THERMOCHEMISTRY

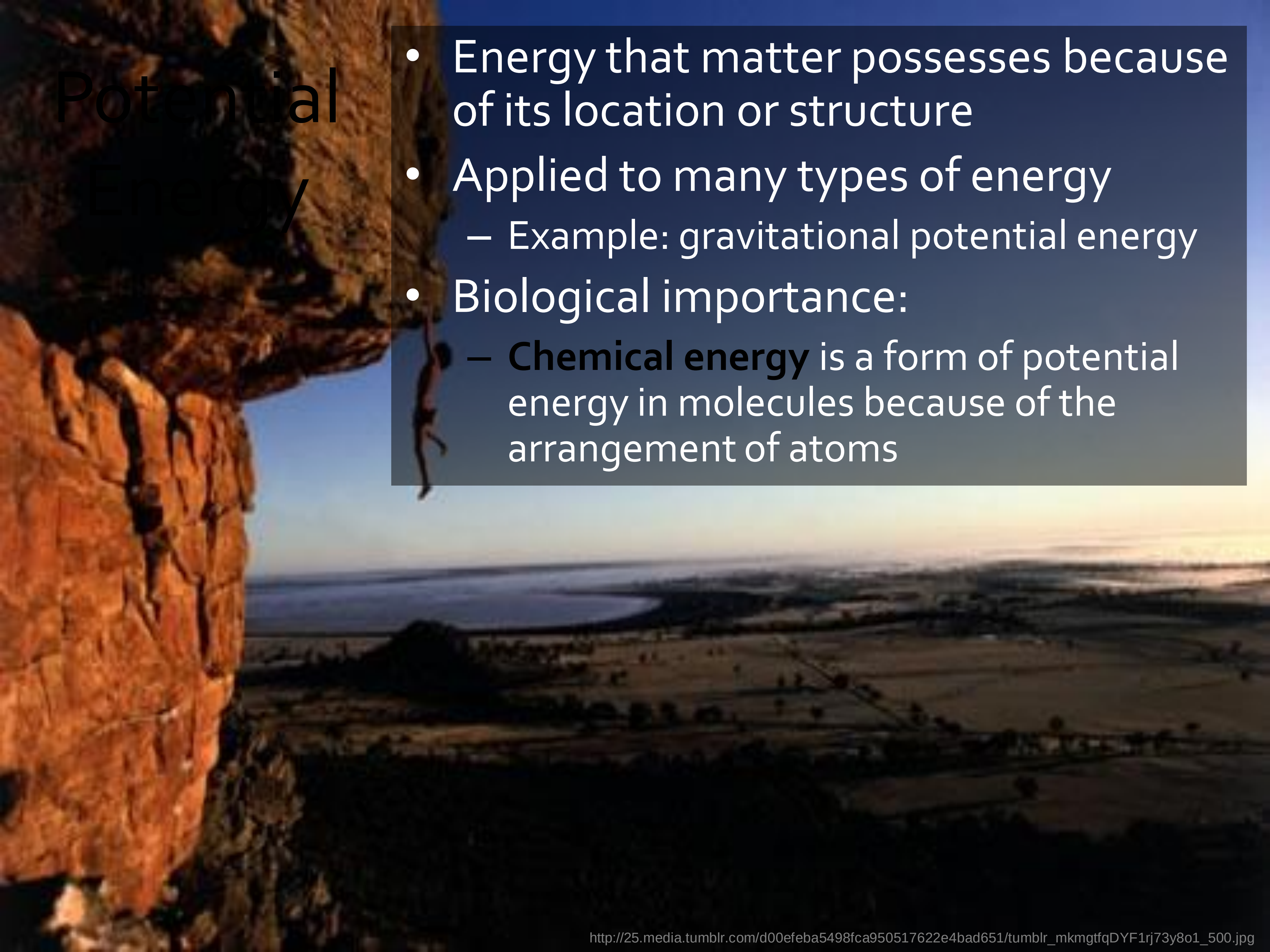
Energy Transformation
ATP Hydrolysis & Coupling
ATP Synthesis & Redox

Content List

- Types of energy
- Energy transformation (first law)
  - Measuring energy: Gibbs Free energy
  - Harnessing free energy
  - ATP coupling
  - Synthesis of ATP
    - Substrate level phosphorylation
    - Oxidative phosphorylation
      - Redox
- Disorder (second law)
- Equilibrium

Types of Energy

- **Energy**: capacity to do work
- Examples:
  - Kinetic
  - Electric
  - Nuclear
  - Sound
  - Thermal
  - Gravitational
  - Chemical



Potential Energy

- Energy that matter possesses because of its location or structure
- Applied to many types of energy
  - Example: gravitational potential energy
- Biological importance:
  - **Chemical energy** is a form of potential energy in molecules because of the arrangement of atoms

http://25.media.tumblr.com/d00efeba5498fca950517622e4bad651/tumblr_mkmgtfqDYF1rj73y8o1_500.jpg

Potential Energy in Bonds

Bond Type	Average Bond Energy (kJ/mol)
H-H	436
C-H	411
O-H	459
N-H	391
C-C	346
C-O	359
C=O	799
O=O	494

Thermodynamics

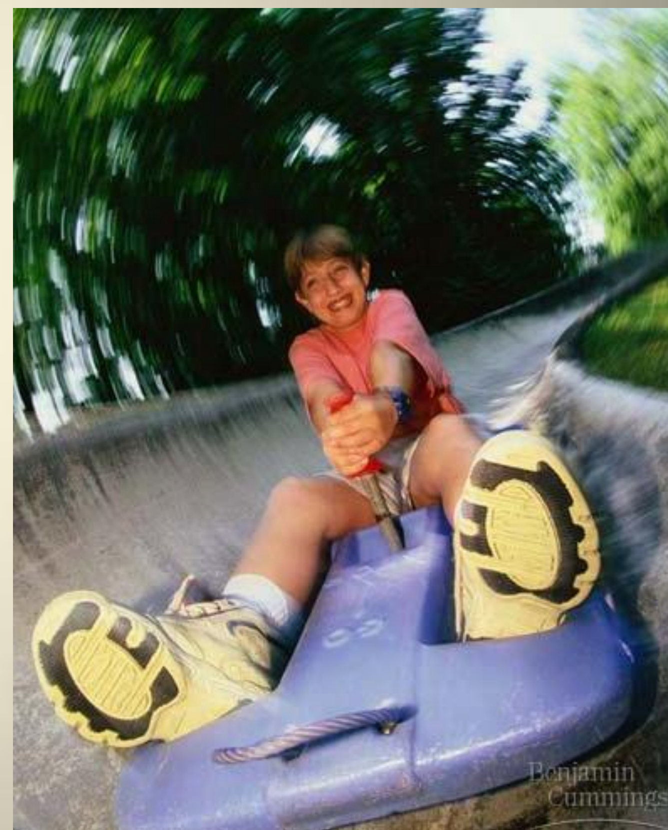
- **Thermodynamics**: study of energy transformations
- **System**: the matter under study
- **Surroundings**: everything outside the system
- **Closed system**: isolated from its surroundings
- **Open system**: energy (and often matter) can be transferred between the system and surroundings
  - Example: Organisms absorb energy in organic molecules and release heat and metabolic waste products

First Law of Thermodynamics

- The total amount of energy in the universe is constant.
- Thus energy cannot be created or destroyed.
- Energy can be transferred and transformed, converting from one form to another

Energy Transformation Example

- Example: Climbing a slide & sliding down
  - Converting kinetic energy to potential energy back to kinetic energy
- Question: Where did the initial kinetic energy for climbing come from?



Energy Transformation

- Answer: From potential energy in food eaten earlier that was stored in the body
- Cellular respiration unleashes the potential energy in the foods that we consume

http://intentblog.com/wp-content/uploads/2013/03/url-19.jpeg

Energy Transformation

- Q: Where did the chemical energy in food come from?
- A: From light energy by plants during photosynthesis

http://media.salon.com/2010/08/the_quiet_vegetarian.jpg

Energy Transformation

- Sunlight provides a daily source of free energy for the photosynthetic organisms.
  - Plants transform light to chemical energy; they do not produce energy.
- Non-photosynthetic organisms depend on a transfer of free energy from photosynthetic organisms in the form of organic molecules.

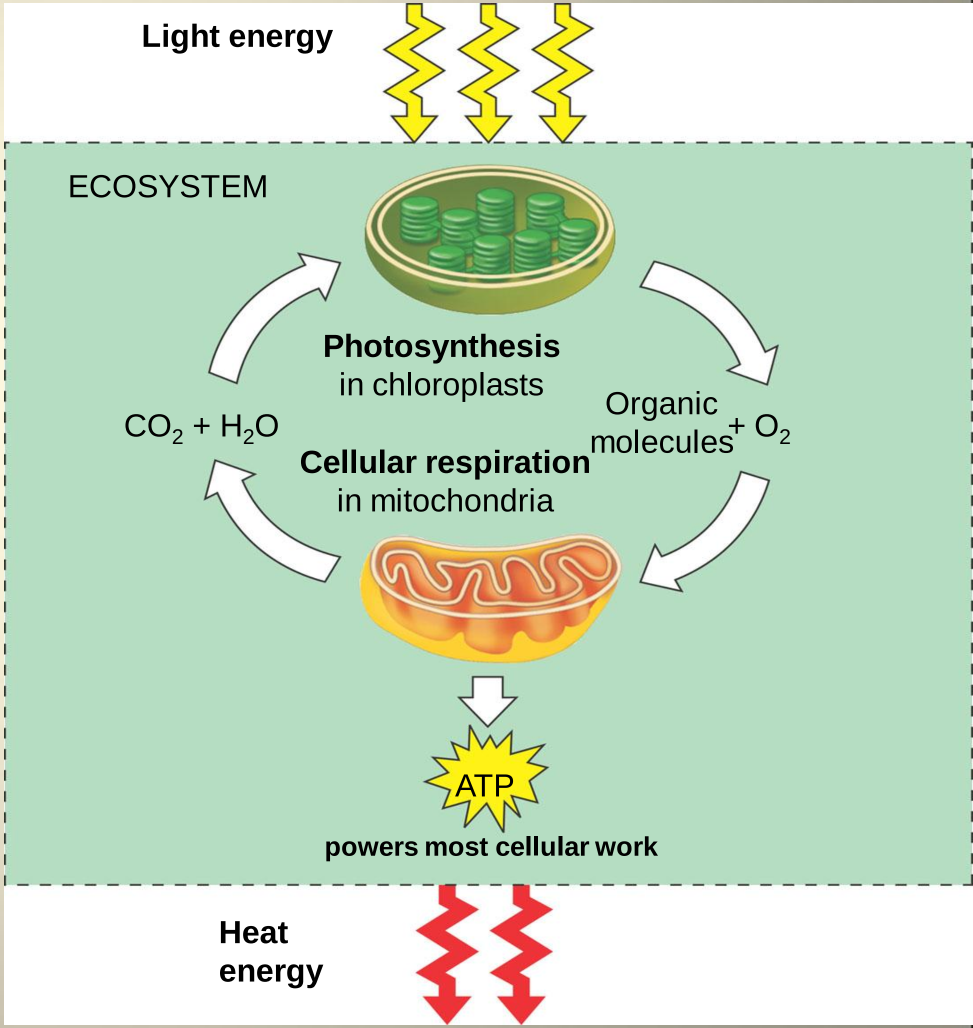


Figure 9.1

Energy Transformation

Light energy

$\downarrow$ Photosynthesis

'food' energy (e.g. glucose)

$\downarrow$ Cellular Respiration

'cellular' energy (e.g. ATP)

