19.7 Cell Potentials under Nonstandard-State Conditions: The Nernst Equation

Cell potentials, like free-energy changes, depend on temperature and on the composition of the reaction mixture—that is, on the concentrations of solutes and the partial pressures of gases. This dependence can be derived from the equation

$$\Delta G = \Delta G^\circ + RT \ \ln Q$$
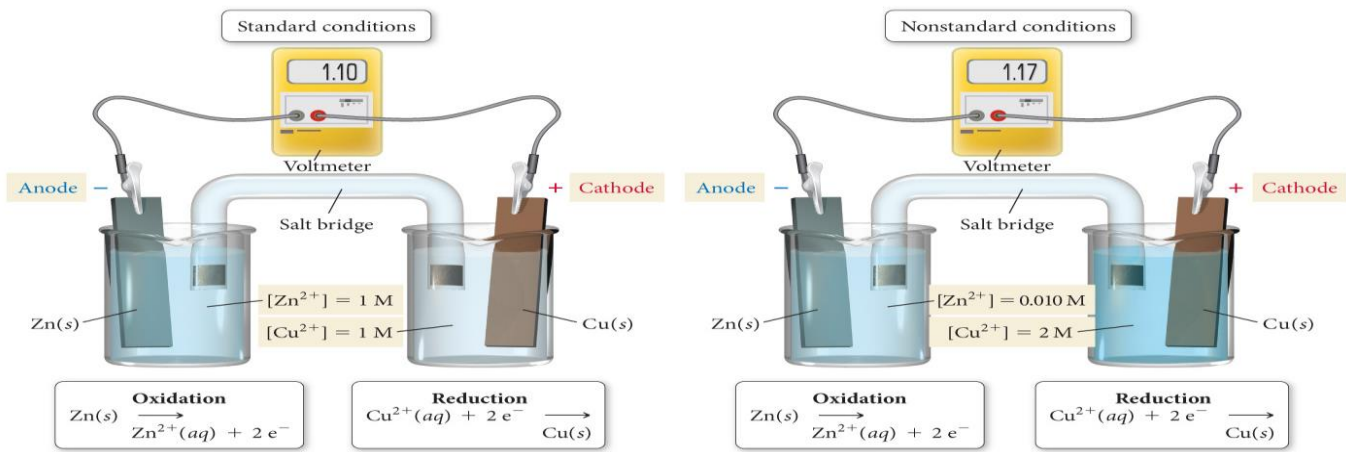$$-nFE_{cell} = -nFE^\circ_{cell} + RT \ \ln Q$$

By dividing -nF, we obtain the Nernst equation

- describe the relationship between E_{cell} and the concentration of species involved in the cell reaction

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

$$E = E^\circ - \frac{\textbf{0.0592 V}}{n} \ \log Q \qquad \text{in volts, at 25 } ^\circ\text{C}$$
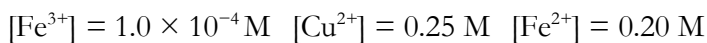
- Changing the concentrations of the reactants and products so they are not 1 M will affect the standard free energy change, ΔG°.

- Because ΔG° determines the cell potential, E^θ_{cell}, the voltage for the cell will be different when the ion concentrations are not 1 M.

- Cell potentials, like free-energy, depend on temperature and on the composition of the reaction mixture-that is, on the concentrations of solutes and the partial pressure of gases.

- It is possible to get a spontaneous reaction when the oxidation and reduction reactions are the same, as long as the electrolyte concentrations are different.

- The difference in energy is due to the entropic difference in the solutions.

- The more concentrated solution has lower entropy than the less concentrated solution

- Electrons will flow from the electrode in the less concentrated solution to the electrode in the more concentrated solution.

  - Oxidation of the electrode in the less concentrated solution will increase the ion concentration in the solution; the less concentrated solution has the anode.

