General Chemistry II
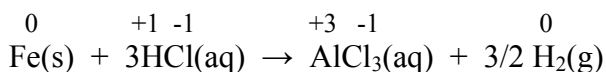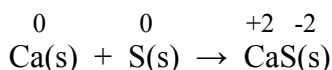## Chapter 19 Lecture Notes

Electrochemistry

Introduction

Electrochemistry deals with interconversion of electrical and chemical energy. Many chemical changes can be clearly related to the electrons that move from one species to another. Often, this electron exchange can be captured to do electrical work external to the chemical system (storage battery, fuel cell). Other times, electrical energy can be used to bring about chemical change (electrolysis, battery charging, etc.).

Redox Reactions

In redox reactions, electrons are transferred from one species to another. A species losing electrons is said to be oxidized; one gaining electrons is said to be reduced. The two processes together are called redox. One can never occur without the other although they can be studied separately.

In redox reactions, it is useful to write the oxidation numbers of each species above the formula to track oxidation and reduction.

$$\overset{0}{Ca}(s) + \overset{0}{S}(s) \rightarrow \overset{+2\ -2}{CaS}(s)$$

$$\overset{0}{Fe}(s) + \overset{+1\ -1}{3HCl}(aq) \rightarrow \overset{+3\ -1}{AlCl_3}(aq) + \overset{0}{3/2\ H_2}(g)$$

Balancing Redox Reactions

The above redox reactions are easy to balance by inspection. Others are more difficult, such as those involving the interaction of the oxyanions CrO_4^{-2}, $Cr_2O_7^{-2}$, NO_3^{-1}, MnO_4^{-1} with water, hydroxide ion or hydrogen ion. Note that in the reaction

$$NO_3^{-1}(aq) + 2H^{+1}(aq) \rightarrow NO_2(g) + H_2O(l)$$
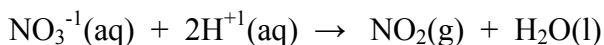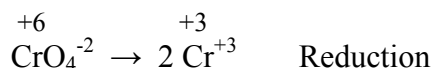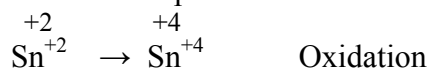
the atoms are balanced but electrons are not. *Both mass and charge must be balanced in any chemical reaction.* How to ensure that both are balanced without spending a lot of time? How to gain insight into the process? Use the **ion-electron method** which divides the reaction into two half reactions, one for oxidation and one for reduction.
Balance each half reaction separately, leaving out water, hydrogen ion and hydroxide ion until the end and then combine the equations so that electrons cancel out. Then the redox reaction is balanced.
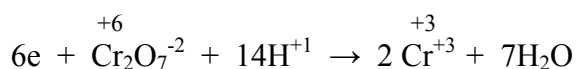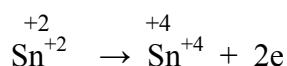
Ex: Balance the reaction between tin(II) and chromate ion in acid solution to give tin(IV) and chromium(III) as chromic ion. Note that in many of the stated problems, acid is not shown and the products water, H^{+1} and OH^{-1} are left out initially.

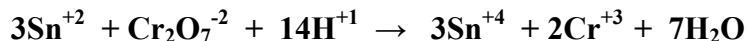$$Sn^{+2}(aq) \ + \ Cr_2O_7^{-2}(aq) \ \rightarrow \ Sn^{+4}(aq) \ + \ Cr^{+3}(aq)$$
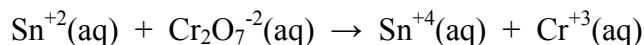
Write the oxidation and the reduction equations separately, with the oxidation numbers written above each species. Write the electrons lost or gained by each. Balance all atoms except H and O.

$$\overset{+2}{Sn^{+2}} \ \rightarrow \ \overset{+4}{Sn^{+4}} \qquad \underline{Oxidation}$$

$$\overset{+6}{CrO_4^{-2}} \ \rightarrow \ 2 \ \overset{+3}{Cr^{+3}} \qquad \underline{Reduction}$$

The reaction takes place in acid, but this has no effect on the tin atoms. In the half-reaction involving chromium, the only way protons can be accommodated is to use them to make water from the dichromate oxygen atoms. Once the necessary H and O atoms have been balanced, finish balancing the half-reactions by inserting electrons as reactants in the reduction equation and as products in the oxidation equation.

$$\overset{+2}{Sn^{+2}} \ \rightarrow \ \overset{+4}{Sn^{+4}} \ + \ 2e$$

$$6e \ + \ \overset{+6}{Cr_2O_7^{-2}} \ + \ 14H^{+1} \ \rightarrow \ 2 \ \overset{+3}{Cr^{+3}} \ + \ 7H_2O$$

