Chapter 18: Electrochemistry

Key topics:
Galvanic cells
Nernst equation
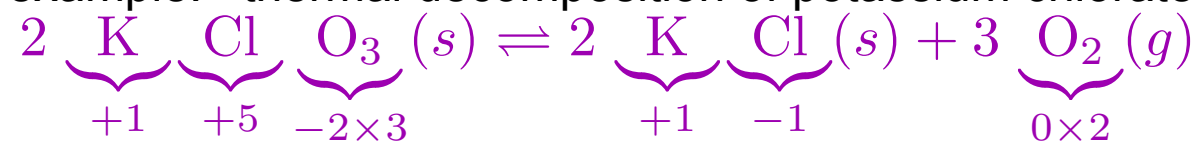***Batteries; electrolysis***

Balancing Redox Reactions

A redox reaction involves a transfer of electrons from one species to another. This results in a change in oxidation number.
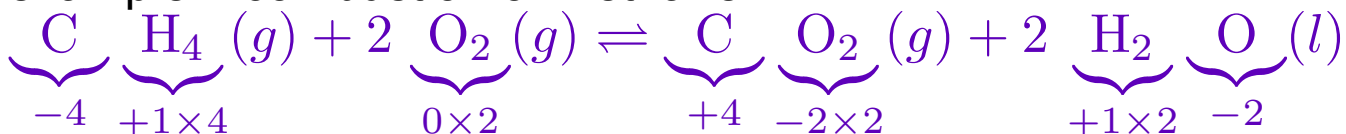
Oxidation (reducing agent):   loss of electrons
Reduction (oxidizing agent):   gain of electrons
     these reactions must occur together
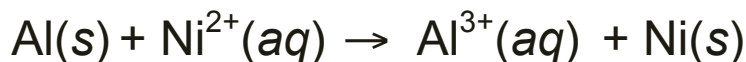
example: thermal decomposition of potassium chlorate

$$2\ \underbrace{K}_{+1}\ \underbrace{Cl}_{+5}\ \underbrace{O_3}_{-2\times3}\ (s) \rightleftharpoons 2\ \underbrace{K}_{+1}\ \underbrace{Cl}_{-1}\ (s) + 3\ \underbrace{O_2}_{0\times2}\ (g)$$

example: combustion of methane

$$\underbrace{C}_{-4}\ \underbrace{H_4}_{+1\times4}\ (g) + 2\ \underbrace{O_2}_{0\times2}\ (g) \rightleftharpoons \underbrace{C}_{+4}\ \underbrace{O_2}_{-2\times2}\ (g) + 2\ \underbrace{H_2}_{+1\times2}\ \underbrace{O}_{-2}\ (l)$$

Balancing Simple Redox Reactions

In a redox reaction both the mass and the charge must be balanced
example: (net ionic equation)

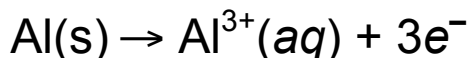$$Al(s) + Ni^{2+}(aq) \rightarrow Al^{3+}(aq) + Ni(s)$$
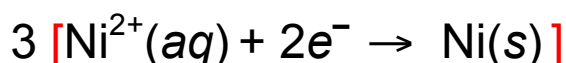
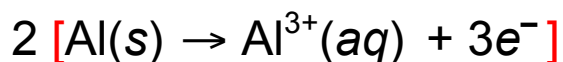balanced by mass, **but *not* by charge**

What do we do?

1. Divide reaction into two half-reactions and add e^- to each half-reaction to balance the charge.
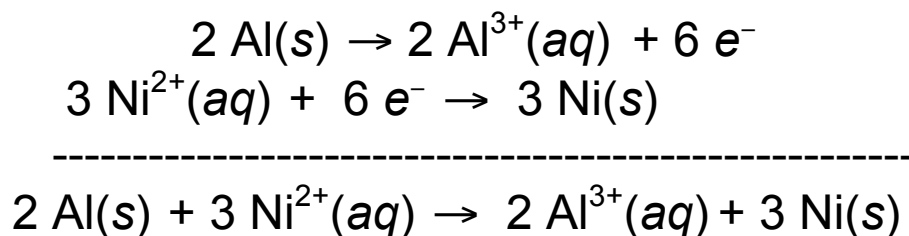The two half-reactions correspond to reduction and oxidation

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$$

$$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$$

2. Multiply to get same number of e^- in each reaction:
   (number of e^- lost must equal number of e^- gained)

$$2\,[Al(s) \rightarrow Al^{3+}(aq) + 3e^-]$$

$$3\,[Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)]$$

3. Cancel e^- to get the balanced net ionic reaction:

$$2\,Al(s) \rightarrow 2\,Al^{3+}(aq) + 6\,e^-$$
$$3\,Ni^{2+}(aq) + 6\,e^- \rightarrow 3\,Ni(s)$$

$$2\,Al(s) + 3\,Ni^{2+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,Ni(s)$$

Balancing Redox Reactions involving H *and* O
   o you will be told if the reaction occurs under acidic or basic conditions
   o use H_2O to balance oxygen
   o use H^+ to balance hydrogen
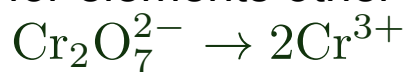   o use OH^- to make basic (under basic conditions)

example: balance the following reaction (acidic conditions)
$$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$$

1. Half reactions

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

$$Fe^{2+} \rightarrow Fe^{3+}$$
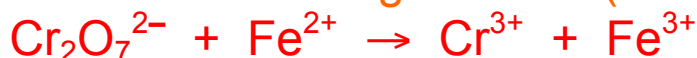
2. Balance by mass for elements other than H and O

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

$$Fe^{2+} \rightarrow Fe^{3+}$$

3. Balance O using H_2O

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

$$Fe^{2+} \rightarrow Fe^{3+}$$

4. Balance H using H^+

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

$$Fe^{2+} \rightarrow Fe^{3+}$$

5. Balance change using e^-

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

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

6. Balance e^- in two half reactions to add them together

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

$$6\left[Fe^{2+} \rightarrow Fe^{3+} + e^-\right]$$
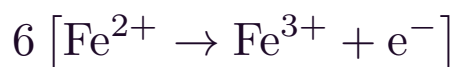
7. Add half reactions and cancel species common to both sides
$$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

8. Check your answer for mass and charge balance

Under basic conditions:
  ○ balance as if under acidic conditions
  ○ for each H^+ in the final equation, add OH^- to both sides
  ○ combine H^+ and OH^- to produce H_2O
  ○ cancel H_2O from both sides if needed

example: balance the following reaction (basic conditions)
$$SO_3^{2-} + MnO_4^- \rightarrow SO_4^{2-} + MnO_2$$

Balancing under acidic conditions gives
$$2H^+ + 3SO_3^{2-} + 2MnO_4^- \rightarrow 3SO_4^{2-} + 2MnO_2 + H_2O$$
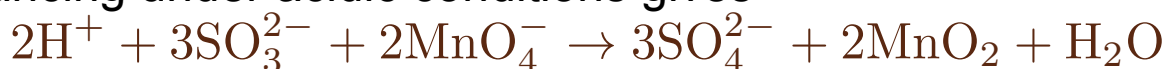
Then we add $2OH^-$ to both sides to obtain
$$H_2O + 3SO_3^{2-} + 2MnO_4^- \rightarrow 3SO_4^{2-} + 2MnO_2 + 2OH^-$$

Galvanic Cells

If we put a piece of copper metal into a $AgNO_3$ solution, a redox reaction occurs: $2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$