  - Reduction of the solution ions at the electrode in the more concentrated solution reduces the ion concentration; the more concentrated solution has the cathode

Standard conditions — Voltmeter 1.10

Anode − / + Cathode

Salt bridge

Zn(s) — $[Zn^{2+}] = 1\,M$ / $[Cu^{2+}] = 1\,M$ — Cu(s)

Oxidation: $Zn(s) \xrightarrow{} Zn^{2+}(aq) + 2\,e^-$

Reduction: $Cu^{2+}(aq) + 2\,e^- \xrightarrow{} Cu(s)$

Nonstandard conditions — Voltmeter 1.17

Anode − / + Cathode

Salt bridge

Zn(s) — $[Zn^{2+}] = 0.010\,M$ / $[Cu^{2+}] = 2\,M$ — Cu(s)

Oxidation: $Zn(s) \xrightarrow{} Zn^{2+}(aq) + 2\,e^-$

Reduction: $Cu^{2+}(aq) + 2\,e^- \xrightarrow{} Cu(s)$

Example: Consider a galvanic cell that uses the reaction

$$Cu_{(s)} + 2Fe^{3+}{}_{(aq)} \rightarrow Cu^{2+}{}_{(aq)} + 2\,Fe^{2+}{}_{(aq)}$$
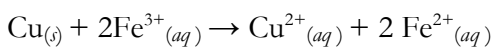
What is the potential of a cell (E_{cell}) at 25 °C that has the following ion concentrations?

$[Fe^{3+}] = 1.0 \times 10^{-4}\,M$ $[Cu^{2+}] = 0.25\,M$ $[Fe^{2+}] = 0.20\,M$

Example: Consider the following galvanic cell:

Digital voltmeter

$e^- \longrightarrow$ $e^- \longrightarrow$

Na^+ NO_3^-

Pb — NO_3^- / Pb^{2+} / NO_3^- NO_3^- — Ag / Ag^+

What is the change in the cell voltage on increasing the ion concentrations in the anode compartment by a factor of 10?

19.9 Standard Cell Potentials and Equilibrium Constant

At equilibrium G = 0 and Q = K $E_{cell} = 0$

Using $\Delta G^\circ = -nFE^\circ$ and $\Delta G^\circ = -RT\ln K$

$-nFE^\circ = -RT\ln K$

$$E^\circ = \frac{RT}{nF} \ln K = \frac{2.303\ RT}{nF} \log K$$

$$E^\circ = \frac{0.0592\ V}{n} \log K$$

in Volts at 25°C

Equilibrium constants for redox reactions tend to be either very large or very small compared to equilibrium constants for acid–base reactions, which are in the range of 10^{14} to 10^{-14} . Thus, redox reactions typically go either essentially to completion or almost not at all.

Figure 19.8 The relationship between the equilibrium constant K for a redox reaction with E°_{cell} and the standard cell potential E°.
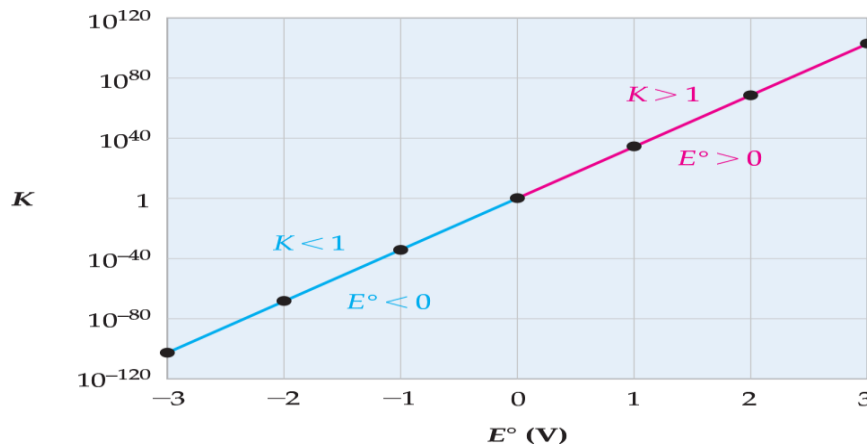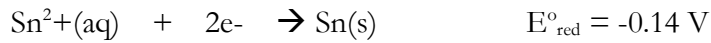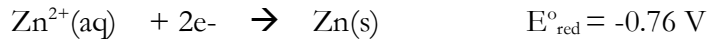

The relationships that we have developed based on properties of the system—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity ($\Delta G^\circ < 0$) can be shown in the triangle below:
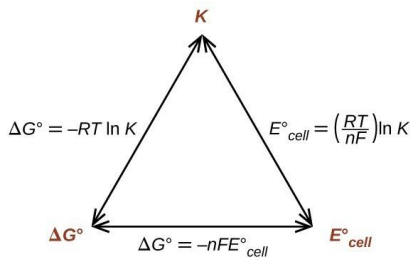
ΔG°	E°_{cell}	K	Direction of reaction
< 0	> 0	> 1	Spontaneous forward
> 0	< 0	< 1	Spontaneous revers
= 0	= 0	= 1	Equilibrium

