Getting Around the Carnot Cycle: Fuel Cells

Anode (oxidation half-reaction):

H^0 $H_2(g) + 2H_2O(l) \rightarrow 2\ H_3O^+(aq) + 2e^-$

H^{1+}

Cathode (reduction half-reaction):

O^0 $\frac{1}{2}\ O_2(g) + 2\ H_3O^+(aq) + 2e^- \rightarrow 3\ H_2O(l)$

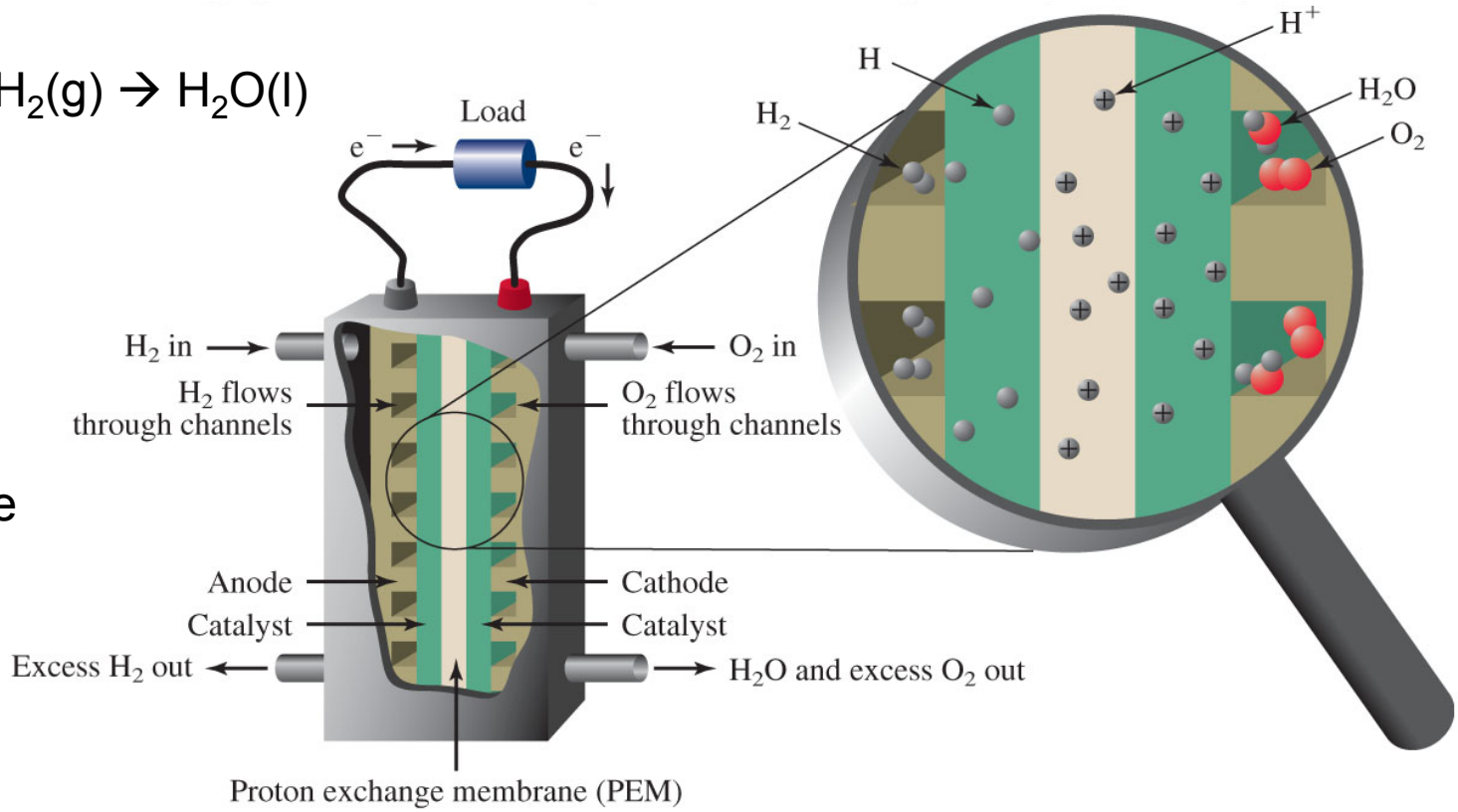
O^{2-}

Overall:

$\frac{1}{2}\ O_2(g) + H_2(g) \rightarrow H_2O(l)$

Fuel Cells: galvanic cells that use fuels for chemical energy

Where does the H_2 come from?



(Photo)Electrolysis for Splitting Water

photoanode (oxidation takes place here)

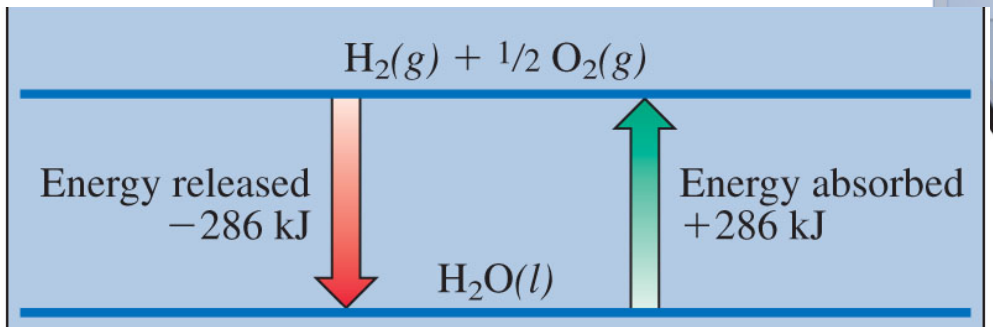
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