Then multiply each equation by the coefficient that will make the number of electrons lost the same as the number gained, add the equations together to cancel the electrons. Check for mass and *charge* balance.
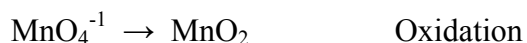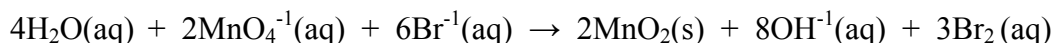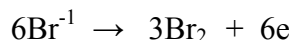
$$3Sn^{+2} \ \rightarrow \ 3Sn^{+4} \ + \ 6e \qquad\qquad\qquad \underline{Oxidation}$$

$$6e \ + \ Cr_2O_7^{-2} \ + \ 14H^{+1} \ \rightarrow \ 2 \ Cr^{+3} \ + \ 7H_2O \qquad \underline{Reduction}$$

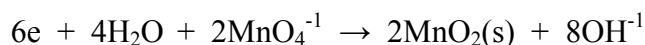$$\mathbf{3Sn^{+2} \ + \ Cr_2O_7^{-2} \ + \ 14H^{+1} \ \rightarrow \ 3Sn^{+4} \ + 2Cr^{+3} \ + \ 7H_2O}$$
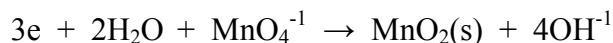
Equation is balanced in atoms and charge

Some redox reaction rules:
- If an oxyanion loses its oxygens, they are converted to water in an acidic medium or converted to hydroxide ion in a basic medium.
- In an acidic medium, hydrogen ion must be consumed or created.
- In a basic medium, hydroxide ion must be created or consumed.

Ex: Balance the equation $MnO_4^{-1}(aq) + Br^{-1}(aq) \ \rightarrow \ MnO_2(s) \ + \ Br_2(aq)$

$$MnO_4^{-1} \ \rightarrow \ MnO_2 \qquad \underline{Oxidation}$$

$$Br^{-1} \ \rightarrow \ Br_2 \qquad \underline{Reduction}$$

$$2H_2O + \overset{+7}{MnO_4^{-1}} \rightarrow \overset{+4}{MnO_2}(s) + 4OH^{-1}$$

$$2\overset{-1}{Br^{-1}} \rightarrow \overset{0}{Br_2}$$

$$3e + 2H_2O + MnO_4^{-1} \rightarrow MnO_2(s) + 4OH^{-1}$$

$$2Br^{-1} \rightarrow Br_2 + 2e$$

$$6e + 4H_2O + 2MnO_4^{-1} \rightarrow 2MnO_2(s) + 8OH^{-1}$$

$$6Br^{-1} \rightarrow 3Br_2 + 6e$$

$$4H_2O(aq) + 2MnO_4^{-1}(aq) + 6Br^{-1}(aq) \rightarrow 2MnO_2(s) + 8OH^{-1}(aq) + 3Br_2(aq)$$
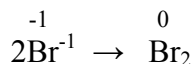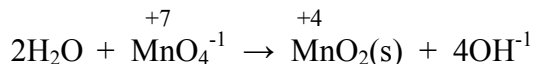
Electrochemical Cells

An electrochemical or *voltaic* or *galvanic* cell is an experimental apparatus for generating an electric current with a *spontaneous* redox reaction. Practical applications include the many kinds of batteries, which generate electric current for practical purposes. Electrochemical cells have various refinements so they will generate reproducible voltages under standard conditions.

(Contributions of Allesandro Volta and Luigi Galvani)

The (historic) Daniell cell: (Use in old west telegraph offices)
Define (Zn) Anode, (Cu) Cathode, Need to keep the reactants separate (Why?)
External connection for electrons, $CuSO_4$(aq) and $ZnSO_4$(aq) electrolytes.
The inert sulfate (or chloride, nitrate, etc.) counterions do not often affect emf.
Detailed description of Daniell cell, oxidation and reduction processes and external circuitry

The difference between the anode and cathode emfs is the measured emf (electromotive force or voltage) of the cell and is characteristic of that cell. Emf of the Daniell Cell is 1.10 volt at 25^oC.

