Electrochemistry

I. Basics:

A. Electrochemistry-

1. The study of systems in which electricity plays a role in the changes that occur during a reaction.
2. **Redox reaction**- a reaction in which a transfer of electrons takes place.
   a. One reactant is the electron acceptor, **oxidizing agent**,
   b. The other reactant is the electron donor, **reducing agent**.
   c. **Reduction**- the process in which electrons are gained by a reactant.
   d. **Oxidation**- the process in which electrons are donated by a reactant.

B. Galvanic Cells:

1. **Galvanic Cell**- a battery in which the power comes from a spontaneous redox reaction in which electron transfer is forced to take place through a wire.
   a. **Half-cells**-the separate containers used in the galvanic cells that house the solutions, electrodes, and salt bridge as connectors between the cells.
      i. Silver electrode(cathode) dipped into a solution of silver nitrate,
      ii. Copper electrode(anode) into a solution of copper nitrate.
      iii. The electrodes are connected to each other through an external electrical circuit.
      iv. The two solutions in the half cells are connected with a salt bridge.

When the circuit is completed, the reduction of the silver cation, Ag^+, to Ag occurs spontaneously, and oxidation occurs spontaneously of $Cu \rightarrow Cu^{2+} + 2e^-$. The electrons are then transferred through the wire and are used in the reduction of the silver ions.

C. Net overall reaction-

1. **Cell reaction**- the overall reaction that takes place in the galvanic cell. It is obtained by summing the half reactions together.
   a. ***Make sure to balance the electrons prior to adding the chemical equations.*** (Review ion-electron method)
2. **Cathode**- the electrode at which reduction occurs.
3. **Anode**- electrode at which oxidation takes place.

D. Conduction-

1. **Metallic conduction**-when the electrons are moved through a wire as mentioned above. From anode to the cathode.
2. **Electrolytic conduction**- when the transport of charge is achieved through the movement of ions through the liquid.

   ***Note for a galvanic cell to work, the solutions in the half cells must b e electrically neutral.**

   a. this is what drives the movement of the electrons.

   i. the accumulation of the ions in the solution causes an attraction of the opposite ion into that half cell.

   1. For instance, the reduction of the silver ions then attracts positive charge to the negative charges.
3. **Salt Bridge**- a tube filled with a solution of salt composed of ions not involved in the cell reaction. The tube has porous plugs at the ends the prevent the solution from pouring out while still allowing the bridge to exchange ions with the solutions of the half cells.

   a. Often KCl or KNO_3

   b. The negative ions diffuse from the salt bridge into the copper half cell or Cu^{2+} ions leave the solution into the salt bridge to help maintain a neutral solution in the half cell.

   c. Positive ions from the salt bridge can enter the cell or the NO_3^- ions can leave the half cell again to keep the half cell neutral.

E. Charges on the electrodes-

1. Anode→

   a. Copper atoms spontaneously leave the electrode and enter the solution as Cu^{2+} ions.

   b. This results in a slightly negative charge from the electrons being left behind that is referred to as negative polarity.
2. Cathode→

   a. Silver ions from the solution come to the electrons that have been brought through the wire to the silver electrode.

   b. This results in the electrode acquiring a slightly positive character referred to as a positive polarity.

***Note- the solution has the opposite charge than that of the electron it surrounds!**

F. Cell notation-

1. Standard cell notation:

$\boldsymbol{Anode(s)electrode} \vdots \boldsymbol{anode\ electrolyte(aq)} \vdots\vdots \boldsymbol{cathode\ electrolyte(aq)} \vdots \boldsymbol{cathode(s)electrode}$

⋮ - represents the phase boundary that exist between the solid electrode and the aqueous solution that surrounds

⁝⁝ **-** represents the salt bridge.