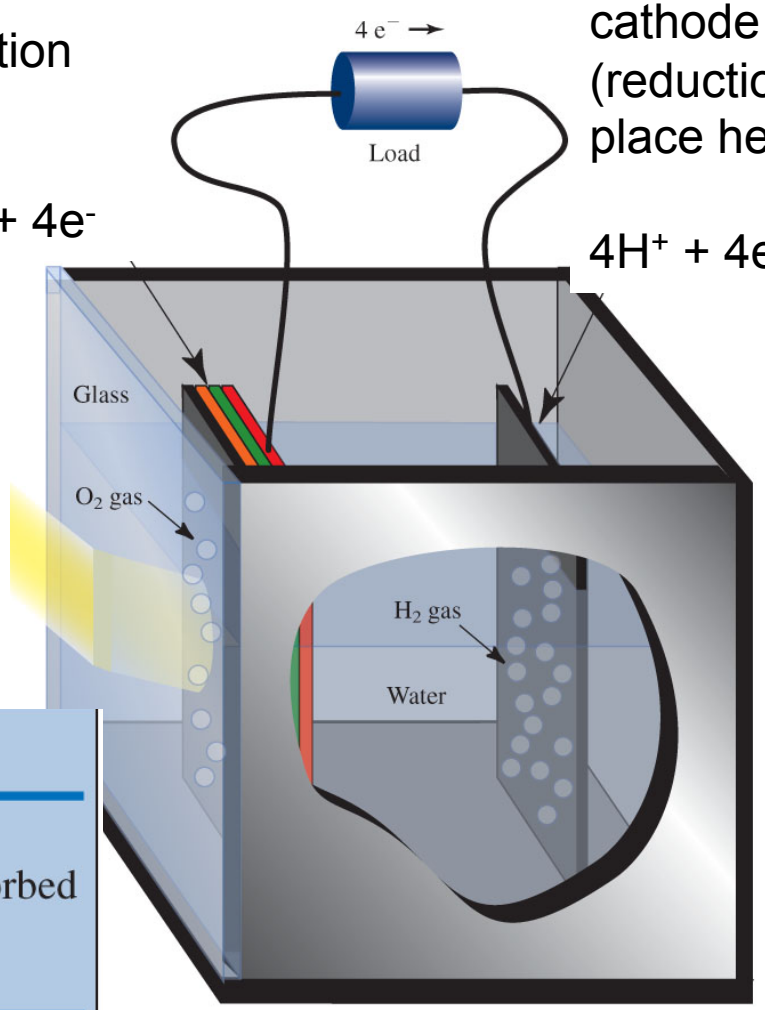
Platinum (Pt) cathode (reduction takes place here)

$4H^+ + 4e^- \rightarrow 2H_2$

4.3 Energy Content of Fuels

Source	kJ/g
Hydrogen	140
Methane	56
Propane	51
Gasoline	48
Coal (hard)	31
Ethanol	30
Wood (oak)	14





Sunlight

Example of Redox in Biology: Oxidative Stress

- Situation: parts of a living being produce **reactive oxygen species** faster than other parts can remove those species, creating an imbalance in compounds that can damage cell tissue and function

- Impacts for proteins:
  - Atherosclerosis
  - Parkinson's disease
  - Myocardial infarction
  - Alzheimer's disease
  - Schizophrenia
  - Bipolar Disorder
  - Chronic fatigue syndrome
- Impacts for DNA:
  - Cancer
  - Mutations

If you're looking to read more, Wikipedia isn't a terrible place to start:

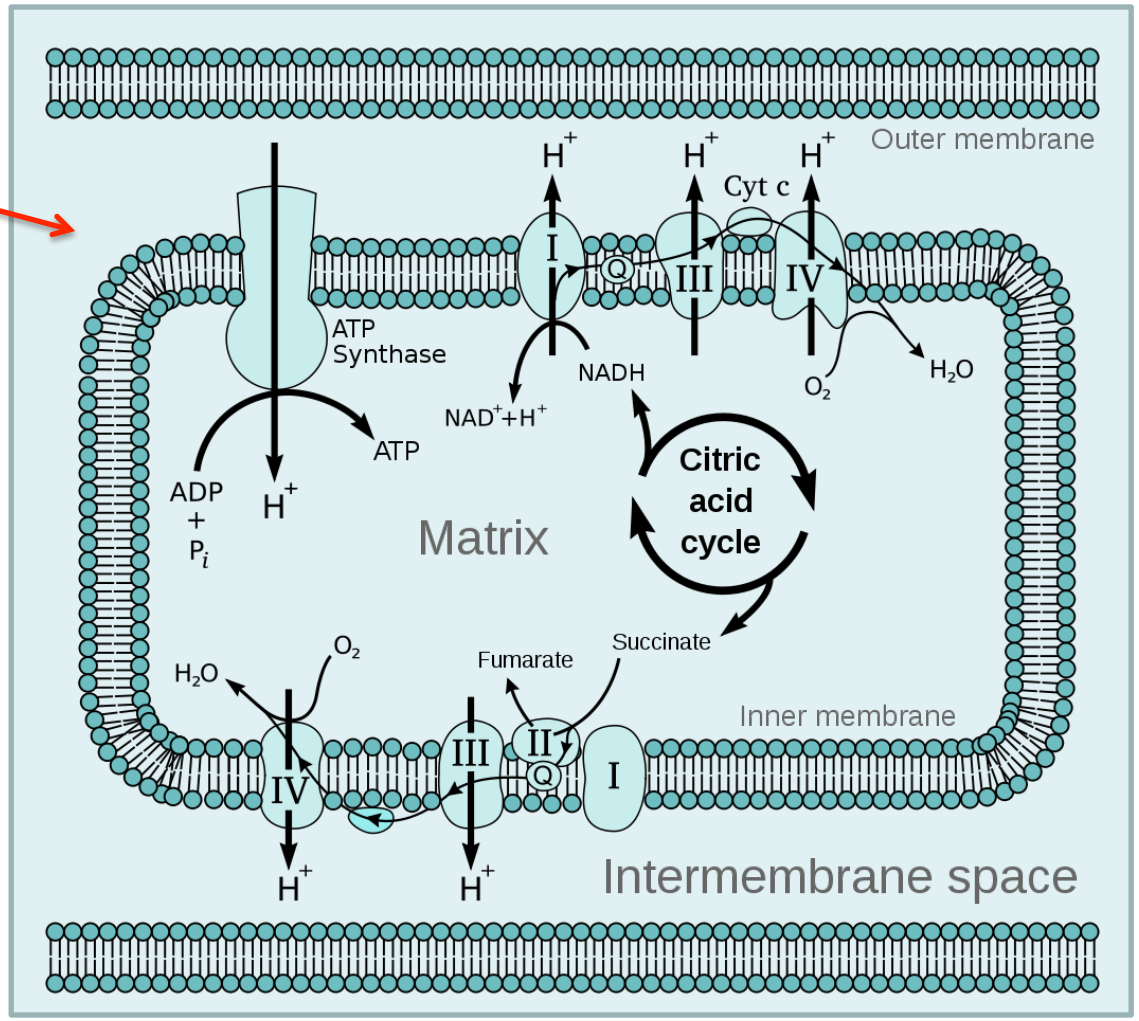
http://en.wikipedia.org/wiki/Oxidative_stress

Oxidative Phosphorylation

Mitocondria
"cellular power house"
Generates ATP

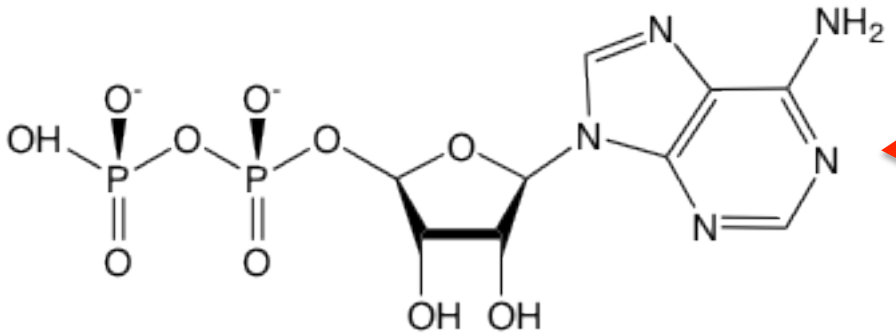
Cellular machinery = complicated

Energy released from oxidation of food drives protons (hydronium ions) through the matrix; in the process, ADP is converted to ATP



http://en.wikipedia.org/wiki/Oxidative_phosphorylation

Oxidative Phosphorylation: Potential Precursor to ROS



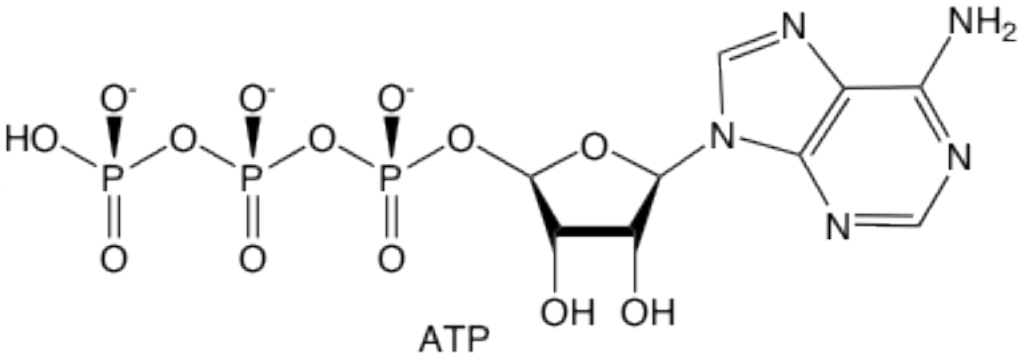
ADP

cell's spent fuel

$$ADP + PO_4^{3-} + 4H_3O^+(\text{intermembrane}) \longrightarrow ATP + H_2O + 4H_3O^+(\text{matrix})$$

$$O_2 + 8H_3O^+(\text{matrix}) + 4e^- \longrightarrow 6H_2O + 4H_3O^+(\text{intermembrane})$$