$\downarrow$

cellular work + lost as heat

Bond Energy

- All chemical reactions break and form bonds
- The greater the bond energy:
  - the more chemically stable the bond
  - the more energy is required to break the bond
- As bonds are broken and formed, energy is transferred from bond to bond

Bond Type	Average Bond Energy (kJ/mol)
H-H	436
C-H	411
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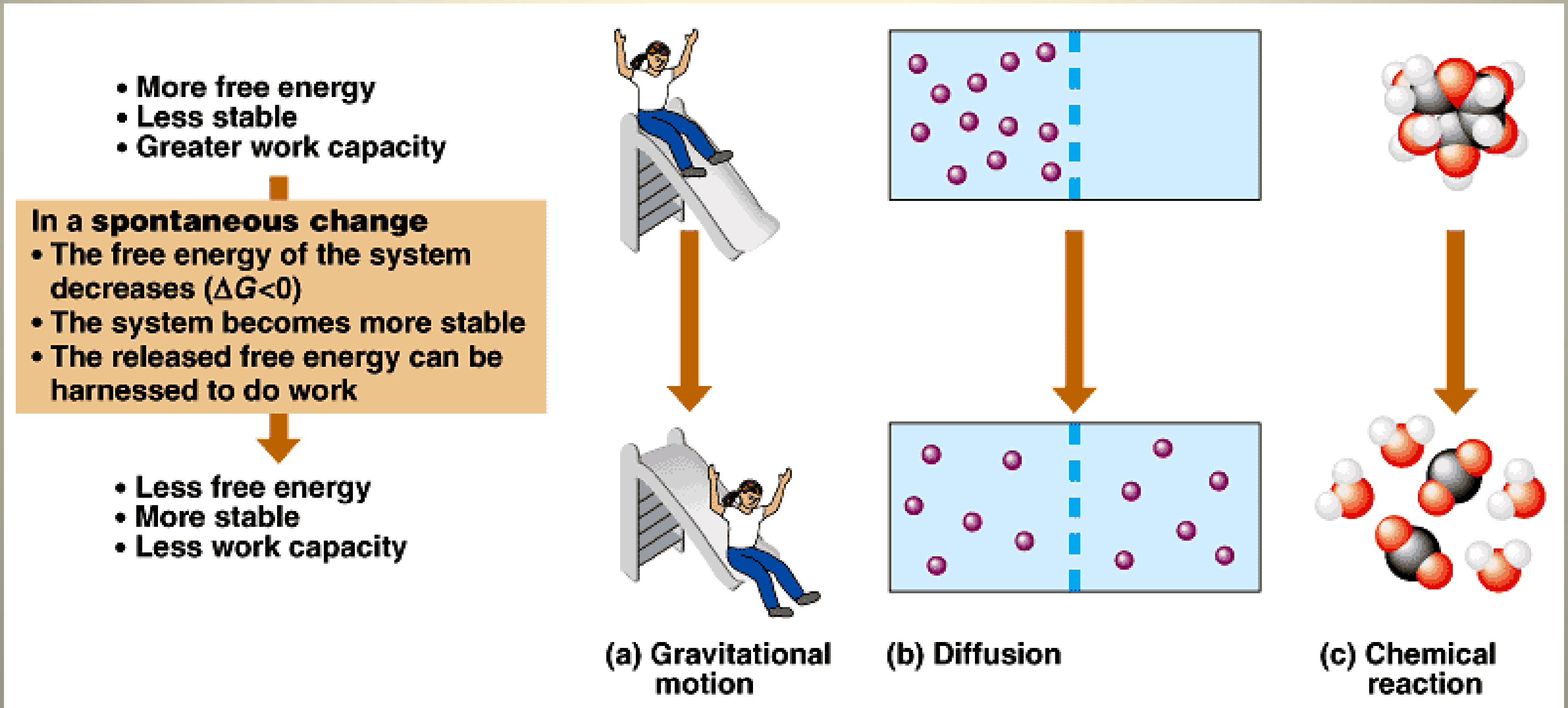
N-H	391
C-C	346
C-O	359
C=O	799
O=O	494

Bond Energy

- The net energetic effect of a chemical reaction is:
  - **Exergonic** when energy for breaking and forming bonds is **released**
  - **Endergonic** when energy for breaking and forming bonds is **absorbed**

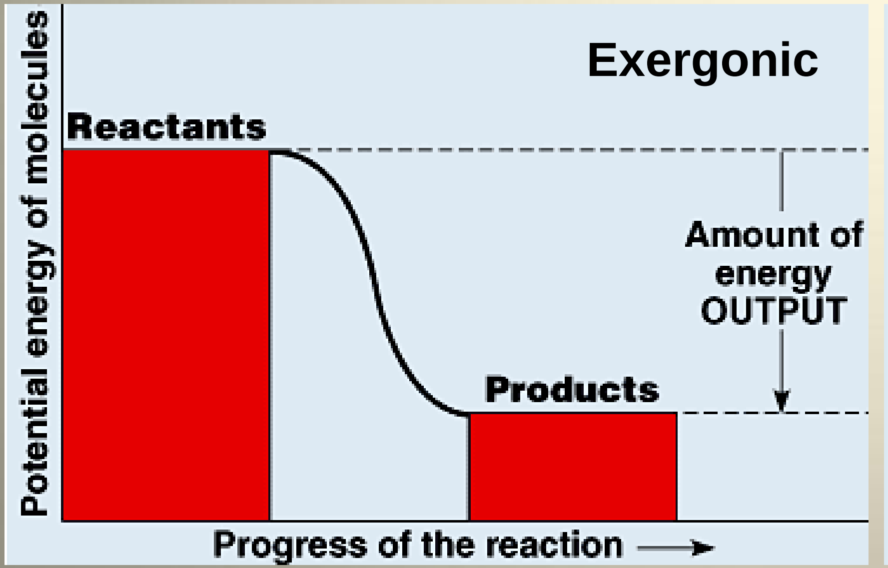
Gibbs Free Energy

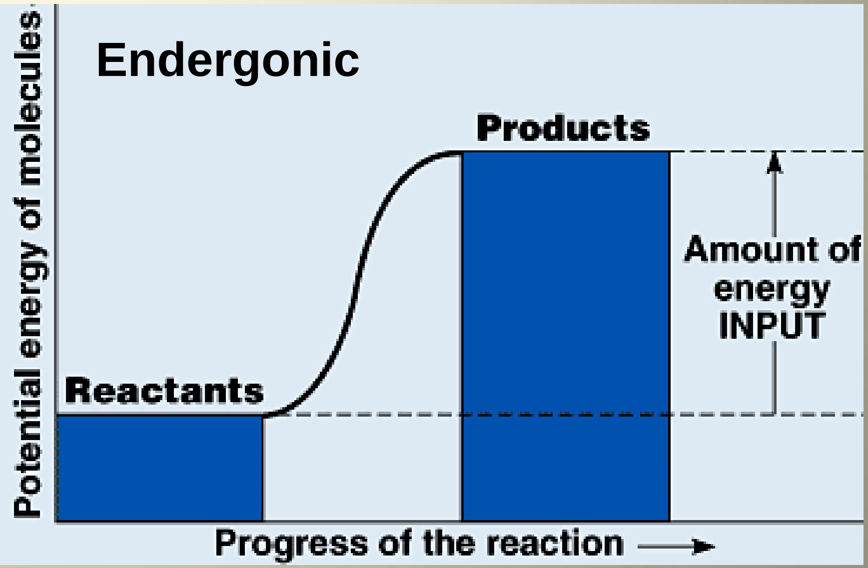
- The energy that is able to perform work
- $\Delta G = G_{final} - G_{initial} = G_{products} - G_{reactants}$



Gibbs Free Energy

Characteristics	Exergonic	Endergonic
Energy	Released	Absorbed
ΔG	Negative	Positive
Reaction	Spontaneous	Nonspontaneous
Products	More stable, less energy	Less stable, more energy

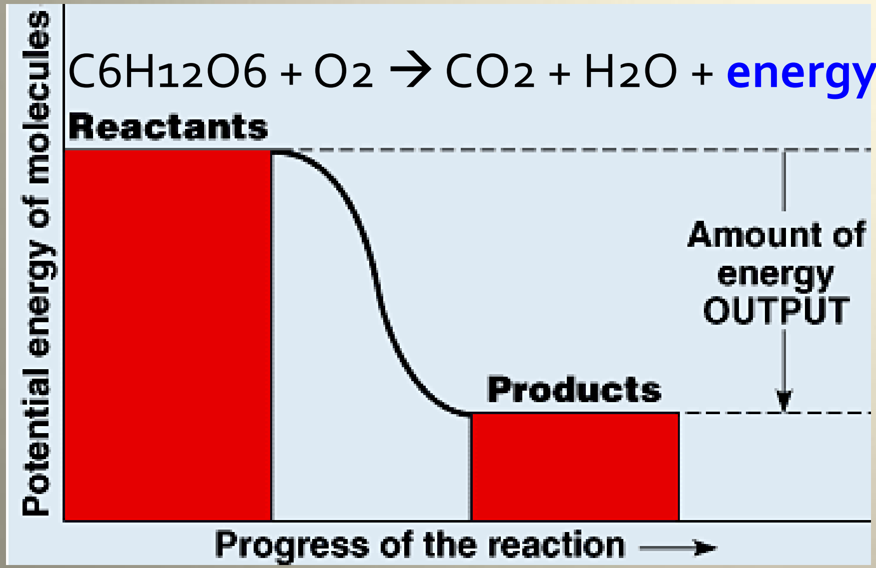




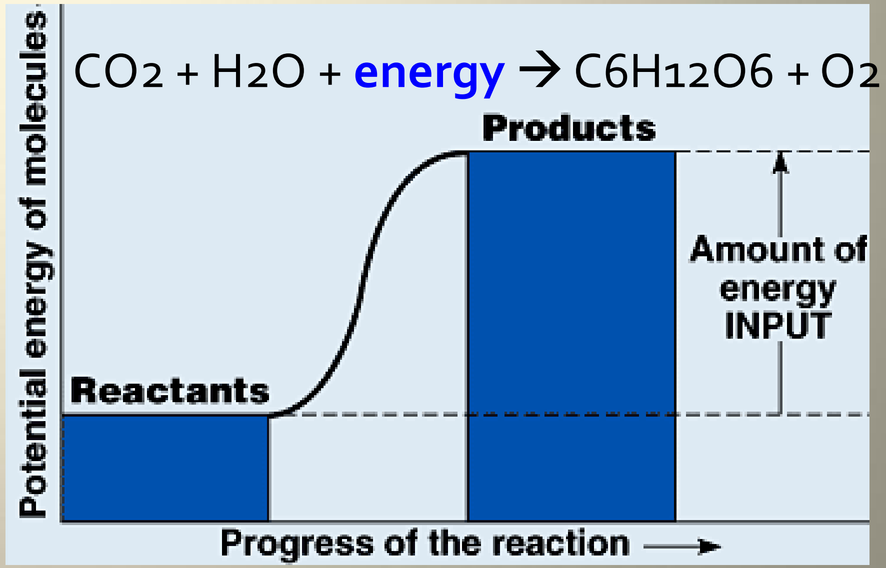
Gibbs Free Energy

Characteristics	Exergonic	Endergonic
Example	Cellular Respiration	Photosynthesis
ΔG	-2870 kJ/mol -686 kcal/mol	+2870 kJ/mol +686 kcal/mol