II. Cell potentials and reduction potentials:

A. Basics-

1. **<u>Potential</u>**- the magnitude of the ability of a galvanic cell to push electrons through the external circuit.
   a. **<u>Volt (V)</u>**- the potential's electrical unit. Defined as the amount of energy, in joules, that can be delivered per SI unit of charge, the coulomb, as the current moves through the circuit.
   1 V = 1 J/C

2. **<u>Cell potential</u>**- the maximum potential that a given cell can generate.
   a. The voltage/potential of a galvanic cell varies with the amount of current flowing through the circuit.
   b. The cell potential varies according to three factors:
      i. Composition of electrodes,
      ii. Concentrations of the ions in the half cells,
      iii. Temperature.
3. **<u>Standard Cell potential</u>**- In order to compare potentials for different cells, the potential of the cell in which all of the ion concentrations are 1.00 M, the temperature is 25°C, and any gases that are involved in the cell reaction are at a pressure of 1 atm.

   ***Note- most cells have potentials that are less than 2 V, to get higher potentials, the cells can be arranged in series.**

4. **<u>Reduction potential</u>**- the magnitude of the half cell's tendency to acquire electrons and proceed as a reduction. If done under standard conditions, then it is referred to as the **<u>standard reduction potential.</u>**
   Notation- the ion being reduced is subscript→ E°_{ion}

   This is still the difference between the standard reduction potential of the substance in the reduced form and the oxidized form.

   When two half cells are connected, the half cell with the higher reduction potential acquires electrons from the half cell with the lower reduction potential, thereby forcing it to undergo oxidation.

In the silver/copper galvanic cell,

$Ag^+(aq) + e^- \rightarrow Ag(s)$

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

are the two reduction reactions. The silver ions must have a greater tendency to proceed through the reduction. In other words, the standard reduction potential for silver is larger than that of the copper reaction. This is what drives the copper reaction towards oxidation.

Therefore,

$$E^\circ_{cell} = E^\circ_{larger} - E^\circ_{smaller} = E^\circ_{reduced} - E^\circ_{oxidized} = E^\circ_{Ag^+} - E^\circ_{Cu^{2+}}$$

5. **Standard hydrogen electrode**- a reference electrode that is used because the standard reduction potential has arbitrarily chosen to be 0 V.
   a. Gaseous hydrogen is bubbled at a pressure of 1 atm over a platinum electrode coated with very finely divided platinum. This finely divided platinum provides a large catalytic surface for the electrode reaction to occur.
   $2\ H^+\ (aq\ 1M) + 2e^- \rightleftharpoons H_2\ E^\circ_{H^\circ}$
   b. The charge on the electrodes will reveal which is the cathode and which is the anode. Positive→cathode; Negative→anode.
   c. The voltage potential can then be deciphered by
   $E^\circ_{cell} = E^\circ_{larger} - E^\circ_{smaller}$ **or** $E^\circ_{reduced} - E^\circ_{oxidized}$

   By measuring the voltage potential, E_{cell} , the smaller is that of hydrogen, leaving only the larger potential left to calculate algebraically.
6. When comparing the reduction potentials of two half reactions, the more positive the potential, the more likely it shall undergo reduction. When comparing two reactions found on a table, the one on top(more positive) is the one that shall undergo reduction. The other shall undergo oxidation in which the potential value's sign must be reversed.
7. Redox reactions predicted with potentials:
   a. If the reaction's potential is positive, then the forward reaction is spontaneous.
   b. If the reaction's potential is negative, then the reverse reaction is spontaneous.

III. Cell potentials are related to free energy changes-

A. Relationship-

1. There must be a relationship if the potential can determine spontaneity, which is normally Gibb's territory.

$-\Delta G$ = maximum work=nFE°_{cell} **n- the # of moles of electrons transferd**
F- 9.65 e 4 C/ mol electrons

F-Faraday's constant is calculated by the number of coulombs of charge equivalent to 1 mol of electrons.

$\Delta G = -nFE^\circ_{cell}$ can then be used as the relationship.

