Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals may be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic tablets, watches, pacemakers, and many others use batteries for power.

17.2 By the end of this section, you will be able to:

- Use cell notation to describe galvanic cells
- Describe the basic components of galvanic cells
- 17.3 By the end of this section, you will be able to:
 - Determine standard cell potentials for oxidation-reduction reactions
 - Use standard reduction potentials to determine the better oxidizing or reducing agent from among several possible choices
- 17.4 By the end of this section, you will be able to:
 - Relate cell potentials to free energy changes
 - Use the Nernst equation to determine cell potentials at nonstandard conditions
 - Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants
- 17.5 By the end of this section, you will be able to: (read this section)
 - Classify batteries as primary or secondary
 - List some of the characteristics and limitations of batteries
 - Provide a general description of a fuel cell
- 17.7 By the end of this section, you will be able to:
 - Describe electrolytic cells and their relationship to galvanic cells
 - Perform various calculations related to electrolysis

General Thoughts on Electrochemistry!

- In solving numerical problems from this chapter, remember that T is always in Kelvin
- Electrochemistry deals with the relation between electricity and chemical reactions
- A chemical reaction can generate electricity
- Electricity can be used to force a chemical reaction to take place
- In a redox reaction, oxidation and reduction take place simultaneously
- Know the definition of oxidation, reduction, oxidizing agent and reducing agent.
- You should be able to identify a half reaction as oxidation or reduction
- In a Voltaic or Galcanic cell
- There are two electrodes, each in contact with a electrolyte solution (called the Half cell)
- The cathode is where reduction takes place and anode is where oxidation takes place
- The anode is written on the left, the cathode on the right.
- The two half cells are connected by a salt bridge

- The electrons flow from the anode to the cathode
- The salt bridge helps in the transport of ions across the two half cells
- A metal electrode must be used. If the half reaction contains a piece of solid metal (not ionic) it is the electrode, if not, use Pt.
- A line notation is used to represent a cell
- You should be able to look at the line notation and be able to describe the cell and draw the cell diagram and write the overall redox reaction
- Alternatively, you should be able to look at a redox reaction and convert it to the line notation
- A voltaic cell is an Electrochemical cell where the chemical reaction generates a cell potential... Where E[°]_{cell} is positive.
- Calculating the standard cell EMF using the following formula

$$\mathbf{E}_{cell}^{\circ} = \mathbf{E}_{red, cathode}^{\circ} - \mathbf{E}_{red, anode}^{\circ}$$

Where the – means that we flip and add the potential at the anode.

- The half cell with the more positive value of the reduction potential is chosen as the cathode. (the first half reaction you find on the chart.)
- The second reaction you find on the chart you will need to flip and add as the anode.
- From a redox reaction, you should be able to identify the oxidation and reduction reaction and thus the cathode and the anode
- You must also be able to identify the number of electrons participating in the reaction.
- If the Cell EMF is positive, the reaction is said to be spontaneous
- You should be able to use the charts to find the best oxidizing and reducing agents.
- E°_{cell} and ΔG° are related as
- $\Delta G^0 = -nFE^0$, where F is the Faraday constant
- n is the number of electrons transferred in the balanced redox reaction
- F = 96485 Coulomb/mole electrons
- 1 Volt is 1 Joule/Coulomb
- Cell potential and Equilibrium Constant are related as
- $\Delta G^{\circ} = RT InK_{eq}$
- Cell potential under non-standard conditions is calculated using the Nernst equation

$$E = E^{\circ} - \frac{RT}{(moles e-)F} lnQ \qquad \text{or} \qquad E = E^{\circ} - \frac{.0592}{moles e-} logQ$$

- A concentration cell is when both the half cells are made of the same material and the cell potential is generated due to the difference in concentration between the two half cells.
- An electrolytic cell is when current is used to force a chemical reaction to take place. This is the principle of Electrolysis.
- Faradays Law: The amount of metal deposited during electrolysis is directly proportional to the charge on the cation, the current, and the length of time the cell runs. Amp = coulomb/second
- Charge that flows through the cell = current in Amperes x time in seconds
- From the charge, we can calculate the moles of electrons (1 mol electron = 96485 C)

