

Chapter 17 – Electrochemistry

17.1 Galvanic Cells

A. Oxidation-Reduction Reactions (Redox Rxns)

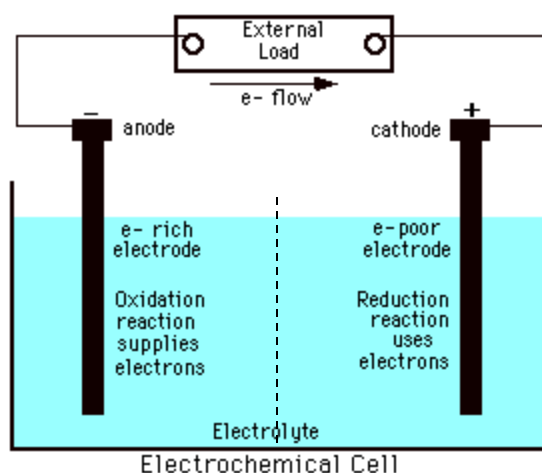
1. Oxidation = loss of electrons
 - a. the substance oxidized is the reducing agent
2. Reduction = gain of electrons
 - a. the substance reduced is the oxidizing agent

B. Redox energy

1. Heat is produced
2. Electricity can be produced if the reactants are separated
 - a. Reactants can be separated by a salt bridge
 - b. Reactants can be separated by a porous partition
 - c. Electrons travel through a wire

C. Galvanic Cell

1. A device in which chemical energy is changed to electrical energy
 - a. Oxidation occurs at the anode
 - b. Reduction occurs at the cathode



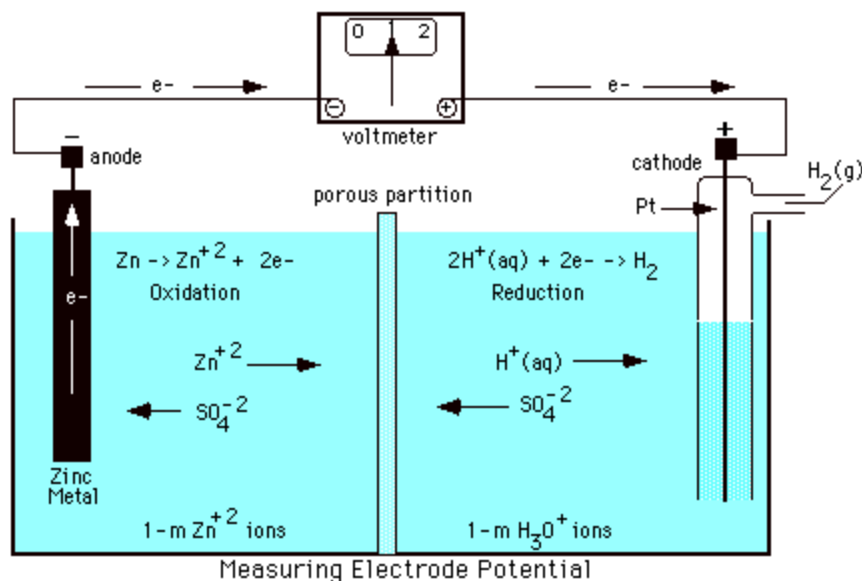
D. Cell Potential ($\mathcal{U}_{\text{cell}}$)

1. The driving force (electromotive force, emf) on the electrons
2. Potential is measured in volts

17.2 Standard Reduction Potentials

A. Measuring Potential

1. Electrode potential is measured in reference to a hydrogen electrode which is arbitrarily assigned a potential of zero volts

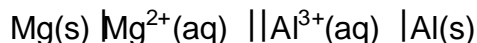


B. Calculating Electrode Potential

1. One of the reduction half reactions must be reversed, changing the sign on the potential for the reversed reaction
2. Potentials are not multiplied by the coefficients in the balanced equation
3. Galvanic cell potentials must be a positive number