Cell diagram convention with anode written to the left: $Zn(s) |Zn^{+2}$ (1M)$||Cu^{+2}$ (1M)$| Cu(s)$

Standard Reduction Potentials

Standard refers to 25^oC, 1 atm pressure and 1M electrolyte solutions. (Oxidation potentials were once tabulated but the convention now is to use reduction reactions.) To find the corresponding *oxidation* cell potential, simply reverse the direction of the reaction and change the emf sign. (Make use of Table 19.1)
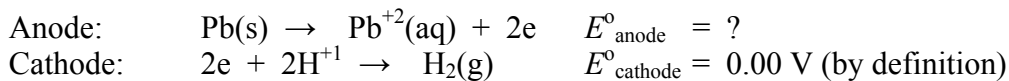
- The cell voltage (cell potential electromotive force, emf or *E)* of the Daniell Cell or any other cell can be calculated from the tabulated standard electrode potentials of the anode and cathode materials.
- However, there can be no oxidation without a simultaneous reduction so it is impossible to know the **absolute emf** for the reduction of any **one** substance.
- Only the *difference* between two half-cell emfs can be determined experimentally, that is by measuring the emf of a real cell.
- It is useful to have a table of *relative* emfs. These are tabulated as *Standard Reduction Potentials* for *Half Reactions* of the form M^{+n}(aq) (1M) + ne $\rightarrow$ M(s).
- The cell potentials of real cells are calculated by adding the appropriate reduction cell potential to the appropriate oxidation cell potential.
- One half-reaction, the reduction of 1 M hydrogen ion on a (catalytic) platinum electrode to hydrogen gas at 1 atm is arbitrarily assigned a standard reduction potential of zero volts.
  $2H^{+1}$ (aq) (1M) + 2e $\rightarrow$ H_2(g) (1atm) E^o = 0.00 volt *by definition*
- All other half-cell potentials are calculated relative to the hydrogen half-cell voltage. Any other arbitrarily chosen hydrogen half-cell voltage would give the same values (differences) for the calculated cell potentials of *real* cells. If the reduction cell potential for hydrogen were given as 3.00 V instead of 0.00 V, all other reduction cell potentials would be 3.00 V higher and the differences between them would stay the same.

Page 775 of the Chang text tabulates 49 reduction cell potentials under standard conditions which can be combined to calculate the E^o values of many real or hypothetical cells.
- The most positive E^o values represent reactions with the greatest forward tendency and the most negative E^o values represent reactions with the greatest backward tendency.
- The equations are all reversible and any electrode can be used as an anode or as a cathode.
- In principal, under standard-state conditions, any combination of oxidation half-cell and reduction half-cell reactions where the reactants are physically separated, will proceed spontaneously if E^o is greater than zero. If E^o is negative, the reaction will not proceed spontaneously. Its reverse reaction, having a positive E^o will be spontaneous.
- How are reactants kept physically separated (and why) by the KCl bridge.

Ex: Calculate the standard half cell reduction potential of lead metal if the measured E^o of the cell $Pb(s) | Pb^{+2}$(1M) $|| H^{+1}$(1 M) $| H_2$(1 atm)$| Pt(s)$ is + 0.13 V.

The anode where oxidation occurs is listed first. The double bar refers to the salt bridge. The right side of the cell diagram refers to the cathode where reduction occurs.
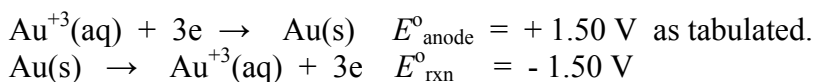
Anode: $Pb(s) \rightarrow Pb^{+2}$(aq) + 2e E^o_{anode} = ?
Cathode: 2e + $2H^{+1} \rightarrow H_2$(g) $E^o_{cathode}$ = 0.00 V (by definition)

E^o_{cell} = $E^o_{cathode}$ - E^o_{anode} = 0.00 V - E^o_{anode} = +0.13 V
E^o_{anode} = 0.00 V - 0.13 V = - 0.13 V

Ex: What is the emf of the (hypothetical) cell I_2 (s) $| I^{-1}$(1M) $|| Au^{+3}$ (1M) $| Au(s)$ |? Is the reaction of the cell as written spontaneous? Write the spontaneous chemical reaction that occurs in the cell.
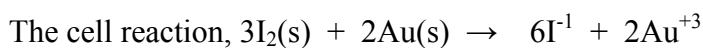
The anode reaction (oxidation) comes first (left) in the cell diagram so the direction of the equation and the sign of the $E°$ value *in the table* must changed.

$I^{-1}(aq) \rightarrow I_2(s) + 2e$ $E°_{cathode} = -0.53V$
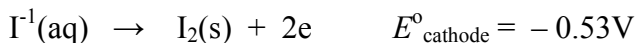
The cathode reaction is on the right where reduction occurs as it is written in table 19.1.

