

•CHEM 1212 - Principles of Chemistry II

Chapter 17 - Electrochemistry

- electrochemistry is best defined as the study of the interchange of chemical and electrical energy

17.1 Galvanic Cells

- an **oxidation-reduction (redox) reaction** involves a transfer of electrons from the **reducing agent** to the **oxidizing agent**
- **oxidation** involves the loss of electrons; **reduction** involves a gain of electrons
 - see Figure 17.1
 - see Figure 17.2
 - see Figure 17.3
- a **galvanic cell** uses a spontaneous redox reaction to produce a current that can be used to do work
- oxidation occurs at the anode (negative electrode); reduction occurs at the cathode (positive electrode)

Cell Potential

- the driving force on the electrons is called the **cell potential** or the electromotive force (emf) of the cell
- the unit of electrical potential is the **volt (V)** which is defined as 1 joule of work per coulomb of charge transferred

17.2 Standard Reduction Potential

- the reaction in a galvanic cell is always an oxidation-reduction reaction that can be broken down into two half-reactions
- it would be convenient to assign a potential to each half-reaction so that when we construct a cell from a given pair of half reactions, we can obtain the cell potential by summing the half-cell potentials
- see Figure 17.5
- the standard hydrogen electrode's potential is arbitrarily set to zero volts
- see Table 17.1

Line Notation

- in this notation the anode components are listed on the left and the cathode components are listed on the right, separated by double vertical lines (indicating the salt bridge or porous disk)

- the phase difference is indicated by the single vertical line

Complete Description of a Galvanic Cell

- a cell will always run spontaneously in the direction that produces a positive cell potential

17.3 Cell Potential, Electrical Work, and Free Energy

- for standard conditions, $\Delta G^\circ = -nFE^\circ$, where n is the number of electrons transferred, F , is a faraday (98,485 C/mol of electrons), and E° is the emf for a cell

17.4 Dependence of Cell Potential on Concentration

- so far have described cells under standard conditions; now consider the dependence of the cell potential on concentration

Concentration Cells

- see Figure 17.9
- a cell in which both compartments have the same components but at different concentrations is called a concentration cell

The Nernst Equation

- using the Nernst equation can calculate the potential of a cell in which some or all of the components are not in their standard states
- the potential calculated from the Nernst equation is the maximum potential before any current flow has occurred; as the cell discharges and current flows from the anode to cathode, the concentration will change, and as a result E_{cell} will change; in fact the cell will spontaneously discharge until it reaches equilibrium, at which point $Q = K$ (equilibrium constant) and the cell potential is zero; a dead battery

Ion-Selective Electrodes

- because the cell potential is sensitive to the concentrations of the reactants and products involved in the cell reaction, measured potentials can be used to determine the concentration of an ion
- a pH meter is a familiar example of an instrument that measures concentration using an observed potential
- the pH meter has three main components: a standard electrode of known potential, a special glass electrode that changes potential depending on the concentration of H^+ ions in the solution into which it is dipped, and a potentiometer that measures the potential between the two electrodes
- see Figure 17.12

- see Table 17.2

Calculation of Equilibrium Constants for Redox Reactions

- the quantitative relationship between E° and G° allows calculation of equilibrium constants for redox reactions
- for a cell at equilibrium, $E_{\text{cell}} = 0$ and $Q = K$, then $\log(K) = n E^\circ / 0.0592$

17.5 Batteries

- a battery is a galvanic cell or a group of galvanic cells connected in series

Lead Storage Battery

- lead storage battery have been used in automobiles since around 1915 with the introduction of self-starter
- in this battery lead serves as the anode, and lead coated with lead dioxide serves as the cathode; both electrodes dip into an electrolyte solution of sulfuric acid
- the electrode reactions are:

anode reaction: $\text{Pb} + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + \text{H}^+ + 2\text{e}^-$

cathode reaction: $\text{PbO}_2 + \text{HSO}_4^- + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$

cell reaction: $\text{Pb(s)} + \text{PbO}_2\text{(s)} + 2\text{H}^+\text{(aq)} + 2\text{HSO}_4^-\text{(aq)} \rightarrow 2\text{PbSO}_4\text{(s)} + 2\text{H}_2\text{O}$

