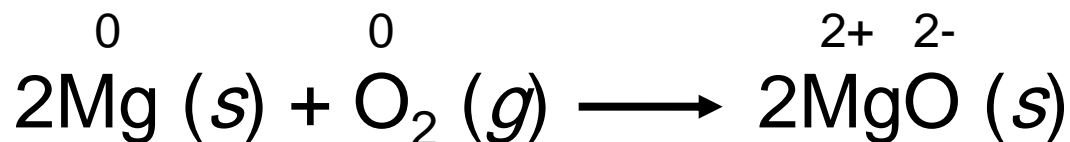


Electrochemistry

Chapter 19

Electrochemical processes are oxidation-reduction reactions in which:

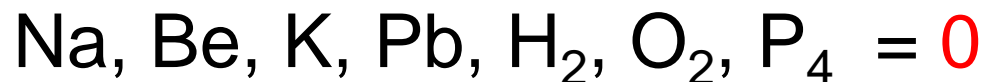
- the energy released by a spontaneous reaction is converted to electricity or
- electrical energy is used to cause a nonspontaneous reaction to occur



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.

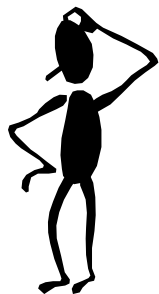


2. In monatomic ions, the oxidation number is equal to the charge on the ion.



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

- 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**.
- Group IA metals are **+1**, IIA metals are **+2** and fluorine is always **-1**.
- 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.



Oxidation numbers of all the atoms in HCO_3^- ?



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

$$3x(-2) + 1 + ? = -1$$

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

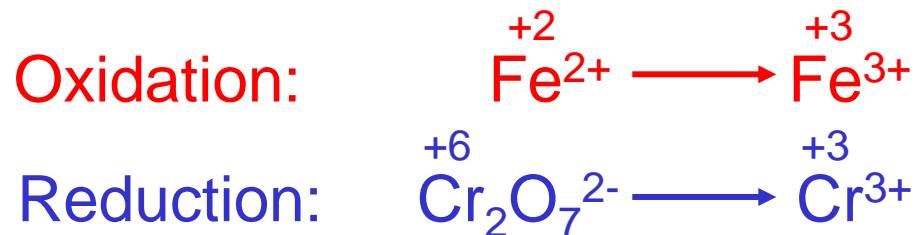
Balancing Redox Equations

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.

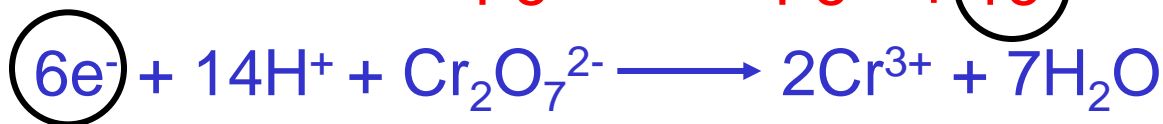
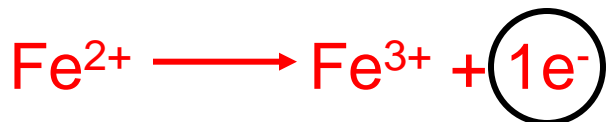


Balancing Redox Equations

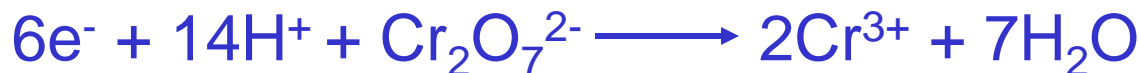
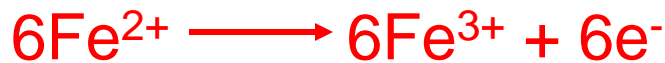
4. For reactions in acid, add H_2O to balance O atoms and H^+ to balance H atoms.



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.**

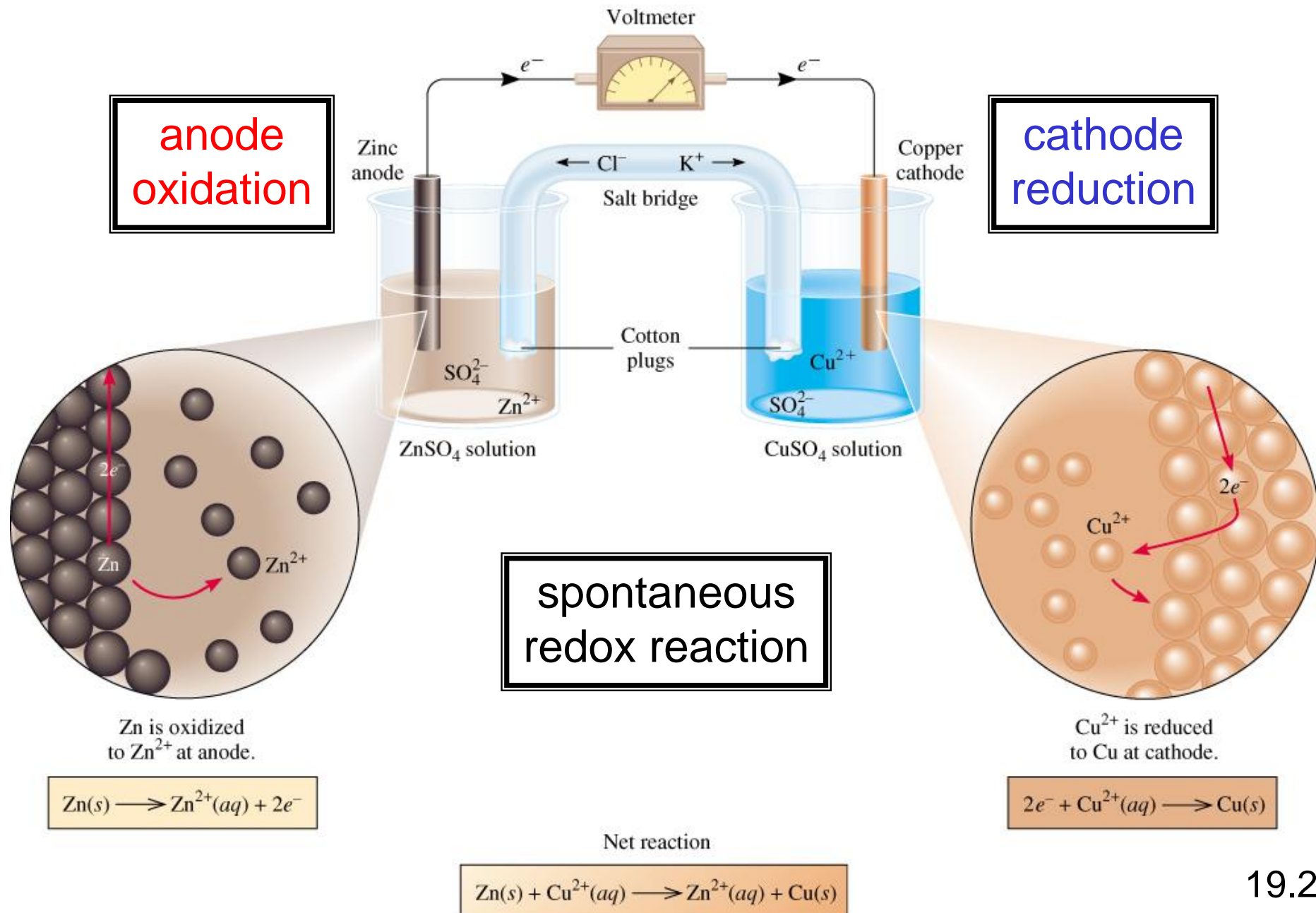


8. Verify that the number of atoms and the charges are balanced.

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

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

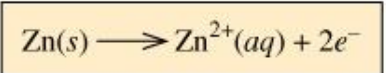


**anode
oxidation**

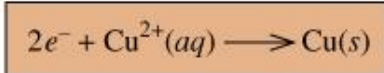
**cathode
reduction**

**spontaneous
redox reaction**

Zn is oxidized to Zn²⁺ at anode.