$Au^{+3}(aq) + 3e \rightarrow Au(s)$ $E°_{anode} = +1.50\ V$ as tabulated.
$Au(s) \rightarrow Au^{+3}(aq) + 3e$ $E°_{rxn} = -1.50\ V$

$E°_{cell} = E°_{cathode} - E°_{anode} = +0.53\ V - (+1.50\ V) = -0.97\ V$

The cell reaction, $3I_2(s) + 2Au(s) \rightarrow 6I^{-1} + 2Au^{+3}$
The spontaneous reaction is the reverse, where iodide is reduced by auric ion to elemental iodine.
$6I^{-1} + 2Au^{+3} \rightarrow 3I_2(s) + 2Au(s)$

Spontaneity of Redox Reactions

How does $E°_{cell}$ relate to ΔG, and K_{eq}?
The Electrical Work done *by* a voltaic cell or done *on* an electrolytic cell is the same as the *Free (useful) Energy*, ΔG.

How to calculate Electrical Work?   (Contrast actual work obtained with W_{max})

Electrical work done is the movement of charge (electrons) across an electrical gradient, the voltage.
Electrical Energy(J) = emf(volts or J/cou) x charge(cou)

Electric charge(cou) = no of electrons x charge per electron (inconvenient)
            = moles of electrons x electric charge per mole
            = n(mol) x F(coulombs/mol)
            = n(mol) x 96,485.3 coulombs/mol

Electrical Energy = - emf(volts or J/cou) x electric charge(cou)
            = - $E°_{cell}$ (volts) x n(mole) x F(cou/mol)

        $W_{max} = -nFE_{cell}$ or $\Delta G = -nFE_{cell}$

Earlier, $\Delta G = -RTlnK$ $\therefore nFE_{cell} = RTlnK$ and

    $E_{cell} = (RT/nF)\ lnK_{eq}$

$R = 8.314$ J/K and, under standard conditions, $(T = 298K)$

$E°_{cell}$ (V) = $(0.0257/n)ln\ K_{eq}$ or since $ln\ K_{eq} = 2.302\ log\ K_{eq}$, then

E^o_{cell} (V) = (0.0592/n)log K_{eq}

(This equation will be supplied for tests. Know how to solve for both E_{cell} and K_{eq}.

Now can calculate K_{eq} values from measured cell potentials or E_{cell} values from measured K_{eq}

Ex: Calculate the (difficult to measure) K_{eq} of any cell reaction using half-cell reduction potentials.
Under standard conditions, calculate K_{eq} for the reaction $Ag^{+1}(aq) + Al(s) \rightarrow 3Ag(s) + Al^{+3}(aq)$

To get E^o_{cell} values, add together the actual half cell potentials for the two reactions as they occur:
or S*ubtract* the listed reduction potential for the anode (*oxidation*) from the listed reduction
potential for the cathode (reduction).

E^o_{cell} = E^o_{Ag}(actual, reduction) + E^o_{Al} (actual, oxidation) = +0.80V + +1.66V = +2.46V
or

E^o_{cell} = E^o_{Ag}(actual, reduction) − E^o_{Al} (as a reduction)   = +0.80V − −1.66V = +2.46V

Now calculate K_{eq} from E_{cell} (V) = (0.0592/n)log K_{eq}

log K_{eq} = E_{cell} x (3/0.0592) = 2.46 x (3/0.0592) = 125

K_{eq} = 1 x 10^{125} (This value could not have been obtained from reactant concentrations)
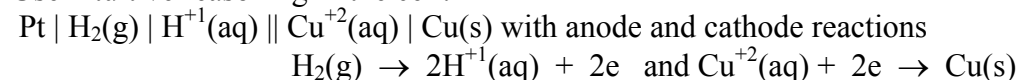

The Effect of Concentration on Cell Emf

Just as the direction of equilibrium is affected by changing reactant and product concentrations, so
is the Emf of a cell can be affected by changing concentrations of cell components.

The Nernst Equation:

Remember the effect of reactant and product concentration of the direction of equilibrium.

Similarly, cell component concentrations affect the cell Emf (E_{cell}).
Use intuitive reasoning in the cell:
 Pt | H_2(g) | H^{+1}(aq) || Cu^{+2}(aq) | Cu(s) with anode and cathode reactions
                    H_2(g) $\rightarrow$ $2H^{+1}$(aq) + 2e and Cu^{+2}(aq) + 2e $\rightarrow$ Cu(s)

The overall reaction is H_2(g) + Cu^{+2}(aq) $\rightarrow$ $2H^{+1}$(aq) + Cu(s)

The forward reaction is driven by increased pH_2, and $[Cu^{+2}]$.
The backward reaction is favored by increased $[H^{+1}]$.
How to quantify these facts?

