Bioenergetics (634 فح ج)

Lecture 2

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Bioenergetics

- Molecular transduction.
- First Law of Bioenergetics.
- Second Law of Bioenergetics.
- Third Law of Bioenergetics.
- The electrochemical potential difference in H+ ions.
- Human one Day energetics.
- Evolution of Bioenergetic Mechanisms.
  - Adenosine Triphosphate.

Molecular transduction

- a particular bond in a molecule can absorb energy from the surrounding environment and alter its structure.
- this bond is sensitive to a particular wavelength of electromagnetic radiation, due to a match of the electron oscillation frequency of the bond and the external radiation frequency.

Molecular transduction (continued)

- Planck postulated that the energy ε of the quantum is not fixed, but will increase as the frequency ν of the oscillation increases, with Planck's constant (h) as the proportionality factor

$$\epsilon = h\nu$$

- The frequency of electromagnetic radiation is inversely proportional to the wavelength λ of the electromagnetic wave, with the product equal to the speed of light c in a vacuum

$$c = \lambda\nu$$

Molecular transduction (continued)

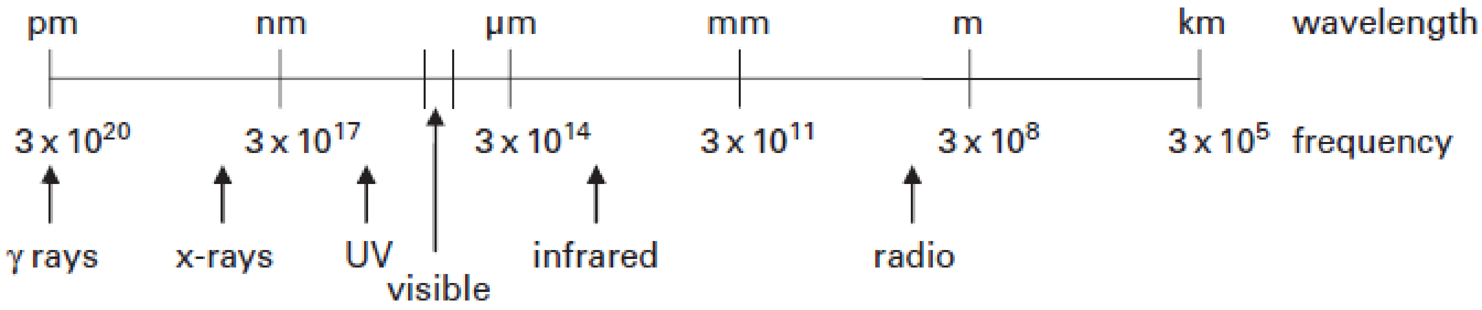


Figure 1.4 Electromagnetic spectrum. Wave energy is directly proportional to frequency and inversely proportional to wavelength.

Molecular transduction

(continued)

- Quantum mechanics limits the states of electrons (Pauli exclusion principle).
- The ground state for an electron is the S_0 singlet state, from which a photon can excite an electron to the S_1 singlet state.
- The electron can spontaneously release this energy as a photon of light: this is fluorescence. Or, there may be an energetic transfer to an adjacent triplet state T_1, from which a photon of light can be released at a different frequency: this is phosphorescence. Fluorescent radiation (10^{-9} to 10^{-5} s) is faster than phosphorescent radiation ($> 10^{-5}$ s) due to the greater stability of the T_1 state (Glaser, 2001).

Molecular transduction

(continued)

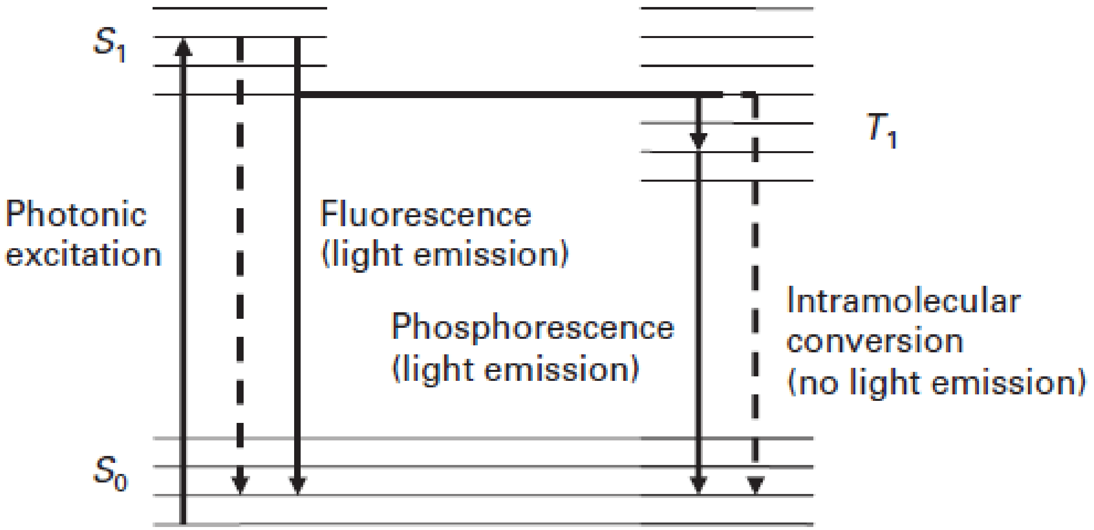


Figure 1.5 At the single atom level, the different quantum states (S_0, S_1, T_1) have thermal variations at each quantum level, indicated by the horizontal parallel lines. Fluorescence and phosphorescence do not play a role in human physiology. Intramolecular conversion occurs in phototransduction, and the destructive effects of ultraviolet and x-rays.

Molecular transduction

(continued)

- The third path, indicated by the dashed lines in Figure 1.5, shows an energy release after quantum absorption of energy without light emission from either the S_1 or T_1 state. In this case, a portion of the energy remains within the molecule and alters its structure. The retinal portion of rhodopsin is an example of this path.