Dang3

Example: Calculate the equilibrium constant, K_{eq}, for the reaction below

$$Zn^{2+}(aq) + 2e- \rightarrow Zn(s) \qquad E^{\circ}_{red} = -0.76 \text{ V}$$

$$Sn^{2}+(aq) + 2e- \rightarrow Sn(s) \qquad E^{\circ}_{red} = -0.14 \text{ V}$$

Example: What is the value of E° for a redox reaction involving the transfer of 2 mol of electrons if its equilibrium constant is 1.8×10^{-5}?
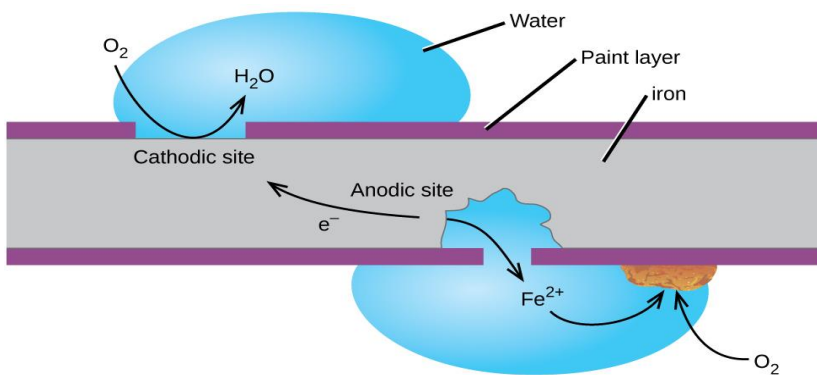
19.10 – Corrosion

- occur when exposing metal to oxidizing agent environment

- some reactant can be defined as the degradation of metals due to an electrochemical process.

   - The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion.
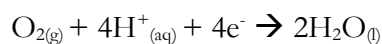
The total cost of corrosion in the United States is significant, with estimates in excess of half a trillion dollars a year.
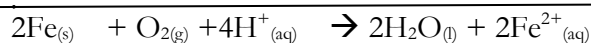

Once the paint is scratched on a painted iron surface, corrosion occurs and rust begins to form. The speed of the spontaneous reaction is increased in the presence of electrolytes, such as the sodium chloride used on roads to melt ice and snow or in salt water.

Dang4

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e- \qquad\qquad E°_{ox} = -0.45V$$

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)} \qquad\qquad E°_{red} = 1.23$$
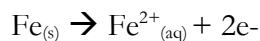
$$2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)} + 2Fe^{2+}_{(aq)} \qquad\qquad E° = 1.68\ V$$

The Fe^{2+} ion formed the anodic regions can migrate through moisture on the surface of the iron to cathodic regions, where they are further oxidized by the reaction with more oxygen.

$$4Fe^{2+}_{(aq)} + O_{2(g)} + (4 + 2n)\ H_2O_{(l)} \rightarrow 2\ Fe_2O_3 \cdot nH_2O_{(s)} + 8H^+_{(aq)}$$
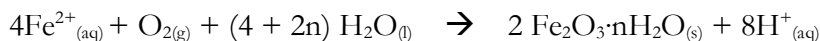
What causes corrosion?

- Moisture must be present for rusting to occur (H_2O is a reactant in the last reaction)

- Additional electrolytes promote rusting (NaCl), enhancing current flow

- The present of acids promote rusting because H^+ ions are involved int the reduction of O_2, lower pH enhances the cathodic reaction, leads to faster rusting.

Prevention:

-painting to keep water away from metals. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron

- Alloying the iron with other metals. For example, stainless steel is mostly iron with a bit of chromium. The chromium tends to collect near the surface, where it forms an oxide layer that protects the iron.