Cu²⁺ is reduced to Cu at cathode.



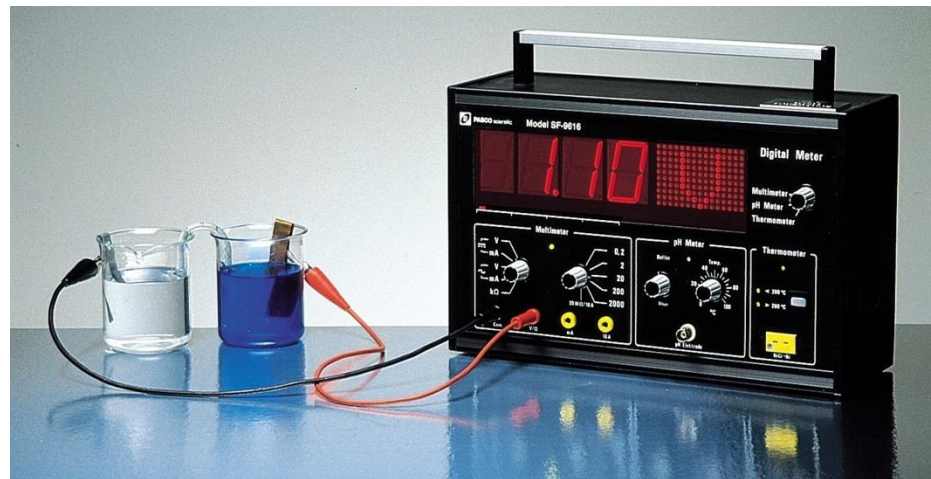
Net reaction



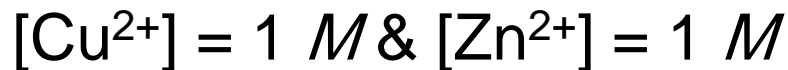
Galvanic Cells

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

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



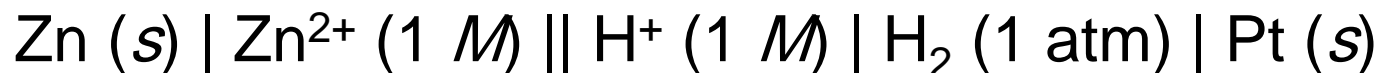
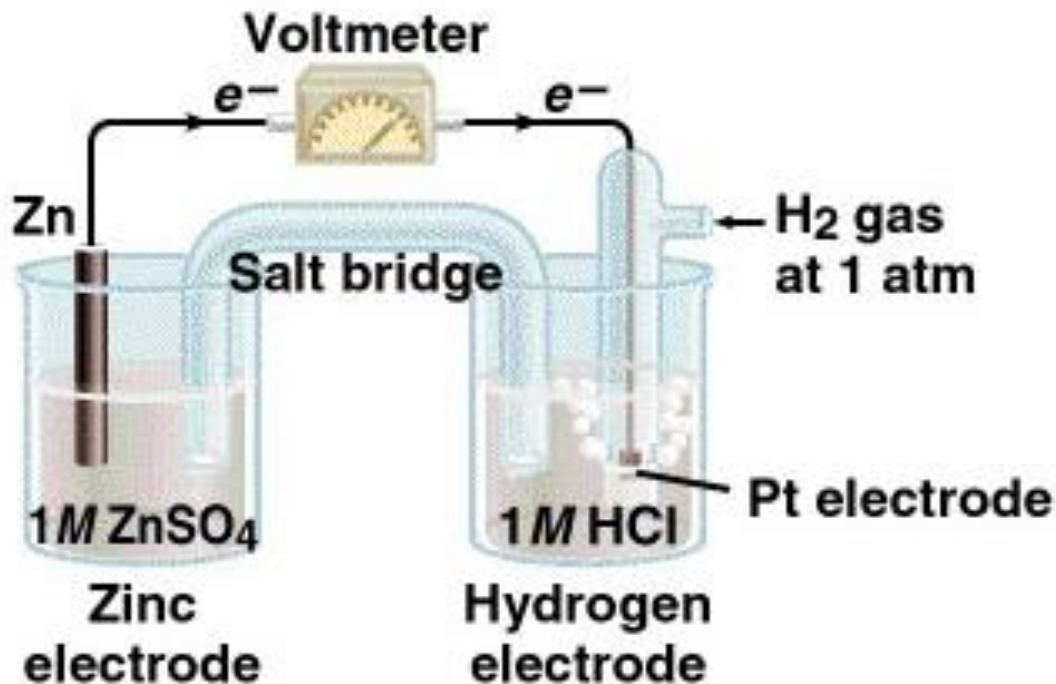
Cell Diagram



anode

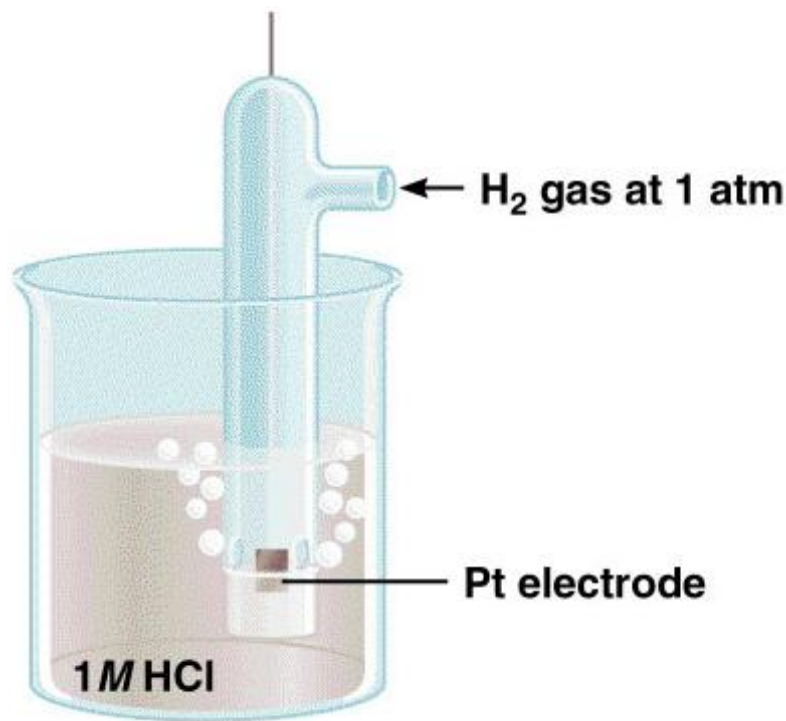
cathode

Standard Electrode Potentials



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 $1\ atm$.