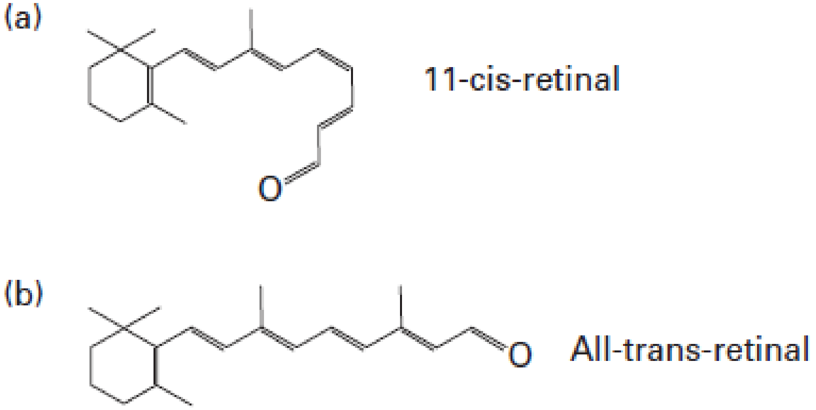


Figure 1.6 Structural forms of retinal: (a) 11-cis-retinal and (b) all-trans-retinal.

Molecular transduction (continued)

- Upon exposure to light, with a maximum absorbance at 500 nm, the 11-cis form of retinal absorbs sufficient energy to be converted to the all-trans form of retinal. The all-trans form partially dissociates from the opsin portion of rhodopsin, triggering the cascade that produces phototransduction. The all-trans form does not spontaneously revert entirely to the 11-cis form, indicating that there is an energy barrier between the forms that exceeds ambient energy.

Molecular transduction

(continued)

- An enzyme, retinal isomerase, is responsible for the conversion back to the 11-cis form.
- Since at equilibrium the 11-cis form predominates, it must have a lower energy minimum than the all-trans form.

First law of bioenergetics

- *Living beings avoid direct utilization of the energy of external sources when performing useful work. They first transform this energy into a convertible form—ATP, $\Delta\bar{\mu}_{H^+}$, or $\Delta\bar{\mu}_{Na^+}$—and then use it in various energy consuming processes.*

$$\text{Energy sources} \longrightarrow \text{ATP},\ \Delta\bar{\mu}_{\mathrm{H}^+},\ \text{or}\ \Delta\bar{\mu}_{\mathrm{Na}^+} \longrightarrow \text{work}$$

Second law of bioenergetics

- *Every living cell has at least two forms of interconvertible energy—ATP, and* $(\Delta\bar{\mu}_{\mathrm{H}^+})$ *or* $\Delta\bar{\mu}_{\mathrm{Na}^+}$

Third law of bioenergetics

- *There is interconversion of three forms of energy stored in a cell. That is why a cell can satisfy all its energy needs if it can obtain at least one of the three interconvertible energy forms from external energy sources.*

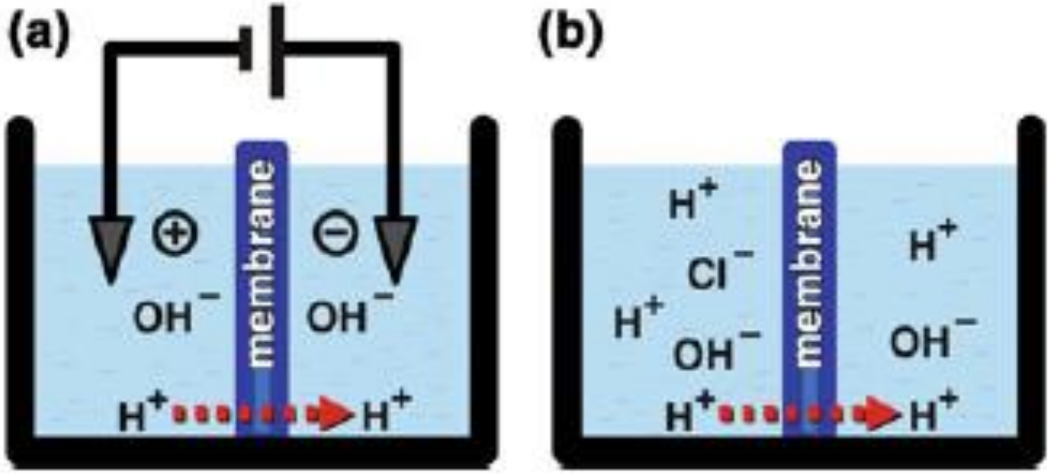
Third law of bioenergetics

(continued)

- There are some kinds of cells that use only one type of energy source.
  - Some of them live by respiration or photosynthesis and produce only $\Delta\bar{\mu}_{H^+}$; they have no glycolysis, hence they have no possibility for direct synthesis of ATP.
  - Others, vice versa, glycolysis (which forms ATP without mediation of $\Delta\bar{\mu}_{H^+}$) is the only energy source.
  - Certain bacteria have neither glycolysis nor respiration nor photosynthesis. They accumulate $\Delta\bar{\mu}_{Na^+}$ via one of the decarboxylation reactions and use $\Delta\bar{\mu}_{Na^+}$ for production of ATP and $\Delta\bar{\mu}_{H^+}$

The electrochemical potential difference in H+ ions $(\Delta\bar{\mu}_{H^+})$

Fig. 1.5 Two forms of H^+ potential between compartments separated by a membrane—electric field gradient $\Delta\Psi$ (a) and acidity gradient ΔpH (b). The direction of proton current is shown by the *dotted arrows*



The electrochemical potential difference in H+ ions $(\Delta\bar{\mu}_{H^+})$ (continued)

- If there is an electric potential difference across the membrane (generated, e.g. by a battery), H+ tends to move from the positively charged to the negatively charged compartment.
- One can reach the same situation by adding for example hydrochloric acid to the left compartment, thus increasing the concentration of H+ in the left compartment in comparison to the right one. In this case, a proton current will also take place downhill, but it is $(\Delta\bar{\mu}_{H^+})$, and not electric potential, that will be the driving force for the process.
- Potential energy accumulated can be utilized if the membrane has a device capable of coupling downhill H+ movement to the performance of useful work.