E under conditions other than standard (1M, 1 atm) is given (without derivation) by
The Nernst Equation:

$$E = E^o - (0.0592/n)\log Q$$

Under standard conditions when all concentrations are 1M, $Q = 1$, $\log Q = 0$ and $E = E^o$.

Ex: Calculate *E* for the cell: $Zn(s) \mid Zn^{+2}(aq) \parallel Br^{-1}(aq) \mid Br_2(l) \mid$ under standard conditions and when $Zn^{+2}(aq) = 3.00$ M and $Br^{-1}(aq) = 2.00$ M.
The overall cell reaction is: $Zn(s) + Br_2(l) \leftrightarrow Zn^{+2}(aq) + 2Br^{-1}(aq)$
Zinc metal (written first in the cell diagram) is the anode and $Br_2(l)$ acts as the cathode.

$E^o_{cell} = E^o_{cathode} - E^o_{anode} = +1.07V -- 0.76V = +1.83V$

Raising $Zn^{+2}(aq)$ *and* $Br^{-1}(aq)$ both shift the equilibrium to the left and will lower E_{cell}

$E_{cell} = E^o_{cell} - (0.0592/n)\log Q = +1.83V - (0.0592/2)\log 6.00 = +1.83V -$
$(0.0592/2)(0.778)$
$$= +1.83V - 0.0230 = +\mathbf{1.81V}$$

Ex: At what $[Fe^{+2}]/[Cd^{+2}]$ ratio will the voltaic cell $Fe(s) \mid Fe^{+2}(aq) \parallel Cd^{+2}(aq) \mid Cd(s)$ have zero Emf?
The anode (oxidation) reaction is $Fe(s) \rightarrow Fe^{+2}(aq) + 2e \qquad E = -0.44$ V
The cathode (reduction) reaction is $Cd^{+2} + 2e \rightarrow Cd(s) \qquad E = -0.40V$
The allover reaction is $Fe(s) + Cd^{+2}(aq) \rightarrow Fe^{+2}(aq) + Cd(s)$

$E^o_{cell} = E^o_{cathode} - E^o_{anode} = -0.40V -- 0.44V = +0.04V \qquad$ (a very small positive Emf)

Zero Emf means $E_{cell} = 0.00V$
$E_{cell} = E^o_{cell} - (0.0592/n)\log Q$, so when $E_{cell} = 0.00V$,
$E^o_{cell} = +(0.0592/n)\log Q$
$+0.04V = +(0.0592/2)\log Q$

$\log Q = +0.04V \cdot (2/0.0592) = 1.35$ (good to one significant figure)

$Q = [Fe^{+2}]/[Cd^{+2}] = 22 \cong 2 \times 10^1$
(Does this make sense intuitively? Look at the overall reaction.)

Concentration Cells

Since the concentrations of cell components can influence cell Emf, a cell can be constructed having the same metal for anode and cathode and the same metal ions, but at different concentrations in the two parts of the cell.

A Concentration Probe can be constructed from a metal anode and its (for convenience) 1M cation solution with a salt bridge which is inserted in a solution of the same metal of unknown

concentration. A small Emf will be generated that depends on the concentration of the metal ion solution being tested (and on the number of electrons transferred).

From the Nernst Equation, $E = E^o - (0.0592/n)\log Q$

E^o is zero since both anode and cathode are the same material.

Therefore, $E = -(0.0592/n)\log Q$

$\log Q = -nE/(0.0592)$

(Note that since E^o is zero, the Emf generated by such a cell depends on the ratio of the anode and cathode cell concentrations, and not on the nature of the reacting species. Moreover, it does not matter if the concentration ratio or its reciprocal is used. The sign will change but not the magnitude of the ratio. A test solution concentration less than 1M will give a positive E; one with a higher concentration will have a negative E value.

Ex: What is the concentration of a $Zn^{+2}(aq)$ solution when a 1M Zn^{+2} probe gives a voltage of +0.014V?