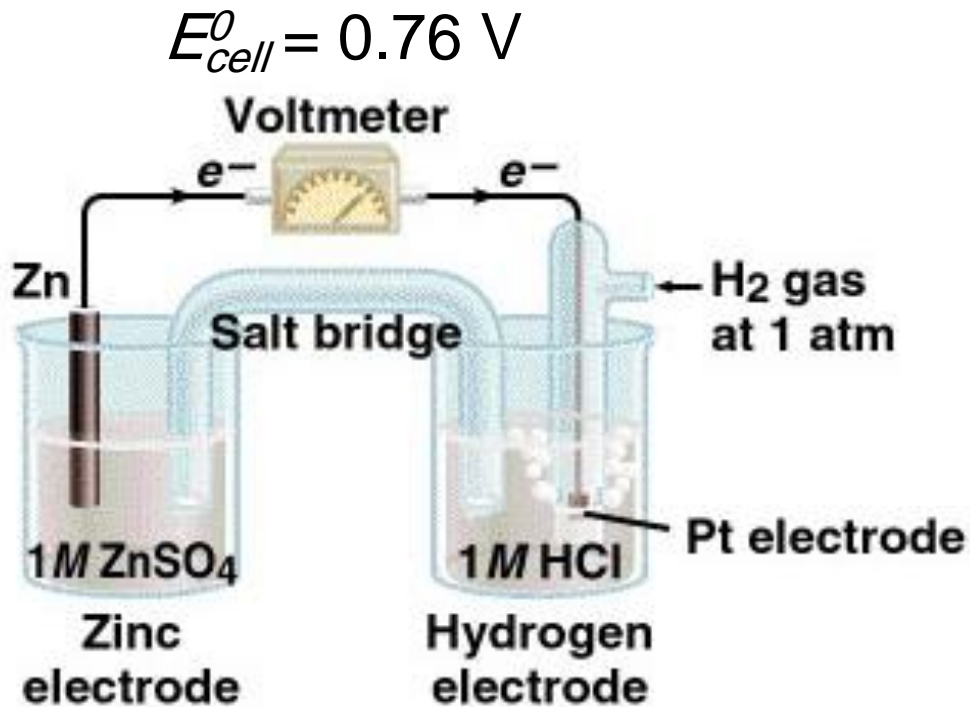
Reduction Reaction



$$E^0 = 0\ V$$

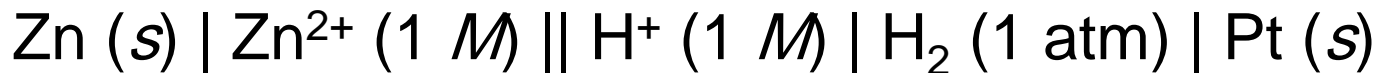
Standard hydrogen electrode (SHE)

Standard Electrode Potentials



Standard emf (E_{cell}^0)

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



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

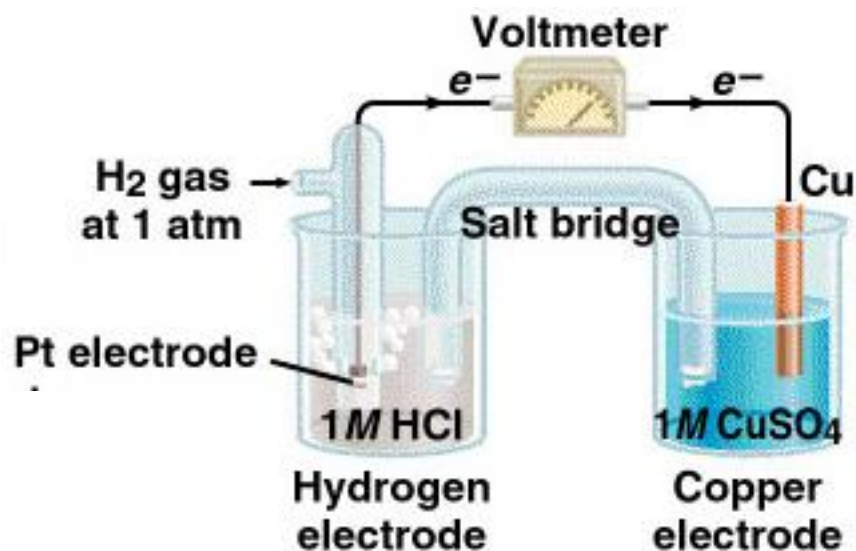
$$0.76 \text{ V} = 0 - E_{\text{Zn}^{2+}/\text{Zn}}^0$$

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



Standard Electrode Potentials

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

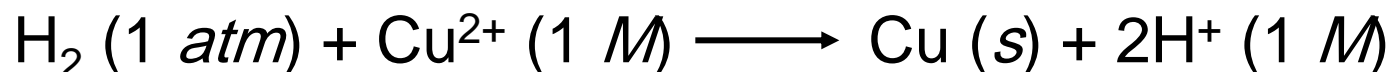
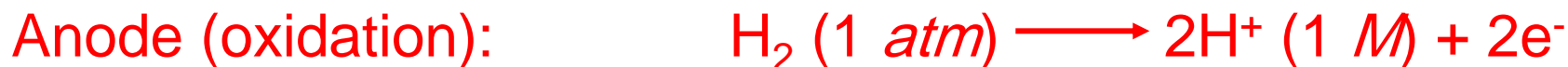
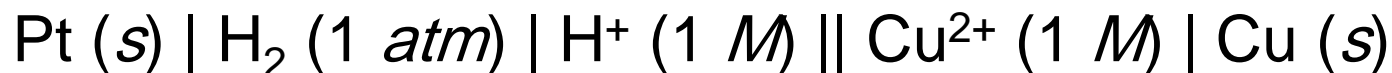


$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0$$

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

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

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



+ve

↑ Oxidizing agent

↓ reducing agent

-ve

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

↑ Increasing strength as oxidizing agent

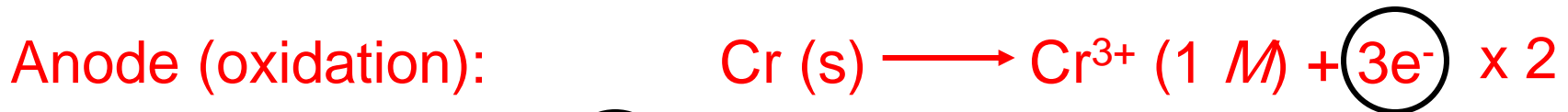
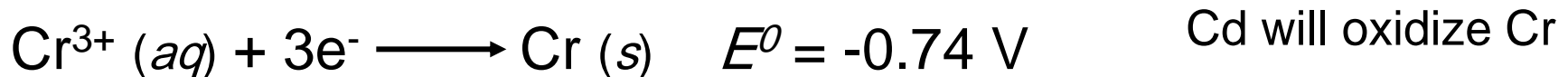
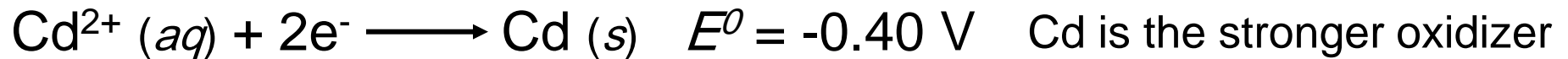
↓ Increasing strength as reducing agent

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

*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 Cd(NO₃)₂ solution and a Cr electrode in a 1.0 M Cr(NO₃)₃ solution?