- Cathodic protection is a way to make the metal as a cathode in Galvanic cell.
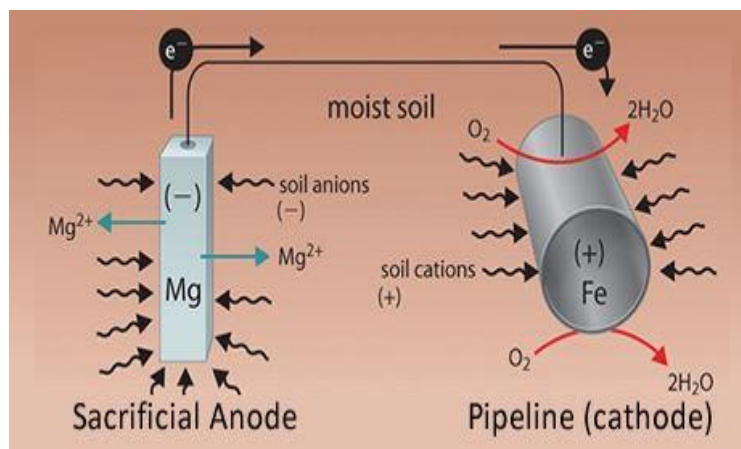
One way to protect an underground iron storage tank is through cathodic protection. Using an active metal like zinc or magnesium for the anode, preventing it from corroding (oxidizing)

19.12 Electrolysis and Electrolytic Cells

- Electrolysis: The process of using an electric current to bring about chemical change

- The processes occurring in galvanic and electrolytic cells are the reverse of each other: A galvanic cell converts chemical energy to electrical energy when a reaction with a positive value of E (and a negative value of) proceeds toward equilibrium; an electrolytic cell converts electrical energy to chemical energy when an electric current drives a reaction with a negative value of E (and a positive value of G) in a direction away from equilibrium.

Table 19.2 Relationship between Cell Potentials E and Free-Energy Changes

| Reaction Type	E	ΔG	Cell Type
Spontaneous	+	–	Galvanic (battery)
Nonspontaneous	–	+	Electrolytic
Equilibrium	0	0	Dead battery

- In electrolytic cells
    - The source of e- is the external source
    - Electrons are drawn off the anode, connected to the positive terminal of the battery.
    - Electrons are forced toward the cathode, connected to negative terminal of the battery.
- Process occurring in galvanic cell and electrolytic cells are the reverse of each other

In an electrolytic cell, two inert electrodes are dipped into an aqueous solution

- The reaction that takes place is the opposite of the spontaneous process.

    $2 H_{2(g)} + O_{2(g)} \rightarrow 2 H_2O_{(l)}$ spontaneous

    $2 H_2O_{(l)} \rightarrow 2 H_{2(g)} + O_{2(g)}$ electrolysis
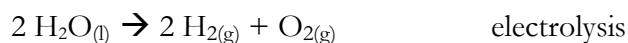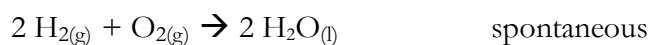
- Some applications are
- metal extraction from minerals and purification,
- production of H_2 for fuel cells,
- metal plating.
- The electrical energy is supplied by a direct current power supply.
- AC alternates the flow of electrons so the reaction won't be able to proceed.
- Some electrolysis reactions require more voltage than E_{cell} predicts. This is called the overvoltage.
- The source of energy is a battery or DC power supply.
- Electrolyte can be either an aqueous salt solution or a molten ionic salt.
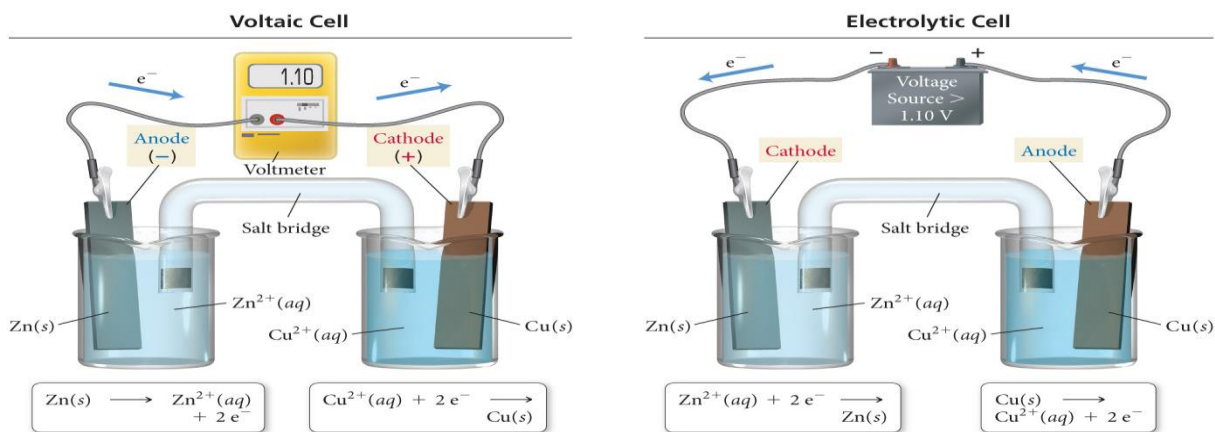
Electrolysis of Molten Sodium Chloride