The reaction will stop when the copper metal gets covered with silver.
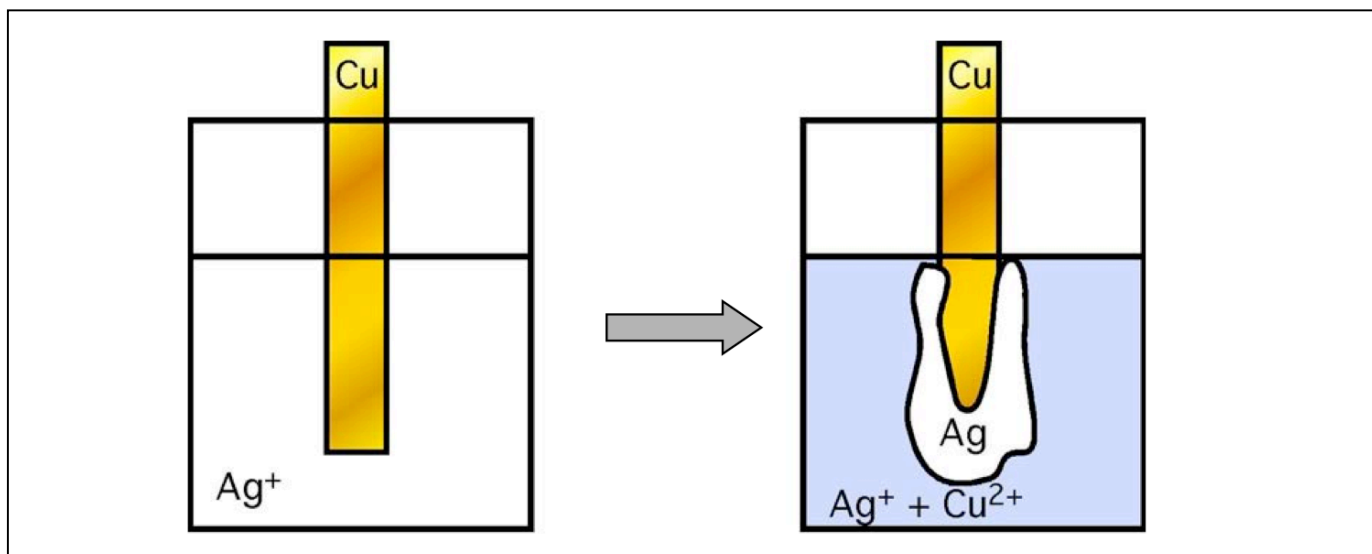
If we want to use this spontaneous reaction to extract energy and do work we need to separate the two half reactions by building a galvanic cell (also called a voltaic cell):
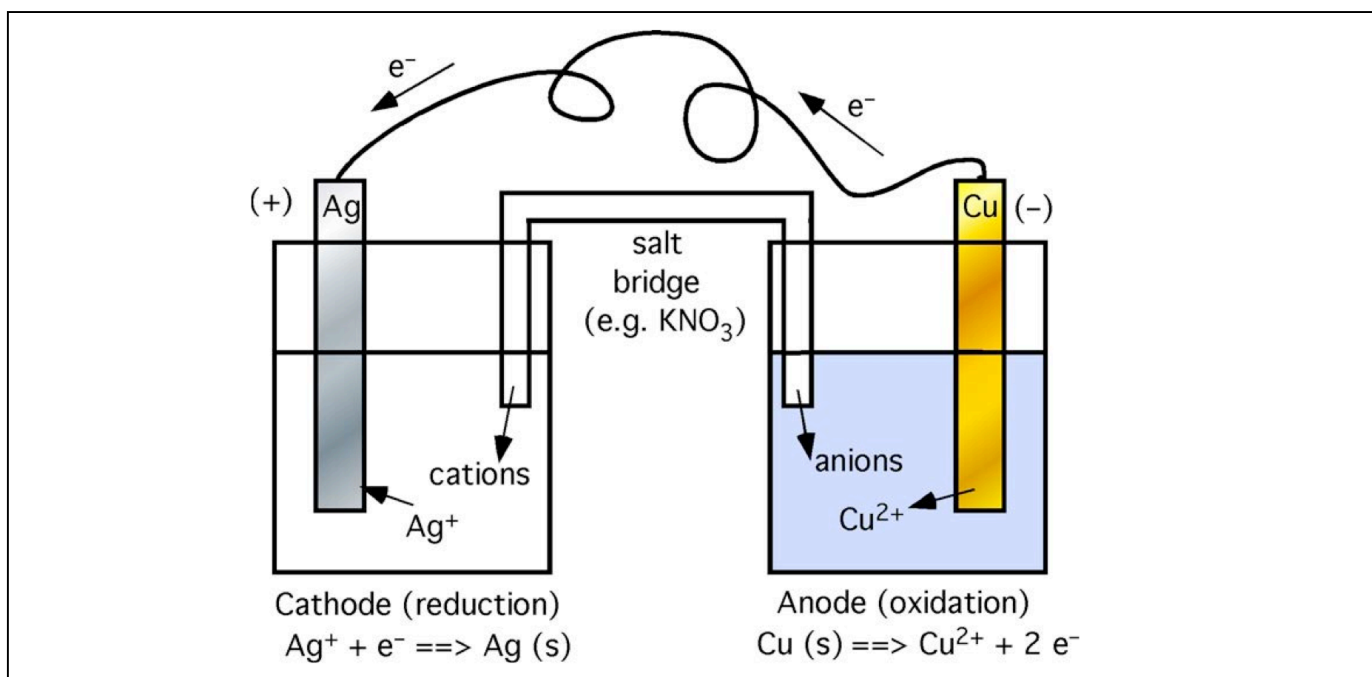
Electrodes
- anode, oxidation
- cathode, reduction

Half-cell
- one container, electrode, and solution

Salt bridge
- conducting medium through which ions can move from one half-cell to the other half-cell
- this is electrolytic conduction (the movement of ions carrying electrical charge)
- contrast with metallic conduction (electrons through wire)

Ion migration
- anions migrate towards the anode
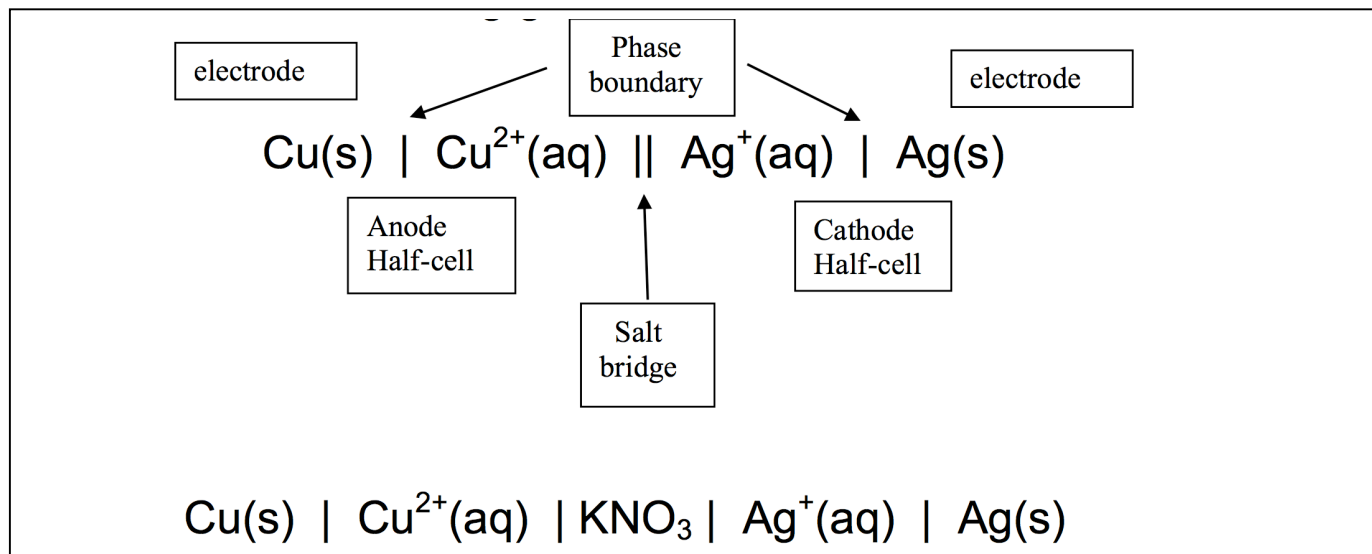- cations migrate towards the cathode

Conduction of charge
- Cu^{2+} enters anode solution (+ charge builds up)
- anions from the salt bridge counter this buildup
- Ag^+ leaves cathode solution (– charge builds up)
- cations from the salt bridge counter this buildup
- salt bridge maintains electrical neutrality (otherwise the reaction will quickly stop)

Charge on the electrodes
- anode: negative (electrons left by Cu oxidation)
- cathode: positive (Ag^+ becomes part of electrode)

*Cell Notation (shorthand for describing a galvanic cell):*

electrode		Phase boundary		electrode

$$Cu(s) \mid Cu^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$$

	Anode Half-cell		Cathode Half-cell	

Salt bridge

$$Cu(s) \mid Cu^{2+}(aq) \mid KNO_3 \mid Ag^{+}(aq) \mid Ag(s)$$

Standard Reduction Potentials

Electrical current flows from the anode to the cathode due to a difference in electrical potential energy between the electrodes

This current is measured, in volts (V), by a voltmeter.

Measured current
- called the overall cell potential (E_{cell})
- is the difference between the electrical potentials at the two electrodes (the two half-cell potentials)
- varies with concentration, temperature, metals/ions used.

Standard cell potential : The cell potential under standard state conditions, [ions] = 1 *M*, *T* = 25°C, 1 atm gas pressure.