cellular gasoline

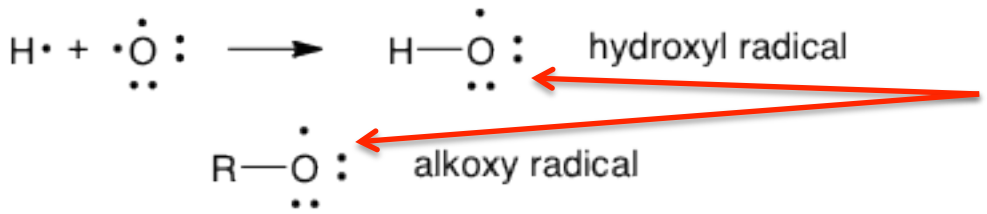


ATP

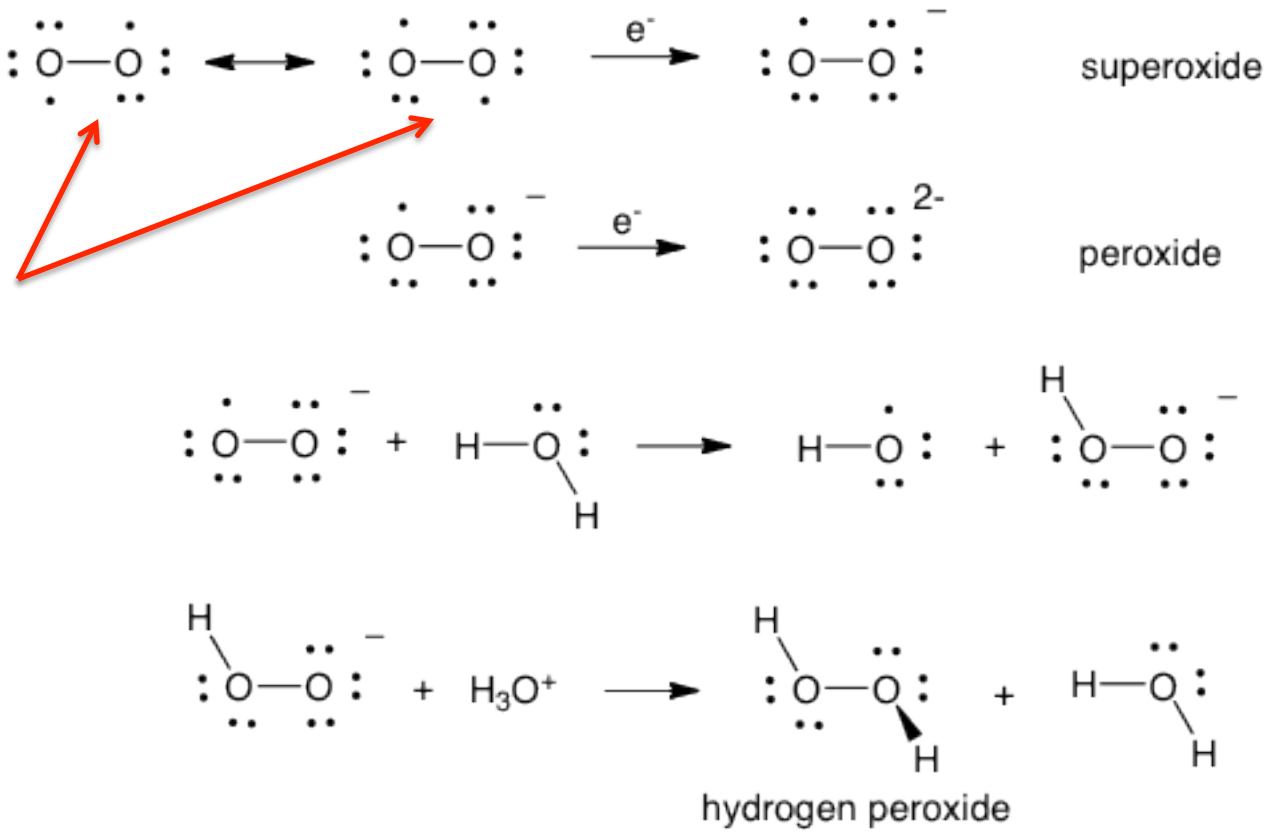
$$ATP + H_2O \rightarrow ADP + PO_4^{3-} \quad \Delta G^{0'} = -31.0 \text{ kJ/mol } (-7.41 \text{ kcal/mol}); \Delta H^{0'} = -24.3 \text{ kJ/mol } (-5.81 \text{ kcal/mol})$$

During ATP production from ADP, e^- can leak out of the mitochondria & react: oxygen is a plentiful and willing target (large electronegativity)

Reactive Oxygen Species (ROS)

