AP Chemistry
Chapter 20 Outline

A. Oxidation States
   a. Rules for assigning <u>oxidation numbers</u>:
      i. Uncombined elements have an oxidation number of 0.
      ii. For monatomic ions, the ion charge is the oxidation number.
      iii. In compounds, hydrogen usually has an oxidation number of +1
         1. In metal hydrides, hydrogen has an oxidation number of -1.
      iv. In compounds, oxygen usually has an oxidation number of -2.
         1. In peroxides, oxygen has an oxidation number of -1.
         2. In a binary compound with fluorine, oxygen has an oxidation number of +2.
      v. In compounds, fluorine always has an oxidation number of -1.
      vi. The sum of the oxidation numbers is 0 for a neutral compound
      vii. For a polyatomic ion, the sum of the oxidation numbers is the charge of a the ion.
   b. A <u>redox reaction</u> is a reaction in which oxidation numbers change
         *If one substance loses electrons, another substance must gain electrons
      i. Oxidation = loss of electrons
         1. When a substance is oxidized, its oxidation number increases
      ii. Reduction = gain of electrons
         1. When a substance is reduced, its oxidation number decreases.
      iii. Mnemonics: LEO the lion says GER, or OIL RIG
      iv. The species that is oxidized is the REDUCING AGENT
      v. The species that is reduced is the OXIDIZING AGENT

B. Balancing oxidation-reduction reactions
   a. Both mass and charge must be conserved.
      i. Use "half reactions", i.e., write out the oxidation step and the reduction step separately
      ii. The number of electrons lost must equal the number of electrons gained.
   b. <u>Balancing redox reactions</u>
      i. Write skeletons for the oxidation and reduction half reactions.
      ii. For each half reaction,   BE SURE YOU CAN DO THIS!
         1. Balance the elements other than H and O.
         2. Add H_2O to balance O atoms.
         3. Add H^+ to balance H atoms.
         4. Add e^- to balance charge; the sum of the charges should be the same on both sides.
         5. Multiply the half-reactions by integers to equal the numbers of electrons in both half reactions.
         6. Add the two half-reactions and simplify.
      iii. If balancing in basic conditions, then add OH^- to neutralize any H^+ and simplify.

C. Voltaic Cells (aka galvanic cells)
   a. The energy released in a spontaneous redox reaction can be used to perform electrical work.
      i. Physically separate the reduction half from the oxidation half to create a flow of electrons through an external circuit.
   b. A electrode is a strip of solid metal, connected to external circuit
      i. The anode is the electrode where oxidation occurs
         1. Negative electrode (by convention)
         2. During reaction, the anode will lose mass (as metal turns into ions in solution)
      ii. The cathode is the electrode where reduction occurs
         1. Positive electrode (by convention)
         2. During reduction, the cathode will gain mass (as ions gaining electrons deposit on electrode)
      iii. Useful mnemonics:
         1. AN OX
         2. RED CAT
   c. A half cell is a (metal) electrode immersed in a solution of its own ions
      i. anode solution will become more concentrated during reaction
      ii. cathode solution will become less concentrated during reaction
      iii. Electrons travel from the anode through the external wire to the cathode.
      iv. Salt bridge = allows ions to move to maintain charge neutrality in both half-cells
         1.   Anions travel toward the anode
         2.   Cations travel toward the cathode
You need to be able to generate correctly labeled sketches of the components of a voltaic cell