C. Line Notation

1. Anode components listed on the left
2. Cathode components listed on the right
3. Double line represents salt bridge or porous disk



D. Complete Description of a Galvanic Cell

1. The cell potential (always positive for a galvanic cell)
2. The direction of electron flow (the direction that yields a positive potential)
3. Designation of the anode and cathode
4. The nature of each electrode and the ions present in each compartment. A chemically inert conductor (such as Pt) is required if none of the substances participating in the reaction is a conducting solid

17.3 Cell Potential, Electrical Work, and Free Energy

A. Driving Force

1. $\text{emf} = \text{potential difference} = \frac{\text{work (joules)}}{\text{charge (coulombs)}}$
 - a. Work leaving the system has a negative charge

$$\Delta U = -w/q \quad -w = q\Delta U$$

$$q = nF$$

(1) n is the number of moles of electrons

(2) F (a faraday) is the charge on a mole of electrons

$$F = (96\,485 \text{ C/mol e}^-)$$

2. emf is not converted to work with 100% efficiency
 - a. Energy is always lost in the form of heat, but w_{max} is useful for calculating the efficiency of conversion

$$w_{\text{max}} = -q\Delta U_{\text{max}}$$

B. Relation to Free Energy

1. $w_{\text{max}} = \Delta G$
2. $\Delta G = -q\Delta U_{\text{max}} = -nF\Delta U_{\text{max}}$
3. $\Delta G = -q\Delta U_{\text{max}}$
4. $\Delta G^0 = -nF\Delta U^0$
 - a. When ΔU_{cell} is positive (spontaneous), ΔG will be negative (spontaneous), so there is agreement

17.4 Dependence of Cell Potential on Concentration

A. Standard Potentials

1. All concentrations are 1M

B. Variation in concentrations

1. Write balanced equation for the cell
2. Use Le Chatelier's principle to determine the effect on potential
 - a. Shift to the left reduces potential
 - b. Shift to the right increases potential

C. Concentration Cells

1. Cells in which both compartments contain the same components, but in different concentrations
2. Reaction proceeds in the direction that will equalize the ion concentration in the compartments
3. Voltages are typically small

D. The Nernst Equation

1. Derivation

$$\Delta G = \Delta G^0 + RT \ln(Q) \quad (\text{from Chapter 16})$$

$$-nF\Delta U = -nF\Delta U^0 + RT \ln(Q)$$

$$\Delta U = \Delta U^0 - \left(\frac{RT}{nF} \right) \ln(Q)$$

2. At 25°C

$$\Delta U = \Delta U^0 - \left(\frac{0.0592}{n} \right) \log(Q)$$

3. As cells discharge, concentration changes, ΔU_{cell} changes.
4. Cells spontaneously discharge until they achieve equilibrium
 - a. At equilibrium, the cell is "dead"

E. Ion-Selective Electrodes

1. Electrodes that are sensitive to the concentration of a particular ion
2. Electrodes can be manufactured to be selective to a cation/anion pair

F. Calculation of Equilibrium Constants for Redox Reactions

1. At equilibrium, $\Delta U_{\text{cell}} = 0$ and $Q = K$
2. Substituting into the Nernst equation

$$0 = \Delta U^0 - \left(\frac{0.0592}{n} \right) \log(K)$$

$$\log(K) = \frac{n\Delta U^0}{0.0592} \quad (\text{at } 25^\circ\text{C})$$

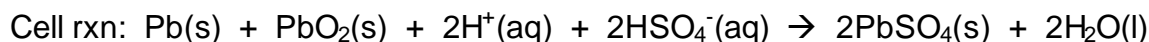
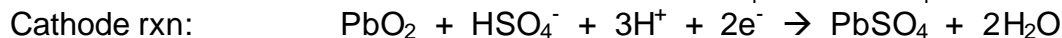
17.5 Batteries

A. Batteries

1. A galvanic cell, or group of galvanic cells, connected in series
2. Source of direct current

B. Lead Storage Battery

1. Six two-volt cells in series



2. Discharge lowers the concentration of sulfuric acid, and the density of the solution
3. Note this – If you learn nothing else in chemistry...