An electrolytic cell has two electrodes that dip into an electrolyte and are connected to a battery or some other source of direct electric current. A cell for electrolysis of molten sodium chloride, for example, is illustrated in **Figure 19.13**. The battery serves as an electron pump, pushing electrons into one electrode and pulling them out of the other.
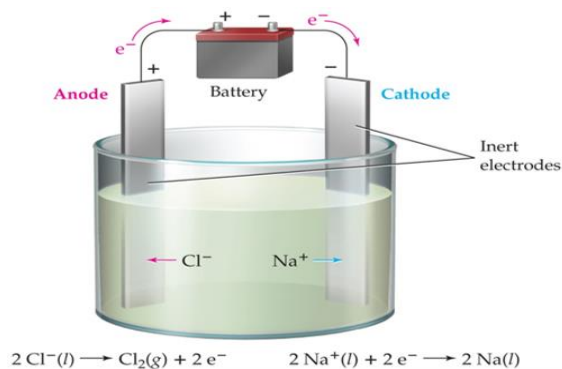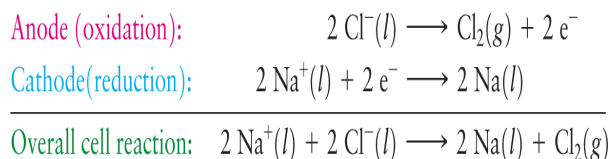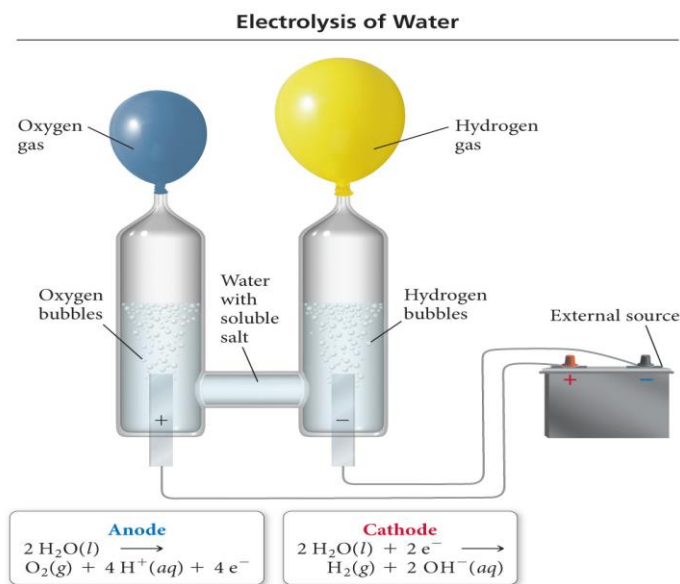
Anode (oxidation): $2 Cl^-(l) \longrightarrow Cl_2(g) + 2 e^-$

Cathode (reduction): $2 Na^+(l) + 2 e^- \longrightarrow 2 Na(l)$

Overall cell reaction: $2 Na^+(l) + 2 Cl^-(l) \longrightarrow 2 Na(l) + Cl_2(g)$

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

Figure 19.13 Electrolysis of molten sodium chloride

Electrolysis of Water

Water decomposes into oxygen and hydrogen gas during electrolysis. H_2SO_4 was added to increase the concentration of H^+ and the total ions in solution, but does not take part in the reaction.