Exergonic



Endergonic

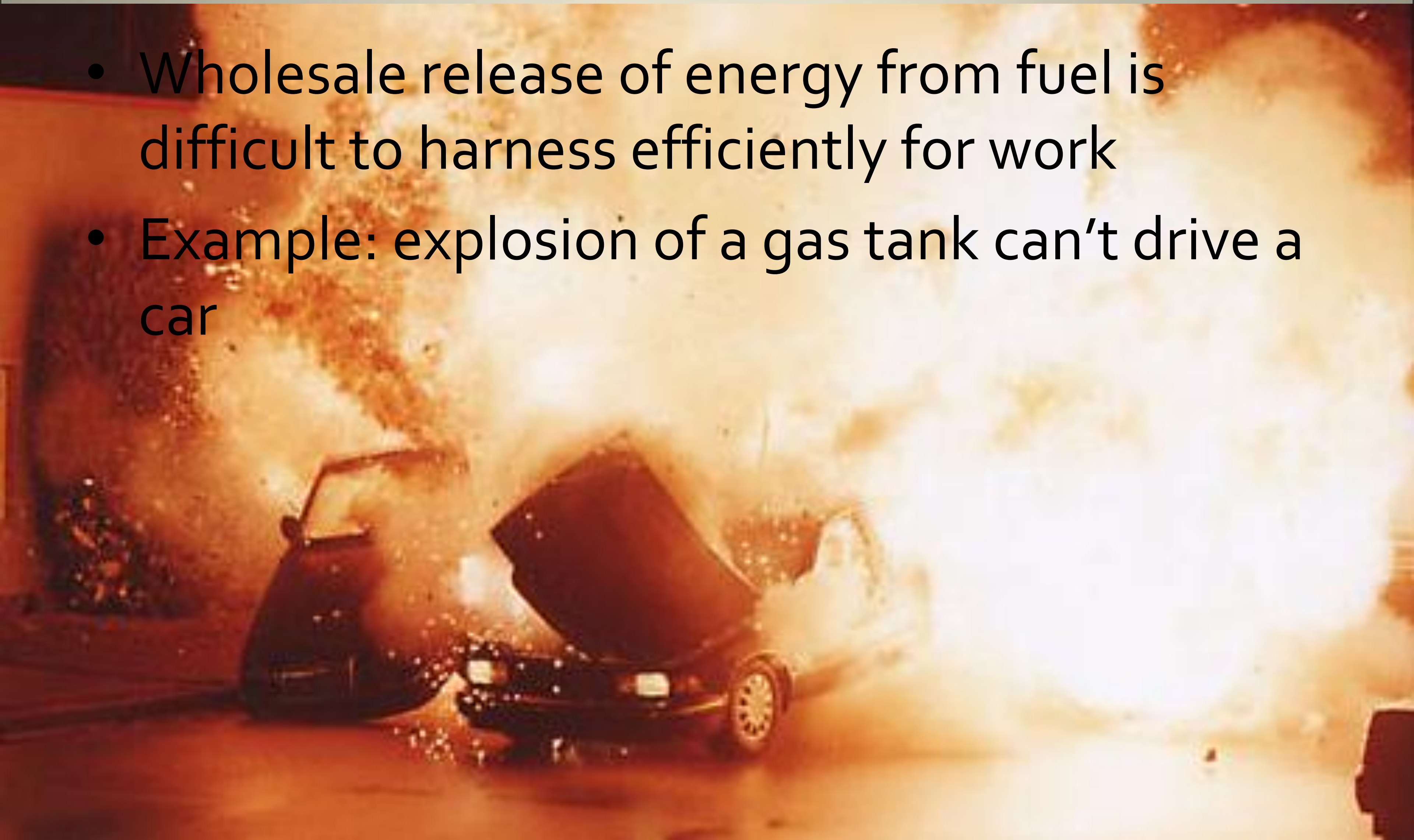


Gibbs Free Energy

Characteristics	Exergonic	Endergonic
Energy	Released	Absorbed
ΔG	Negative	Positive
Reaction	Spontaneous	Non-spontaneous
Products	More stable Less energy	Less stable More energy

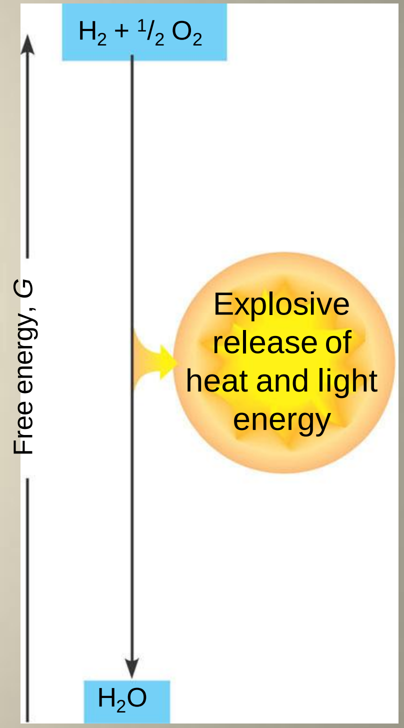
Harnessing Free Energy

- Wholesale release of energy from fuel is difficult to harness efficiently for work
- Example: explosion of a gas tank can't drive a car



Harnessing Free Energy

- A large release of energy occurs
- Example: Oxidation of sugar
  - http://www.youtube.com/watch?v=K8DRM3k39Pg
  - http://www.youtube.com/watch?v=KZq7W2cqf8I
  - http://www.youtube.com/watch?v=nN8xD_bv2aQ&feature=related
  - http://www.youtube.com/watch?v=mamoT11TEV4&feature=related
- Example: Reaction of hydrogen and oxygen to form water
  - http://www.youtube.com/watch?v=NYC23ANpEds

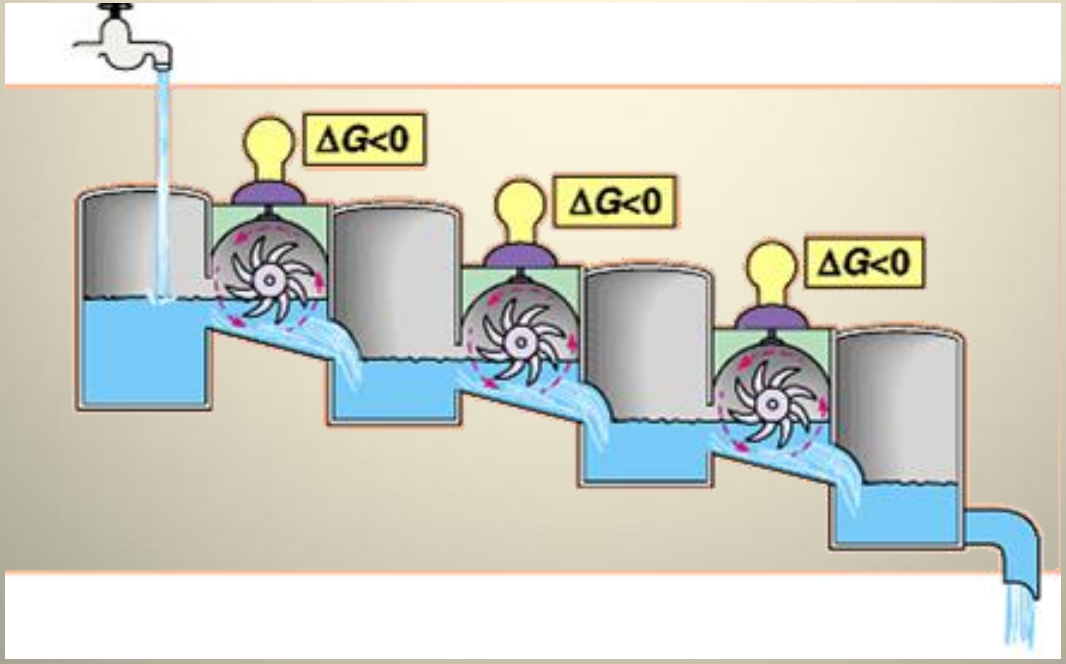


Uncontrolled reaction

Figure 9.5 A

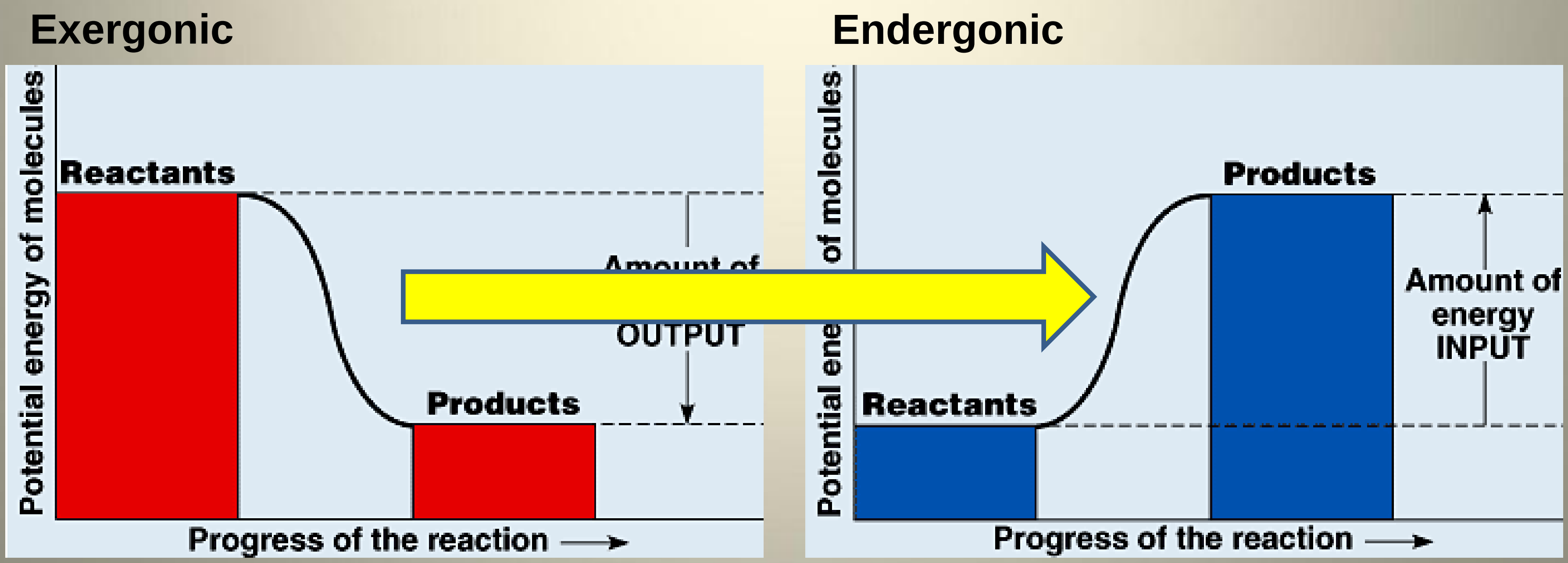
Harnessing Free Energy

- Cells release free energy by gradually breaking down organic fuel in a series of reactions each catalyzed by an enzyme