When jump starting a car, you MUST connect the ground cable on the DEAD car to a metallic contact AWAY from the battery. Otherwise, BOOM! (maybe)

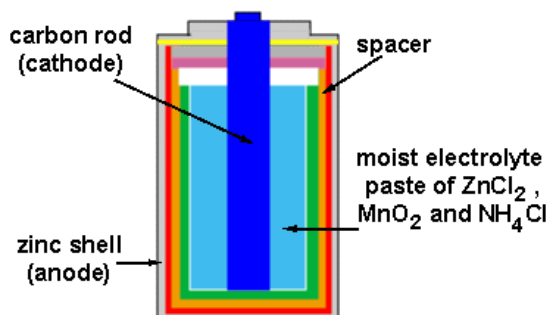
C. Common Dry Cell Battery

1. Acid version

- a. zinc inner case acts as the anode
- b. carbon rod in contact with a moist paste of solid MnO_2 , solid NH_4Cl and carbon is the cathode

2. Alkaline dry cell

- a. NH_4Cl is replaced with KOH or NaOH
- b. Alkaline cells last longer than acid cells because zinc corrodes more slowly in a basic environment



D. Fuel Cells

1. Galvanic cells for which the reactants are continuously supplied
2. Energy normally lost as heat is captured and used to produce an electric current
3. The reaction taking place must be a redox reaction

17.6 Corrosion

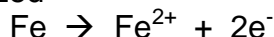
A. Corrosion = Oxidation of a metal

1. The oxidation of most metals by oxygen is spontaneous
2. Many metals develop a thin coating of metal oxide on the outside that prevents further oxidation

B. Corrosion of Iron

1. Anode regions

- a. Regions of a piece of steel alloy where the iron is more easily oxidized



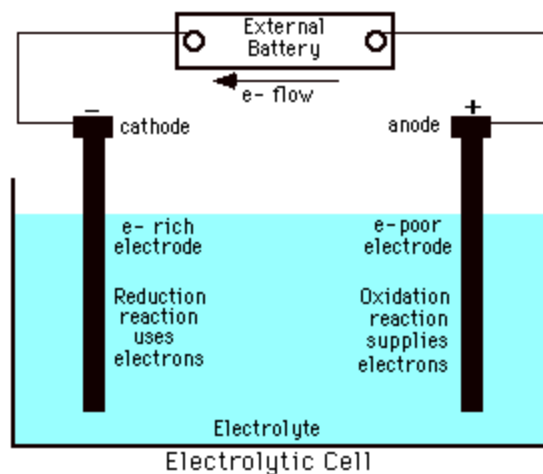
2. Cathodic regions
 - a. Areas that are resistant to oxidation
 - b. Electrons flow from anodic regions and react with oxygen

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$$
 3. Presence of water is essential to corrosion of iron
 4. Presence of salt accelerates the corrosion process by increasing the ease with which electrons are conducted from anodic to cathodic regions
- C. Prevention of Corrosion
1. Coating with a metal that will form an oxide coat to protect a metal that would not develop a protective coat
 2. Galvanizing
 - a. Placing a “sacrificial” of a more easily oxidized metal on top of the metal you desire to protect
 - (1) zinc over iron
 3. Alloying
 - a. Addition of metals that change steel’s reduction potential
 - (1) nickel and chromium alloyed to iron
 4. Cathodic Protection
 - a. Connection of easily oxidized metals (an anode) to less easily oxidized metals keeps the less from experiencing corrosion
 - b. The anode corrodes and must be replaced periodically
 - (1) Magnesium as anode to iron pipe
 - (2) Titanium as anode to a steel ship’s hull

