Redox

Electrochemical Cells
Redox reactions

- Electron transfer
  - Oxidation
  - Reduction

- Oxidation numbers
  - Balancing redox reactions
  - Half reactions

- Electrolytic cell
  - Voltaic cell
  - Anode & cathode
  - Cell potentials
  - Standard reduction potentials

Redox unit advance organizer
Assigning Oxidation Numbers

- Elemental samples of matter have an oxidation number of 0.
  Examples:
Assigning Oxidation Numbers

- For a monotomic ion, the charge of the ion is the oxidation number.

- Examples:
Assigning Oxidation Numbers

- Hydrogen in a compound usually has an oxidation number of +1.
- Example:
Assigning Oxidation Numbers

- Hydrogen in a compound usually has an oxidation number of +1.

- Exception:
  - When in a metal hydride, H has an oxidation number of -1.

  Ex.
Assigning Oxidation Numbers

- Fluorine in a compound has an oxidation number of -1.
- Ex
Assigning Oxidation Numbers

- Oxygen in a compound usually has an oxidation number of -2.

- Ex.
Assigning Oxidation Numbers

- Oxygen in a compound usually has an oxidation number of -2.
- Exception: In peroxides, oxygen has an oxidation number of -1.
  - Ex.
Assigning Oxidation Numbers

- Exception: In compounds with fluorine, oxygen has an oxidation number of +2.
- Ex.
Assigning Oxidation Numbers

- In a neutral compound, the sum of the oxidation numbers equals zero.
- In a polyatomic ion, the sum of the oxidation numbers equals the overall charge of the ion.
Oxidation

- Oxidation = loss of electrons
- In oxidation, the oxidation number increases
- Oxidation half reactions:
  - Na → Na\(^+\) + e\(^-\)
  - Mg → Mg\(^{2+}\) + 2e\(^-\)
Reduction

- Reduction = gain of electrons
- In reduction, the oxidation number decreases
- Reduction half reactions:
  - Fe\(^{3+}\) + 3e\(^-\) → Fe
  - F\(_2\) + 2e\(^-\) → 2F\(^-\)
Redox

- Oxidation can’t occur without reduction!
- The number of electrons lost must equal the number of electrons gained.
- In a redox reaction, oxidation numbers change.
Are these redox reactions?

- \( \text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O} \)
- \( \text{H}_2\text{SO}_4 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \)
- \( \text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2 \)
- \( \text{I}_2\text{O}_5 + \text{CO} \rightarrow \text{I}_2 + \text{CO}_2 \)
- \( \text{P}_4 + \text{S}_8 \rightarrow \text{P}_2\text{S}_5 \)
Mnemonics

- LEO the lion says GER
- OIL RIG
What is oxidized? What is reduced?

- $2\text{Na} + \text{Br}_2 \rightarrow 2 \text{NaBr}$
- $\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$
- $\text{Mg} + \text{CuSO}_4 \rightarrow \text{MgSO}_4 + \text{Cu}$
More about redox reactions

- Oxidizing agent = the substance that gets reduced
- Reducing agent = the substance that gets oxidized
Identify the oxidizing agent. Identify the reducing agent.

- \(2Na + Br_2 \rightarrow 2 NaBr\)
- \(N_2 + 3 H_2 \rightarrow 2 NH_3\)
- \(Mg + CuSO_4 \rightarrow MgSO_4 + Cu\)
Electrochemical cells

- Voltaic cells
  - Aka galvanic cells
  - Set up to release electrical energy
  - Batteries
Electrochemical cells

- Electrolytic cells
  - Consume electrical energy to drive a chemical reaction
  - Electroplating
Galvanic cells

- **Electrode** = metal strip
- **Half-cell** = electrode immersed in a solution of its ions
- **Two half cells are needed for an electrochemical cell**
Completing the circuit

- Connect the electrodes with an external wire
- Connect the half-cells with a “salt bridge” to complete the circuit
- The salt bridge allows the movement of ions, but keeps the solutions physically separated
Parts of the galvanic cell

- Oxidation occurs at the anode
  - The anode is the negative electrode
- Reduction occurs at the cathode
  - The cathode is the positive electrode
Parts of the galvanic cell

- Electrons flow from the anode to the cathode
- Mnemonic: RED CAT
  - AN OX
A galvanic cell

Zn(s) $\rightarrow$ Zn$^{2+}$ (aq) + 2 e$^-$  Cu$^{2+}$ (aq) + 2 e$^-$ $\rightarrow$ Cu(s)

Movement of cations

Movement of anions

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A visual summary
As the galvanic cell runs...

- The anode will get less massive, as cations are generated
  - $A \rightarrow A^+ + e^-$
- The concentration of metal cations will increase in the anode compartment
As the galvanic cell runs...

- The cathode will get more massive, as cations are reduced to form the metal
  - $C^+ + e^- \rightarrow C$
- The concentration of metal cations in the cathode will decrease
A virtual model

Go to
http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/galvan5.swf
Standard Reduction Potentials

- A relative measure of tendency to undergo reduction
  - More positive $E^0$ value (Higher up): greater tendency to reduce
  - Less positive $E^0$ value (lower down): greater tendency to oxidize

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>Reduction Half-Reaction</th>
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<tbody>
<tr>
<td>+2.87</td>
<td>$F_2(g) + 2e^- \rightarrow 2F^-(aq)$</td>
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<td>+1.51</td>
<td>$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$</td>
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<tr>
<td>+1.36</td>
<td>$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$</td>
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<td>+1.33</td>
<td>$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$</td>
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<td>+1.23</td>
<td>$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$</td>
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<tr>
<td>+1.06</td>
<td>$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$</td>
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<tr>
<td>+0.96</td>
<td>$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$</td>
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<td>+0.80</td>
<td>$Ag^+(aq) + e^- \rightarrow Ag(s)$</td>
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<td>$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$</td>
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<td>$I_2(s) + 2e^- \rightarrow 2I^-(aq)$</td>
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<td>$Li^+(aq) + e^- \rightarrow Li(s)$</td>
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Calculating $E_{\text{cell}}$

- Find the half-reactions on the Table of Standard Reduction Potentials.
- The reaction that is higher on the table:
  - Greater tendency to reduce, so keep as written.
  - This reaction will occur at the cathode.
- The reaction that is lower on the table:
  - Lesser tendency to reduce, so flip it to be an oxidation half reaction, change sign of $E^{\circ}$.
  - This reaction will occur at the anode.
- Add the $E^{\circ}$ values to find $E_{\text{cell}}$. 
Calculate \( E_{\text{cell}} \)

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