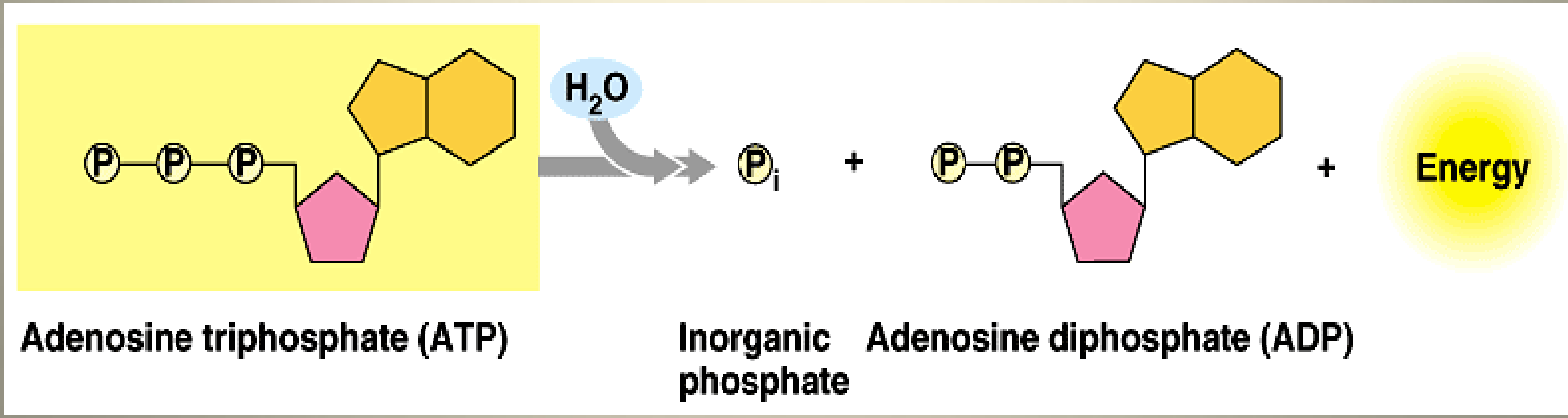
Energy Transformation: Coupling

- Exergonic reactions drive endergonic reactions
- Example:
  - Energy in the bonds of the food we eat drives (or is transferred to) the production of ATP
  - ATP hydrolysis drives cellular work



ATP Hydrolysis

- Hydrolysis of phosphate bonds yields energy
  - phosphate groups require low energy to break
  - new bonds formed release more energy than the energy required to break the bond
  - products are more stable

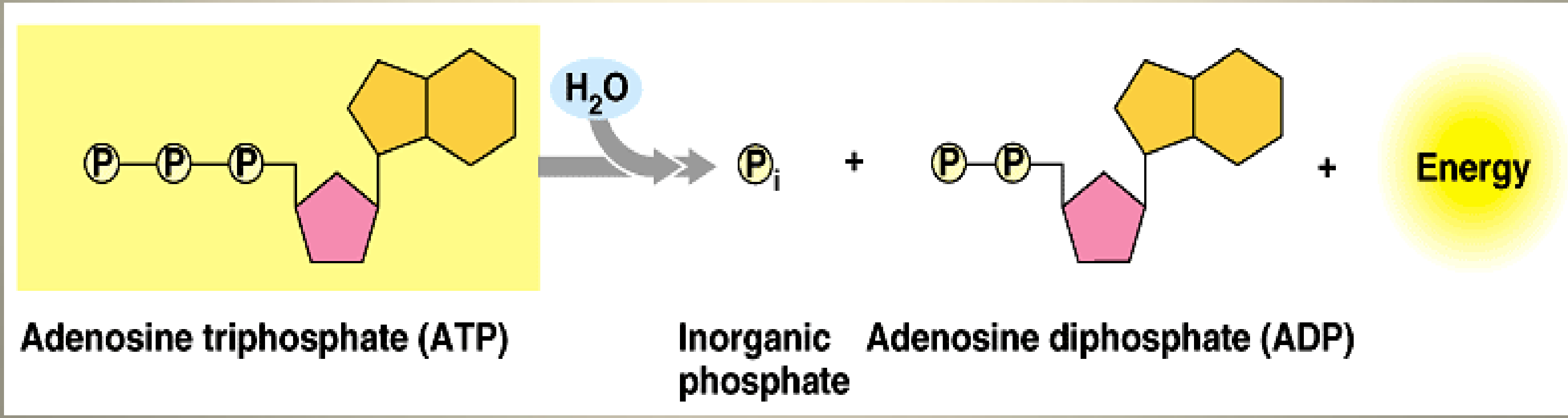


Phosphate Bonds

- Referred to as high-energy phosphate bonds but are actually fairly weak covalent bonds
  - Each of the three phosphate groups has a negative charge
  - Their **repulsion contributes to the instability** of this region of the ATP molecule.

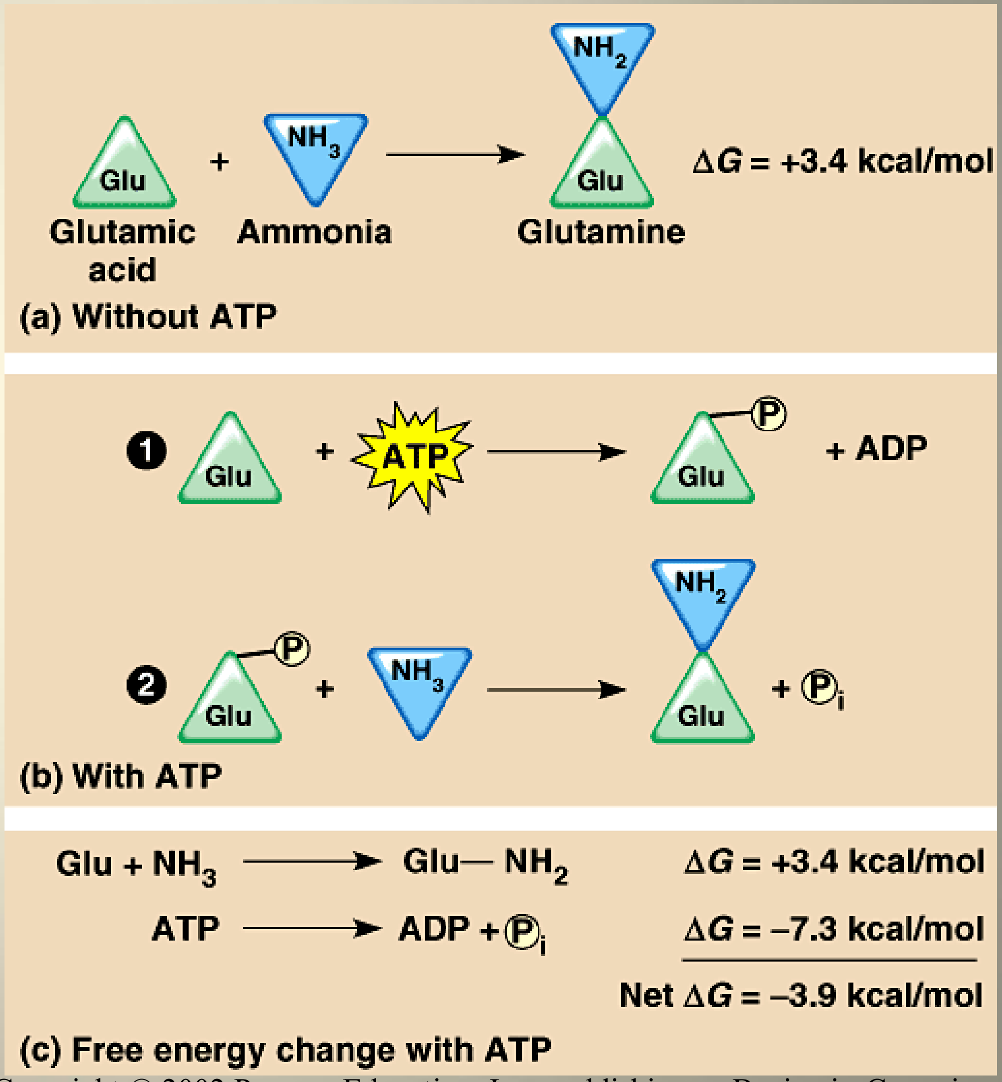
ATP Hydrolysis

- ΔG is -7.3 kcal/mol under standard conditions
- ΔG is -13 kcal/mol in a cell
- ATP is (in most cases) the immediate source of energy that powers cellular work



Energy Transformation: ATP Coupling

- Energy from the hydrolysis of ATP is coupled to endergonic processes by transferring the phosphate group to another molecule.
- The phosphorylated molecule is now more reactive.



Types of Cellular Work

- Transport work
  - pumping substances across membranes against the direction of spontaneous movement
- Mechanical work
  - beating of cilia
  - contraction of muscle cells
  - movement of chromosomes
- Chemical work
  - synthesis of polymers from monomers
  - many enzymatic reactions