D. Cell EMF under standard conditions
   a. 1 volt = 1 J/1 C   (a couloumb is a mole of electrons)
   b. Electrons flow from the anode to the cathode because of a difference in potential energy.
      i. Potential energy of electrons is higher in the anode than in the cathode.
      ii. Electromotive force (EMF) is the potential difference that pushes electrons through the external circuit
      iii. Cell potential = the EMF of a voltaic cell = cell voltage = E_{cell}
      iv. For spontaneous reactions (i.e. voltaic cells), $E_{cell} > 0$
      v. Standard conditions = 1 M concentration, 1 atm (for gases), $25^{o}C$
   c. Standard reduction potential = a measure of the tendency of a reduction half-reaction to occur, relative to a standard= E^{o}
      i. Standard hydrogen electrode $E^{o} = 0$ by convention
      ii. The more positive the value of E^{o}, the greater the tendency of the reactant of the half-reaction to be reduced.
         1. Half reaction with the higher E^{o} → stronger oxidizing agent

  iii. The more negative the value of E^o, the less tendency for this reduction reaction to occur
    1. i.e, the reverse, oxidation half-reaction becomes more likely!
    2. Half reaction with the lower E^o → stronger reducing agent
  iv. Tabulated for many reduction half-reactions
  v. E^o is an intensive property!
    1. *Multiplying a half-reaction by a constant value does not change the value of E^o*

 d. To find E_{cell},
  i. Find half-reactions on table of standard reduction potentials
  ii. The reaction that is higher: keep as written (i.e., reduction)
    This reaction occurs at the CATHODE
  iii. The reaction that is lower: reverse, and change the sign of E^o
    This reaction occurs at the ANODE
  iv. The sum of the Eo values gives E_{cell}
  v. The sum of the reactions (after equalizing the number of e- lost and gained) gives the overall reaction for the cell

E. Free energy and redox reactions
 a. Any reaction that can occur in a voltaic cell to produce a positive EMF must be spontaneous.
  i. A positive EMF value indicates a spontaneous process.
  ii. A negative EMF value indicates a non-spontaneous process.
 b. $\Delta G^o = -nFE^o$ You need to be able to apply this equation

  n = the number of electrons transferred in the reaction
  $\mathcal{F}$ = Faraday's constant = the quantity of electrical charge on one mole of electrons = 96485 C/mol

F. Cell EMF under nonstandard conditions
 a. As a battery runs, the reactant and product concentrations change. Eventually, the battery is "dead."
  i. A dead battery is a system at equilibrium!
  ii. Cell EMF depends on reactant and product concentrations
 b. Nernst equation
  i. In general, if reactants increase relative to products, EMF increases
  ii. If products increase relative to reactants, EMF decreases
  iii. $E_{cell} = E^o - \dfrac{0.0592}{n} log Q = E^o - \dfrac{0.0592}{n} log \dfrac{[products]}{[reactants]}$
  iv. As Q increases, E_{cell} will decrease
  v. If Q decreases (perhaps if the concentration of reactants is altered when the cell is constructed), Ecell will increase compared to E^o
 c. Concentration cell = cell based solely on the EMF generated because of a difference in concentration
  i. E^o = 0 for these cells, so the ratio of product to reactant concentrations in the two half-cells is responsible for E_{cell}
  ii. Basis for pH meters & function of nerve cells

You are not expected to know sections 20.7 and 20.8 in any detail for the AP exam

G. Electrolysis
  a. It is possible to use electrical energy to cause non-spontaneous redox reactions to occur.
      i.   Electrolysis reactions = reactions driven by an outside source of electrical energy
      ii. E_{cell} is < 0
  b. Electrolytic cells consist of two electrodes in a molten salt or solution
      i.   Oxidation occurs at the anode
      ii.   In electrolytic cells, the anode is the positive electrode
      iii. Reduction occurs at the cathode
            In electrolytic cells, the cathode is the negative electrode
      iv.   For a more detailed discussion of electrolysis reactions, go to the packet on electrolysis from the Ultimate Chemical Equations book.
  c. Quantitative aspects of electrolyis
      i.   Couloumb = amperes x seconds
      ii. To calculate the quantities of substances involved in an electrolytic process:
           1.

$$grams\ metal = (amperes) \times (\sec onds)\left(\frac{1mole\ e-}{96485\ C}\right)\left(\frac{1mole\ metal}{n\ e-}\right)\left(\frac{gfm\ of\ metal}{1\ mole}\right)$$

           2. n = number of electrons needed to go from cation to neutral atom for that metal
      You must be able to do these calculations!