Zn(s) | Zn^{2+} (1 M) || Cu^{2+} (1 M) | Cu(s)
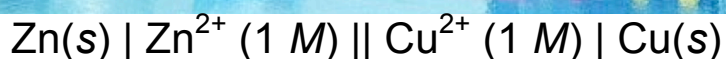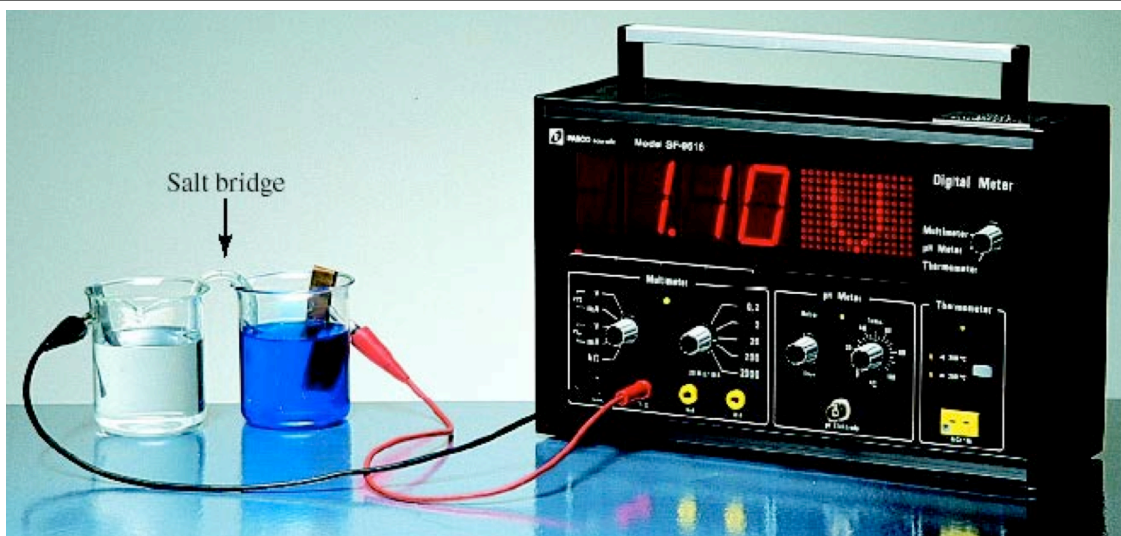
Each half-reaction can be considered to have a reduction potential associated with it. This measures the natural tendency of the half-reaction to proceed as a reduction.

Standard reduction potential ($E°$ or $E°_{red}$): Reduction potential for a half-reaction under standard state conditions.

When two half-reactions are connected
- the one with the larger (more positive) $E°_{red}$ goes as a reduction
- the other one (less positive $E°_{red}$) goes as an oxidation with $E°_{ox}$ = -($E°_{red}$)

$$E°_{cell} = \underbrace{E°_{red}}_{cathode} + \underbrace{E°_{ox}}_{anode}$$

We can only measure E_{cell} so how do we get $E°_{red}$ and $E°_{ox}$? We select a specific half-cell as our reference (defined as zero) and then use this one to get $E°_{red}$ for all other half-cells.

Reference half-cell : standard hydrogen electrode (SHE)
- o standard state conditions
- o assigned a value of 0 V
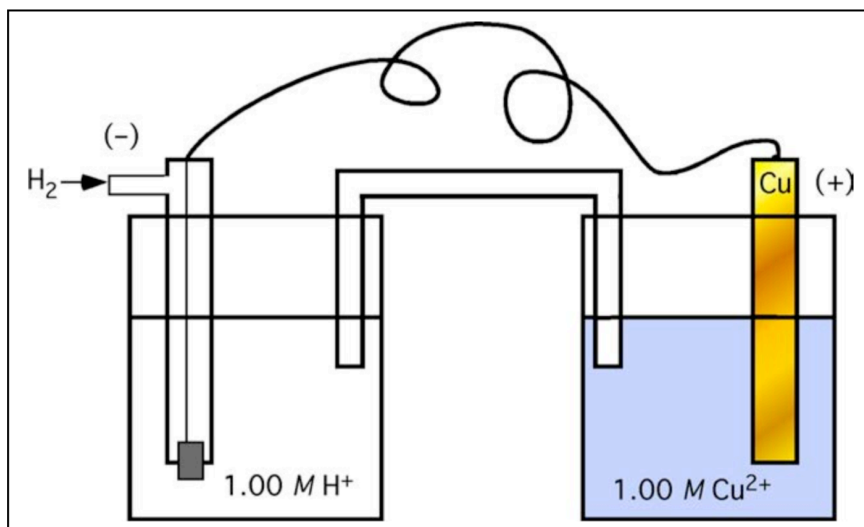- o reaction is $2H^+$ (1 M) + $2e^-$ → H_2 (1 atm)

$$E^{\circ}_{H^+/H_2} = 0 \text{ V}$$
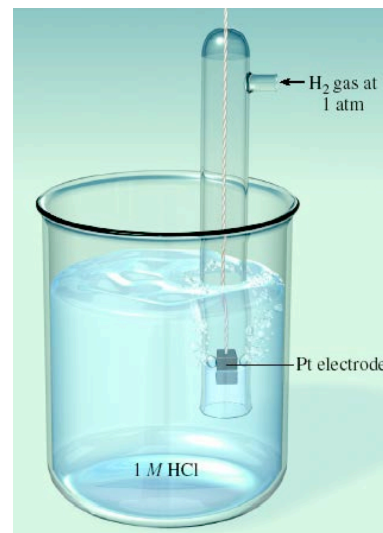
How to measure the Cu^{2+} standard reduction potential:

Measure the charge on the electrodes:
Cu (+) ⇒ cathode
H_2 (−) ⇒ anode

Measure the current: 0.34 V

$$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}(s)$$
$$\text{H}_2(g) \rightarrow 2\text{H}^+ + 2e^-$$
$$\overline{}$$
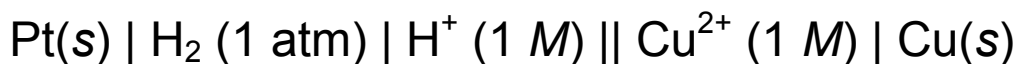$$\text{Cu}^{2+} + \text{H}_2(g) \rightarrow 2\text{H}^+ + \text{Cu}(s)$$
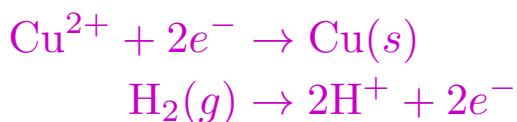
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red, Cu}^{2+}/\text{Cu}} + E^{\circ}_{\text{ox, H}^+/\text{H}_2}$$
$$0.34 \text{ V} = E^{\circ}_{\text{red, Cu}^{2+}/\text{Cu}} + 0$$

$$E^{\circ}_{\text{red, Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$$

Pt(s) | H$_2$ (1 atm) | H$^+$ (1 M) || Cu^{2+} (1 M) | Cu(s)
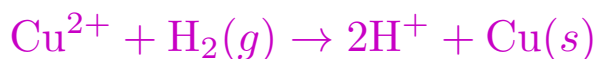
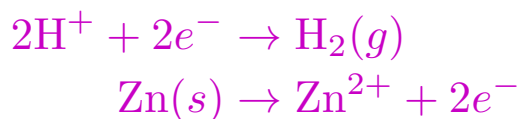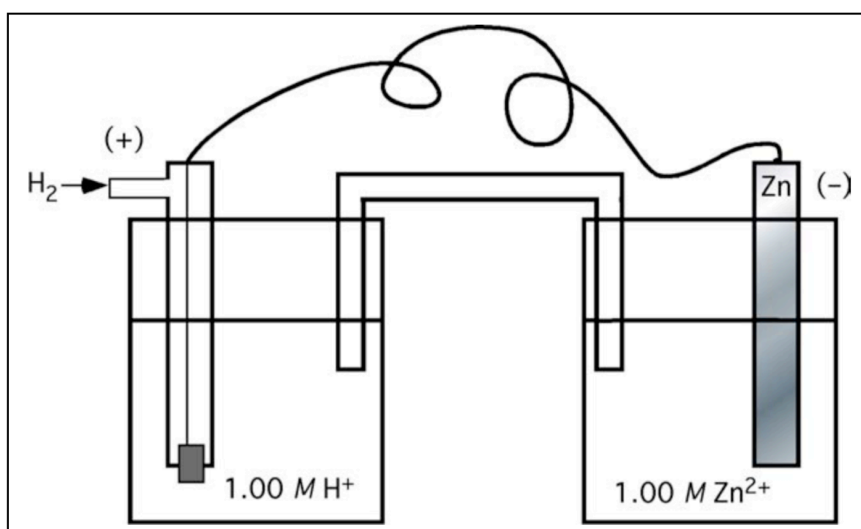*How to measure the Zn^{2+} standard reduction potential:*