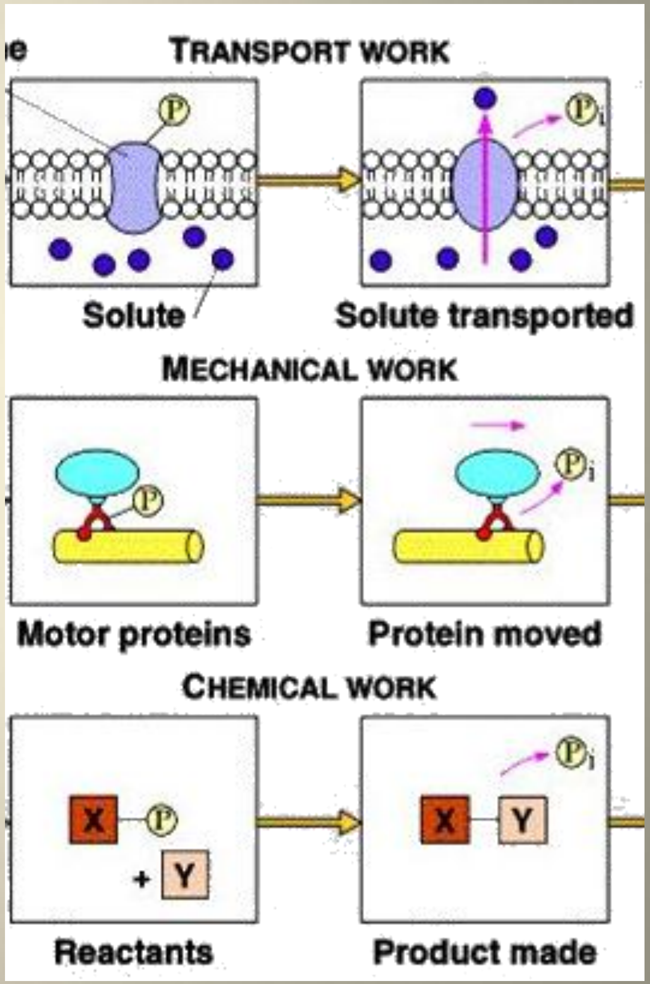


Fig 9.2

ATP Coupling and work

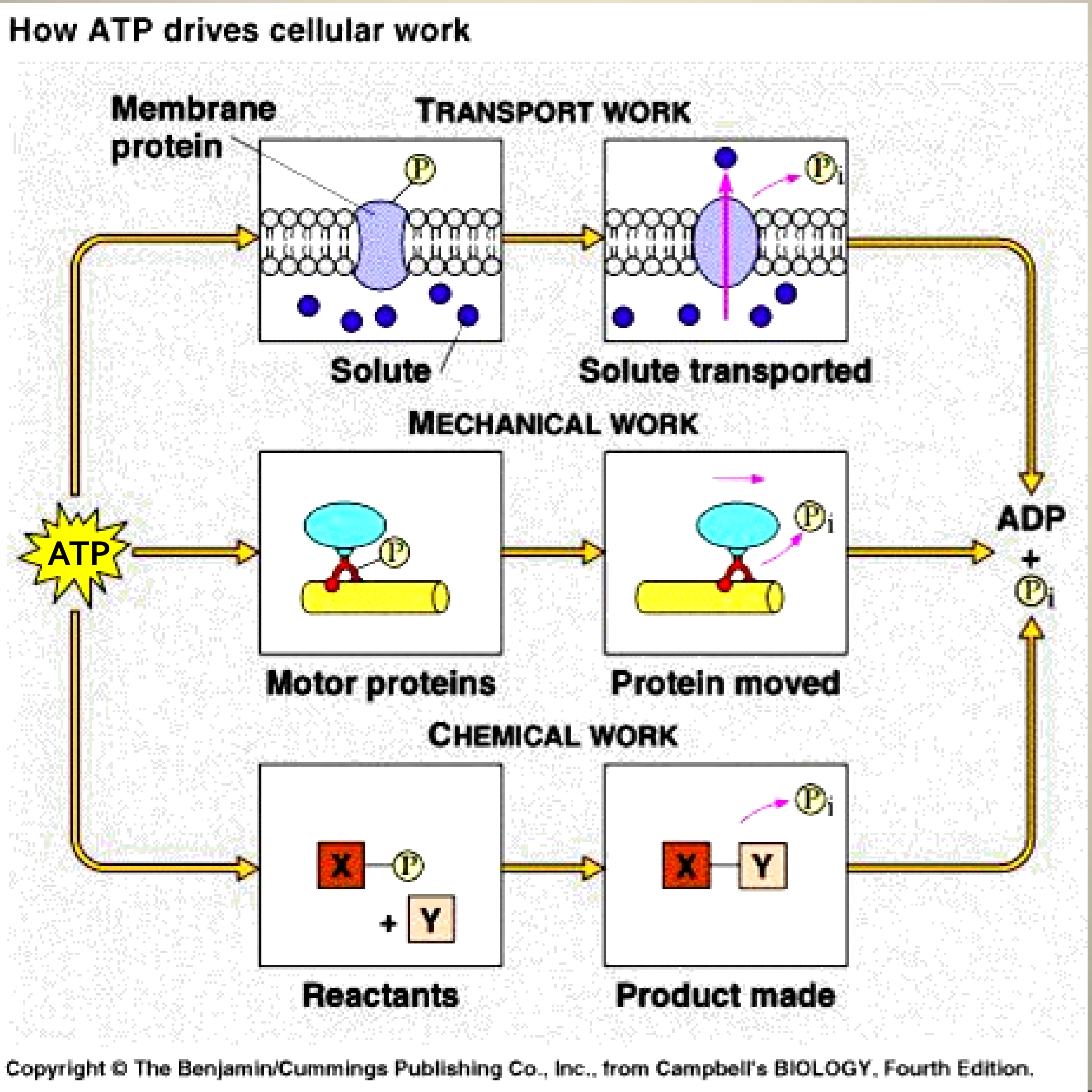
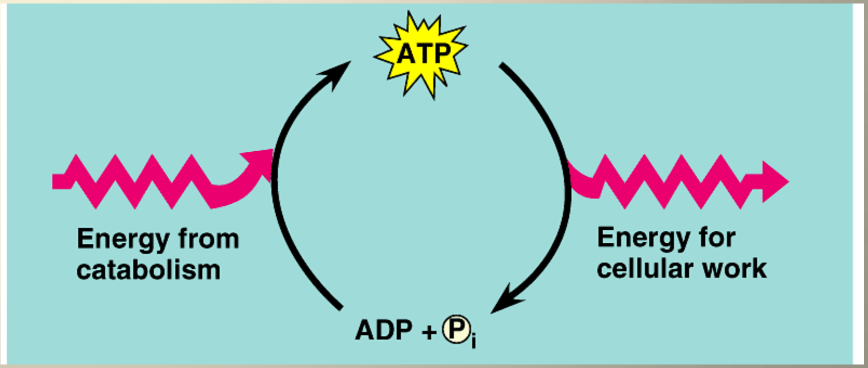


Figure 9.2

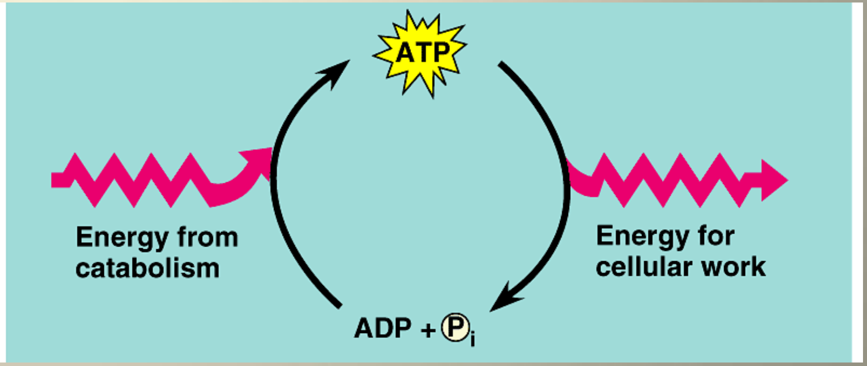
ATP Synthesis

- ATP is continually regenerated by adding a phosphate group to ADP
  - In a working muscle cell the entire pool of ATP is recycled once each minute
  - Over 10 million ATP consumed and regenerated per second per cell



ATP Synthesis

- Regeneration of ATP is an endergonic process:
  - investment of energy: $\Delta G = +7.3$ kcal/mol
- Energy for renewal comes from catabolic reactions in the cell
- Relocation of electrons in organic compounds releases chemical potential energy to drive synthesis of ATP

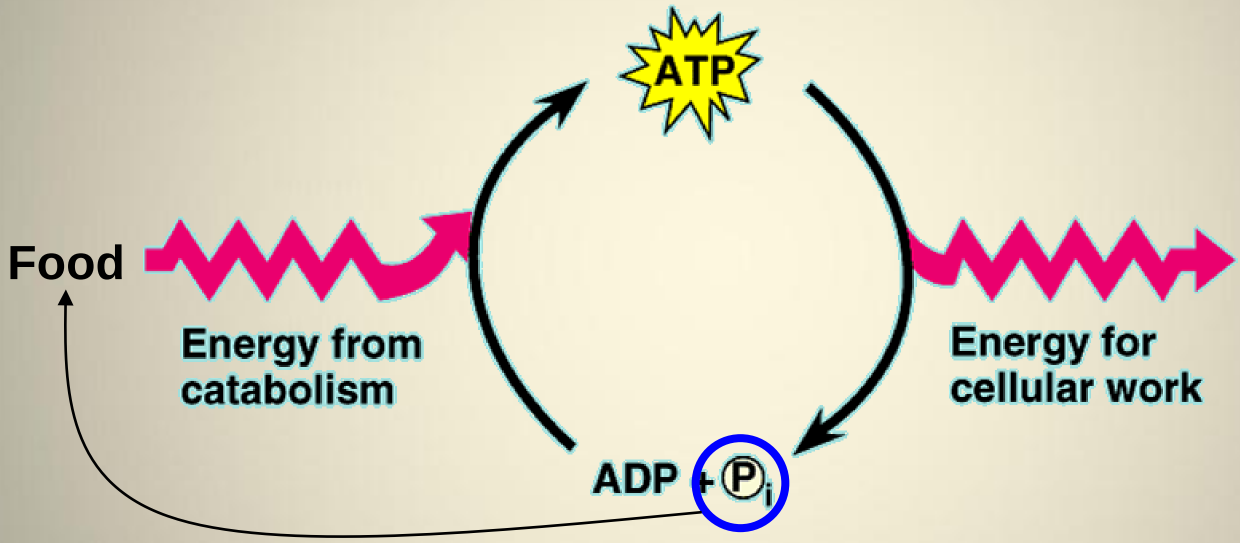


Methods of ATP Synthesis

- Substrate-level phosphorylation
- Oxidative phosphorylation

Substrate-level Phosphorylation

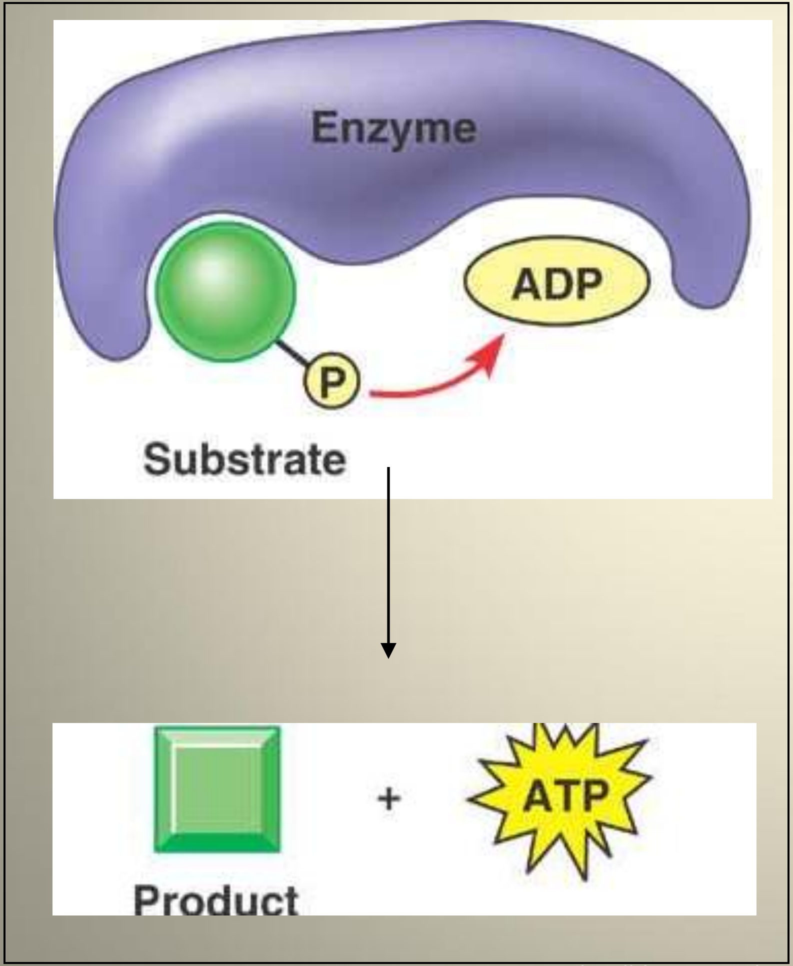
- Direct method of ATP synthesis



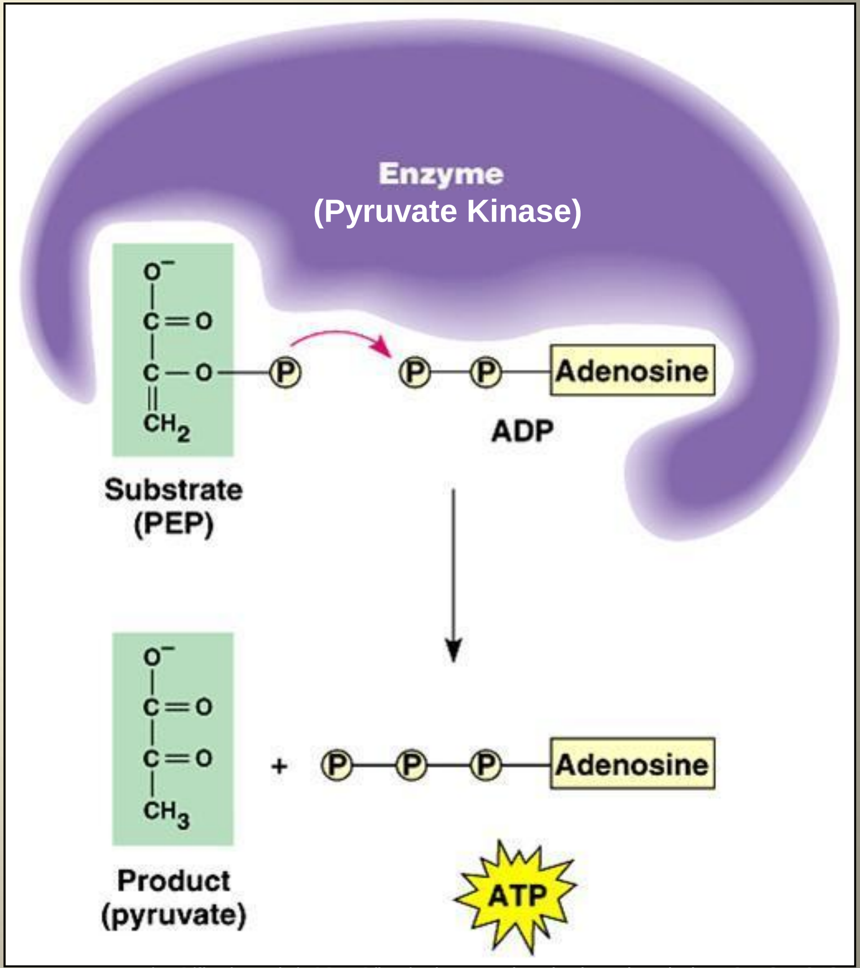
- The phosphate needed to make ATP is actually covalently attached to the “food”
- An enzyme transfers the phosphate from the “food” onto ADP to make ATP