$\log Q = -nE/(0.0592) = -2 \times (+0.014V)/(0.0592) = -0.47$

$Q = [Zn^{+2}]/[1M\ Zn^{+2}] = 0.34$

The unknown solution has $[Zn^{+2}] = 0.34M$

Batteries

The tem battery comes form a series or pile of cells that can be used as a source of direct current at a constant voltage. Modern commercial batteries are constructed to deliver a constant voltage for most of their lifetime, be self-contained, leak-proof and with convenient external electrodes.
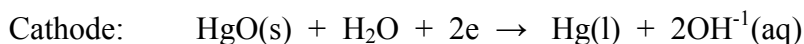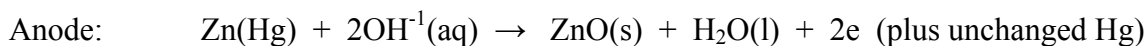
The Dry Cell Battery

(Almost) dry as opposed to the wet Daniell cell. Used in flashlights and cheap electronics, the Leclanché cell delivers 1.5 V using a zinc can as the anode that contains an ammonium chloride-zinc chloride-starch paste designed (almost) to prevent leakage. Higher voltages are attained by wiring several cells in series. The anode is a conductive (unreactive) graphite rod in contact with solid manganese dioxide. Anode and cathode reactions are respectively

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

$$2NH_4^{+1}(aq) = 2MnO_2(s) + 2e \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$$
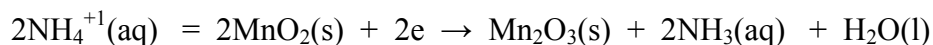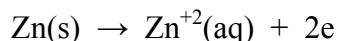
Battery life ends when much of the MnO_2 is used up or extensive *polarization* of the electrolyte occurs. (A rest from service is helpful) Dead dry-cell batteries leak in time and ruin equipment.
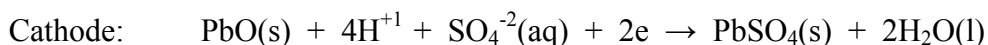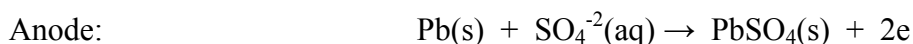
The Mercury Battery

Consists of *amalgamated* zinc anode and a stainless steel casing which supports the mercuric oxide cathodic material. Only the solid components change, not the electrolyte, keeping volume and internal pressure constant. Used in high-end applications where removing battery is inconvenient.

Anode: $Zn(Hg) + 2OH^{-1}(aq) \rightarrow ZnO(s) + H_2O(l) + 2e$ (plus unchanged Hg)

Cathode: $HgO(s) + H_2O + 2e \rightarrow Hg(l) + 2OH^{-1}(aq)$

The Lead Storage Battery

The 2 V lead –acid battery is rechargeable. Must be kept upright to prevent spillage of sulfuric acid electrolyte. Automotive 6V and 12V (soon 42V?) batteries are built from multiple cells. Loss of power in cold weather is due to increased viscosity of cold electrolyte which hinders movement of ions.

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

Cathode: $PbO(s) + 4H^{+1} + SO_4^{-2}(aq) + 2e \rightarrow PbSO_4(s) + 2H_2O(l)$

The sulfuric acid electrolyte changes to water as the battery is discharged, with a corresponding decrease in viscosity which can be measures with a hydrometer.

Charging a battery requires the input of electrical energy from the generator which reverses the reactions and replenishes the battery's "charge". Battery engineering involves building longer-lasting batteries that sustain little electrode damage in repeated charge-discharge cycles. Batteries are recycled to recover the expensive and environmentally harmful lead metal.

The Solid State Lithium Battery

Nontoxic lithium has the largest reduction potential on the table and has the lowest density, making a battery that has a high power/weight ratio.

Fuel Cells

Many fuels are burned in internal or external combustion engines to produce power for locomotion or electric generation. These engines are notoriously inefficient. In a fuel cell the electrons could be captured during the (redox) burning, electric generation would be more efficient. Oxygen and

fuels such as hydrogen or simple hydrocarbons are bubbled over catalytic metal electrodes where oxidation and reduction takes place under standard, not flame conditions. .

Anode: $2H_2(g) + 4OH^{-1}(aq) \rightarrow 4H_2O(l) + 4e$

Cathode: $O_2(g) + 4H_2O(l) + 4e \rightarrow 4OH^{-1}(aq)$
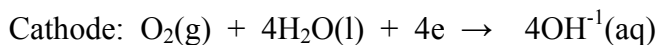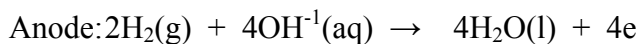
$E^o_{cell} = E^o_{cathode} - E^o_{anode} = +0.40 \text{ V} - (-0.83\text{V}) = 1.23 \text{ V}$
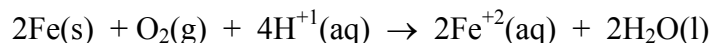

Corrosion

Corrosion is defined as the deterioration of metal by an electrochemical process. Rusting of iron metal is the prime example. Other examples are pitting of aluminum and the patina on outdoors copper and brass.