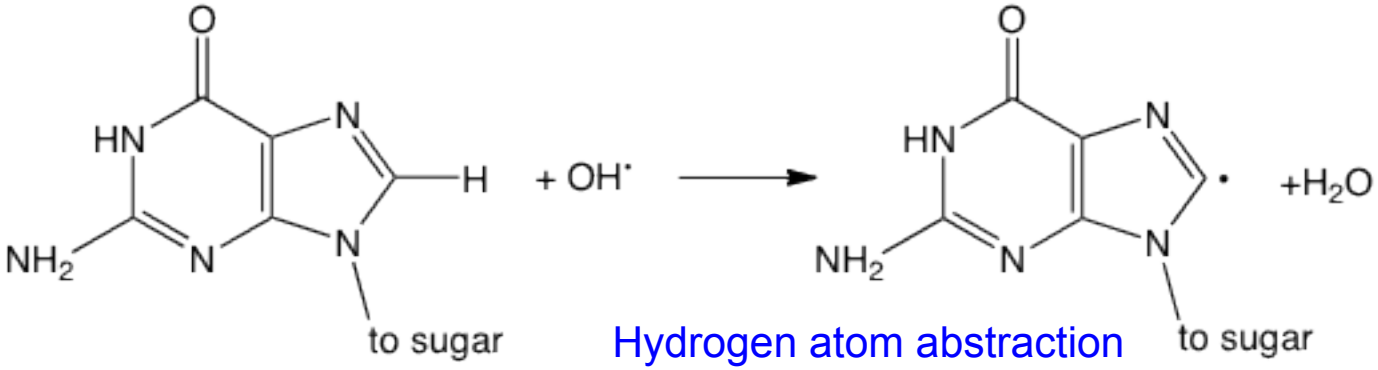


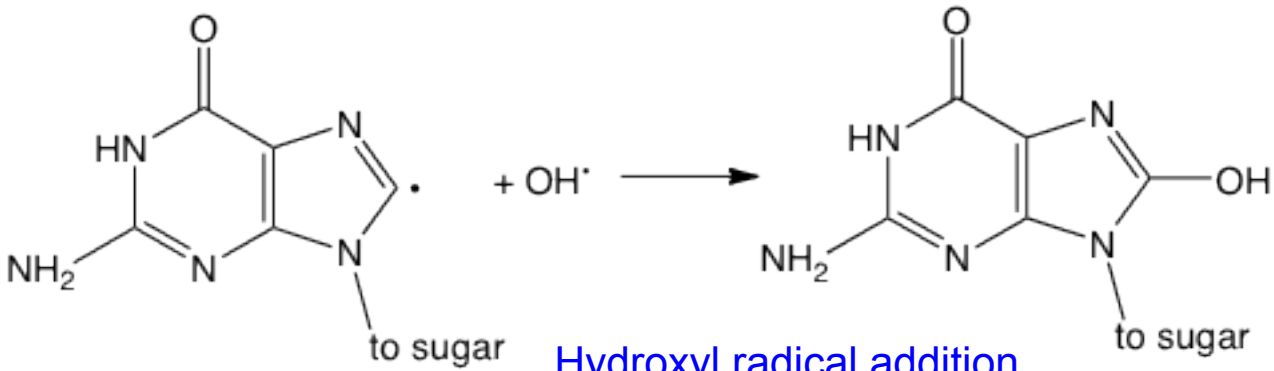
Oxygen does not have Noble gas configuration