17.7 Electrolysis

A. Electrolysis

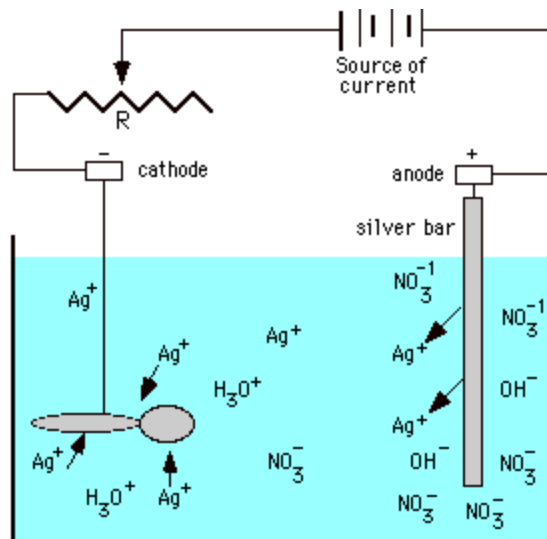
1. Forcing a current through a cell to produce change for which the cell potential is negative



- a. oxidation at the anode
- b. reduction at the cathode

B. Electroplating

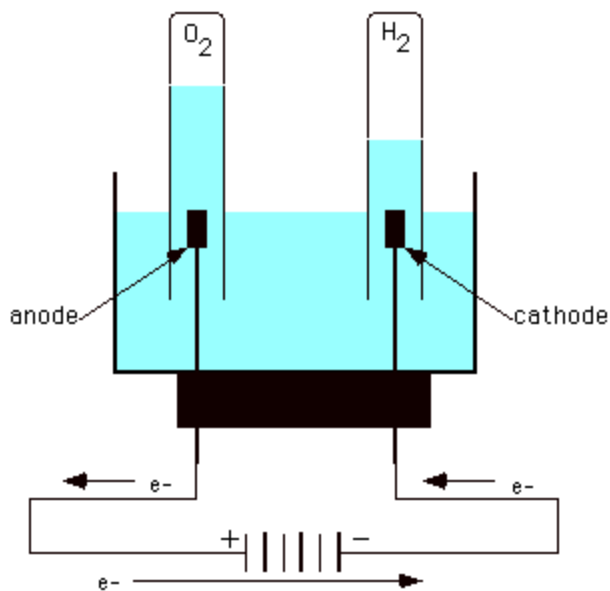
1. Depositing neutral metal atoms on the electrode by reducing the metal ions in solution.



- a. Anode is a piece of the plating metal
- b. Cathode is the object to be plated

C. Electrolysis of Water

1. Requires the presence of a soluble salt or dilute acid to serve as an electrolyte
 - a. $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$



D. Electrolysis of Mixtures of Ions

1. Most easily reduced metals (highest values of \tilde{U}^0) will be plated first

E. Stoichiometry of Electrolytic Processes

1. Step 1 – convert current and time to quantity of charge in coulombs
 - a. Amps x time = total charge transferred in coulombs

$$(\text{Coulomb/sec}) \times \text{sec} = \text{coulombs}$$

2. Step 2 – convert quantity of charge in coulombs to moles of electrons

$$\text{coulombs} \div (96,485 \text{ coulomb/mol e}^-) = \text{mol e}^-$$

3. Step 3 – Convert moles of electrons to moles of substance

$$\text{Mol e}^- \times (\text{mole substance/mol e}^-) = \text{mol substance}$$

4. Step 4 – Convert moles of substance to grams of substance

$$\text{Mol substance} \times \text{formula mass of substance} = \text{mass of substance}$$

17.8 Commercial Electrolytic Processes

A. Production of Aluminum

1. Purification of aluminum from bauxite ore
2. See table 17.3 for prices of aluminum over the last century

B. Electrefining of Metals

C. Metal Plating

D. Electrolysis of Sodium Chloride