$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ}$$

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

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

Spontaneity of Redox Reactions

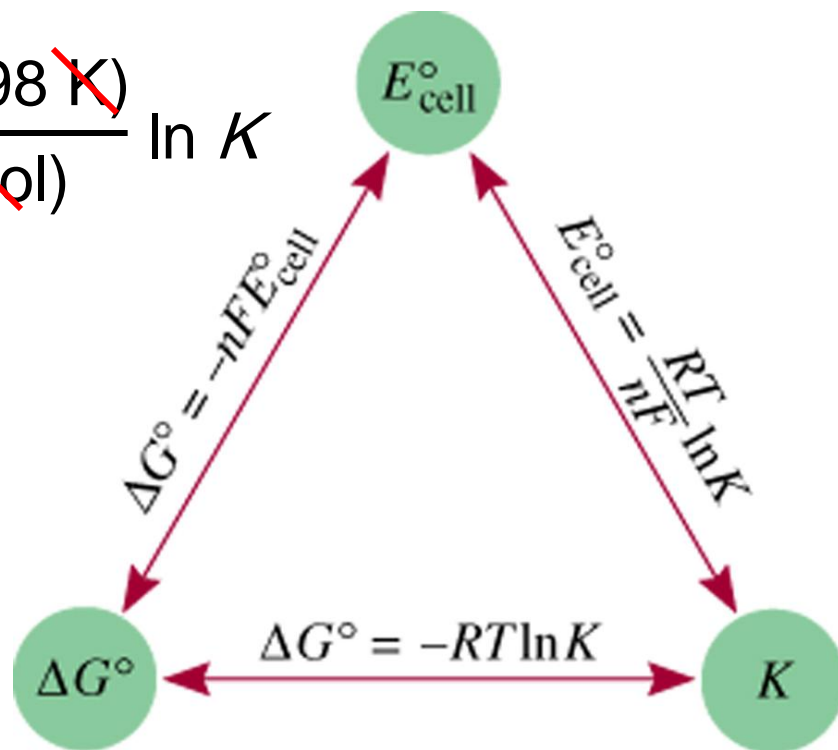
$$\Delta G = -nFE_{\text{cell}} \quad n = \text{number of moles of electrons in reaction}$$

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

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

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

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



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.



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

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



$$n = 2$$

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

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

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

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

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

The Effect of Concentration on Cell Emf

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

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

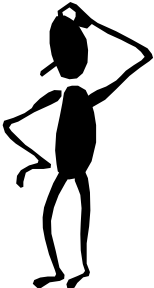
Nernst equation

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

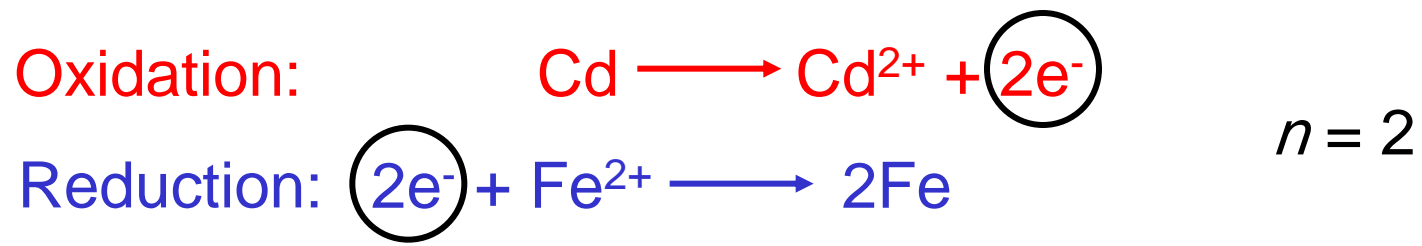
At 298

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

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



Will the following reaction occur spontaneously at 25°C if [Fe²⁺] = 0.60 M and [Cd²⁺] = 0.010 M?



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

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

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

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

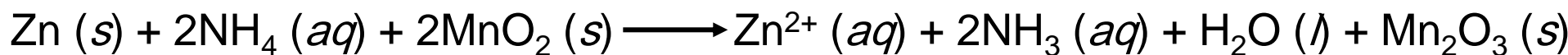
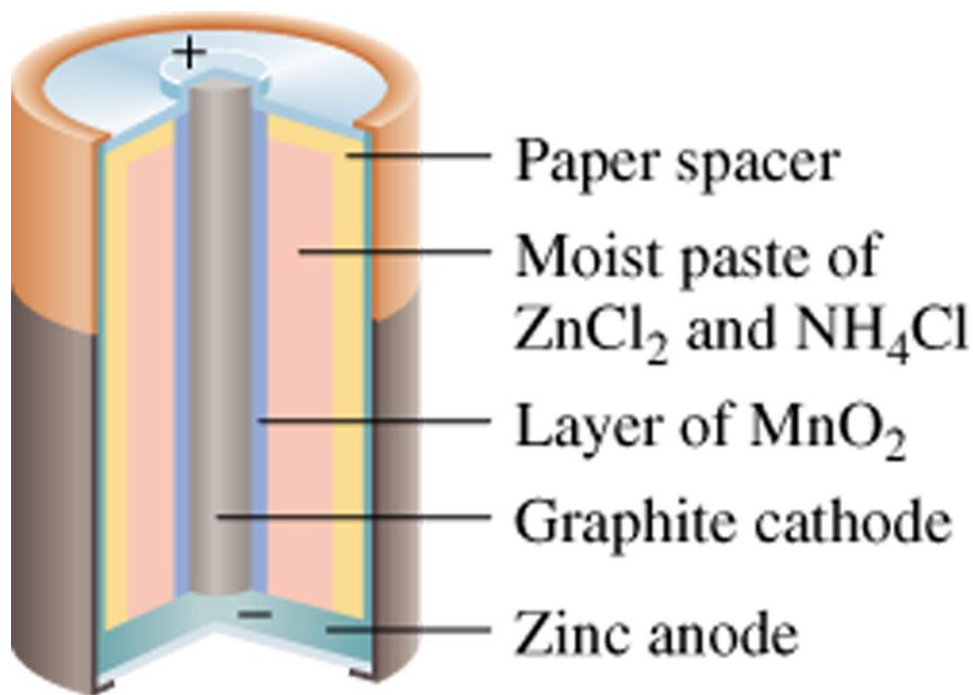
$$E = -0.04 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.010}{0.60}$$