Measure the charge
on the electrodes:
H$_2$ (+) $\Rightarrow$ cathode
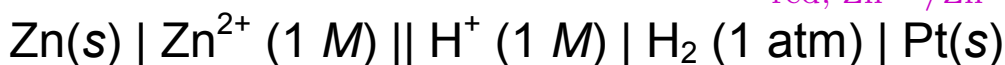Zn (−) $\Rightarrow$ anode

Measure the
current: 0.76 V

(+)
H$_2\rightarrow$

Zn (−)

1.00 M H$^+$ 1.00 M Zn^{2+}

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g)$$
$$\text{Zn}(s) \rightarrow \text{Zn}^{2+} + 2e^-$$
$$\overline{}$$
$$2\text{H}^+ + \text{Zn}(s) \rightarrow \text{Zn}^{2+} + \text{H}_2(g)$$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red, H}^+/\text{H}_2} + E^{\circ}_{\text{ox, Zn}^{2+}/\text{Zn}}$$
$$0.76 \text{ V} = 0 + E^{\circ}_{\text{ox, Zn}^{2+}/\text{Zn}}$$

$$E^{\circ}_{\text{ox, Zn}^{2+}/\text{Zn}} = +0.76 \text{ V}$$
$$E^{\circ}_{\text{red, Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$$

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

Once the half-cell potentials are determined, we can calculate E°_{cell}
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} + E^{\circ}_{\text{ox}}$$
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red, Cu}^{2+}/\text{Cu}} + E^{\circ}_{\text{ox, Zn}^{2+}/\text{Zn}}$$

$$= 0.34 \text{ V} + 0.76 \text{ V} = 1.10 \text{ V}$$

Table 18.1: $E°$ values for several half reactions

TABLE 18.1	Standard Reduction Potentials at 25°C*	
Half-Reaction		**$E°$(V)**
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$		+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O(l)$		+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$		+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$		+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$		+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$		+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$		+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$		+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$		+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$		+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$		+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$		+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$		+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$		+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
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$		+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$		+0.53
$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$		+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$		+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$		+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O(l)$		+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
$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$		−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

Increasing strength as oxidizing agent

Increasing strength as reducing agent

more (+) : more likely to be reduced, better oxidizing agent

more (−) : more likely to be oxidized, better reducing agent

Using standard reduction potentials :

When connecting two half-cells
- o can use $E°$ for each half-reaction to predict the redox rxn
- o half-reaction with more positive $E°$ will go as reduction
- o other half-reaction will go as oxidation
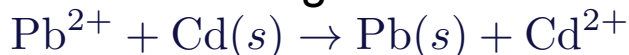- o overall $E°$ is *always* positive for a spontaneous reaction

e.g., Determine the overall cell reaction and $E°_{cell}$ of a galvanic cell made of a Cd electrode in a 1.0 *M* $Cd(NO_3)_2$ solution and a Pb electrode in a 1.0 *M* $Pb(NO_3)_2$ solution.

Solution:
The relevant entries in Table 18.1 are:
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$, $E° = -0.13$ V
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$, $E° = -0.40$ V
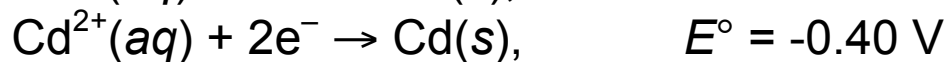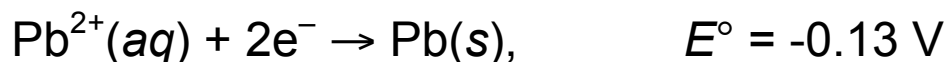
Pb will therefore go as a reduction, and Cd as an oxidation.
$$Pb^{2+} + Cd(s) \rightarrow Pb(s) + Cd^{2+}$$
$$E°_{cell} = E°_{red,\ Pb^{2+}/Pb} + E°_{ox,\ Cd^{2+}/Cd} = E°_{red,\ Pb^{2+}/Pb} - E°_{red,\ Cd^{2+}/Cd}$$
$$= -0.13\text{ V} - (-0.40\text{ V}) = 0.27\text{ V}$$

e.g., Determine what redox reaction, if any, occurs when lead metal (Pb) is added to (a) a 1.0 *M* solution of $NiCl_2$ and (b) a 1.0 *M* solution of HCl

Solution:
The relevant entries in Table 18.1 are:
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$, $E° = -0.13$ V
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$, $E° = -0.25$ V
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $E° = +1.36$ V
$2H^+(aq) + 2e^- \rightarrow H_2(g)$ $E° = 0$ V
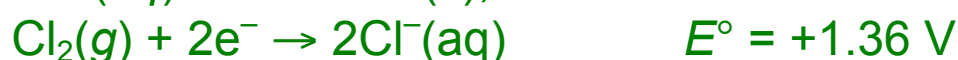
The Cl half-reaction will not occur because it would have to run as a reduction, but there is no $Cl_2(g)$ present.
(a) The Pb half-reaction will not occur because it would have to run as a reduction, but there are no $Pb^{2+}(aq)$ ions present.
(b) The Pb half-reaction would have to run as an oxidation and the hydrogen reaction would have to run as a reduction. This works because $Pb(s)$ and $H^+(aq)$ are present. The reaction is
$2H^+(aq) + Pb(s) \rightarrow H_2(g) + Pb^{2+}(aq)$

Spontaneity of Redox Reactions Under Standard State Conditions

ΔG is the maximum useful work that can be obtained.

In a galvanic cell, the work is supplied by the electric current (moving electrons through a wire)

$$\text{maximum work} = n\,\mathcal{F}\,E_{\text{cell}}$$

$$\Delta G = -n\,\mathcal{F}\,E_{\text{cell}} \qquad \Delta G^\circ = -n\,\mathcal{F}\,E_{\text{cell}}^\circ$$

n = number of moles of electrons
$\mathcal{F}$ = Faraday constant = electric charge contained in one mole of electrons
E_{cell}° measured in V

We can introduce the equilibrium constant K through

$$\Delta G^\circ = -n\mathcal{F}E_{\text{cell}}^\circ = -RT\ln K$$

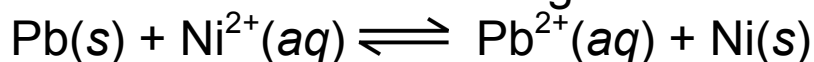and rearrange to get $\qquad E_{\text{cell}}^\circ = \dfrac{RT}{n\mathcal{F}}\ln K$

plug in the values of R, $\mathcal{F}$, and room temperature (298 K) :

$$E_{\text{cell}}^\circ = \dfrac{0.0257\,\text{V}}{n}\ln K$$
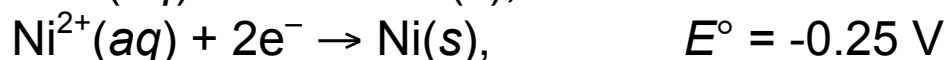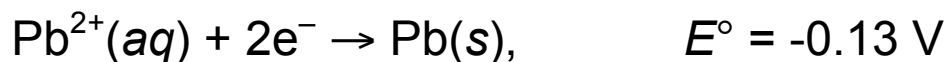
and then convert "ln" to "log"

$$E^{\circ}_{\text{cell}} = \frac{0.0592\,\text{V}}{n} \log K$$

e.g., Calculate ΔG° for the following reaction at 25°C
$$Pb(s) + Ni^{2+}(aq) \rightleftharpoons Pb^{2+}(aq) + Ni(s)$$

Solution:
The relevant entries in Table 18.1 are:
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$, E° = -0.13 V
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$, E° = -0.25 V

The given reaction runs nickel as a reduction and lead as an oxidation reaction, thus E°_{cell} = -0.25 V + 0.13 V = -0.12 V.
Since E°_{cell} < 0 this reaction is not spontaneous and ΔG° > 0.

$$\Delta G^{\circ} = -n\mathcal{F}E^{\circ}_{\text{cell}} = -(2)(96500)(-0.12) = 23.16\,\text{kJ/mol}$$

e.g., Calculate the equilibrium constant for the following reaction at 25°C $2Ag(s) + Fe^{2+}(aq) \rightleftharpoons 2Ag^+(aq) + Fe(s)$

Solution:
The relevant entries in Table 18.1 are:
$Ag^+(aq) + e^- \rightarrow Ag(s)$, E° = +0.80 V
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$, E° = -0.44 V