- the typical automobile lead storage battery has six cells connected in series
 - see Figure 17.13
- note as the battery discharges sulfuric acid is consumed; the density of the electrolyte solution decreases from an initial value of 1.28 g/cm^3
- an alternator driven by the car's engine recharges the battery
- traditional storage batteries require periodic "topping" off, because the water in the electrolyte solution is depleted by the electrolysis that accompanies the charging process
- recent types of batteries have electrodes made of an alloy of calcium and lead that inhibits the electrolysis of water; these batteries can be sealed since they do not require the addition of water
- a car battery will last from 3-5 years; physical damage from road shock and chemical side-reaction eventually cause it to fail

Other Batteries

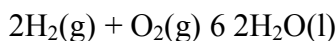
- the common dry cell battery was invented more than 100 years ago by **George Leclanché** (1839-1882)
- in its acid version the dry cell battery contains a zinc inner case that acts as the anode and a

carbon rod in contact with a moist paste of solid MnO_2 , solid NH_4Cl , and carbon that acts as the cathode; the cell produces a potential of about 1.5 V

- see Figure 17.14
- in the alkaline version of the dry cell battery, the solid NH_4Cl is replaced with KOH or NaOH
- the alkaline dry cell lasts longer mainly because the zinc anode corrodes less rapidly under basic conditions than under acidic conditions
- the silver cell has a Zn anode and a cathode that employs Ag_2O as the oxidizing agent in a basic environment
- mercury cells (often used in calculators) have a Zn anode and a cathode involving HgO as the oxidizing agent in a basic medium
- an important type of battery is the nickel-cadmium battery; as in the lead storage battery the products adhere to the electrodes; therefore, a nickel-cadmium battery can be recharged an indefinite number of times

Fuel Cells

- a fuel cell is a galvanic cell for which the reactants are continuously supplied
- the US space program has supported extensive research to develop fuel cells; the Apollo missions used a fuel cell based on the reaction of hydrogen and oxygen to form water:



- see Figure 17.16
- the half reactions are:

anode reaction: $2\text{H}_2 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$

cathode reaction: $4\text{e}^- + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-$

- a cell of this type weighing about 500 pounds has been designed for space vehicles

17.6 Corrosion

- corrosion can be viewed as the process of returning metals to their natural state - the ores from which they were originally obtained
- corrosion involves oxidation of the metal; since there is a loss in structural integrity and attractiveness there is a great economic impact
- approximately one-fifth of the iron and steel produced annually is used to replace rusted metal
- except for gold, commonly used metals have standard reduction potential less positive than that of oxygen gas; thus the oxidation of most metals by oxygen is spontaneous (says nothing about the rate)
- most metals develop a thin oxide which greatly inhibits further corrosion; example is aluminum

- iron also can form a protective oxide coating; however, when steel is exposed to oxygen in moist air, the oxide that forms tends to scale off and expose new metal surface to corrosion
- copper forms an external layer of greenish copper carbonate called patina
- silver tarnish is silver sulfide which in thin layers gives the silver surface a richer appearance

Corrosion of Iron

- see Figure 17.17
- because of the migration of ions and electrons, rust often forms at sites that are remote from those where the iron dissolved to form pits in the steel
- the degree of hydration of the iron oxide affects the color of the rust, which may vary from black to yellow to the familiar reddish brown
- moisture must be present to act as a kind of salt bridge between anodic and cathodic regions
- steel does not rust in dry air
- salt accelerates rusting; increases the conductivity of the aqueous solution formed there and thus accelerates the electrochemical corrosion process
- chloride ions also form very stable complex ions with Fe^{3+} , and this factor tends to encourage the dissolving of the iron, again accelerating the corrosion

Prevention of Corrosion

- prevention of corrosion is an important way of conserving our natural resources of energy and metals
- primary means of protection is application of a coating, commonly painting or metal plating
- chromium and tin used for plating; form durable, effective oxide layer
- zinc used in process called galvanization; zinc does not form oxide layer; rather zinc is oxidized before steel; “sacrificial” coating on steel
- alloying used; stainless steel contains chromium and nickel; both form oxide layers
- also have cathodic protection; magnesium bar attached to steel pipe or titanium bar attached to hull of ship
- see Figure 17.18
- see Figure 17.19

17.7 Electrolysis

- recall a galvanic cell is spontaneous
- in an electrolytic cell electrical energy is used to produce a chemical change
- the process of electrolysis involves forcing a current through a cell to produce a chemical change for which the cell potential is negative
- electrolysis has great practical importance; examples, charging a battery, producing aluminum metal, and chrome plating

17.8 Commercial Electrolytic Processes

- read this section