The electrochemical potential difference in H+ ions $(\Delta\bar{\mu}_{H^+})$ (continued)

The energy stored in $\Delta\bar{\mu}_{H^+}$ can be calculated from Eq.

$$\Delta\bar{\mu}_{H^+} = F\Delta\Psi + RT \cdot \ln\frac{[H^+]_p}{[H^+]_n}$$

- where $\Delta\Psi$ is the transmembrane electric potential difference, R is the gas constant, T is the absolute temperature, F is the Faraday constant, and $[H+]_p$ and $[H+]_n$ are the molar concentrations of H+ in the positively charged (or more acidic) and negatively charged (or more alkaline) compartments, respectively.

The electrochemical potential difference in H+ ions $(\Delta\bar{\mu}_{H^+})$ (continued)

- the energy of light or respiratory substrates can be utilized by enzymes of the photosynthetic or respiratory redox chains or by bacteriorhodopsin to form $(\Delta\bar{\mu}_{H^+})$. The latter can support various types of work in the ‘‘protonic’’ membrane, with ATP synthesis being the most important.
- Substrate-level phosphorylations serve as an alternative mechanism of ATP formation that operates with no $(\Delta\bar{\mu}_{H^+})$ involved. Such phosphorylations occur in the glycolytic chain and in oxidative decarboxylation of a-ketoglutarate.

The electrochemical potential difference in H+ ions $(\Delta\bar{\mu}_{\mathrm{H}^+})$ (continued)

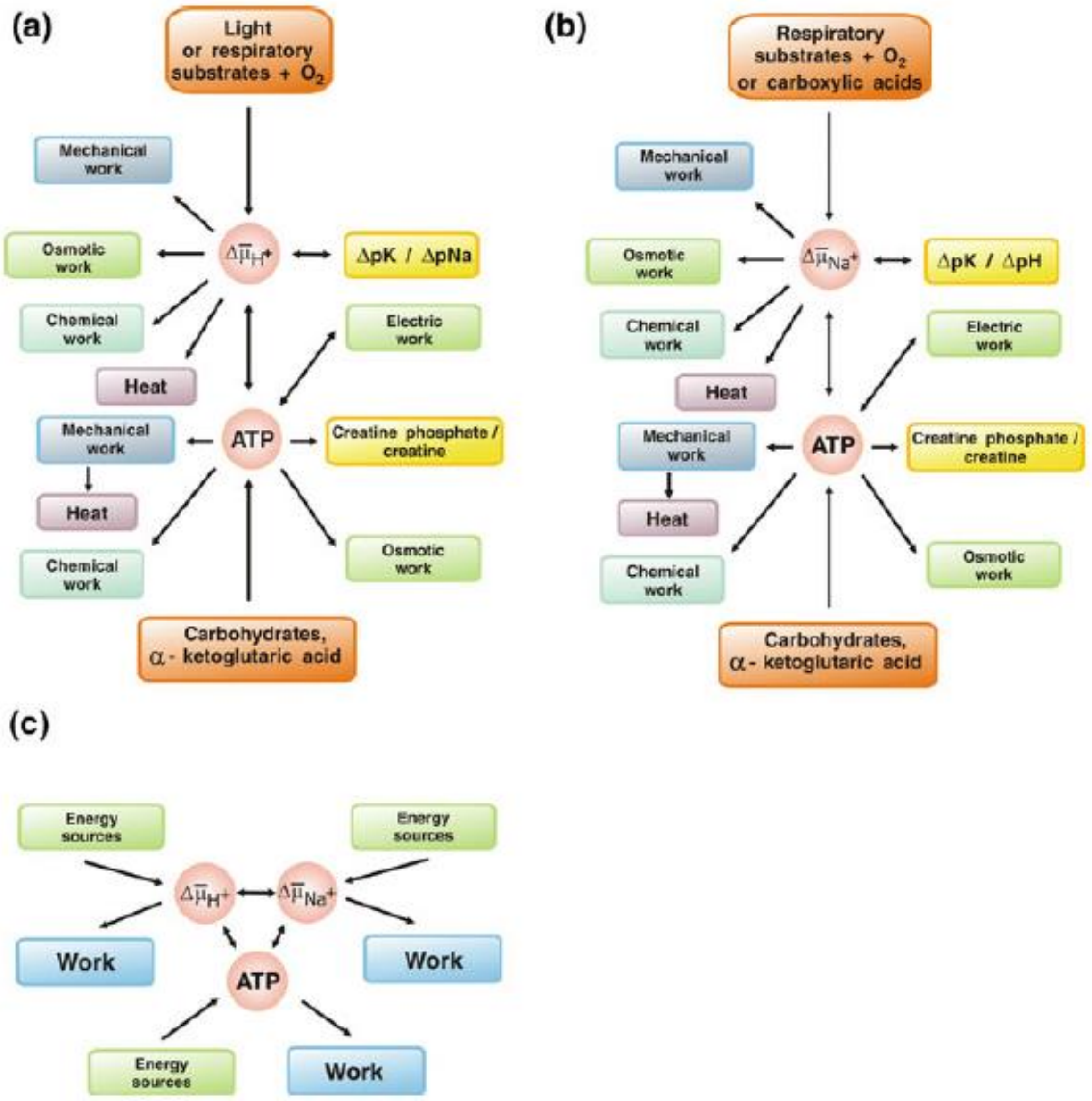
- The $(\Delta\bar{\mu}_{\mathrm{H}^+})$ linked formation of ATP is a major but not the only process of transformation of $(\Delta\bar{\mu}_{\mathrm{H}^+})$ into chemical work. The $(\Delta\bar{\mu}_{\mathrm{H}^+})$-supported synthesis of inorganic pyrophosphate and transfer of reducing equivalents in the direction of more negative redox potentials are also of this type of energy transduction.

The electrochemical potential difference in H+ ions $(\Delta\bar{\mu}_{H^+})$ (continued)

- Osmotic, mechanical and heat energy transduction have also been described for the non-membranous parts of cells. Here they are supported by the energy of ATP or other high-energy compounds.
- In certain bacteria, $\Delta\bar{\mu}_{Na^+}$ instead of $(\Delta\bar{\mu}_{H^+})$ is formed at the expense of energy released by respiration or by nonoxidative decarboxylation of some organic acids. Then the $\Delta\bar{\mu}_{Na^+}$ can be used to support chemical, osmotic, or mechanical work. The K+/H+ gradient can serve as a buffering system for $\Delta\bar{\mu}_{Na^+}$

The electrochemical potential difference in H+ ions $(\Delta\bar{\mu}_{H^+})$ (continued)

- The most complicated pattern of energy transduction is inherent in animal cells, where there are three different interconvertible energy currencies—$(\Delta\bar{\mu}_{H^+})$ for mitochondria and some other intracellular vesicles, $\Delta\bar{\mu}_{Na^+}$ for the outer cell membrane, and ATP for nonmembranous cell constituents.
- Coming back to the first law of bioenergetics, we should state that its three components (ATP, $(\Delta\bar{\mu}_{H^+})$ and $\Delta\bar{\mu}_{Na^+}$) do not have equal value. ATP is always present, while the two other components are interchangeable, and hence some organisms have only one or the other. But one of the latter two should always be present.