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

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

Write the net-equation:

19.14 Quantitative Aspects of Electrolysis

Quantitative Aspects of Electrolysis and Stoichiometry of Electrolysis

Recall: Charge (C) = Current (A) x Time (sec)

Faraday constant: 96,500 C/mole e-

In electrolytic cell, electrical current is used to drive a particular chemical reaction. The electron act as a reactant and therefore have a stoichiometric relationship with another reactants and products
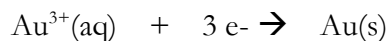
Cu^{2+}(aq)   +   2e-   →   Cu(s)

1mol ion   2 mole e-   1 mol Cu = 63.55 g
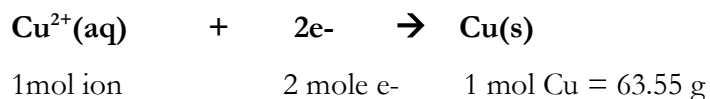
Ratio: 2 mol e- : 1 mole Cu(s)

Redox stoichiometry: Electric current   →   moles electrons → moles sample   →   grams

Grams →   moles   →   mole e- →   minutes

Example: Gold can be plated out of a solution containing Au^{3+} according to the half-reaction

Au^{3+}(aq)   +   3 e- →   Au(s)

What mass of gold (in grams) is plated by a 25 minutes flow of 5.5 A current?

Example: A constant current of 30.0 A is passed through an aqueous solution of NaCl for 1.00 h. How many grams of NaOH and how many liters of Cl_2 gas at STP are produced?

*Read the following section in the text.   Students are responsible for the types of batteries and what substance(s) are used at the anode and cathode.

19.10 Batteries

Battery is an electrochemical cell or series that produces an electric current.

- Ideal battery would never run down, produce an unchanging voltage, and be capable of withstanding environmental extremes of heat and humidity.

- There are two basic types of batteries: primary and secondary.

Primary batteries

- Single-use batteries because they cannot be recharged. A common battery is the dry cell called zinc-carbon battery (flashlight battery).

- **Alkaline batteries**

- Same basic cell as acidic dry cell, except electrolyte is alkaline, KOH paste

- Cell voltage = 1.54 V

- Longer shelf life than acidic dry cells and rechargeable, with little corrosion of zinc.

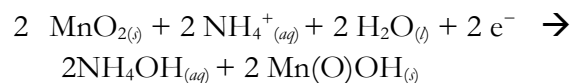- Deliver three to five times the energy of a zinc-carbon dry cell of similar size.

- Anode = Zn (or Mg)

- $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\ e^-$
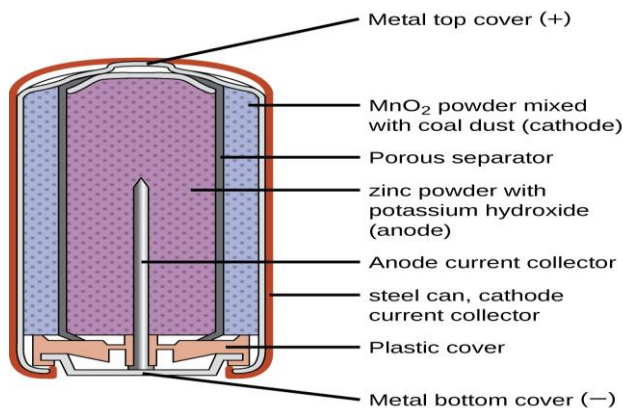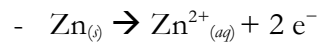
- Cathode = graphite or brass rod

- MnO_2 is reduced.

$2\ MnO_{2(s)} + 2\ NH_4^+_{(aq)} + 2\ H_2O_{(l)} + 2\ e^- \rightarrow 2NH_4OH_{(aq)} + 2\ Mn(O)OH_{(s)}$
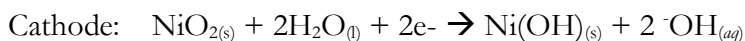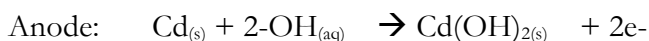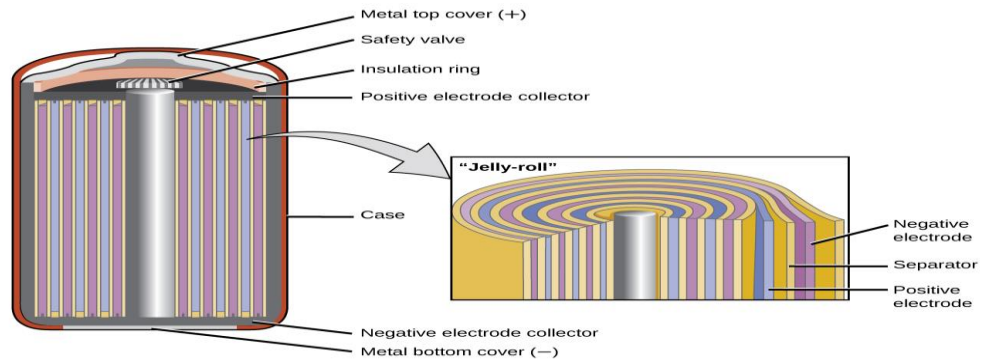
Secondary Battery

- Are rechargeable and found in devices such as smartphones, electronic tablet and automobiles.

