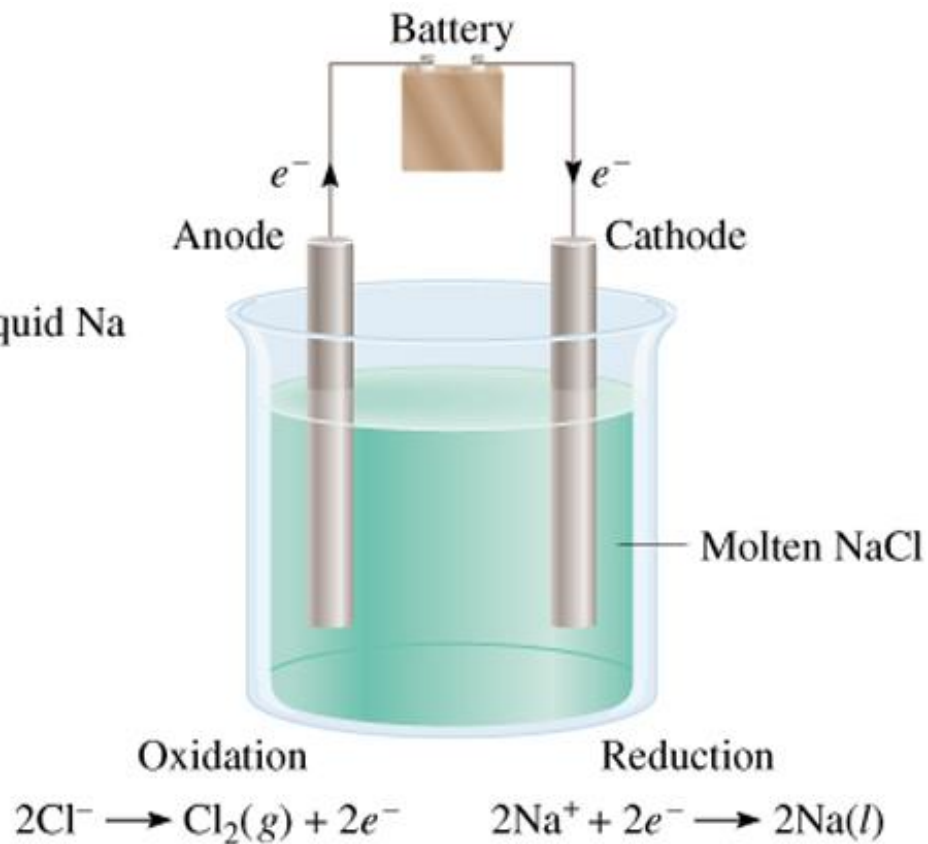Anode: $2H_2\ (g) + 4OH^-\ (aq) \longrightarrow 4H_2O\ (l) + 4e^-$

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

$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (l)$

19.6

Corrosion

Air

O$_2$

Water

Fe^{2+}
Fe^{3+}

Rust

Iron

e^-

Anode

Cathode

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

$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$

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

19.7

Cathodic Protection of an Iron Storage Tank

Mg

e^-

Iron storage tank

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

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
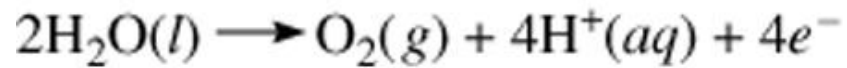
Electrolysis is the process in which electrical energy is used to cause a **nonspontaneous** chemical reaction to occur.

Cl$_2$ gas

NaCl

Liquid Na ←

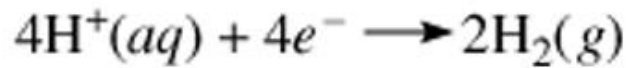→ Liquid Na

Iron cathode   Iron cathode

Carbon anode

Battery

e^- e^-

Anode   Cathode

Molten NaCl

Oxidation   Reduction

$$2Cl^- \longrightarrow Cl_2(g) + 2e^- \qquad 2Na^+ + 2e^- \longrightarrow 2Na(l)$$