2. This implies that the equilibrium constants can be calculated from the potential of the cell.

$-RT\ln K_c = \Delta G = -nF E^{\circ}_{cell}$ can then be manipulated to yield

$$E^{\circ}_{cell} = \frac{RT}{nF} \ln K_C$$ **R-8.314, T-Kelvin, n-# mol of e transfrd.**

3. This relationship can be furthered as follows:

$\Delta G = \Delta G^{\circ} + RT \ln Q$ can be used in conjunction with $\Delta G = -nF E^{\circ}_{cell}$ to yield:

$$E_{cell} = E^{\circ}_{cell} + \frac{RT}{nF} \ln Q$$

IV. Batteries –examples of galvanic cells

A. Basics:

1. **Primary cell**- Not designed to be recharged portable galvanic cells that are able to produce electrical energy.
2. **Secondary cells**- galvanic cells that are able to be recharged for repeated use of electrical energy.

B. Lead storage battery:

1. Several secondary cells that each have a potential of about 2V that are connected in series so that their voltages are additive.
2. One cell in the battery has anode made of lead plates and the cathode made of PbO_2 with the electrolyte of sulfuric acid to yield the following net equation:

   $PbO_2(s) + Pb(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O$

   As the battery uses up the energy, the sulfuric acid ($2H^+(aq) + 2HSO_4^-(aq)$) is used up. Therefore, the sulfuric acid density in the battery is proportional to the amount of charge left.

3. The advantage of the lead battery is that it can be recharged by being exposed to an external potential through electrolysis.
4. Disadvantage is that it is heavy, and sulfuric acid is corrosive and can spill.
5. Modern batteries use lead-calcium alloy as the anode which allows for the batteries to be sealed. The new alloy doesn't need venting.

C. Zinc-magnesium dioxide batteries:

1. Typical battery that you might use in a flashlight that produces about 1.5V.
   a. Outer shell made of zinc, anode, with the exposed bottom negative end,
      i. Oxidation of zinc occurs at the anode- $Zn(s) \rightarrow Zn^{2+} + 2e^-$
   b. Cathode, positive terminal of the battery, consists of a carbon(graphite) rod surrounded with a moist paste of graphite powder, manganese dioxide, and ammonium chloride.
      i. With so many reactants there are many reactions taking place, but the major one that takes place: $2MnO_2(s) + 2NH_4^+(aq) + 2e^- \rightarrow MnO_3(s) + 2NH_3(aq) + 2H_2O$
      ii. The ammonia, $NH_3(aq)$, reacts with the zinc cation to form a complex ion of $Zn(NH_3)_4^{+2}$… Many more complex reactions.

2. The disadvantage is that these type of batteries cannot stand heavy current drain.
   a. But if unused they can rejuvinate themselves.
   b. Cannot be recharged.

3. Alkaline batteries are also used. The same reactants as above, but under basic conditions.

D. Nickel-Cadmium batteries

1. Produces a voltage of about 1.4V.
2. Anode is made of cadmium coating over a steel mesh – $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$
3. Cathode is made of metal support with a porous coating of Nickel that holds NiO_2 which places Ni in its +4 oxidation state- $NiO_2(s) + 2H_2O \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$
4. Net cell reaction- $Cd(s) + NiO_2(s) + 2H_2O \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$
5. Can be recharged by reversing the above reactions to remake the reactants.
6. Can be sealed, can release energy quickly, and recharge quickly which make them good candidates for electronic devices. Only problem is that the cadmium is toxic to dispose.