$$E = 0.013$$

$E > 0$ Spontaneous

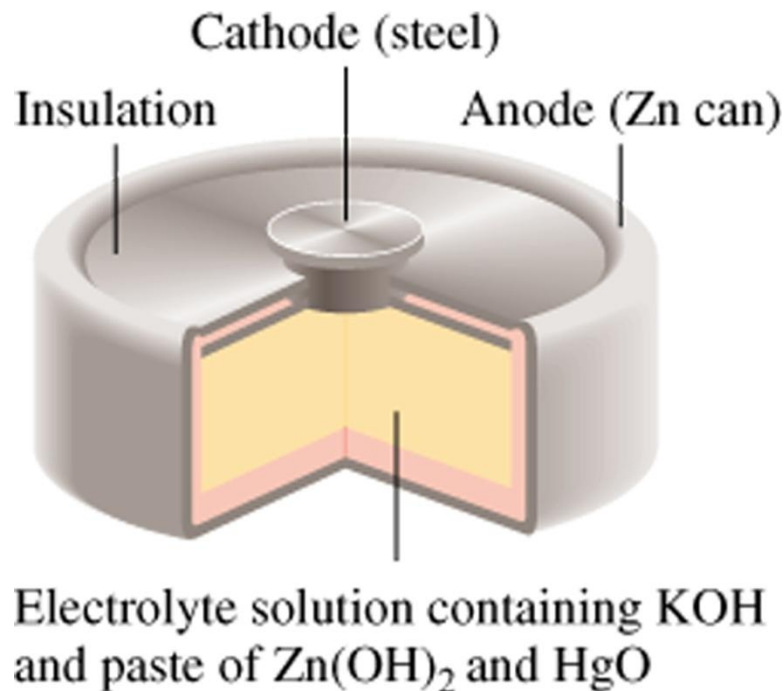
Batteries

Dry cell
Leclanché cell



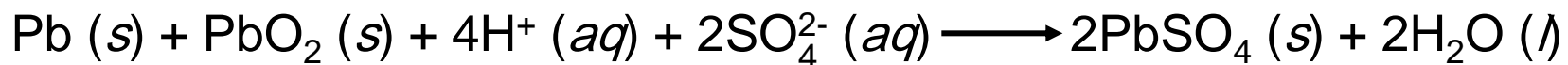
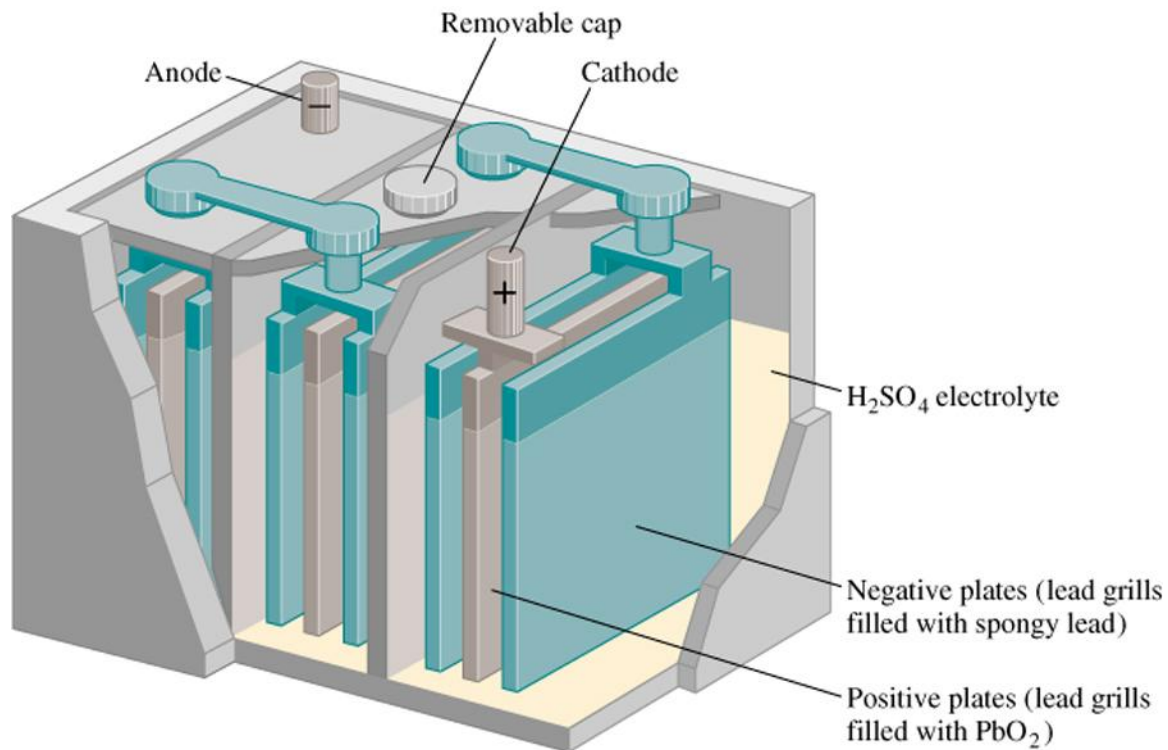
Batteries