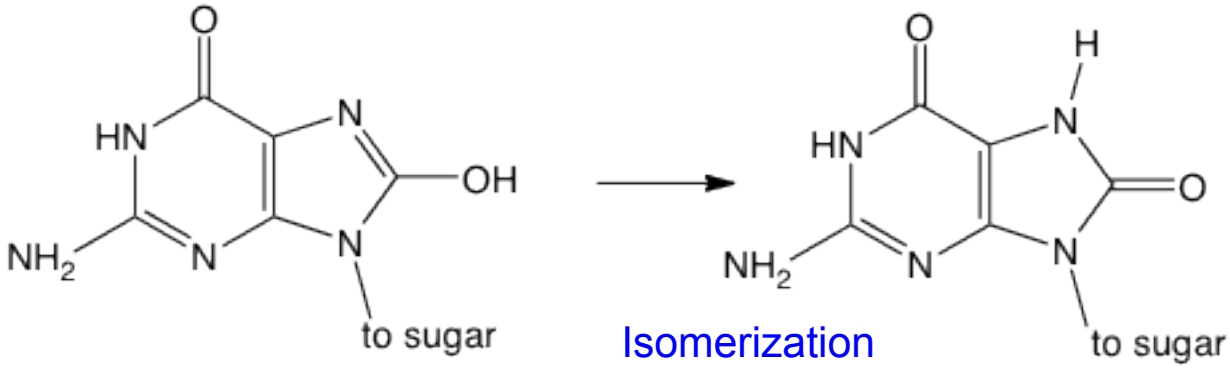


A more accurate Lewis dot structure for O_2

Consequence of ROS Production: Guanine Oxidation

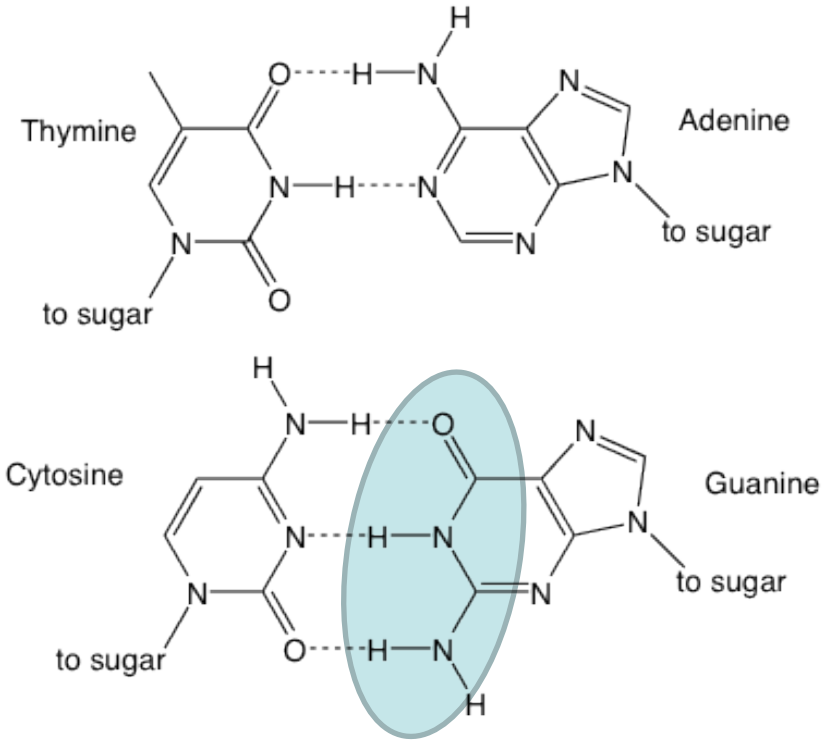






Guanine Oxidation Leads to Base-Pairing Disruption

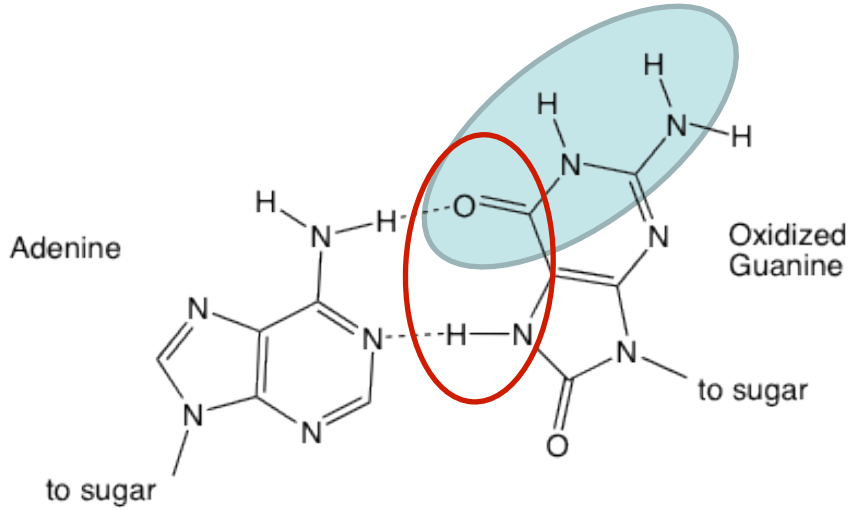
Normal base-pairing



T – A
C – G

critical to proper DNA replication and transcription

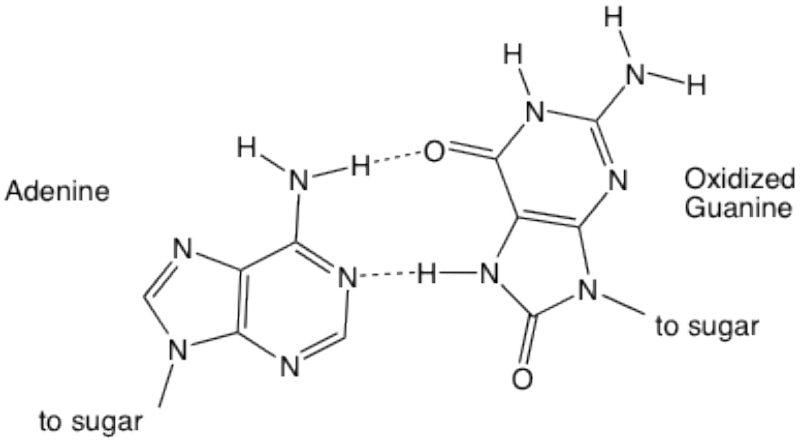
Mismatched base-pairing
Instead of A-T we now have A-G