Substrate-level Phosphorylation

- An enzyme transfers phosphate from substrate to ADP

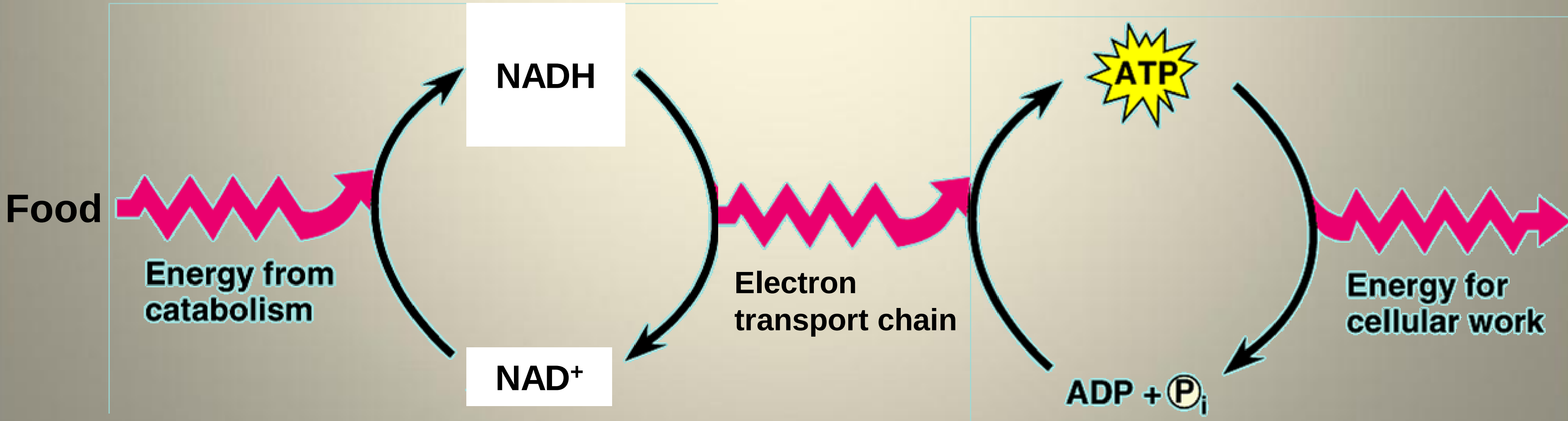


- Example from glycolysis in cellular respiration



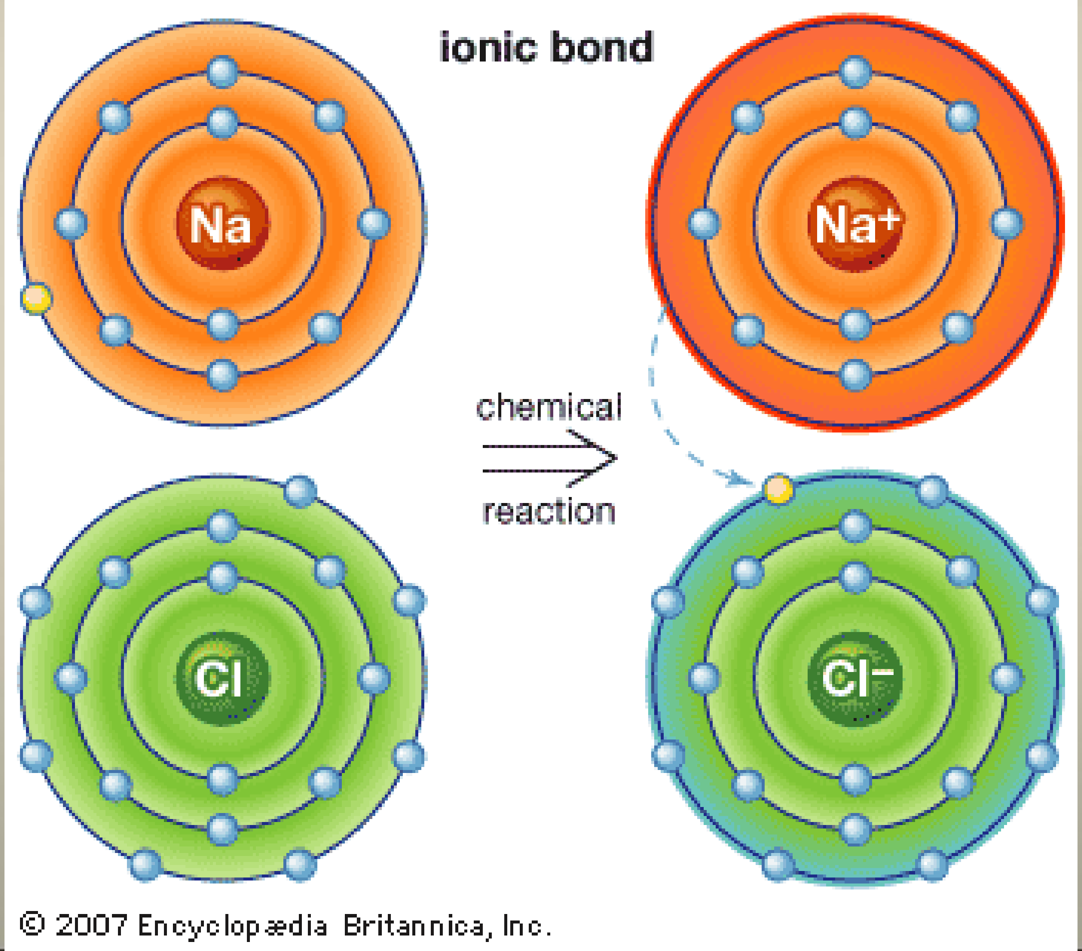
Oxidative Phosphorylation

- Indirect method of ATP synthesis
- Uses redox reactions where electrons are transferred to an intermediate forming high energy molecules (NADH, $FADH_2$)



Redox Reactions

- reactions involving electron transfer



The Principle of Redox

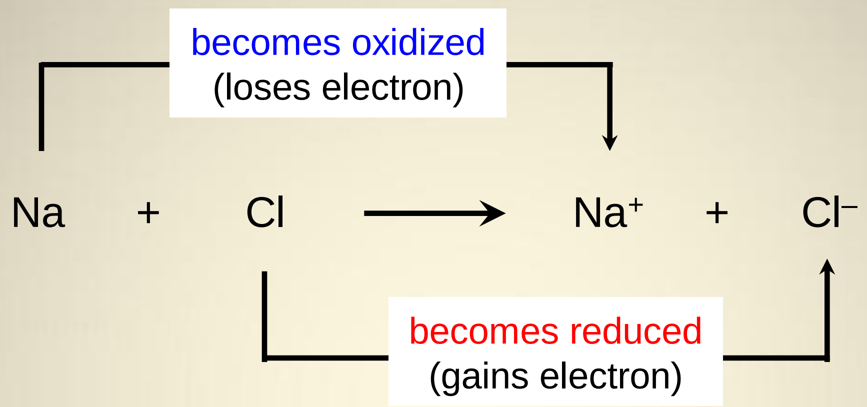
- Oxidation
  - A substance loses electrons
  - Is oxidized
- Reduction
  - A substance gains electrons
  - Is reduced

- LEO the lion says GER
  - Loss of Electrons is Oxidation
  - Gain of Electron is Reduction
- OIL RIG
  - Oxidation is Loss
  - Reduction is Gain

Redox Reactions

- Reducing Agent:
  - substance that LOSES electrons
  - causes the other substance to be reduced
- Oxidizing Agent:
  - substances that GAIN electrons
  - causes the other substance to be oxidized

Example of Redox Reactions



- Na
  - Electron donor: lose electrons, becoming oxidized
- Cl
  - Electron acceptor: gains electrons, becoming reduced

Example of Redox Reactions

becomes oxidized
(loses electron)

$$Na + Cl \longrightarrow Na^+ + Cl^-$$

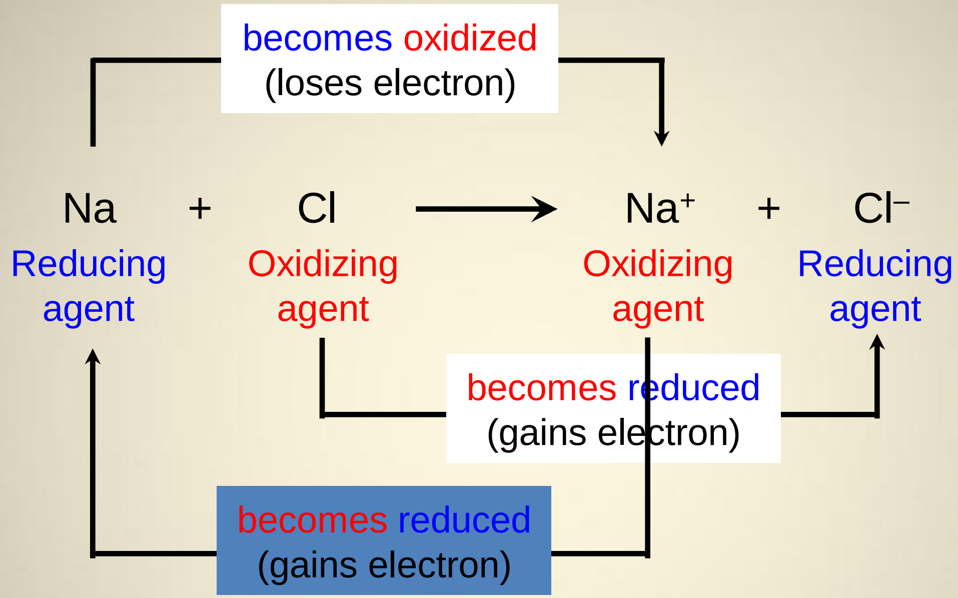
Reducing agent (Na)

Oxidizing agent (Cl)

becomes reduced
(gains electron)

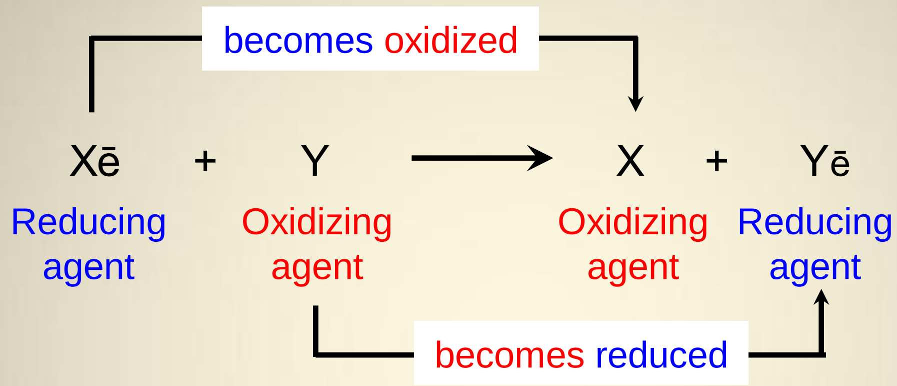
- Na
  - Electron donor: lose electrons, becoming oxidized
  - Reducing agent: cause Cl to accept the donated electron becoming reduced
- Cl
  - Electron acceptor: gains electrons, becoming reduced
  - Oxidizing agent: cause Na to lose electrons becoming oxidized