19.8

Electrolysis of Water

Battery

e^- Anode

e^- Cathode

Dilute H_2SO_4 solution

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

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

19.8
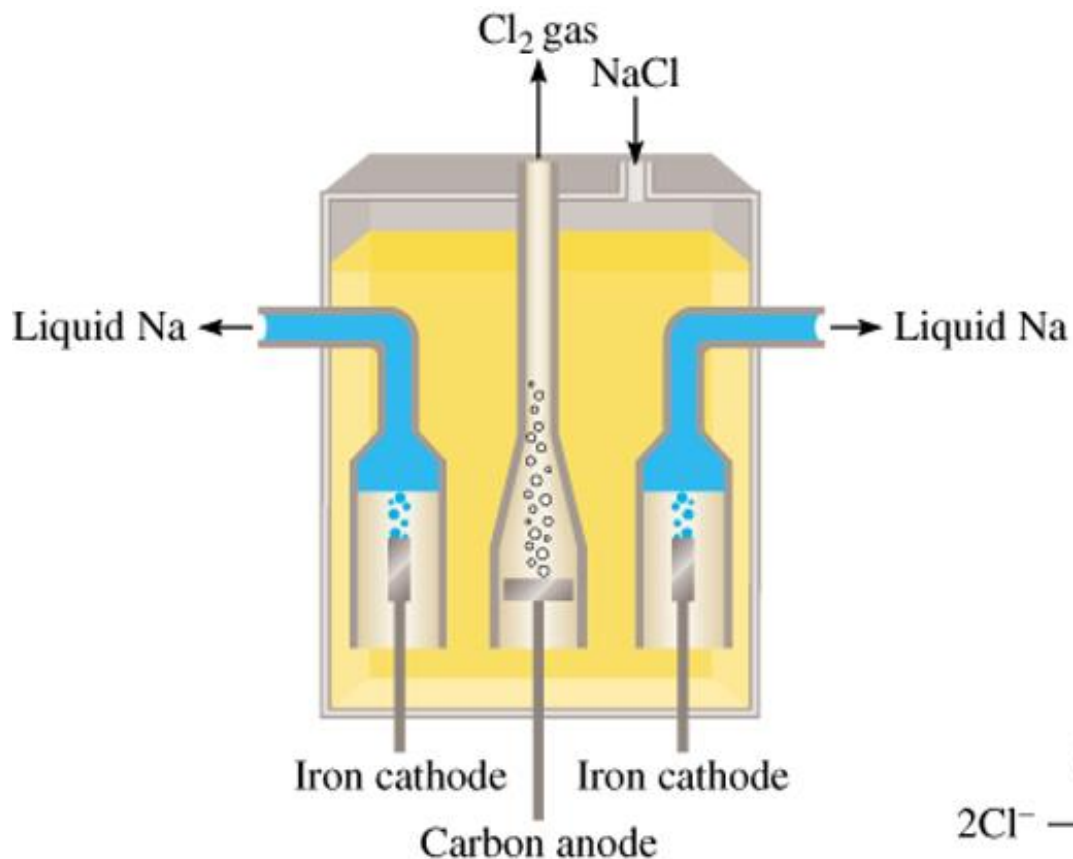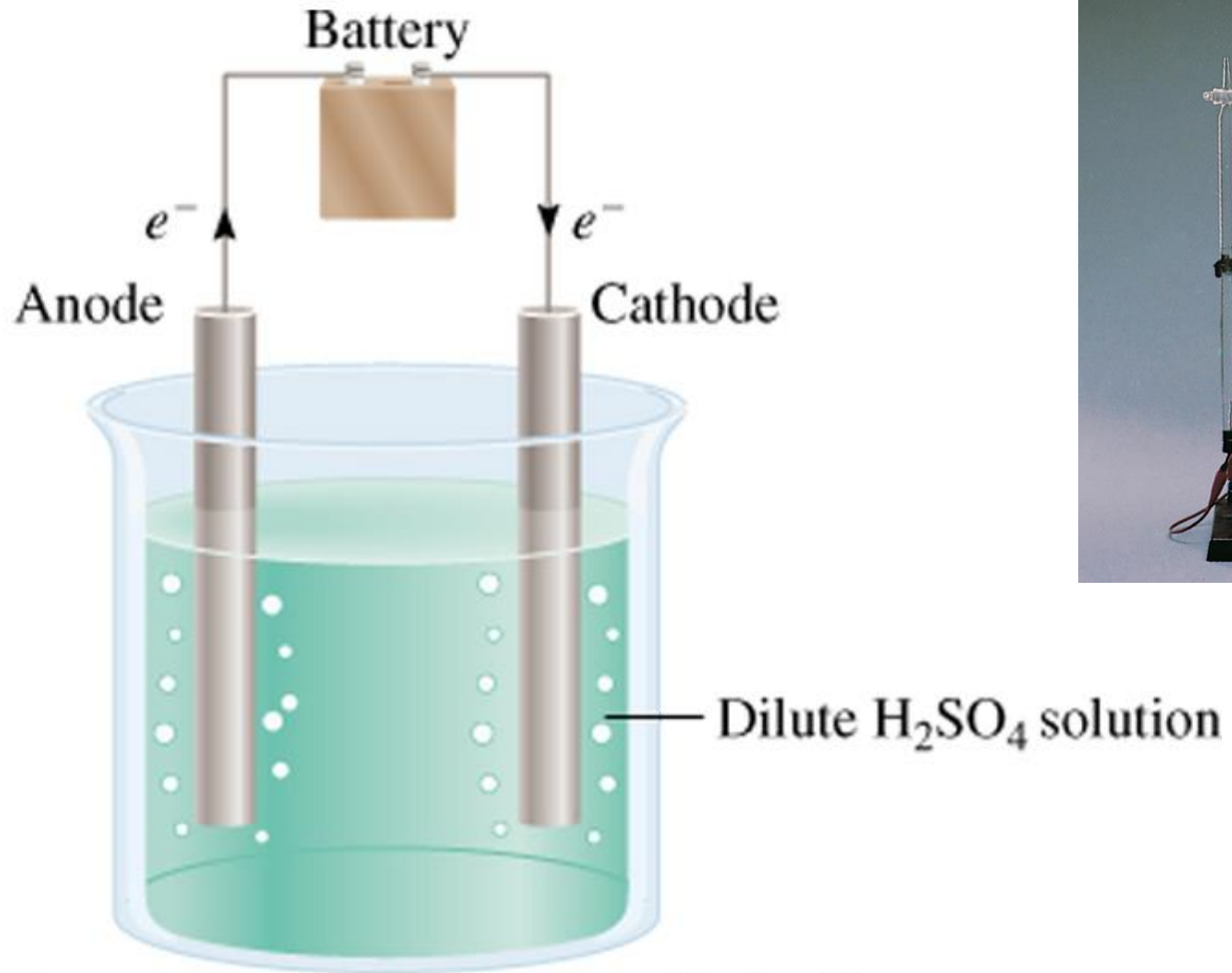
Electrolysis and Mass Changes
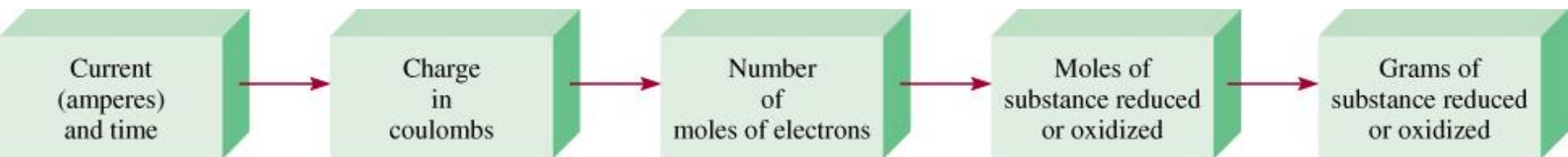
charge (C) = current (A) x time (s)