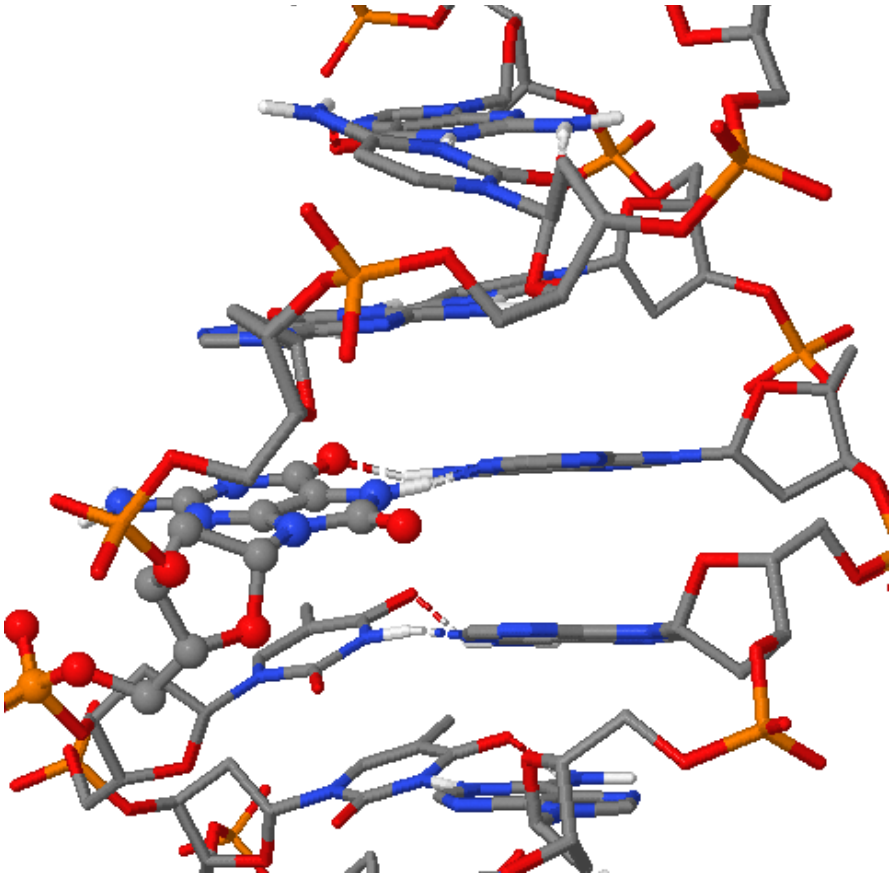


A – G

Rutroh Astro…

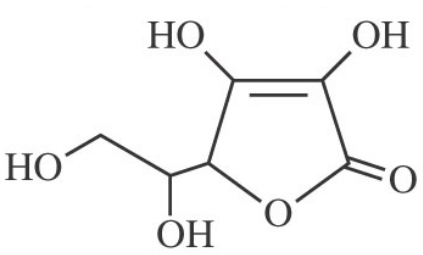
DNA Duplex with Oxidized Guanine



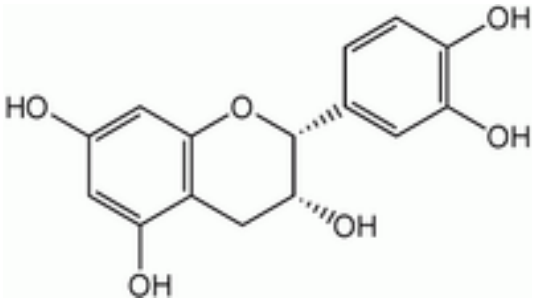


Antioxidants

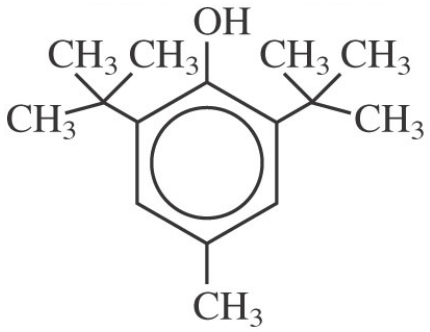
- Reading—chapter 11.9 (6th edition of text)
- Fatty foods become **rancid** after prolonged exposure to oxygen
- **Antioxidants** react with ROS to remove radicals
- Natural and industrial sources
  - berries
  - chocolate
  - red wine
  - BHT, BHA
- Reactions of antioxidants (BHT and BHA):
  - $RO_2^{\cdot} + ArOH \rightarrow ROOH + ArO^{\cdot}$
  - $RO_2^{\cdot} + ArO^{\cdot} \rightarrow$ non-radical products



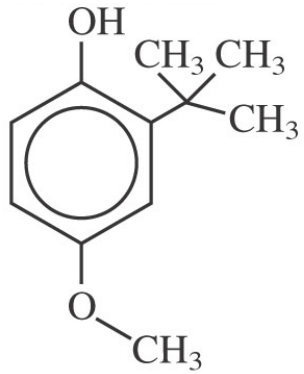
Ascorbic acid
(Vitamin C)



Epicatechin
(**flavonoid** in cocoa)