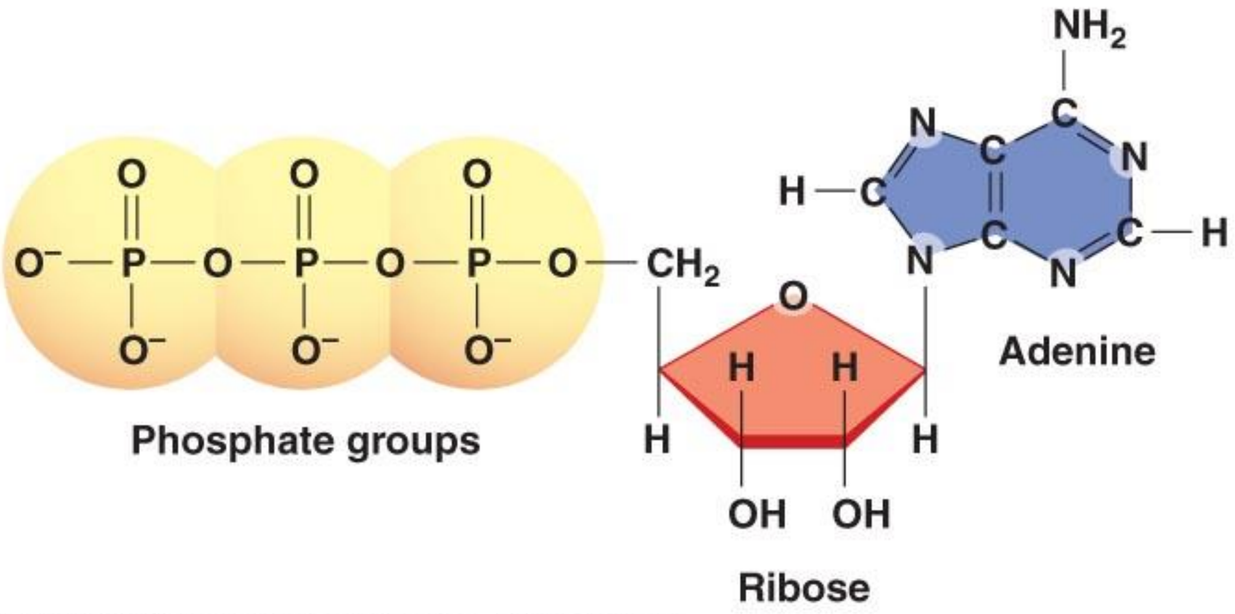

(a)
Light or respiratory substrates + O_2
Mechanical work
Osmotic work
$\Delta\bar{\mu}_{H^+}$
ΔpK / ΔpNa
Chemical work
Electric work
Heat
Mechanical work
ATP
Creatine phosphate / creatine
Heat
Chemical work
Osmotic work
Carbohydrates, α- ketoglutaric acid
(b)
Respiratory substrates + O_2 or carboxylic acids
Mechanical work
Osmotic work
$\Delta\bar{\mu}_{Na^+}$
ΔpK / ΔpH
Chemical work
Electric work
Heat
Mechanical work
ATP
Creatine phosphate / creatine
Heat
Chemical work
Osmotic work
Carbohydrates, α- ketoglutaric acid
(c)
Energy sources
Energy sources
$\Delta\bar{\mu}_{H^+}$
$\Delta\bar{\mu}_{Na^+}$
Work
Work
ATP
Energy sources
Work

Human One Day Energetics

- The average human being consumes about *140 liters of oxygen* per day and synthesizes about *40 kg of ATP*. To obtain such values, about *0.5 kg of protons* needs to be transported across mitochondrial membranes, while $\Delta\bar{\mu}_{H^+}$ generators maintain the voltage of the electric field across the mitochondrial membrane corresponding to *hundreds of kilovolts per centimeter* of the membrane thickness.