Iron rusts in the presence of moisture and air which supplies oxygen and CO_2 which gives H^{+1} via H_2CO_3.

Anode: (iron surface) $Fe(s) \rightarrow Fe^{+2}(aq) + 2e$

Cathode: (also the iron surface) $O_2(g) + 4H^{+1}(aq) + 4e \rightarrow 2H_2O(l)$

The overall redox reaction is

$$2Fe(s) + O_2(g) + 4H^{+1}(aq) \rightarrow 2Fe^{+2}(aq) + 2H_2O(l)$$

$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 1.23 \text{ V} - (-0.44\text{V}) = +1.67 \text{ V}$

Iton(II) is then oxidized by atmospheric O_2 to Fe(III), forming the familiar red-brown flaky solid hydrated iron(III) oxide $Fe_2O_3 \cdot xH_2O$ that we call rust.

Coating iron with paint helps as long as the paint film stays intact.
Alloys of iron with carbon and chromium give "stainless steel", expensive but durable. (Building codes require stainless steel nails and screws in certain seaside areas.)
Aluminum corrodes very quickly in air but is protected by the <u>adherent</u> aluminum oxide film. (Iron rust is flakes off and does not protect.)

Cathodic Protection relies on the preferential corrosion of magnesium metal electrically connected to an underground iron structure. The flow of electrons to the iron resulting from $Mg(s) \rightarrow Mg^{+2} + 2e$ opposes the analogous oxidation of iron,

$$Fe(s) \rightarrow Fe^{+2}(aq) + 2e$$
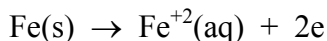
Electrolysis

Electrolysis means literally taking apart with electricity. Electrolysis is a nonspontaneous chemical change produced by electrical energy. It is used commercially to prepare many reactive metals in their elemental form and to prepare fluorine and chlorine gas.

Electrolysis of Molten Sodium Fluoride

Elemental chlorine can be used to oxidize bromide ion to elemental bromine. How would one prepare elemental fluorine, already the strongest elemental oxidizing agent. There is no other halogen with a higher electronegativity that can take electrons away from F^{-1} to make F_2. The solution is to supply the energy from an outside source, a battery, which can supply any voltage. Typically NaF or KF is melted to mobilize the ions. The anode must be an inert material such as graphite to prevent attack by fluorine. The cathode must be a metal which will not amalgamate with molten sodium and the products must be kept separate to prevent the highly exothermic reaction between fluorine gas and molten Na.
(Extreme reactivity of F_2 gas with water, glass and asbestos. Fatal consequences of inhaling F_2.)

Anode: $2F^{-1}(l) \rightarrow F_2(g) + 2e$
Cathode: $2Na^{+1} + 2e \rightarrow 2Na(l)$
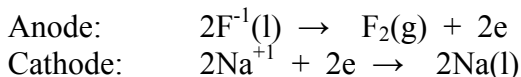
$E^o = E^o{}_{anode} - E^o{}_{cathode} = -2.87\ V - (+2.71\ V) = -5.58\ V$

The large negative E^o shows this is a highly endothermic process requiring a large energy input to drive it. There are no existing cells with E^o approaching 5.58 V but any number of cells of lower E^o can be wired in series to get a voltage of the desired value.

This is the commercial method typically used to prepare pure alkali metals which otherwise could not be prepared from their salts or solutions.

Electrolysis of Water

Electrolysis of water is a common laboratory demonstration. Do not expect water to decompose spontaneously to hydrogen and oxygen.

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \qquad \Delta G = +474.4\ kJ$$
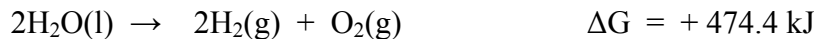
The reaction can be easily driven by an electrical current. Pure water is made conductive with sulfuric acid, chosen because sulfate anion is not easily oxidized.

Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^{+1}(aq) + 4e$
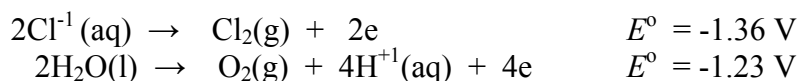Cathode: $4H^{+1}(aq) + 4e \rightarrow 2H_2(g)$
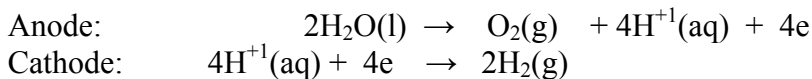
If the gases are collected separately in burets, the volume of hydrogen is exactly twice that of oxygen, illustrating their molar volumes. Why is it important to keep the evolved hydrogen and oxygen gases separate? (Incidental dangerous electrolysis of water in nuclear reactors.)