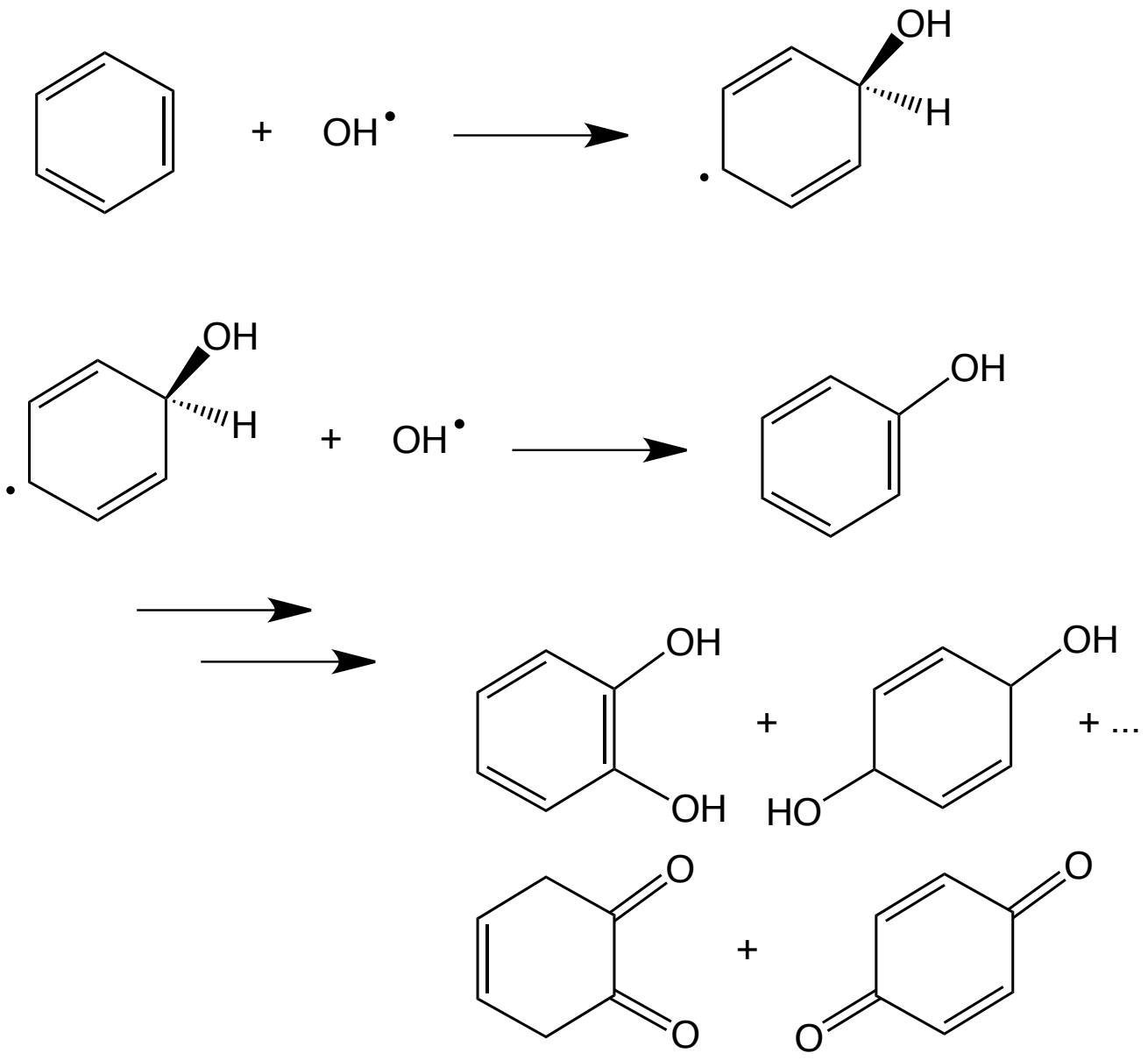
BHT



BHA

BHT = Butylated hydroxytoluene
BHT = Butylated hydroxyanisole

Benzene Oxidation



Thermite Reaction

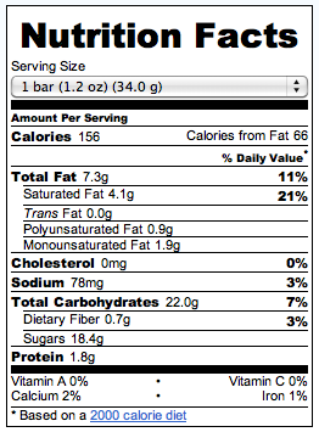
- The main reason to introduce oxidation/reduction chemistry to CHEM 103
- Remember that combustion is a redox reaction
- Metals can “burn” just like hydrocarbons
- Some metals really “want” to be oxides (e.g. Cr, Al)

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$$

- Questions to consider:
  - Which species is being oxidized?
  - Which species is being reduced?
  - Which species is the oxidizing agent?
  - Which species is the reducing agent?

279 kJ/mol Al
(67 kcal/mol Al)
(A Baby Ruth
candy bar is ~160 kcal)

- Thermite reaction used for welding railroad tracks together



Nutrition Facts

Serving Size
1 bar (1.2 oz) (34.0 g)

Amount Per Serving

Calories 156	Calories from Fat 66
	% Daily Value*
Total Fat 7.3g	**11%**
Saturated Fat 4.1g	**21%**
Trans Fat 0.0g	
Polyunsaturated Fat 0.9g	
Monounsaturated Fat 1.9g	
Cholesterol 0mg	**0%**
Sodium 78mg	**3%**
Total Carbohydrates 22.0g	**7%**
Dietary Fiber 0.7g	**3%**
Sugars 18.4g	
Protein 1.8g	

Vitamin A 0% • Vitamin C 0%
Calcium 2% • Iron 1%

* Based on a 2000 calorie diet

Thermite video

$$1000\ \text{lb thermite} \times \frac{454\ \text{g}}{1\ \text{lb}} \times \frac{1\ \text{mole thermite}}{213.7\ \text{g thermite}} \times \frac{2\ \text{mole Al}}{1\ \text{mole thermite}} \times \frac{67\ \text{kcal}}{1\ \text{mole Al}} = 2.85x10^{5}\ \text{kcal}$$

178 Baby Ruths!

Unit 4.3 Summary

- Concepts
  - definitions of redox terms
    - oxidation: a compound loses electron(s)
    - reduction: a compound gains electron(s)
  - determination of oxidation state
  - combustion is a redox reaction: check out the oxidation states of the reactants and products
  - galvanic cells and batteries
    - cathode (+): where the reduction takes place
    - anode (-): where the oxidation takes place
    - V = I*R Voltage = Current * Resistance
  - biological redox
    - reactive oxygen species (hydroxyl, superoxide, peroxide)
    - effects on proteins, DNA
  - thermite reaction: exploiting the propensity of some metals (e.g. Aluminum) to oxidize very easily