Mercury Battery

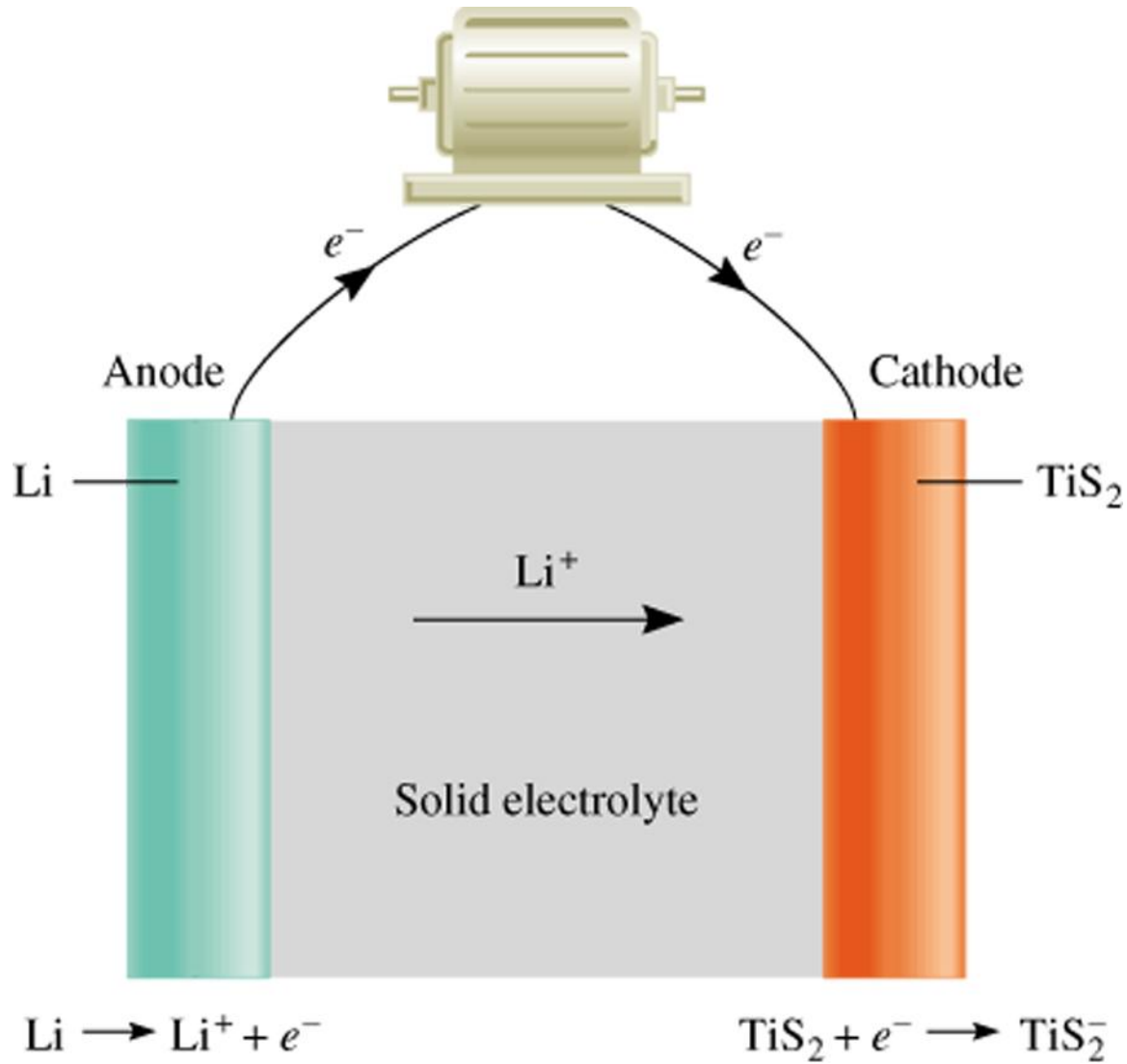


Batteries

Lead storage battery

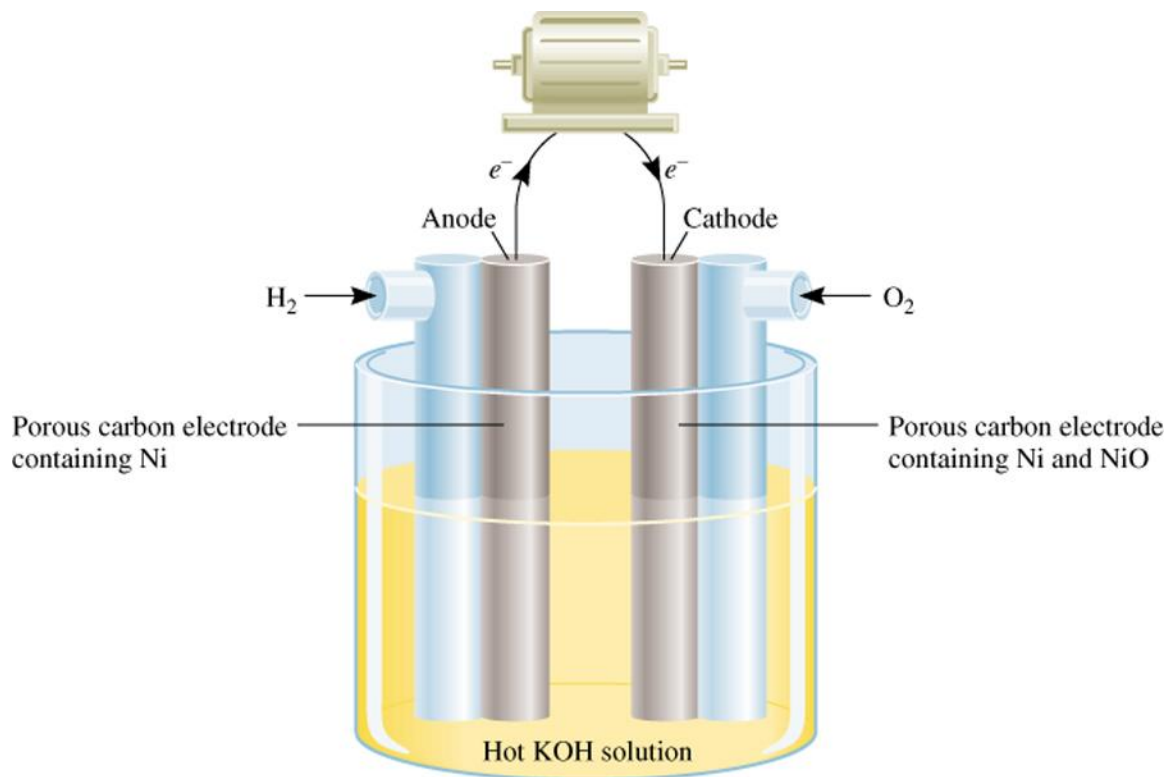


Batteries



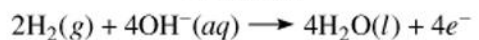
Solid State Lithium Battery

Batteries

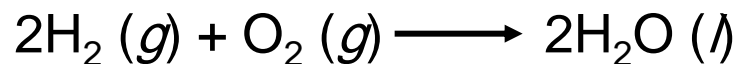
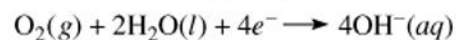


A ***fuel cell*** is an electrochemical cell that requires a continuous supply of reactants to keep functioning