E. Silver Oxide battery:

1. Miniature batteries found in watches and calculators.
2. $Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$ at the anode.
3. $AgO(s) + H_2O + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$ at the cathode.
4. To yield the net reaction: $Zn(s) + AgO(s) + H_2O \rightarrow Zn(OH)_2(s) + 2Ag(s)$

F. High performance batteries:

1. **Energy density**- the ratio of the energy available to the volume of the battery.
2. **Specific energy**- the ratio available energy to weight.
3. **Nickel metal hydride batteries**- secondary cells that are used in cell phones, camcorders, and even electric vehicles.
   a. The reactions are similar to the nickel-cadmium reactions except hydrogen is the anode reactant is hydrogen.
      i. The hydrogen, a gas at room temperature, is used in conjunction with metal alloy to yield a metal hydride allowing hydrogen to participate in reversible reactions.

b. Anode- $MH(s) + OH^-(aq) \rightarrow M(s) + H_2O + e^-$
c. Cathode- $NiO(OH)(s) + H_2O + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$
d. Net cell reaction- $MH(s) + NiO(OH)(s) \rightarrow Ni(OH)_2(s) + M(s)$
e. Can store about 50% more energy than its nickel-cadmium counterpart of equal volume; however, they lose their charge quickly.

4. **Lithium batteries**- Due to the fact that lithium has the lowest reduction potential of all the metals; therefore, it can easily undergo oxidation. Also a very light weight metal.
   a. Reacts violently with water, so initial problem was to avoid unwanted water had to be eliminated from the reaction process. Without aqueous electrolytes, the organic solvent of lithium salt had to be used.
   b. **Lithium ion cell**- a lithium battery that uses lithium ions instead of metallic lithium.

G. Fuel cells-
1. Electrochemical cell in which the electrode reactants are supplied continuously, not in typical redox form, and are able to operate without a theoretical limit as long as the reactants are replenished.
2. Example- Hydrogen-oxygen cell:
   Cathode- $O_2(g) + 2H_2O + 4e^- \rightarrow 4OH$

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

   Net cell reaction- $2H_2(g) + O_2(g) \rightarrow 2H_2O$

3. The advantage is that the fuel cell is no electrode material to replace. Fuel can be fed to continue yielding power.

V. Electrolysis:

A. Basics:
1. When electricity is passed through a molten(melted) ionic compound or through a solution of an electrolyte.
   a. The molten metal or electrolytic solution is exposed to electricity that takes the electrons back to their original positions.
   b. The current acts as a pump that pulls electrons away from one electrode and places them on the other.
      i. This results in one electrode being negatively charged and the other that lost its electrons shall be positive.

B. Electrolytic vs. Galvanic cells
1. Electrolytic cell:
   a. Cathode is negative→ reduction takes place
   b. Anode is positive→ oxidation takes place

2. Galvanic cell:
    a. Cathode is positive→ reduction takes place
    b. Anode is negative→oxidation is negative.
3. The reason they are switched is as follows:
    a. The negatively cathode, for instance, when placed in the molten solution shall be negative and attract a layer or coating of positively charged cations.
    b. When the current is run, the positive cations are then reduced by the negative cathode.
    c. This then causes the neutral atom to leave the electrode freeing up a space for another cation.
    d. The anode has supplied the electrons to give the cathode a negative charge(thanks to the current applied), and therefore, is positive. This results in a coating of anions, and then a similar process occurs as the cathode in which the anions are oxidized, neutralized, and then replaced.
    e. For aqueous solutions, competing redox reactions occur with that of water.
4. The reduction potentials can be used to determine the electrolysis products that would result.
    a. By examining the half reactions that are possible at the cathode, reduction, and the anode, oxidation.
    b. After determining which species shall be oxidized and which shall be reduced,
        i. The reduced and oxidized product shall become part of the net cell reaction equation.
        ii. Doesn't always work because concentration of ions and formation of complex ions can interfere with the prediction of the cell reaction.

VI. Electric current and time:

A. Basics:
1. **Ampere**- the SI unit of electric current.
2. **Coulomb**- the SI unit of charge defined as the amount of charge that passes by a given point on a wire when an electric current of 1 ampere flows for 1 second.
   1 C = 1 A X s ***Remember- 1 mol of e^- has 9.65 e 4 C**
   ***For most of these types of problems: 1. Convert time to seconds 2. Multiply by amps to get the coulombs 3. Convert using Faraday's constant and chemical equation to get from mol e^- to mole of element in question to grams of element in question.**