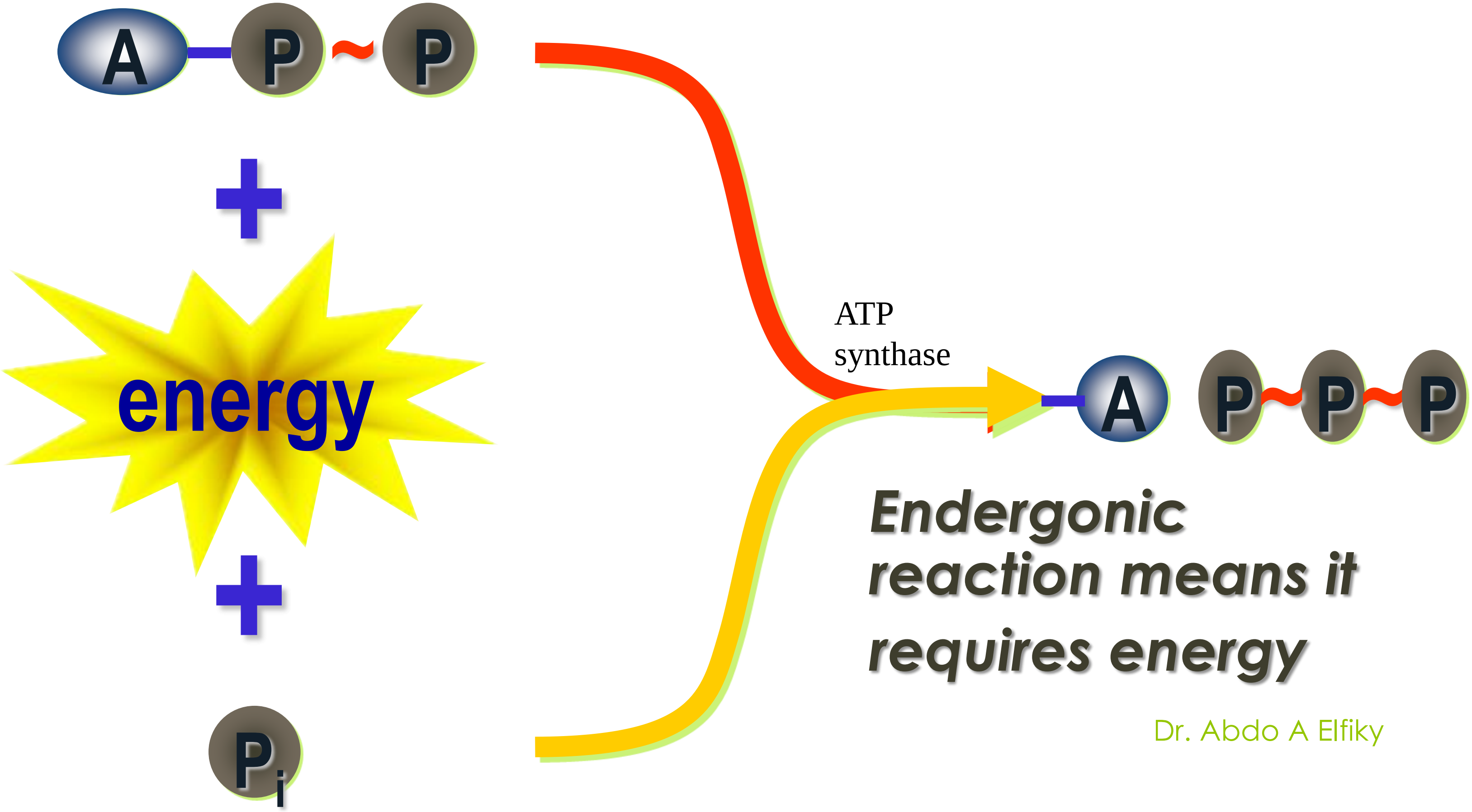
Adenosine Triphosphate

(a) ATP consists of three phosphate groups, ribose, and adenine.



Adenosine Triphosphate

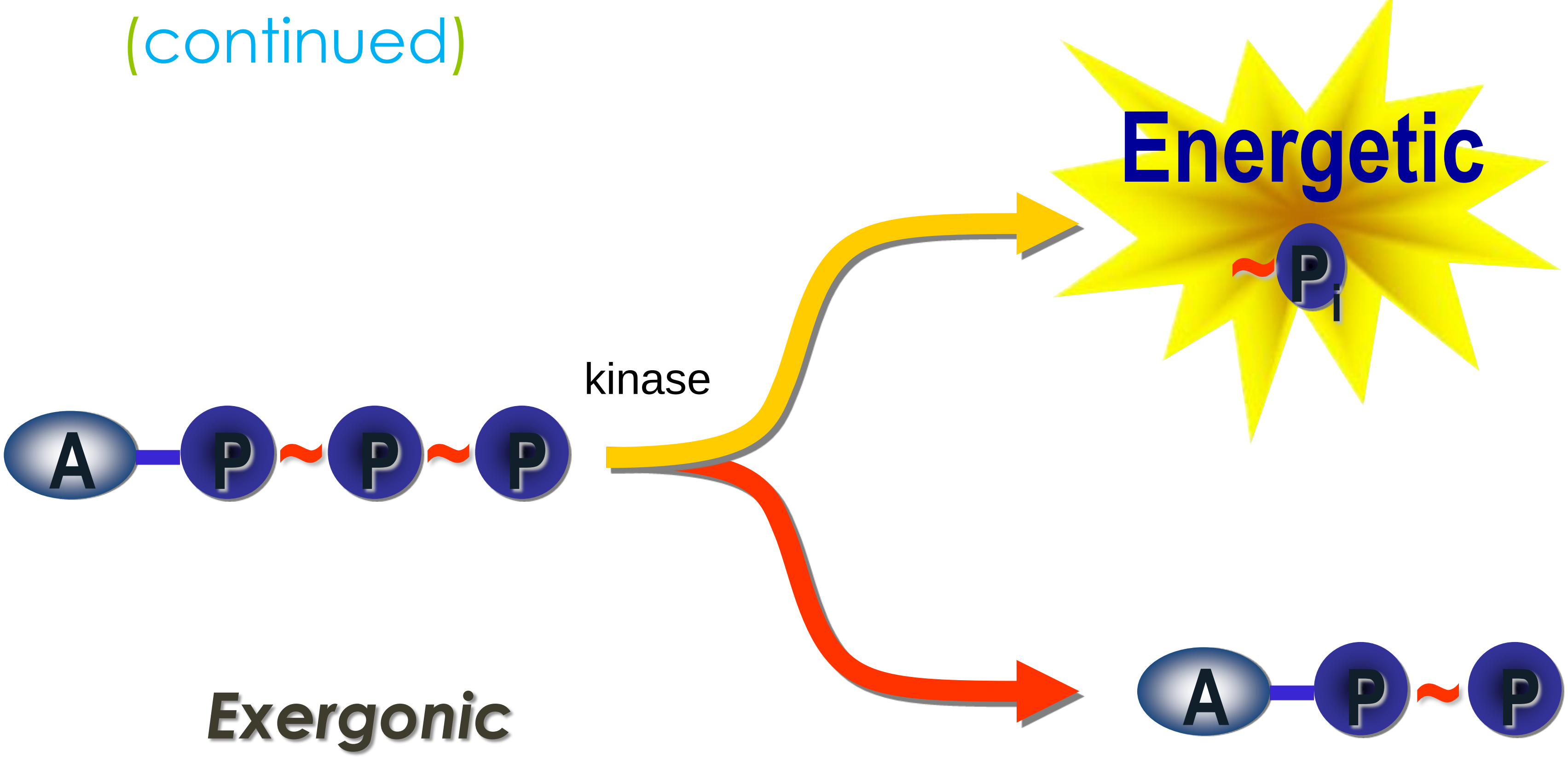
(continued)