1 mole e⁻ = 96,500 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?

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

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

$Ca^{2+} (l) + 2Cl^- (l) \longrightarrow Ca (s) + Cl_2 (g)$
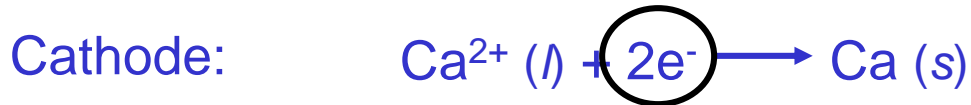
2 mole e^- = 1 mole Ca

96500 = 1mol e , So 2 moles of electrons requires = 2x 96500

Q =I x t = 0.452 x 1.5 x 3600 = 2440 C

193000 C = 1 mole Ca

2440 C   =   x

X = 2440 x 1 / 193000 = 0.0126 mol Ca

Mass = 0.0126 x 40 = 0.5 g Ca

Chemistry In Action: Dental Filling Discomfort

Corrosion of a Dental Filling

Hg_2^{2+}/Ag_2Hg_3 0.85 V

Sn^{2+}/Ag_3Sn -0.05 V

Sn^{2+}/Ag_3Sn -0.05 V

Gold inlay

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

e^-

$Sn_8Hg \longrightarrow Sn^{2+}$

Dental filling