- We can then calculate the moles and amount of metal deposited (from the stoichiometry between the electrons and the metals in the half reaction)
- Batteries are portable electrochemical power sources (chemical reaction generates voltage)
- In a lead acid battery, the Cathode is PbO_2 on a metal grid and the anode is spongy Pb and the electrodes immersed in H_2SO_4
- In an alkaline battery, powdered Zn in contact with concentrated KOH serves as the anode and the cathode is a mixture of MnO₂ and graphite

Corrosion is an example of an undesirable redox reaction. Galvanized iron is Iron coated with Zinc. Zinc acts as a sacrificial anode and prevents the corrosion of Iron.

Define:
anode
cathode
Electrochemical cell
cell notation or line notation
cell potential
galvanic cell
inert electrode
voltaic cell
standard cell potential

$$\mathbf{E}_{cell}^{\circ} = \mathbf{E}_{red, \ cathode}^{\circ} - \mathbf{E}_{red, \ anode}^{\circ}$$

standard reduction potential (E°)

Problems:

1. Determine the redox reaction represented by the following cell notation. Identify the anode and the cathode. Which is the oxidizing agent?

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Mg(s) | Mg^{2+}(aq) || Cu^{2+}(aq) | Cu(s)
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Mg/Mg²⁺ : anode Cu/Cu²⁺ Cathode Cu²⁺ oxidizing agent

2. Determine the cell notation for the redox reaction given below. Identify the anode and the cathode. What is being oxidized?

 $Sn(s) + 2 Ag^{+}(aq) \rightarrow Sn^{2+}(aq) + 2 Ag(s)$

Sn/sn²⁺ : anode Ag/Ag⁺ Cathode Ag⁺ being oxidized.

3. Calculate the standard cell potential for:

Mg(s) | Mg²⁺(aq) || Cu²⁺(aq) | Cu(s)

ɛ • = 2.71 V

And

 $Sn(s) + 2 Ag^{+}(aq) \rightarrow Sn^{2+}(aq) + 2 Ag(s)$

e • = .94 V

4. Determine the <u>cell notation</u> for the redox reaction given below. Calculate the standard cell potential and ΔG° . Is the Cell spontaneous? yes

 $3 \operatorname{Cl}_2(g) + 2 \operatorname{Al}(s) \rightarrow 6 \operatorname{Cl}^-(aq) + 2 \operatorname{Al}^{3+}(aq)$

 $Pt(s) | Cl_2(g) | Cl^-(aq) Al^{3+}(aq) | Al(s)$

ε • = 3.02 V ΔG° = - 1.75 MJ

5. Calculate the standard cell potential, ΔG° and K and for the reaction at 25°C. Is the cell spontaneous? no $2I^{-}(aq) + 2H^{+}(aq) \rightarrow H_{2}(g) + I_{2}(s)$

 $\mathbf{E}^{\circ} = -.54 \text{ V}$ $\Delta G^{\circ} = 102000 \text{ J}$ $K = 1.2 \times 10^{-18}$

6. Calculate the cell potential for the following reaction that takes place in an electrochemical cell at 25°C.

Sn(s) | Sn²⁺(aq, 1.8 M) || Ag⁺(aq, 0.055 M) | Ag(s)

8 = .86 V

7. What mass of aluminum can be plated onto an object in 755 minutes at 5.80 A of current?

24.5 g

8. For the reaction:

 $Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_{2}(g)$ **E** ° = 0.76 V

When the $P_{H_2} = 1.0$ atm and $[Zn^{2+}] = 1.0$ M, the cell potential is 0.66 V. The concentration of H⁺ in the cathode compartment is _____ M.

[H⁺] = 0.020 M

9. Circle the metals that will dissolve in 1.0 M HCl.A) AgB) NaC) MgD) Cu

10. (A) Circle the best oxidizing agent: Cl_2 , Fe^{3+} , K^+ , H_2O_2 , PbO_2 .

(B) Circle the best reducing agent: CI^- , Mn^{2+} , Cr, H_2 , Al.