

Chapter 18

Section 18.1 You should know that **Electrochemistry** is the branch of chemistry that links redox reactions to the production or consumption of electrical energy. Any redox reaction can be broken down into oxidation and reduction half-reactions. The gain of electrons in a reduction half-reaction must be balanced by the loss of electrons in the oxidation half-reaction coupled to it.

Section 18-2 You should know that a **voltaic cell** is an **electrochemical cell** that produces an electrical current in an external circuit as a result of a spontaneous redox reaction in which oxidation occurs at the **anode** and reduction occurs at the **cathode** of the cell. A **cell diagram** used symbols including single and double vertical lines to show how the components of the cathodic and anodic compartments of the cell are connected.

Section 18.3 You should know that the **cell potential (E_{cell})** of a voltaic cell is the **electromotive force** that the cell generates. E_{cell} is related to the change in free energy (ΔG_{cell}) of the cell reaction by the equation:

$$\Delta G_{\text{cell}} = -nFE_{\text{cell}}$$

where F is **Faraday's constant** ($9.65 \times 10^4 \text{ C/mol}$) and n is the number of electrons transferred in the balanced chemical equation describing the cell reactions. This change in free energy is available to do work in an external electric circuit.

Section 18.4 You should know that the E_{cell} under standard conditions is called **standard cell potential (E°_{cell})**. It is calculated by combining the **standard potentials (E°)** of a cell's half-reactions, E°_{red} of the cathode half-reaction and E°_{ox} of the anode half-reaction.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} (\text{cathode}) + E^{\circ}_{\text{ox}} (\text{anode})$$

The standard potentials in Appendix 6 are all reduction potentials, E°_{red} . The corresponding E°_{ox} values for the half-reactions in reverse have the same magnitudes but opposite signs.

Section 18.5 You should know that all standard potentials are referenced to the potential of the **standard hydrogen electrode** ($E_{\text{SHE}} = 0.000 \text{ V}$).

Section 18.6 You should know that the potential of a voltaic cell decreases as reactants turn into products. The **Nernst equation** predicts how the potential of a cell changes with the concentrations of the cell reactants and products. The potential of a voltaic cell approaches zero as the cell reaction approaches chemical equilibrium. At equilibrium $E_{\text{cell}} = 0$ and $Q = K$.

$$\text{Nernst Equation : } E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{R \cdot T}{n \cdot F} \cdot \log Q$$

Section 18.7 You should know that the quantities of reactants consumed in a voltaic cell reaction are directly proportional to the coulombs of electrical charge that the cell delivers. Faraday's constant relates the quantity of electrical charge to the number of moles of electrons, and indirectly to the moles of reactants involved in the cell reaction. Most portable electronic devices are powered by nickel-metal hydride (NiMH) or lithium-ion batteries.

Section 18.8 You should know that reversing a spontaneous reaction by passing electric current through an electrochemical cell turns the cell into an **electrolytic cell**. Reactions in electrolytic cells that produce gases often require application of additional electromotive force, or **over-potential**. The polarities of cathodes and anodes in electrolytic cells are opposite the polarities of these electrodes in voltaic cells.

Section 18.9 You should know that **fuel cells** directly convert the free energy released during the reactions
 $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$ into electrical energy. Fuel cells with proton-exchange membranes have been developed as power supplies for electric vehicles.