Endergonic reaction means it requires energy

Adenosine Triphosphate

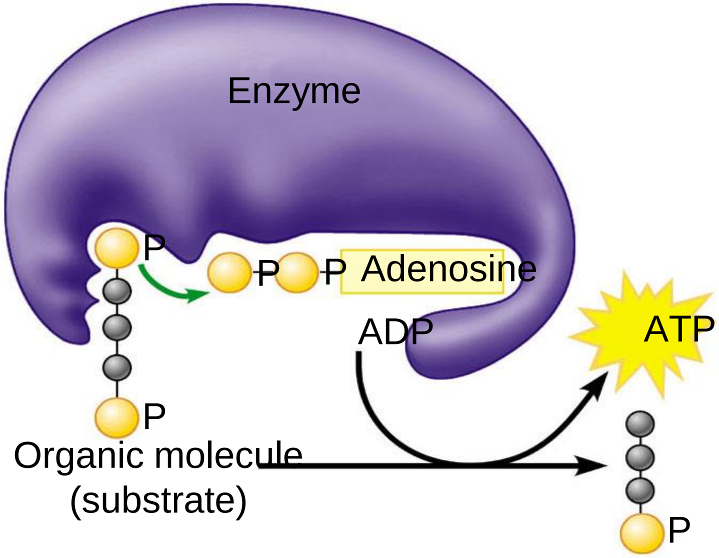
(continued)



Exergonic reaction means it gives energy

Adenosine Triphosphate (continued)

- Glycolysis produces ATP by substrate-level phosphorylation in which a phosphate group is transferred from an organic molecule to ADP



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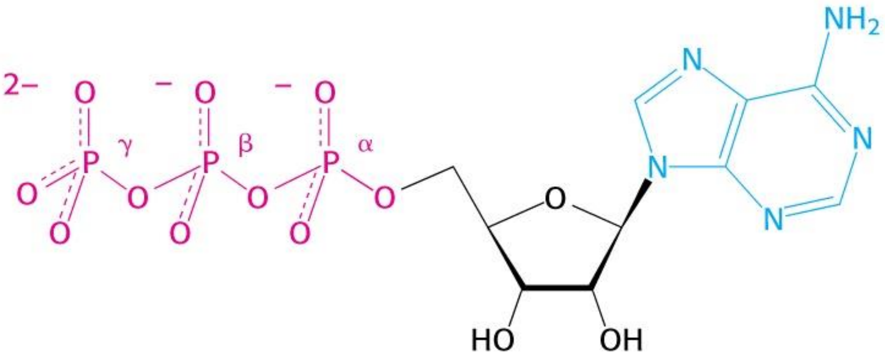
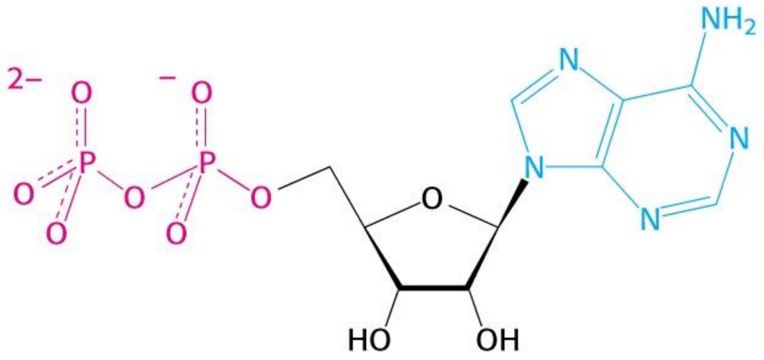
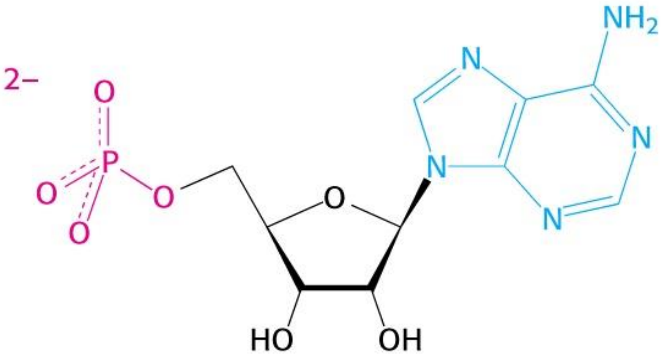
Adenosine Triphosphate (continued)



Adenosine triphosphate (ATP)



Adenosine diphosphate (ADP)

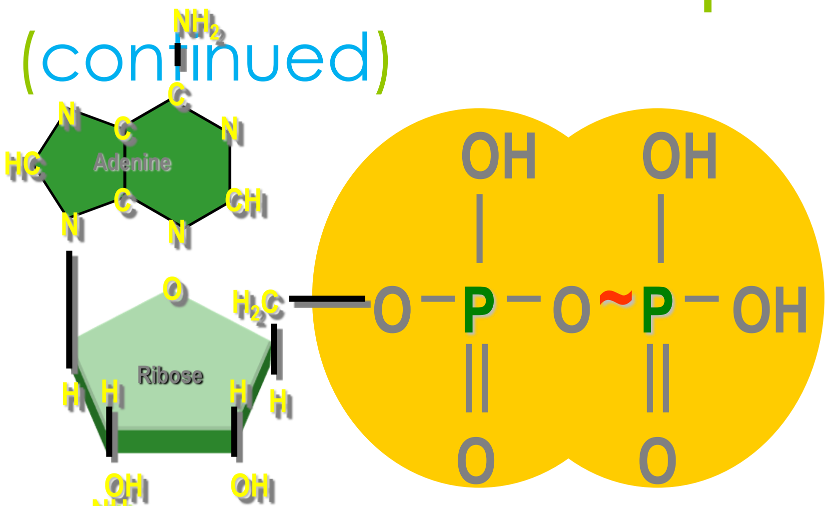


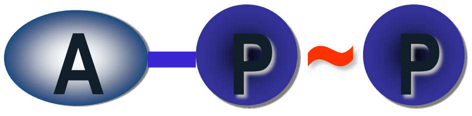
Adenosine monophosphate (AMP)

Adenosine Triphosphate (continued)