Example of Redox Reactions



- The reverse reaction can also occur
- Reducing and oxidizing agents are pairs

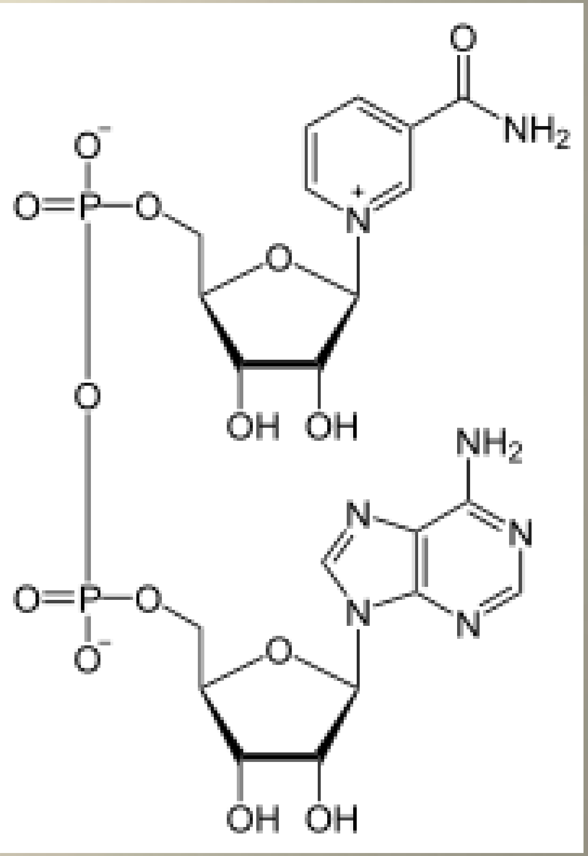
Generalizing Redox Reactions



- X
  - Electron donor: lose electrons, becoming oxidized
  - Reducing agent: cause Y to accept electrons becoming reduced
- Y
  - Electron acceptor: gains electrons, becoming reduced
  - Oxidizing agent: cause X to lose electrons becoming oxidized

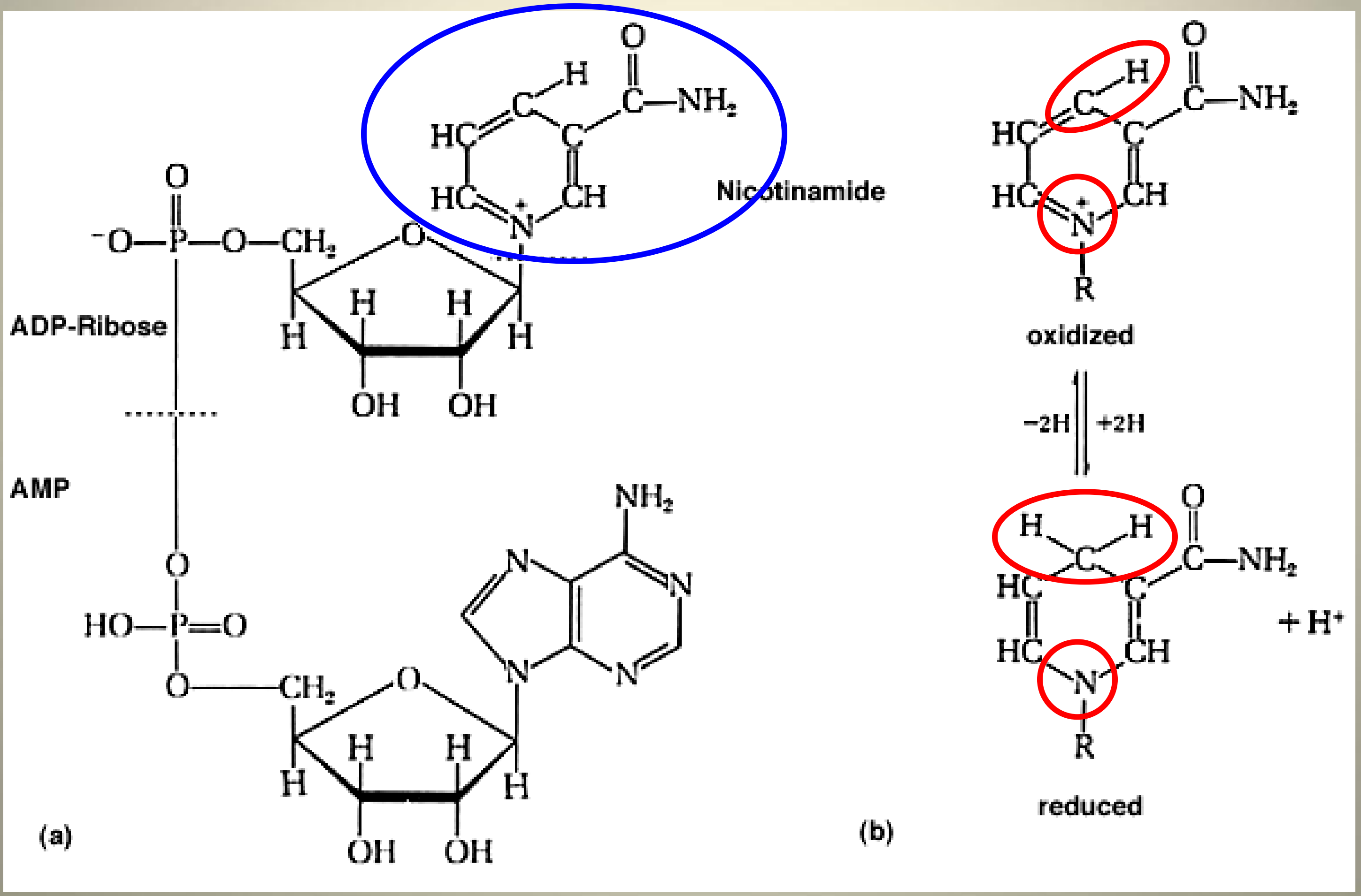
Oxidizing Agent in Metabolism

- NAD+
  - Nicotinamide adenine dinucleotide
  - a coenzyme
  - can accept electrons from organic compounds
    - Gain of electrons is reduction (becomes reduced)
    - forming NADH
  - acts as an oxidizing agent



Redox with NAD+/NADH

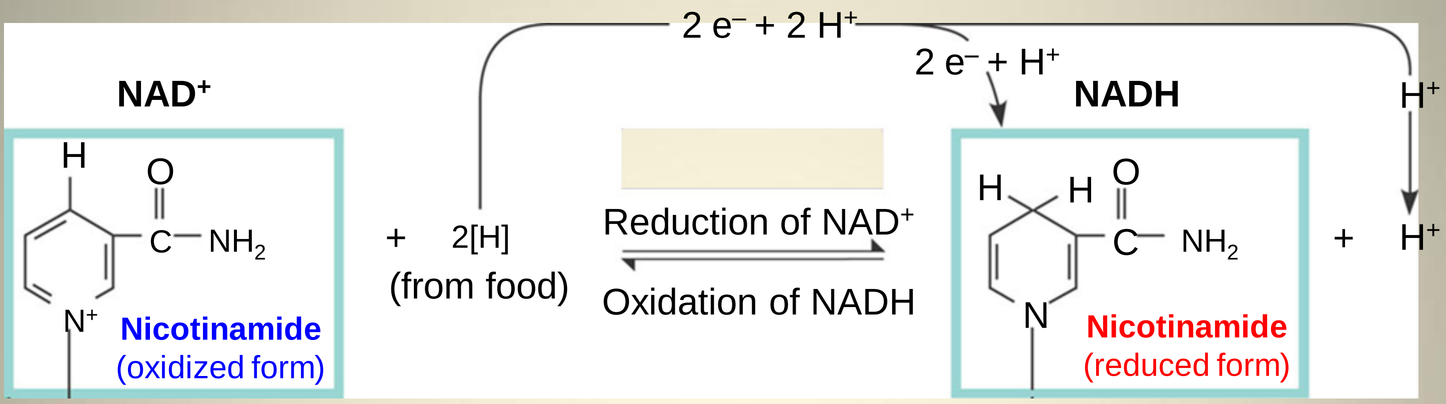
- NAD+ + e- → NADH (electron carrier)



Reducing Agent in Metabolism

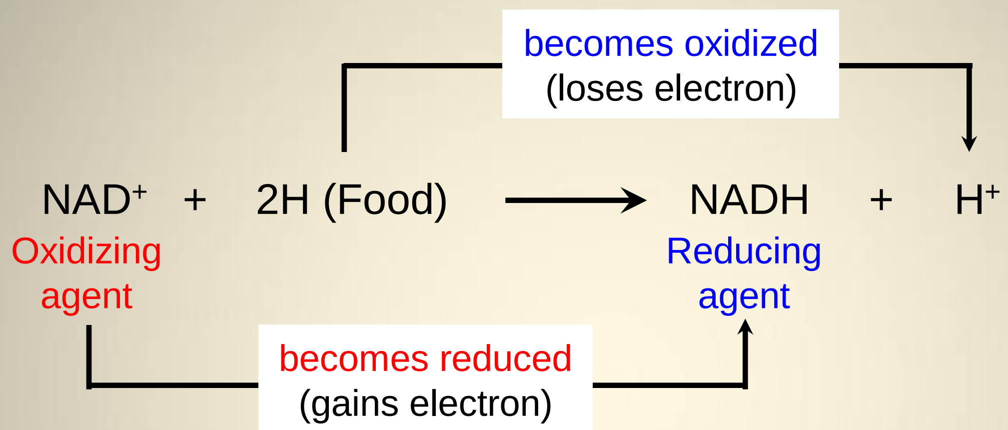
- NADH
  - can donate electrons
    - Loss of electrons is oxidation (becomes oxidzed)
    - reforms NAD^+
  - acts as an reducing agent
- Electrons in NADH:
  - represents stored energy that can make ATP
  - can release a free energy change of -53 kcal/mol

Redox with NAD+/NADH



- Source of electrons is hydrogen
  - Note: hydrogen = proton + electron
- Source of hydrogen is organic compounds (e.g. glucose)

Redox with NAD+/NADH



- Equation: $NAD^+ + 2H \rightarrow NADH + H^+$
- Thus cellular respiration involves:
  - Food (glucose) being oxidized

Redox in Cellular Respiration

- Cellular respiration is the oxidation of glucose
- Organic molecules are excellent fuels because their hydrogens are a source of electrons with a potential to “fall” closer to oxygen