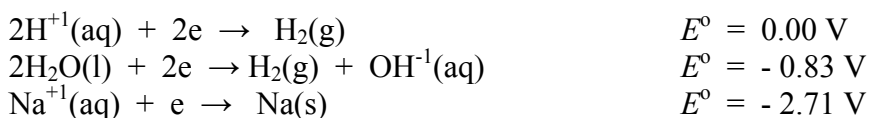**Electrolysis of Aqueous Sodium Chloride Solution**

The result of electrolyzing this solution is not as predicted. The solution contains the oxidizable species chloride and water and the reducible species water, hydrogen ion and sodium ion. What actually is produced in electrolysis of this mixture?

The oxidation of chloride and water have almost the same $E°$.

$$2Cl^{-1}(aq) \rightarrow Cl_2(g) + 2e \qquad\qquad E° = -1.36 \text{ V}$$
$$2H_2O(l) \rightarrow O_2(g) + 4H^{+1}(aq) + 4e \qquad E° = -1.23 \text{ V}$$

Oxygen should be oxidized preferentially at the anode but it is not. Chlorine gas is formed because of the *overvoltage* for water oxidation. (Overvoltage, the difference between the calculated and the actual voltage needed to produce electrolysis is a common phenomenon.)

Possible cathode reactions are:

$$2H^{+1}(aq) + 2e \rightarrow H_2(g) \qquad\qquad E° = 0.00 \text{ V}$$
$$2H_2O(l) + 2e \rightarrow H_2(g) + OH^{-1}(aq) \qquad E° = -0.83 \text{ V}$$
$$Na^{+1}(aq) + e \rightarrow Na(s) \qquad\qquad E° = -2.71 \text{ V}$$

This time the predicted reaction occurs; hydrogen ion is preferential reduced and hydrogen gas evolves. Other useful products of the *Chlor-alkali* process are chlorine gas and sodium hydroxide.
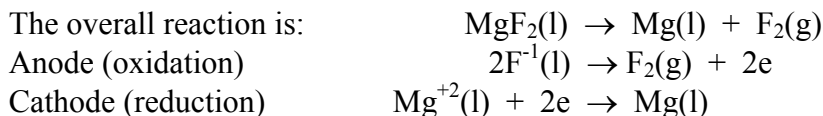

Quantitative Aspects of Electrolysis

Faraday observed that the mass of metal deposited by electrolysis was proportional to the amount of current that flowed through the cell.
Electric current flow is expressed in amperes, and by definition,

Charge(coulombs) = Current(amperes) x Time(s) and
1 mole of electrons = 96500 coulombs

Ex: A 0.430 amp current flowed through a molten magnesium fluoride electrolysis cell for 1 hour, 35.0 minutes. What mass of magnesium and what mass of fluorine was produced?

The overall reaction is: $\qquad MgF_2(l) \rightarrow Mg(l) + F_2(g)$
Anode (oxidation) $\qquad\qquad 2F^{-1}(l) \rightarrow F_2(g) + 2e$
Cathode (reduction) $\qquad Mg^{+2}(l) + 2e \rightarrow Mg(l)$

First, calculate moles of electrons, then calculate moles of fluorine and magnesium.

Charge(coulombs) = Current(amperes) x Time(s)
= 0.430 amp x 5700 s = 1.05 x 10^3 coulomb (Total charge that flowed through the cell.)

1.05 x 10^3 coulomb x 1 mole of electrons/96500 coulombs = 1.09 x 10^{-2} mol electrons

1.09 x 10^{-2} mol electrons x (1 mol Mg/2 mol electrons) x (24.31 g Mg/mol Mg) =
= **0.133 g Mg**

1.09 x 10^{-2} mol electrons x (1 mol F_2/2 mol electrons) x (38.00 g F_2/mol F_2) =
= **0.207 g F_2**

An electrolytic cell can also be used to determine total charge flow or size of current.

Ex: If 1.456 g of silver was deposited in 1.500 hours from Ag^{+1} solution, what was the current flow?

1.456 g Ag x (1 mol Ag/107.9 g Ag) = 1.349 x 10^{-2} mol Ag = 1.349 x 10^{-2} mol electrons

1.349 x 10^{-2} mol electrons x (96,485.3 coulombs/mol electrons) = 1302 coulombs

Charge(coulombs) = Current(amperes) x Time(s)

Current(amperes) = Charge(cou)/Time(s) = 1302 coulombs/5400. s = **0.2411 amps**