The given reaction runs silver as an oxidation and iron as a reduction, thus E°_{cell} = -0.44 – 0.80 = -1.24 V.
$$E^{\circ}_{\text{cell}} = \frac{0.0592\,\text{V}}{n} \log K \quad \Rightarrow \quad \log K = \frac{nE^{\circ}_{\text{cell}}}{0.0592\,\text{V}} = \frac{(2)(-1.24\,\text{V})}{0.0592\,\text{V}}$$

$$\Rightarrow K = 1.28 \times 10^{-42}$$

Spontaneity of Redox Reactions Under Conditions other than Standard State

The concentrations of the half-cell species affect E_{cell}
[ions] = 1 M; P_{gases} = 1 atm: E°_{cell}
[ions] ≠ 1 M; P_{gases} ≠ 1 atm: E_{cell} (potential changes)

The cell potential drops as the reactants are comsumed and the reaction approaches equilibrium
$$\Delta G = -n\mathcal{F}E_{cell} \quad \Rightarrow \quad \text{when } \Delta G = 0, E_{cell} = 0$$

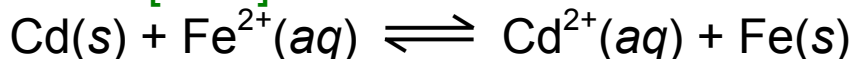From Chapter 15.4, we have $\Delta G = \Delta G^{\circ} + RT \ln Q$
We can rewrite this as

$$-n\mathcal{F}E_{cell} = -n\mathcal{F}E^{\circ}_{cell} + RT \ln Q \quad \Rightarrow \quad E_{cell} = E^{\circ}_{cell} - \frac{RT}{n\mathcal{F}} \ln Q$$

$$E = E^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q \quad \text{or} \quad E = E^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q$$
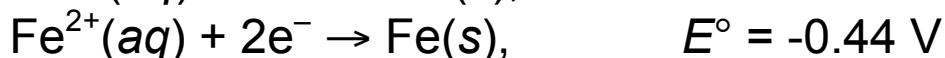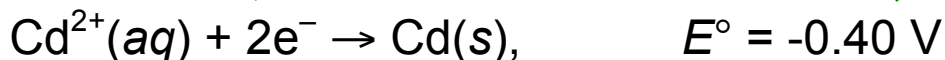
Nernst Equation

e.g., Will the following reaction occur spontaneously at 298 K if [Fe^{2+}] = 0.60 M and [Cd^{2+}] = 0.010 M ?
$$Cd(s) + Fe^{2+}(aq) \rightleftharpoons Cd^{2+}(aq) + Fe(s)$$

Solution:

n = 2 and Q = 0.010 / 0.60 = 0.0167. Also, from Table 18.1,
$Cd^{2+}(aq) + 2e^{-} \rightarrow Cd(s)$, E° = -0.40 V
$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$, E° = -0.44 V
Thus E = (-0.44 V + 0.40 V) – (0.0257 V / 2)(-4.094) = +0.01 V
Yes, since E > 0, this reaction is spontaneous.

e.g., What is $[Cu^{2+}]$ when a standard Ag/Ag^+ half-cell connected to a Cu/Cu^{2+} half-cell (Cu electrode is negative) has E_{cell} = 0.62 V ?

Solution:

The reaction is $2Ag^+(aq) + Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$ and
$Ag^+(aq) + e^- \rightarrow Ag(s),$ $E°$ = +0.80 V
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s),$ $E°$ = +0.34 V

Thus *n* = 2 and $E°_{cell}$ = 0.80 V – 0.34 V = 0.46 V, and
$0.62\,\text{V} = 0.46\,\text{V} - 0.01285\ln Q$ $\Rightarrow$ $Q = 3.91 \times 10^{-6} = [Cu^{2+}]/[Ag^+]^2$
Thus $[Cu^{2+}]$ = 3.9 x 10^{-6} *M*

Concentration Cell : is a galvanic cell composed of the same material but differing in ion concentrations.
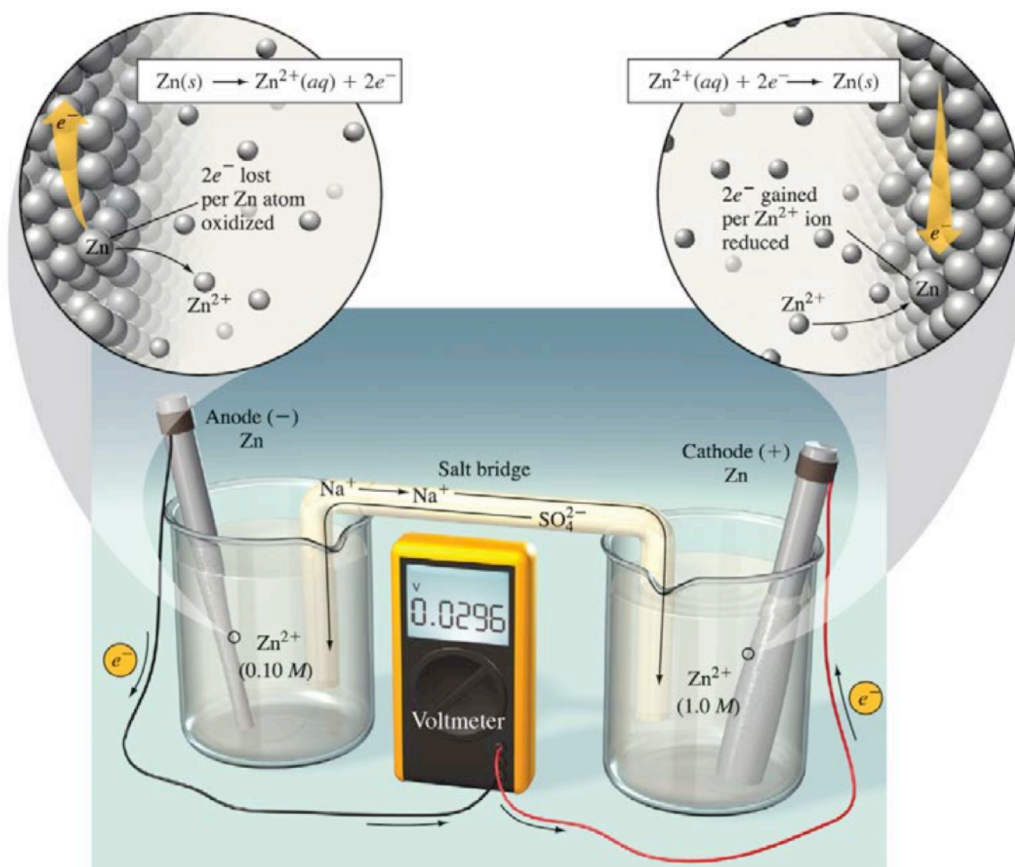
For a zinc concentration cell, the reduction half-reaction
$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$$
will be favored for high $[Zn^{2+}(aq)]$
and the oxidation half-reaction $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
will be favored at low $[Zn^{2+}(aq)]$ from Le Chatelier's principle.

Therefore the reduction takes place in the more concentrated half-cell and the oxidation occurs in the more dilute half-cell.

For a zinc concentration cell of
$Zn(s) \mid Zn^{2+}$ (0.10 M) $\|$ Zn^{2+} (1.0 M) $\mid Zn(s)$

the cell potential is
$$E = 0 - \frac{0.0592 \text{ V}}{2} \log \frac{0.10}{1.0} = 0.030 \text{ V}$$

The cell potential decreases during the operation of the cell until the concentration of ions in the two compartments are equal, at which point E = 0.