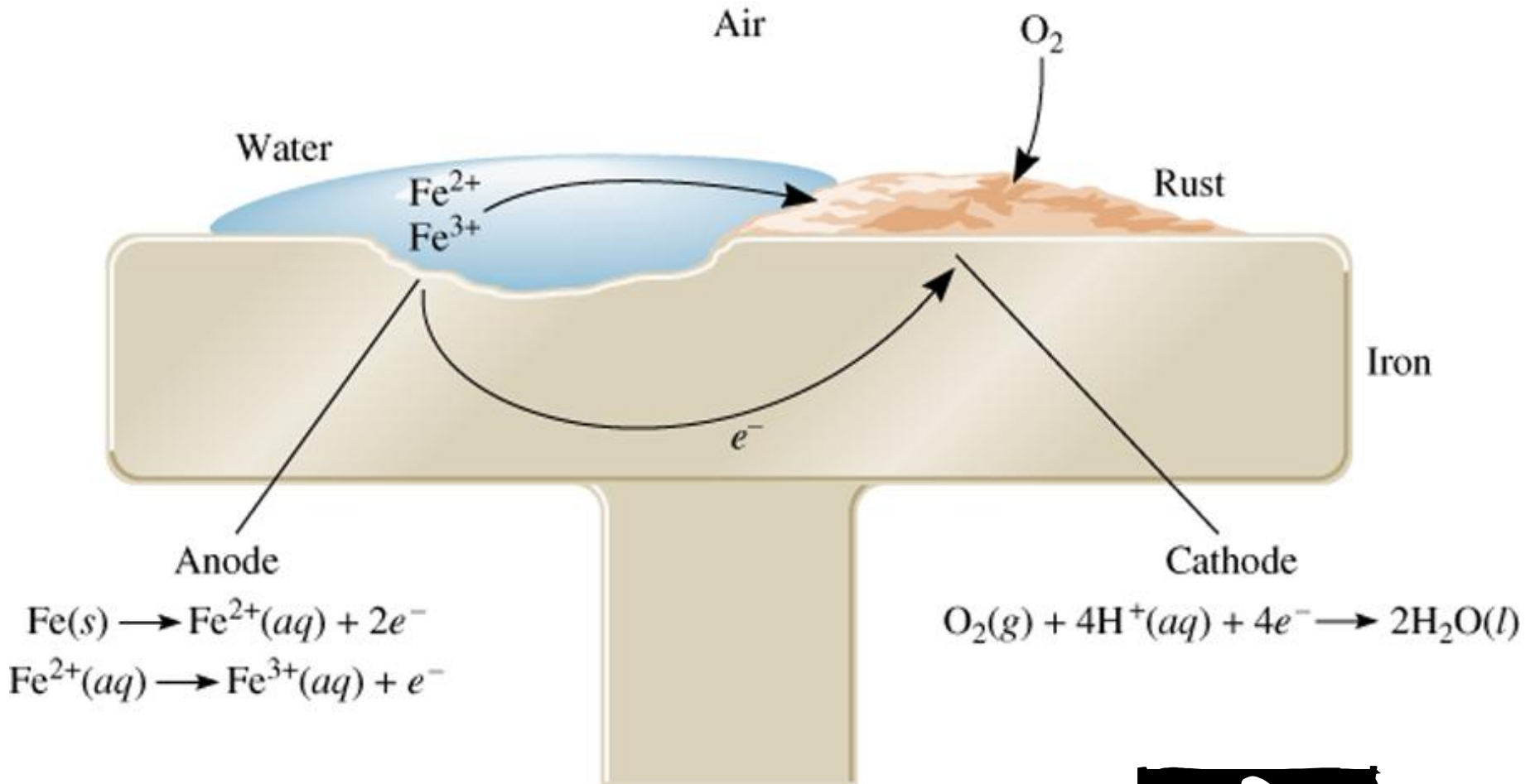
Oxidation



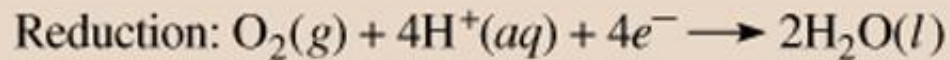
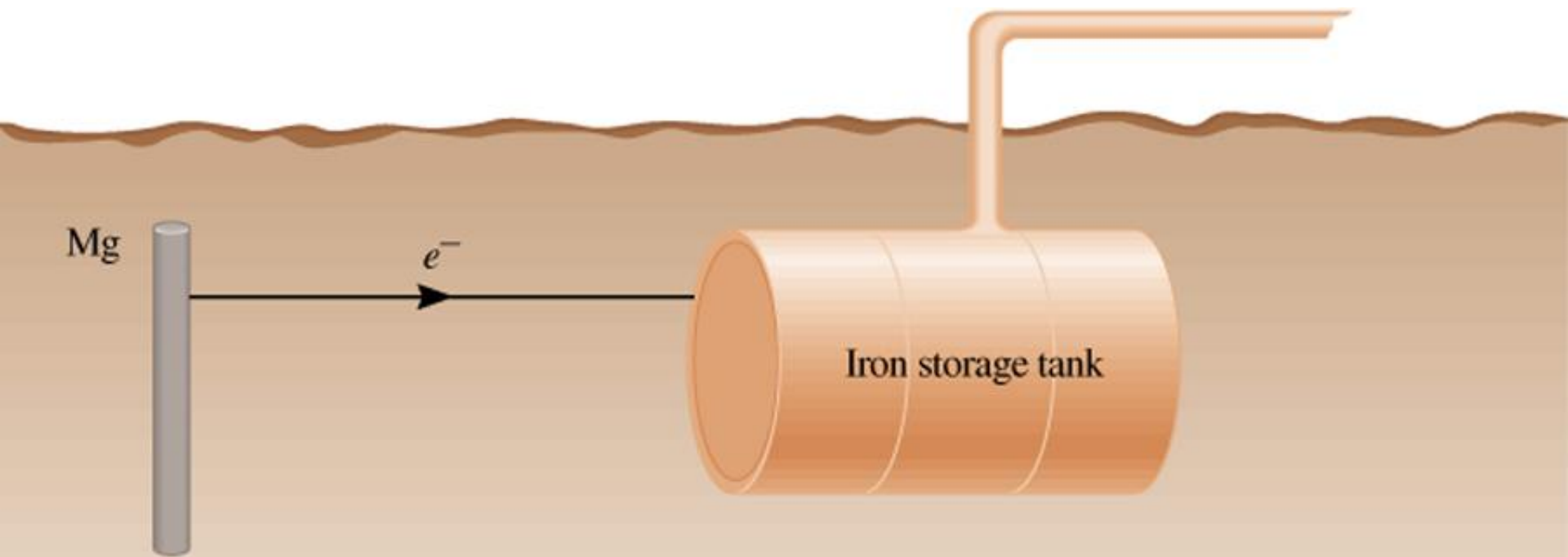
Reduction



