8.1 Oxidation–Reduction Reactions

Redox reactions are chemical reactions that involve a transfer of one or more electrons from one atom to another.

- Oxidation: the loss of one or more electron by a atom, ion, or molecule
- Reduction: the gain of one or more electron by a atom, ion, or molecule

Oxidation State: measure of how many electrons are associated with a given atom within a molecule.

Determining oxidation state:

- Ionic bonding: charge = oxidation state
- Covalent bonding: electrons belong to most electronegative atom
- Metal-ligand: electrons belong to the ligand

**Reactions are only considered to be redox if the oxidation state of any involved atoms change.**

8.2 Electrochemistry and Electrochemical Reactions

- You are able to remove molecules from your half equations if they show up on both sides of the reaction in stoichiometrically equivalent amounts

$$Fe(Br)_3 \text{ (aq)} + Cu(Br) \text{ (aq)} \rightleftarrows Fe(Br)_2 \text{ (aq)} + Cu(Br)_2 \text{ (aq)}$$

Equation 8.4

The redox nature of this reaction can be seen more clearly if the individual ions are written out explicitly (Equation 8.5):

$$Fe^{3+} \text{ (aq)} + Cu^{1+} \text{ (aq)} \rightleftarrows Fe^{2+} \text{ (aq)} + Cu^{2+} \text{ (aq)}$$
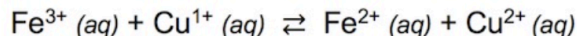
Equation 8.5

- ○

Salt-bridge: is a method for ions to travel during a reaction in order to alleviate charge build-ups.

8.2.1 Chemical Half-Reactions and Balancing Electrochemical Reactions

- Half reactions are a process of splitting the oxidation and reduction steps
  - ○ If the electrons on each side do not cancel out then stoichiometric balances must be made

8.3 The Relationship Between Free Energy and Voltage

- The oxidation half reaction is known as an anode (negative terminal of a battery).
- The reduction half reaction is known as the cathode (positive terminal of a battery)

8.3.1 Cell Potentials, ε – One Way to Directly Measure ΔG

- Gibbs free energy in batteries = electromotive force (EMF)

$$\Delta G = -nF\varepsilon$$

Equation 8.9

Where ε is the cell potential, n is the number of moles of electrons in the balanced redox reaction, and F is Faraday's constant, a measure of the charge of 1 mol of electrons (96485 coulombs/mol = 96485 J/V·mol).

- For a reaction to be spontaneous, G must be negative and cell potential must be positive
- G is calculated per reaction, while potential is per electron

$$\Delta G° = -RT \ln K = -nF\varepsilon°$$

Equation 8.10

8.3.2 Standard Reduction Potentials
Standard hydrogen electrode (SHE) is used as point of reference; cell potential of reduction is 0V.
- In table of reduction values, all potentials are relative to each other. **The more positive a value is, the more likely it is to reduce in relation to another substance.** Conversely, greater negative values are more likely to oxidize in the presence of other substances.

Standard Reduction Potentials for Some Chemical Species	
Reduction Reaction	Standard reduction Potential ($\varepsilon°$) Volts
$F_2 + 2H^+ + 2e^- \longrightarrow 2HF$	3.053
$F_2 + 2e^- \longrightarrow 2F^-$	2.866
$Au^+ + e^- \longrightarrow Au$	1.692
$HClO_2 + 2H^+ + 2e^- \longrightarrow HClO + H_2O$	1.645
$Au^{3+} + 3e^- \longrightarrow Au$	1.498
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	1.358
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.229
$Ir^{3+} + 3e^- \longrightarrow Ir$	1.156
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	0.957
$Ag^+ + e^- \longrightarrow Ag$	0.800
$Cu^{2+} + 2e^- \longrightarrow Cu$	0.342
$PbO_2 + H_2O + 2e^- \longrightarrow PbOH + 2OH^-$	0.247
$2H^+ + 2e^- \longrightarrow H_2$	0.000
$Pb^{2+} + 2e^- \longrightarrow Pb$	-0.126
$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH$	-0.199
$Ni^{2+} + 2e^- \longrightarrow Ni$	-0.257
$S + 2e^- \longrightarrow S^{2-}$	-0.476
$Ga^{3+} + 3e^- \longrightarrow Ga$	-0.549
$Zn^{2+} + 2e^- \longrightarrow Zn$	-0.762
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	-0.828
$Zn(OH)_2 + 2e^- \longrightarrow Zn + 2OH^-$	-1.249
$Al^{3+} + 3e^- \longrightarrow Al$	-1.662
$Na^+ + e^- \longrightarrow Na$	-2.710
$K^+ + e^- \longrightarrow K$	-2.931
$Li^+ + e^- \longrightarrow Li$	-3.040

Table 8.1. Standard Reduction Potentials for some chemical species

$$\varepsilon^{\circ}{}_{cell} = \varepsilon^{\circ}{}_{red} + \varepsilon^{\circ}{}_{ox}$$

Equation 8.14

- **Positive potential of reduction is equivalent to a negative potential of oxidation.**

8.4 Nonstandard Cell Potentials – The Nernst Equation

$$\varepsilon = \varepsilon^{\circ} - \frac{RT}{nF}\ln Q = \varepsilon^{\circ} - \frac{0.0592}{n}\log Q$$
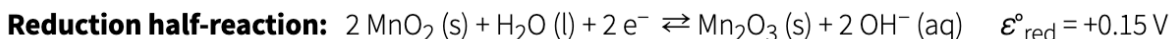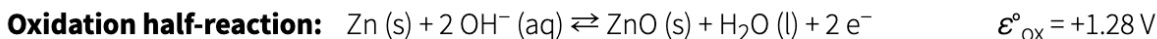
Equation 8.17

Using appropriate values for R (8.314 J/mol K) and F (96,485 J/ V mol of electrons) at a T of 298.15 K as well as changing from natural (ln) to base 10 (log) logarithms, yields a frequently used version of the Nernst equation that depends only on the standard cell potential (ε°), number of electrons transferred (n), and reaction quotient (Q).

8.5 Batteries
Batteries are cells that change chemical energy to electrical energy. Primary batteries are unable to recharge, while secondary batteries can.

8.5.1 Primary Batteries
Alkaline batteries that are made of Zn and MnO_2.

Oxidation half-reaction: $Zn\ (s) + 2\ OH^-\ (aq) \rightleftarrows ZnO\ (s) + H_2O\ (l) + 2\ e^-$ $\varepsilon^{\circ}{}_{ox} = +1.28\ V$

Reduction half-reaction: $2\ MnO_2\ (s) + H_2O\ (l) + 2\ e^- \rightleftarrows Mn_2O_3\ (s) + 2\ OH^-\ (aq)$ $\varepsilon^{\circ}{}_{red} = +0.15\ V$

8.5.2 Secondary Batteries
Nicad batteries use nickel and cadmium. Electric cars use lead-acid batteries.