e.g., Consider a copper concentration cell. One half-cell has 1.00 M $CuNO_3$ and the other contains a saturated solution of CuCl. The cell potential is 0.175 V. Find K_{sp} for CuCl.
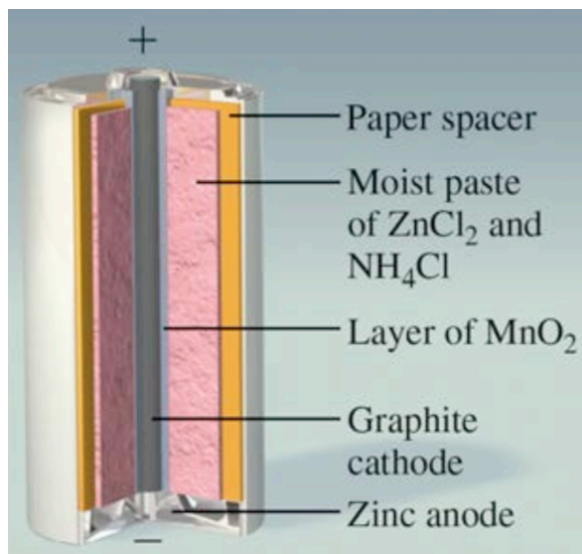
Solution:
We have 0.175 V = 0 – (0.0592 V) (log $[Cu^+]$), Cu^+ of the CuCl
so $[Cu^+]$ = 1.11 x 10^{-3} and K_{sp} = (1.11 x 10^{-3})^2 = 1.22 x 10^{-6}
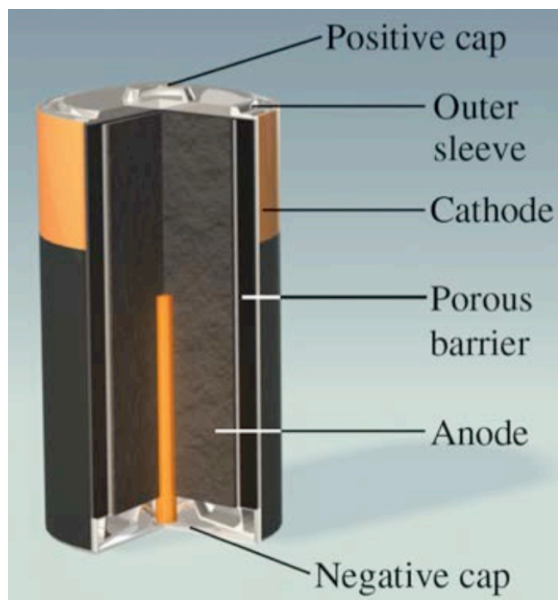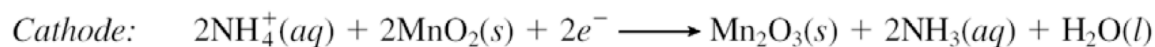
Batteries

A battery is a galvanic cell, or a series of connected galvanic cells, that can be used as a self-contained source of direct electric current.
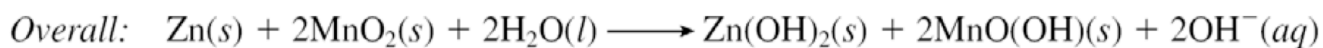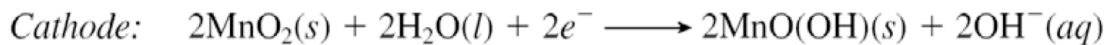
Dry cells and alkaline batteries
involve zinc, manganese oxide, and an electrolyte.

— Paper spacer

— Moist paste of $ZnCl_2$ and NH_4Cl

— Layer of MnO_2

— Graphite cathode

— Zinc anode

Dry Cell, E_{cell} = 1.5 V

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

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

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

— Positive cap

— Outer sleeve

— Cathode

— Porous barrier

— Anode

— Negative cap

Alkaline Cell, E_{cell} = 1.54 V

Cathode: $\quad 2MnO_2(s) + 2H_2O(l) + 2e^- \longrightarrow 2MnO(OH)(s) + 2OH^-(aq)$

Anode: $\quad Zn(s) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s) + 2e^-$

Overall: $\quad Zn(s) + 2MnO_2(s) + 2H_2O(l) \longrightarrow Zn(OH)_2(s) + 2MnO(OH)(s) + 2OH^-(aq)$

Lead acid battery
- made of six identical cells in series (each delivers 2 V)
- lead anode and PbO_2 cathode immersed in H_2SO_4.
- rechargeable (use electrolysis)
- discharge uses H_2SO_4 and the solution density decreases (can measure density with a hydrometer)

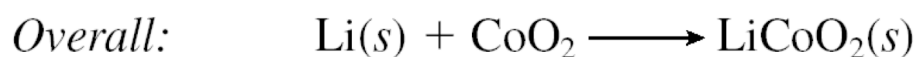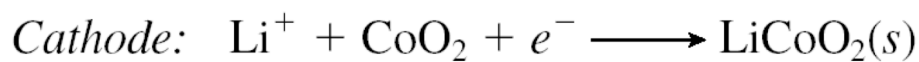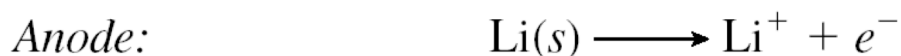Anode, Removable cap, Cathode

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

Overall: $\quad Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$
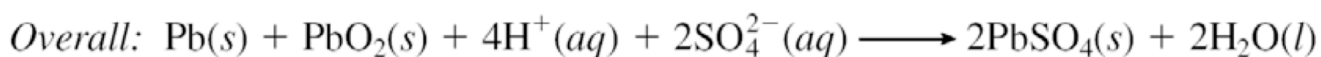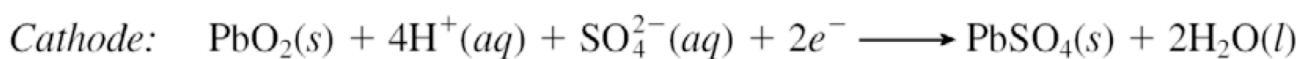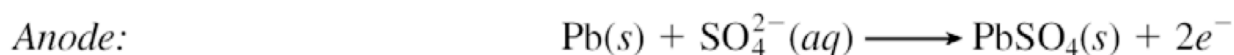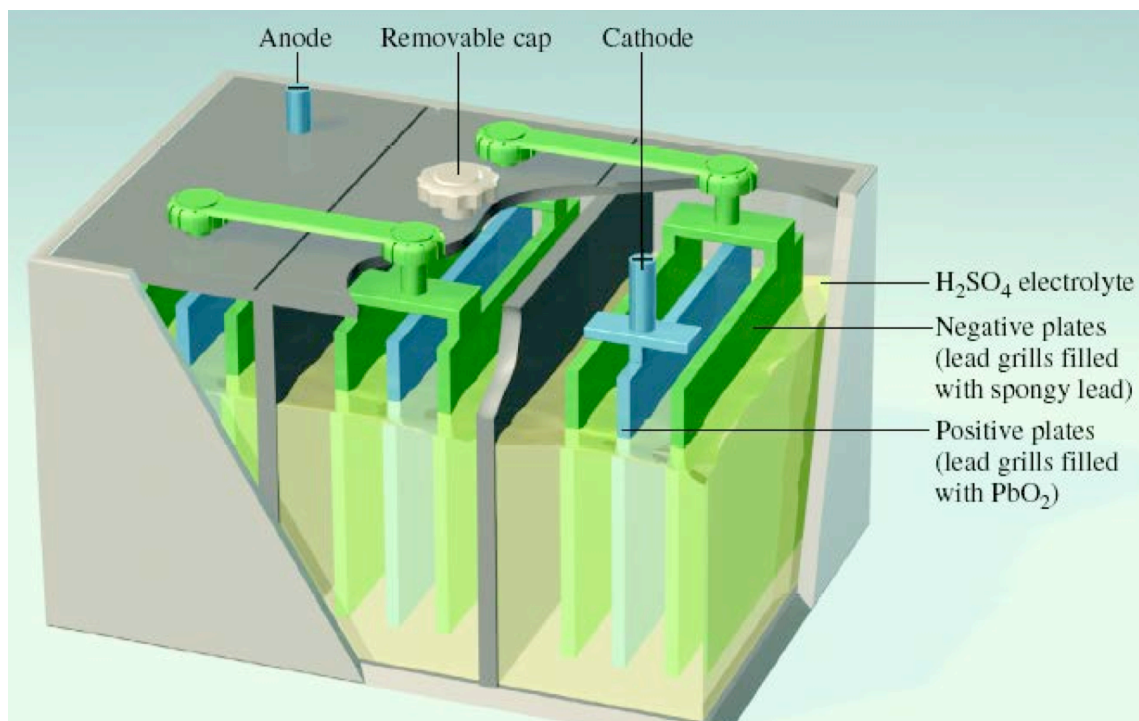
Lithium-ion battery
- E_{cell} = 3.4 V, a relatively large potential
- can be recharged hundreds of times