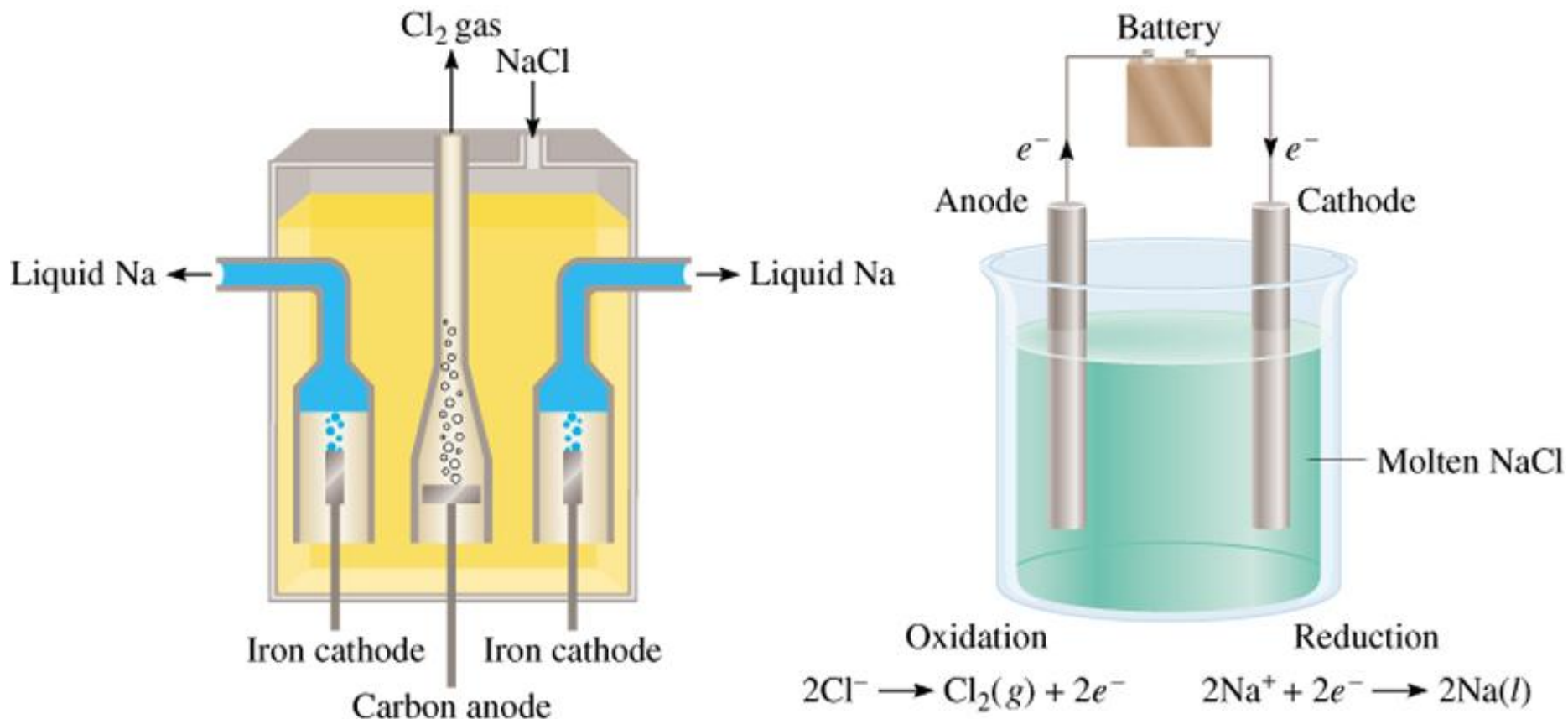
Corrosion



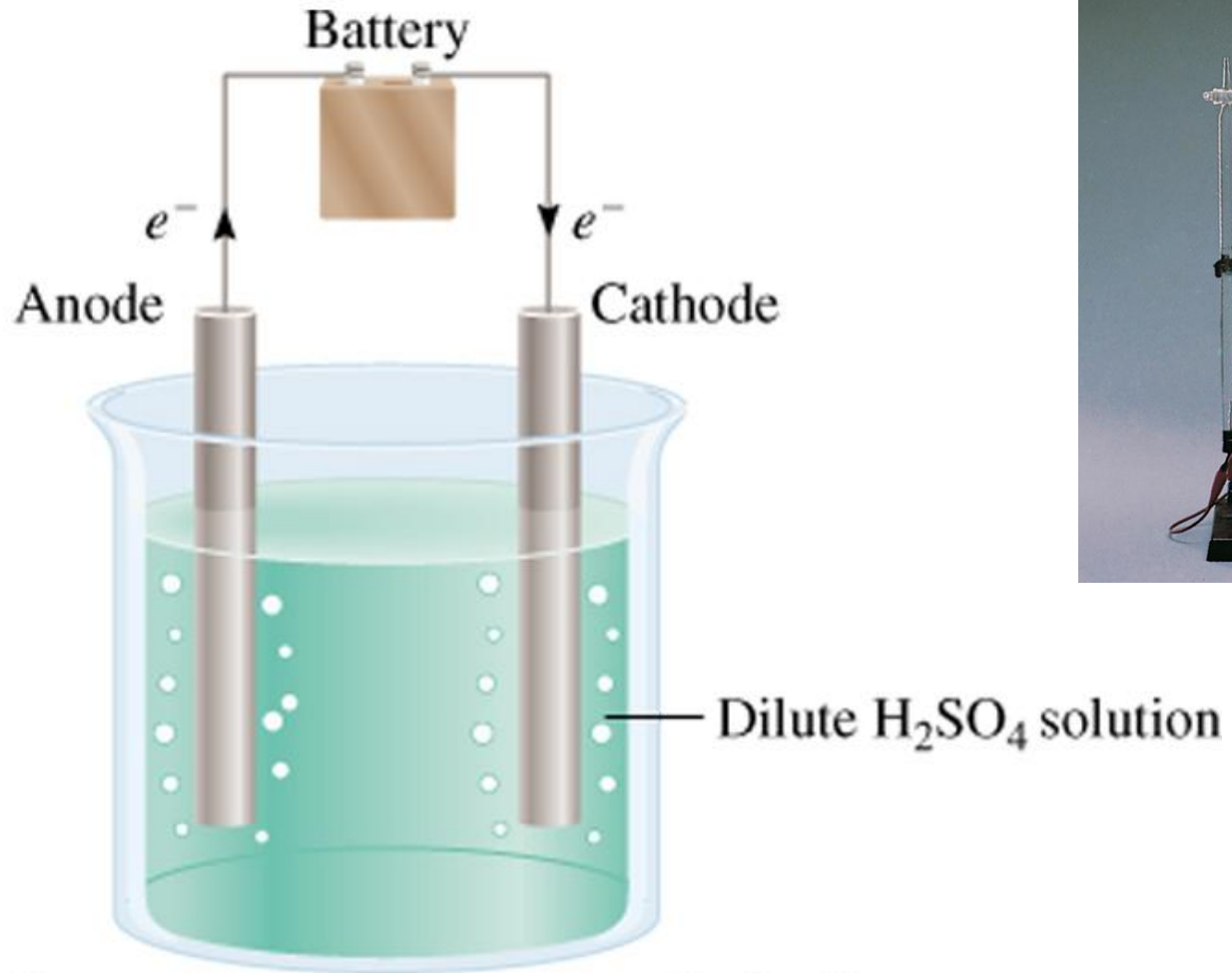
Cathodic Protection of an Iron Storage Tank



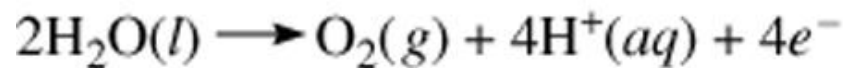
Electrolysis is the process in which electrical energy is used to cause a **nonspontaneous** chemical reaction to occur.



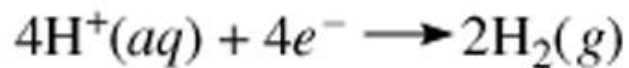
Electrolysis of Water



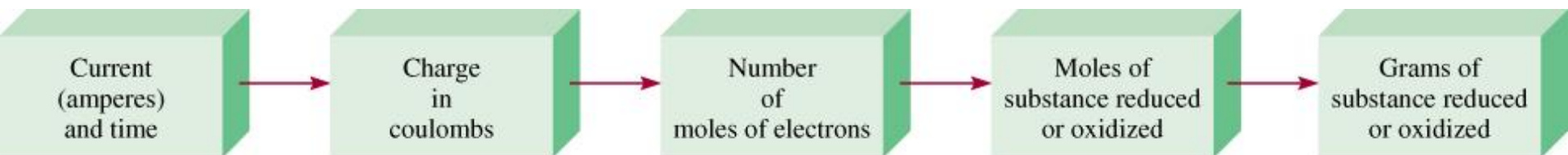
Oxidation



Reduction



Electrolysis and Mass Changes

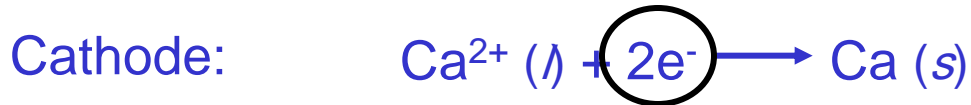


$$\text{charge (C)} = \text{current (A)} \times \text{time (s)}$$

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



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

96500 = 1 mol e^- , So 2 moles of electrons requires = 2×96500

$$Q = I \times t = 0.452 \times 1.5 \times 3600 = 2440 \text{ C}$$

$$193000 \text{ C} = 1 \text{ mole Ca}$$

$$2440 \text{ C} = x$$

$$x = 2440 \times 1 / 193000 = 0.0126 \text{ mol Ca}$$

$$\text{Mass} = 0.0126 \times 40 = 0.5 \text{ g Ca}$$

Chemistry In Action: Dental Filling Discomfort

Corrosion of a Dental Filling