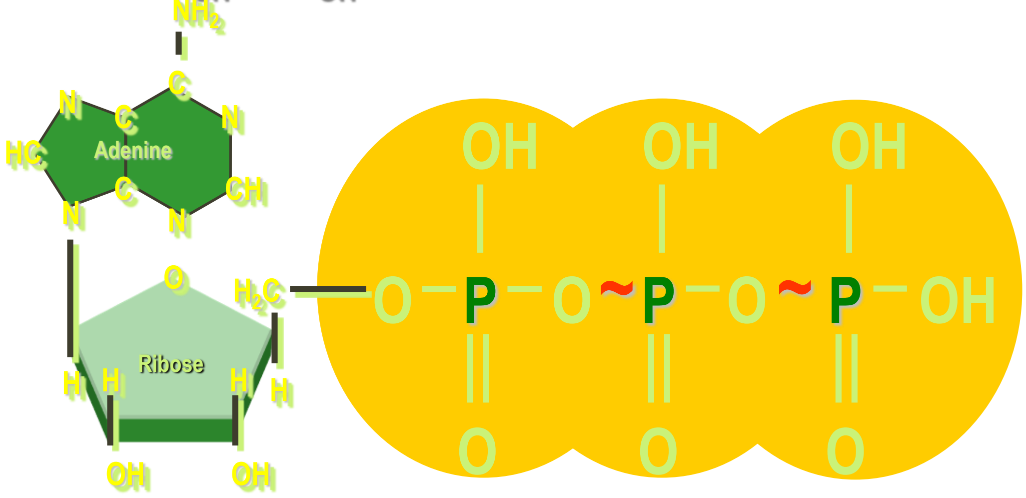
- Terminal phosphate hydrolysis of ATP is shown to take place when the energy consuming process driven by the ATP hydrolysis requires energy less than or equal to 10 kcal/mol. This is also the case when the energy requirement is much larger than 10 kcal/mol. In the latter case, a special mechanism is at work making it possible to use the energy of many ATP molecules simultaneously to perform a functional act.
- If the energy requirement is only slightly higher than 10 kcal/mol ATP is hydrolyzed to AMP and inorganic pyrophosphate.

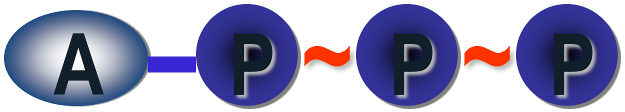
Adenosine Triphosphate (continued)





ADP





ATP

Adenosine Triphosphate (continued)

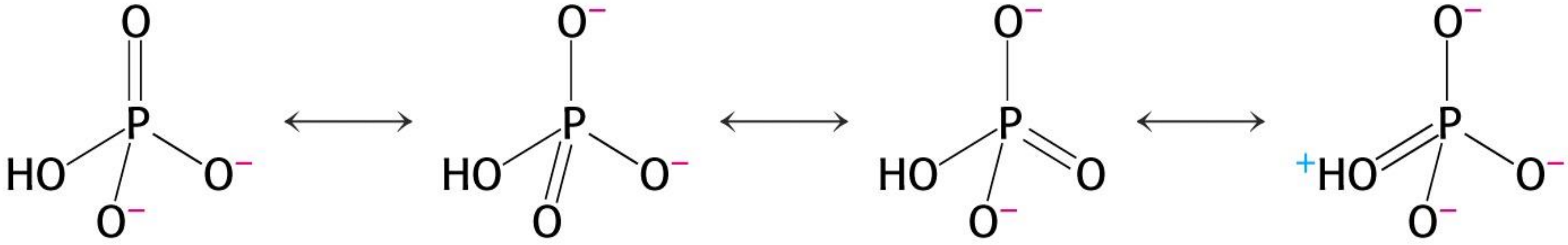
- In the living cell, the energy release is usually 4–5 kcal/mol higher when AMP and PPi are formed instead of ADP and Pi. This is because of a much lower cytosolic concentration of PPi than of Pi. This is due to hydrolysis of PPi by soluble pyrophosphatases.
- So, we can state that the use of adenosine triphosphate rather than adenosine diphosphate (also a high-energy compound) as a convertible energy currency adds some flexibility to the biological energy supply system.

Why does ATP have a high phosphoryl transfer potential?

- ΔG0’ depends on the difference in free energies of products and reactants, therefore, both must be considered.

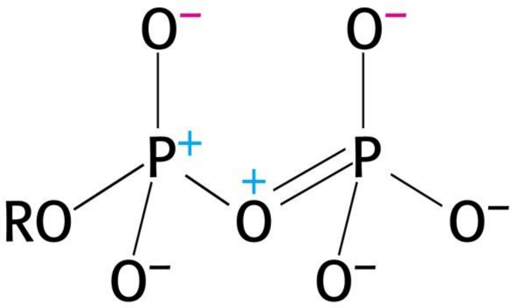
Three factors are important:

1. Resonance stabilization
2. Electrostatic repulsion
3. Stabilization due to hydration



Why does ATP have a high phosphoryl transfer potential?

(continued)



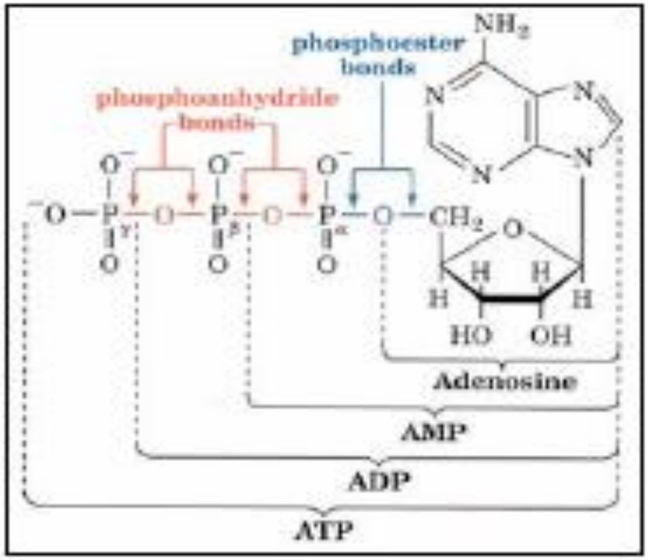
ATP show improbable *resonance* structure.