Anode: $\quad Li(s) \longrightarrow Li^+ + e^-$

Cathode: $\quad Li^+ + CoO_2 + e^- \longrightarrow LiCoO_2(s)$

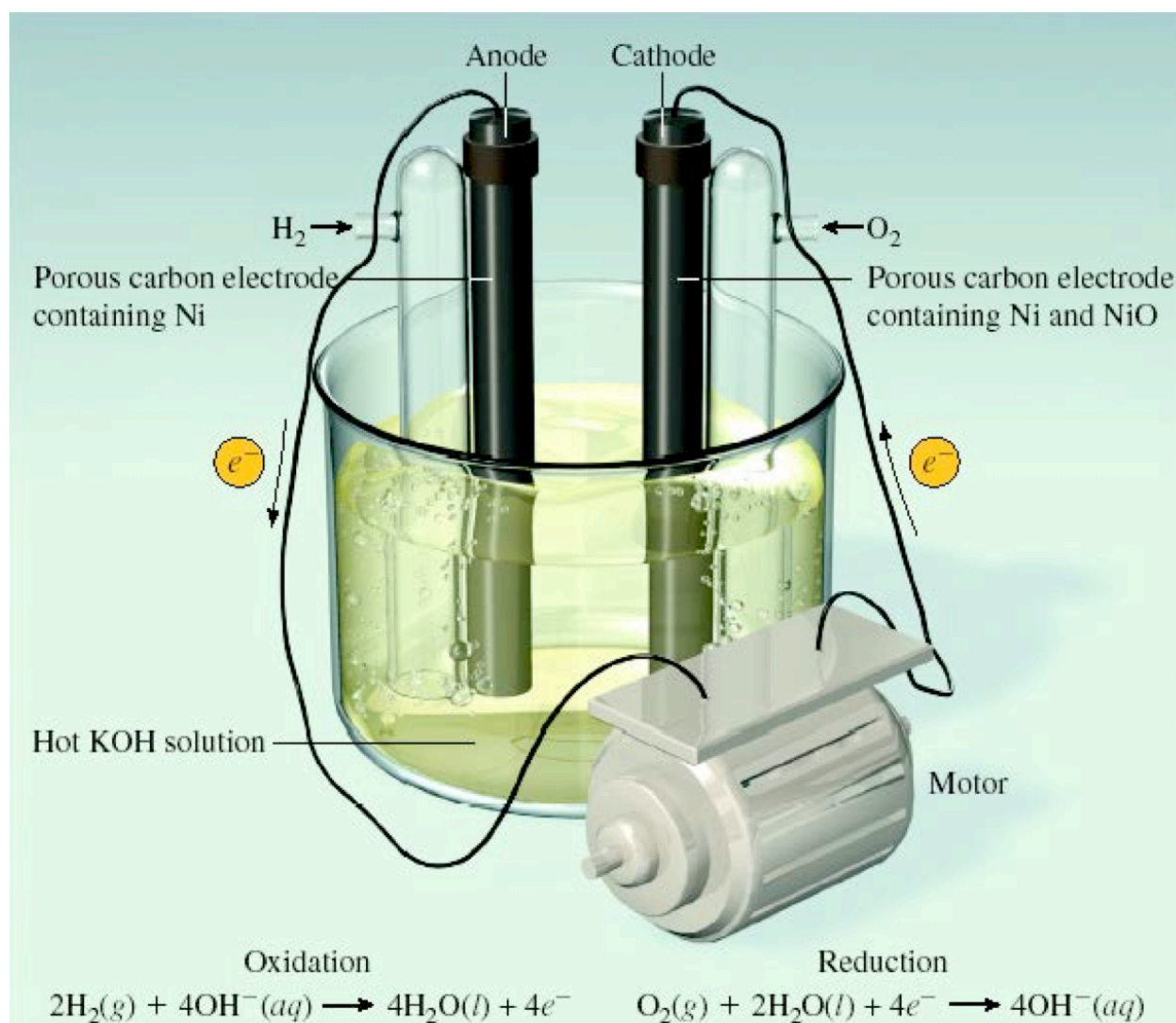*Overall:* $\quad Li(s) + CoO_2 \longrightarrow LiCoO_2(s)$

Fuel cells
- o direct production of electricity (electrochemical process)
- o requires a continuous supply of reactants
- o very efficient
- o the only waste product is water !

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

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

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

$$E^o_{cell} = E^o_{red(cathode)} + E^o_{ox(anode)}$$

$$E^o_{cell} = 0.40\ V + 0.83\ V$$

$$E^o_{cell} = 1.23\ V$$

Anode   Cathode

$H_2 \rightarrow$

Porous carbon electrode containing Ni

$\leftarrow O_2$

Porous carbon electrode containing Ni and NiO

e^-

e^-

Hot KOH solution

Motor

Oxidation

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

Reduction

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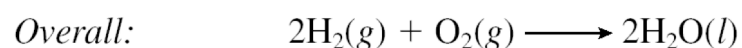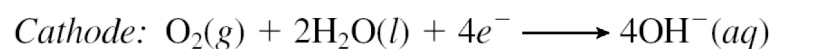
Electrolysis

is the use of electrical energy to drive a *non-spontaneous* redox reaction.

Electrolysis of molten NaCl

- molten state ⇒ ions can move freely
- inert electrodes
- $E°_{cell}$ = -4 V: must supply at least 4 V from a battery
- anions move towards the anode (oxidation site)
- cations move towards the cathode (reduction site)
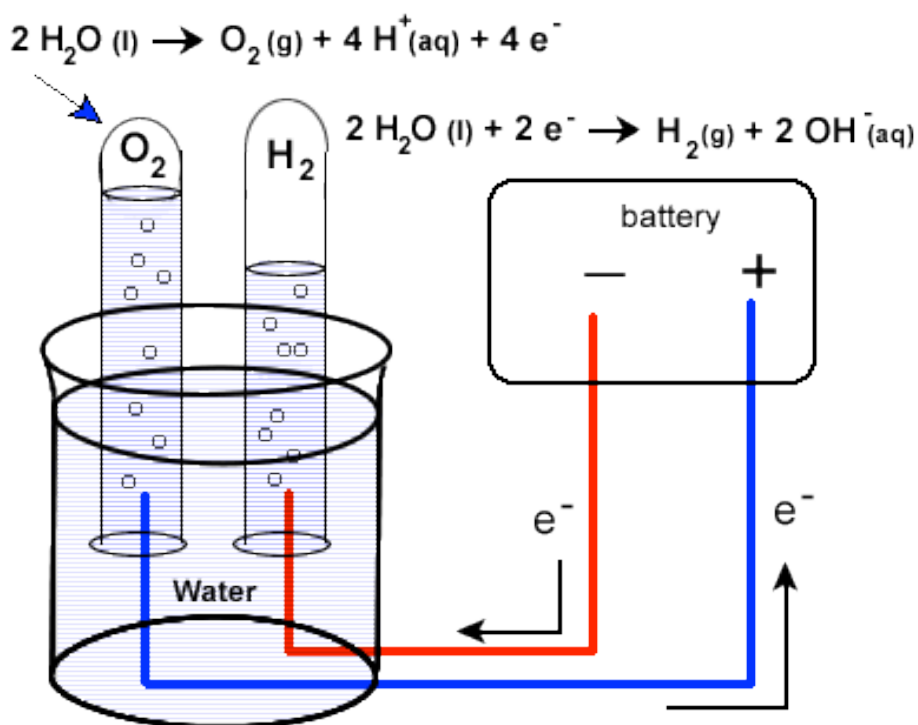- extract electron from Cl⁻, force electron onto Na⁺

Commercial setup

Cathode (reduction) $2Na^+(l) + 2e^- \rightarrow 2Na(l)$
Anode (oxidation) $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
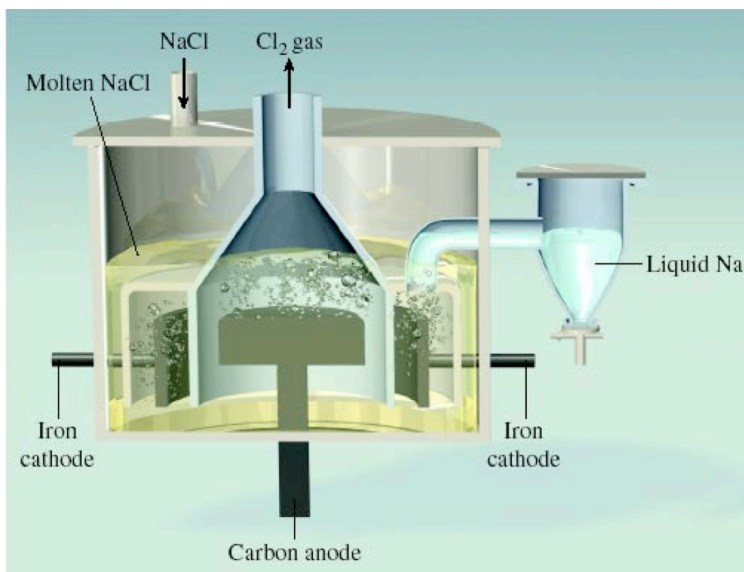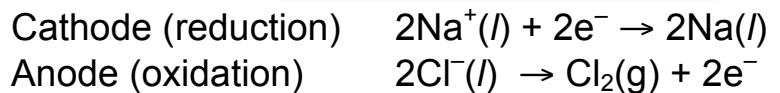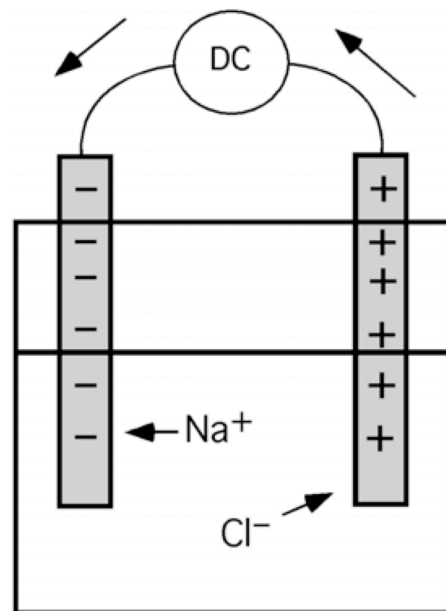
Electrolysis reactions in aqueous solutions
These are more complicated than molten salt electrolysis.