Nickel-Cadmium

- consist of a nickel-platted cathode, cadmium-plated anode, and a potassium hydroxide electrode. The negative and positive plates, are rolled together and put into the case to allow the NiCd cell to deliver much more current than a similar-sized alkaline battery. The voltage is about 1.2V – 1.25 Vas the battery discharges. When treated properly, a NiCd can be recharged about 1000 times. Cadmium is a toxic heavy metal so the battery should not be put into a regular trash.

Anode: $Cd_{(s)} + 2\text{-}OH_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e\text{-}$

Cathode: $NiO_{2(s)} + 2H_2O_{(l)} + 2e\text{-} \rightarrow Ni(OH)_{(s)} + 2\ ^-OH_{(aq)}$

Lithium ion battery

- Charge flows between the electrodes as the lithium ions moves between the anode and cathode.

- Provide a large amount of current, are lighter than comparable batteries of other types, produces a nearly constant voltage as they discharge, and only slowly lose their charge when stored.
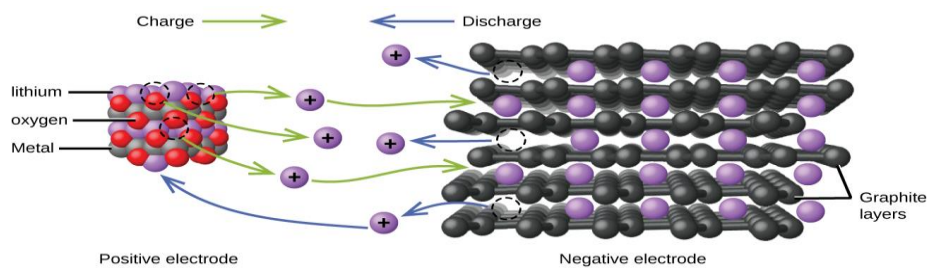

Lead Acid battery

Both the anode and cathode are immersed in H_2SO_4.   As electrical current is drawn from the batter, both electrodes become coated with $PbSO_4(s)$.   However, if the battery run for a long time without recharging, too much $PbSO_4(s)$ develops on the surface of the electrode and the battery goes dead.
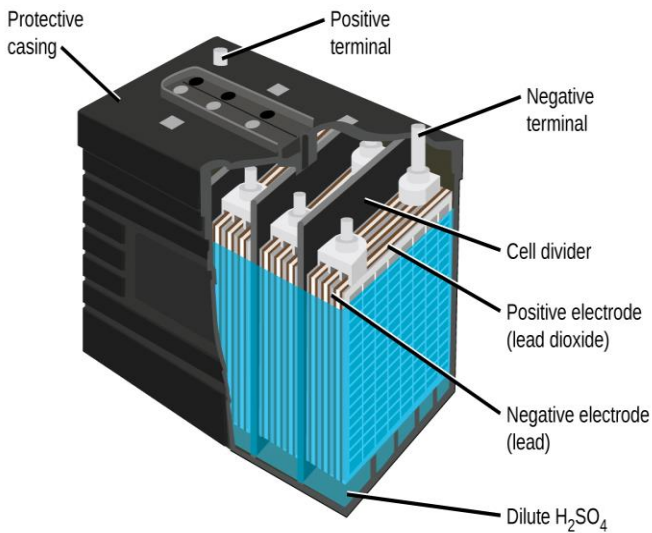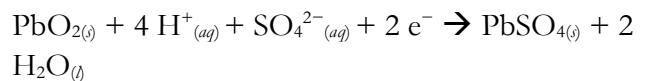

Six cells in series

Electrolyte = 30% H_2SO_4

Anode = Pb

$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2\ e^-$
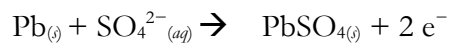
Cathode = Pb coated with PbO_2

PbO_2 is reduced .

$PbO_{2(s)} + 4\ H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2\ e^- \rightarrow PbSO_{4(s)} + 2\ H_2O_{(l)}$

Cell voltage = 2.09 V

Rechargeable, heavy