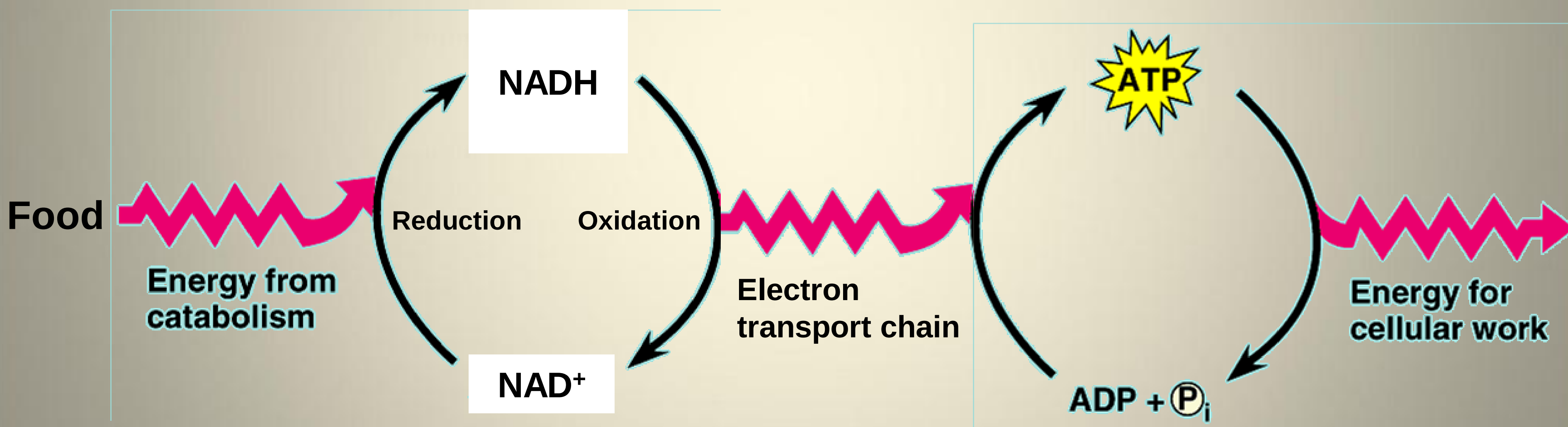
becomes oxidized

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{Energy}$$

becomes reduced

Oxidative Phosphorylation

- Indirect method of ATP Synthesis
- Food → NADH → ATP → Work



Second Law of Thermodynamics

- Energy transformation make the universe more disordered.
  - Example: $C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O$ + **energy**
- **Entropy**: a measure of disorder, chaos, or randomness

- Although order can increase locally in a particular system, it requires the input of energy and the universe will still trend towards randomization.
  - Example: $CO_2 + H_2O$ + **energy** $\rightarrow C_6H_{12}O_6 + O_2$

Energy Transformation

- The quantity of energy is constant, but the quality is not.
- Organisms take in organized energy like light or organic molecules and replace them with less ordered forms, especially heat.

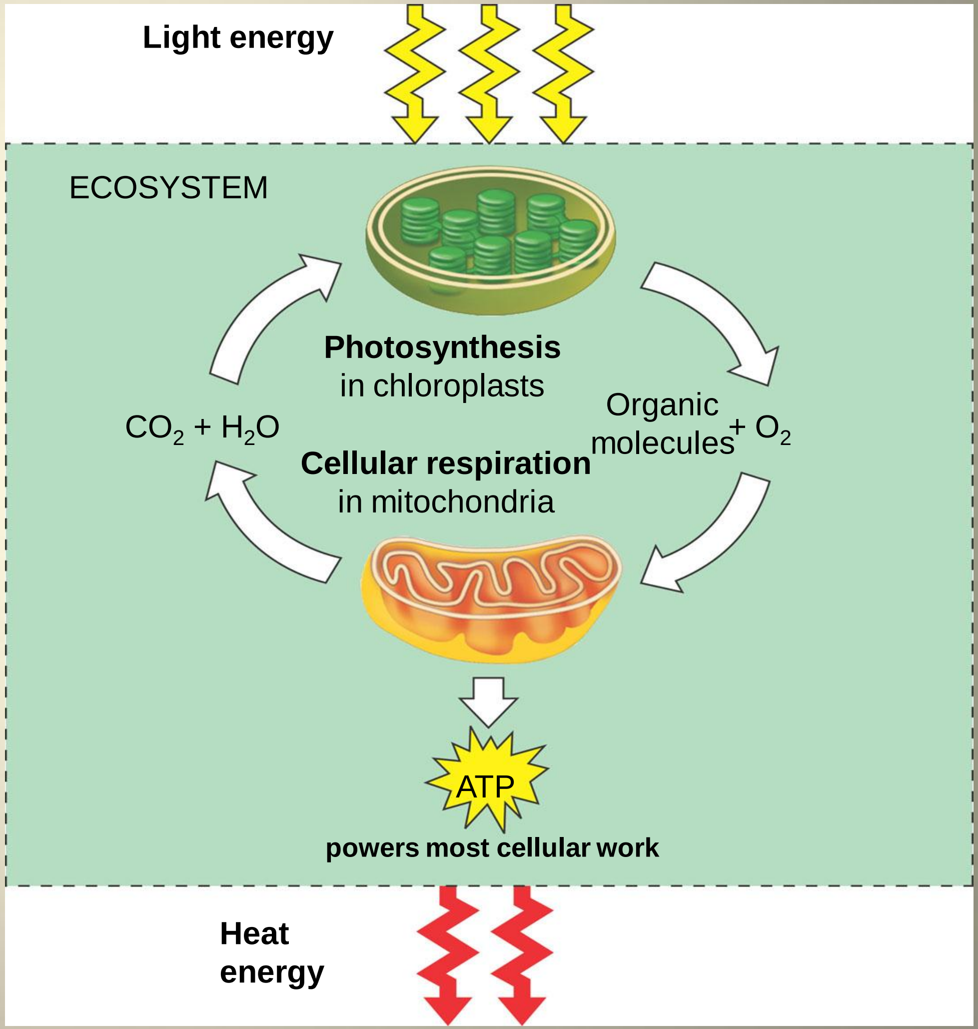


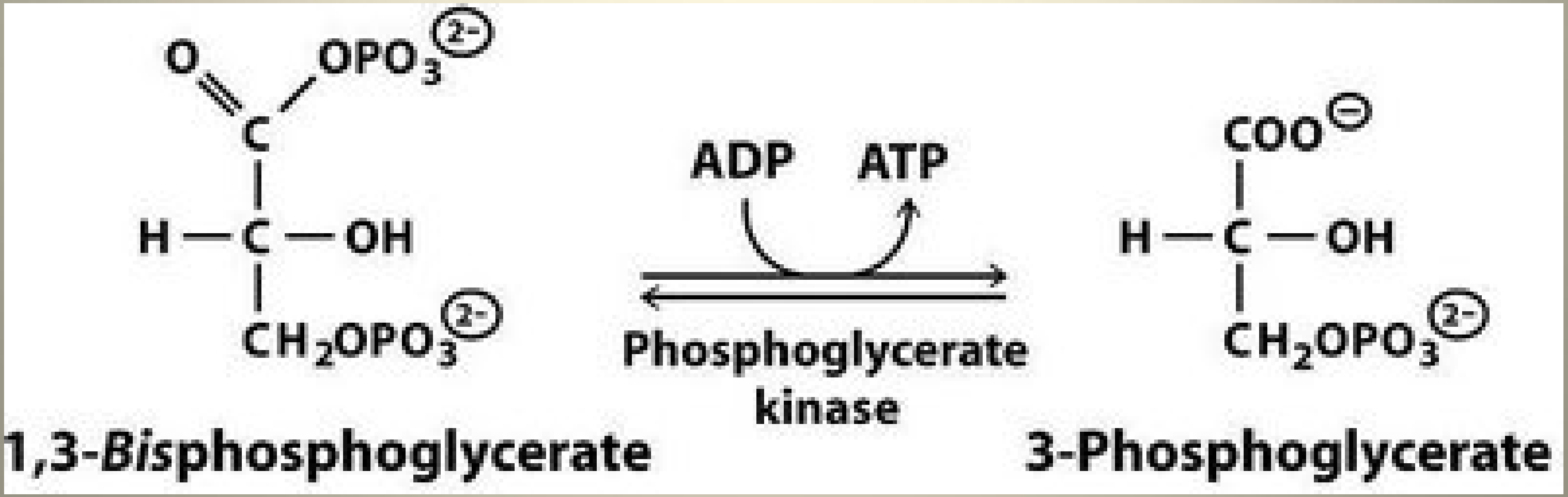
Figure 9.1

Heat

- Energy of random molecular motion; energy in its most random state
- Much of the increased entropy of universe takes the form of increasing heat
  - Living cells unavoidably convert organized forms of energy to heat.
  - The metabolic breakdown of food ultimately is released as heat even if some of it is diverted temporarily to perform work for the organism.

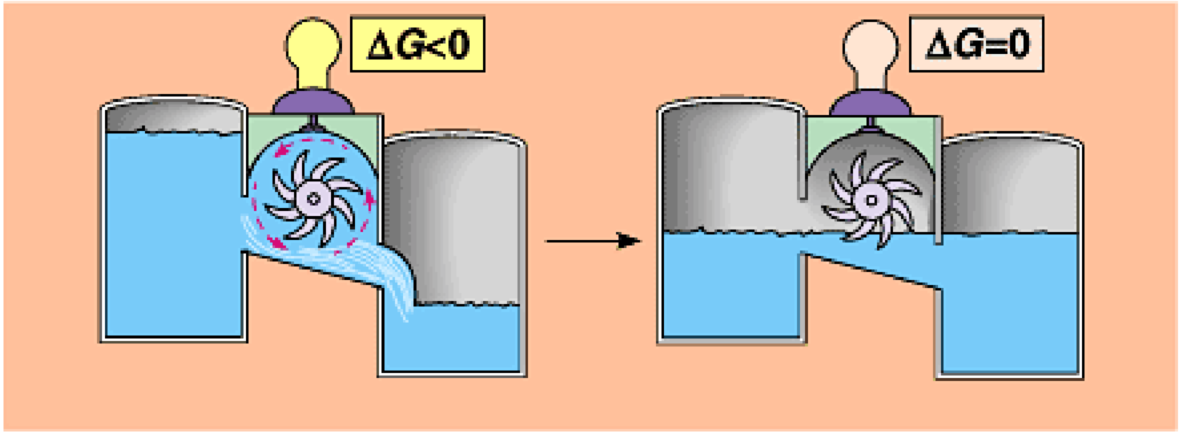
Equilibrium

- A system at equilibrium is at maximum stability.
- Equilibrium reactions convert back and forth with minimal energy. $\Delta G = 0$
- Example: In a chemical reaction, the rate of forward and backward reactions are equal. There is no change in the concentration of products or reactants.



Equilibrium

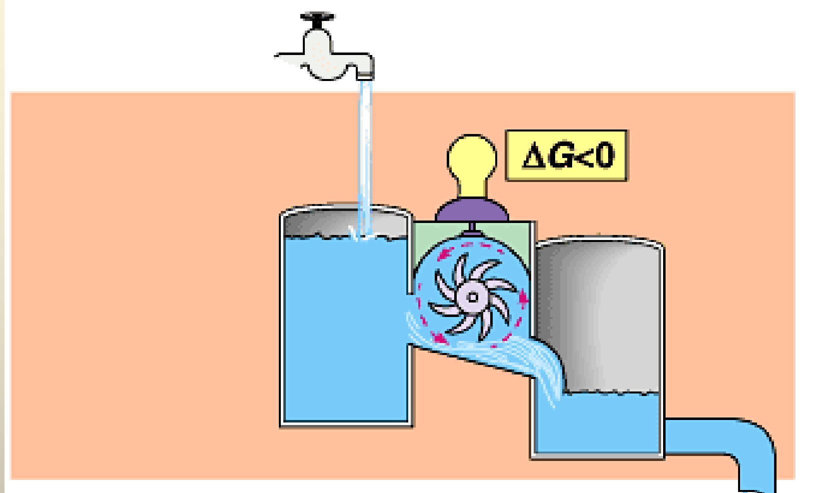
- Reactions in closed systems eventually reach equilibrium and can do no work.
- A biological system that has reached metabolic equilibrium has a $\Delta G = 0$ and is dead!



(a) A closed hydroelectric system

Equilibrium

- Cells are open systems which maintains disequilibrium
- Metabolic disequilibrium is one of the defining features of life



(b) An open hydroelectric system