Electrolysis of water
- o overall reaction is $2H_2O(l) \rightarrow O_2(g) + 2H_2(g)$
- o need to add an electrolyte (e.g., H_2SO_4) to provide enough ions to create a current.

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

$2\ H_2O\ (l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$

battery

$-$ $+$

O_2

H_2

e^- e^-

Water

Electrolysis of aqueous sodium chloride

Possible reductions at the cathode:
- o $2H^+(aq) + 2e^- \rightarrow H_2(g)$ $\qquad\qquad\qquad$ $E° = 0$ V
- o $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\qquad$ $E° = -0.83$ V
- o $Na^+(aq) + e^- \rightarrow Na(s)$ $\qquad\qquad\qquad\qquad$ $E° = -2.71$ V

Na^+ will not be reduced because of the large negative $E°$ value. H^+ is not at standard state conditions (it is 10^{-7} M) so the reduction of water is what occurs.

Possible oxidations at the anode:
- $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $E°_{ox} = -1.36$ V
- $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E°_{ox} = -1.23$ V
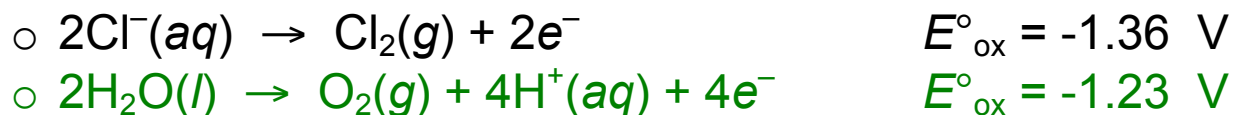
The oxidation of water should occur more readily but
- the conditions are not standard state (typically 25% NaCl)
- the overvoltage for O_2 formation is quite high (≈ 1 V)

As a result the oxidation of Cl^- is what is observed to occur.

The overall reaction is
$2H_2O(l) + 2Cl^-(aq) \rightarrow H_2(g) + 2OH^-(aq) + Cl_2(g)$

Quantitative applications of electrolysis

The amount of product formed is directly proportional to the amount of electrical charge passed through the wire.

electrical current (in amperes) x time (in seconds) = coulombs
$1 A$ x $1 s = 1 C$

1 mole of electrons = 1 Faraday ($\mathcal{F}$) = 9.65 x 10^4 C

e.g., A constant current of 0.912 *A* is passed through an electrolytic cell containing molten $MgCl_2$ for 18 h. What mass of Mg is produced?

Solution:
We know the reduction half-reaction is $Mg^{2+} + 2e^- \rightarrow Mg$

$$\text{grams Mg} = (0.912\ A)(18\ h) \left(\frac{3600\ s}{1\ h} \right) \left(\frac{1\ \text{mol}\ e^-}{9.65 \times 10^4\ C} \right) \left(\frac{1\ \text{mol Mg}}{2\ \text{mol}\ e^-} \right) \left(\frac{24.31\ \text{g Mg}}{1\ \text{mol Mg}} \right)$$

= 7.44 g

e.g., A constant current is passed through an electrolytic cell containing molten $MgCl_2$ for 12 h. If 4.83 L of Cl_2 (at STP) is produced at the anode, what is the current in amperes?

Solution:
We know the oxidation half-reaction is $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

First we convert 4.83 L of Cl_2 to moles

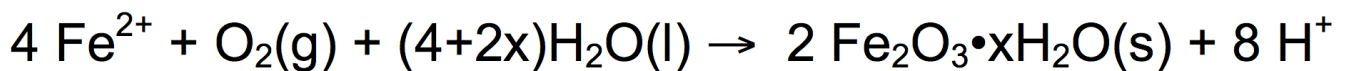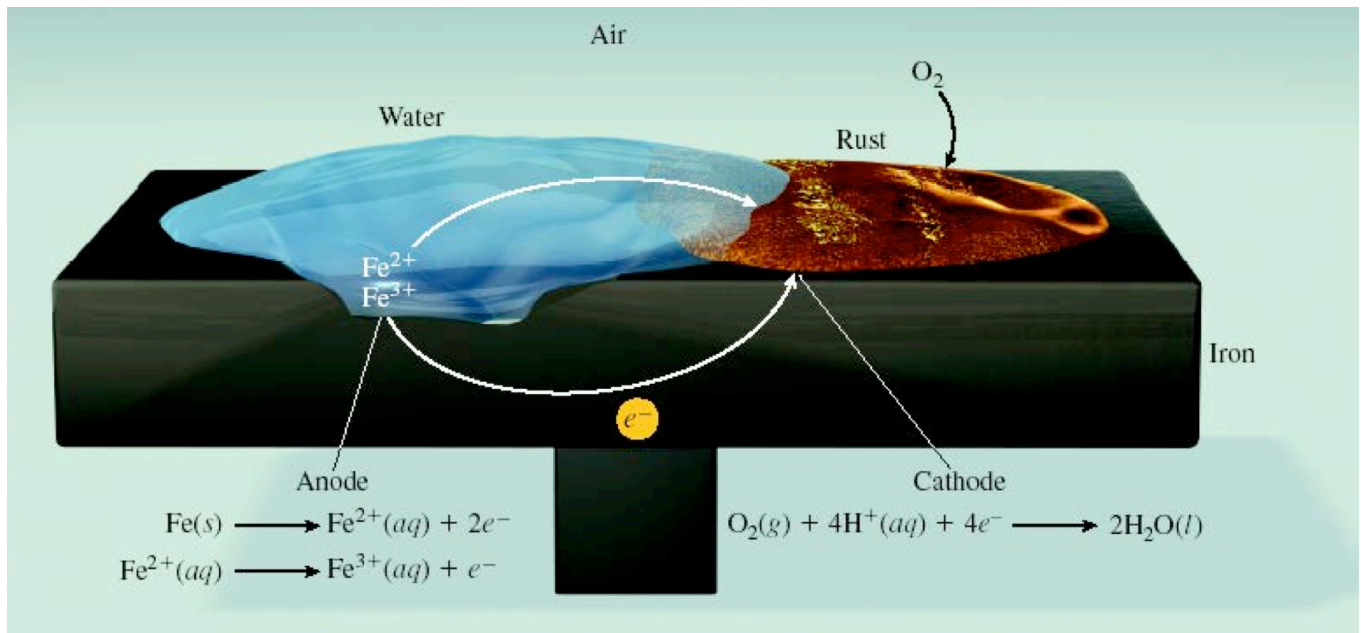$$PV = nRT \implies n = \frac{(1\ \text{atm})(4.83\ \text{L})}{(0.08206\ \text{L atm}\,K^{-1}\,\text{mol}^{-1})(273\ \text{K})} = 0.216\ \text{mol}$$

$$(0.216\ \text{mol}\ Cl_2) \left(\frac{2\ \text{mol}\ e^-}{1\ \text{mol}\ Cl_2} \right) \left(\frac{9.65 \times 10^4\ C}{1\ \text{mol}\ e^-} \right) \left(\frac{1}{12\ h} \right) \left(\frac{1\ h}{3600\ s} \right) = 0.965\ A$$

Corrosion
is the deterioration of a metal by an electrochemical process.
e.g., iron rusts:

$$4\ Fe^{2+} + O_2(g) + (4+2x)H_2O(l) \rightarrow 2\ Fe_2O_3 \cdot xH_2O(s) + 8\ H^+$$

Ways to prevent corrosion
- o passivation (formation of a thin oxide layer by treatment with an oxidizing agent)
- o formation of an alloy (stainless steel)
- o coating with a layer of a less active metal (tin cans)
- o cathodic protection (use zinc or magnesium as a sacrificial metal)