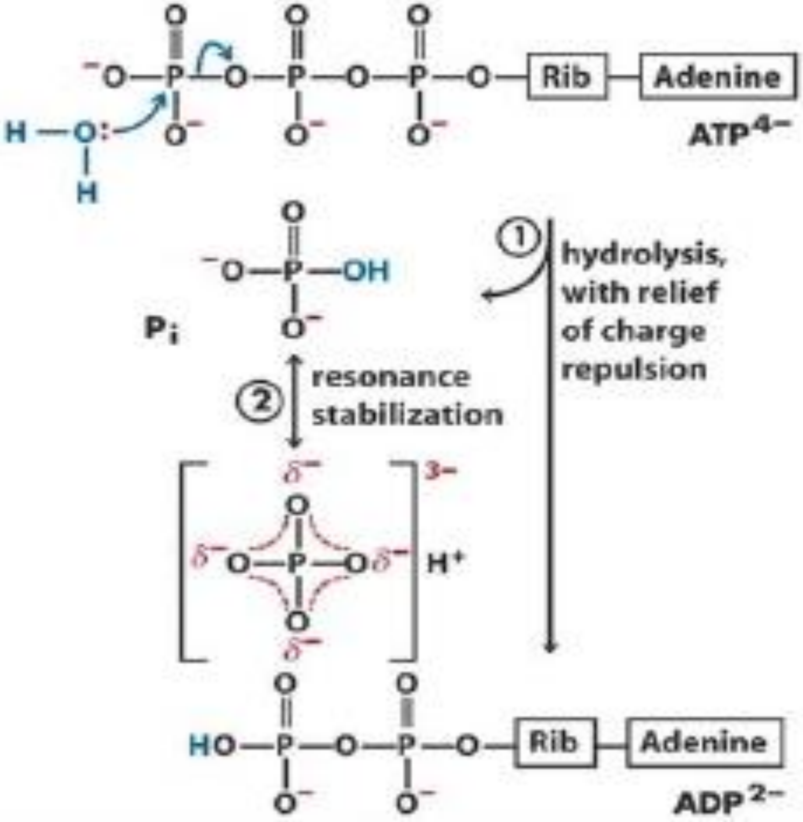
Electrostatic repulsion, reduced by hydrolysis of ATP

stabilizing by hydration: Water can bind more effectively to ADP and Pi than to phosphoanhydride part of ATP.

Chemical Basis for “High Energy” Compounds

ATP - Hydrolysis





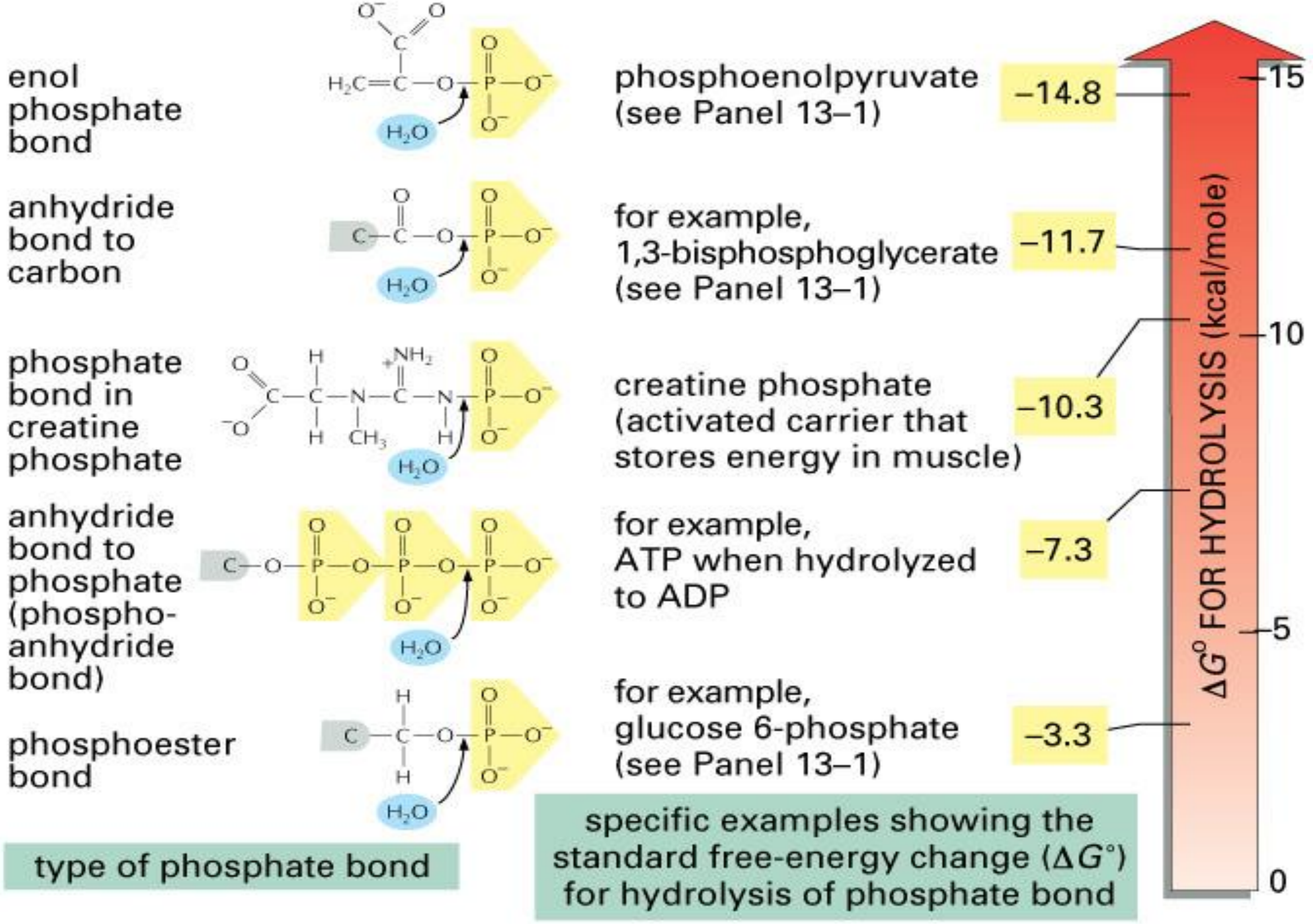
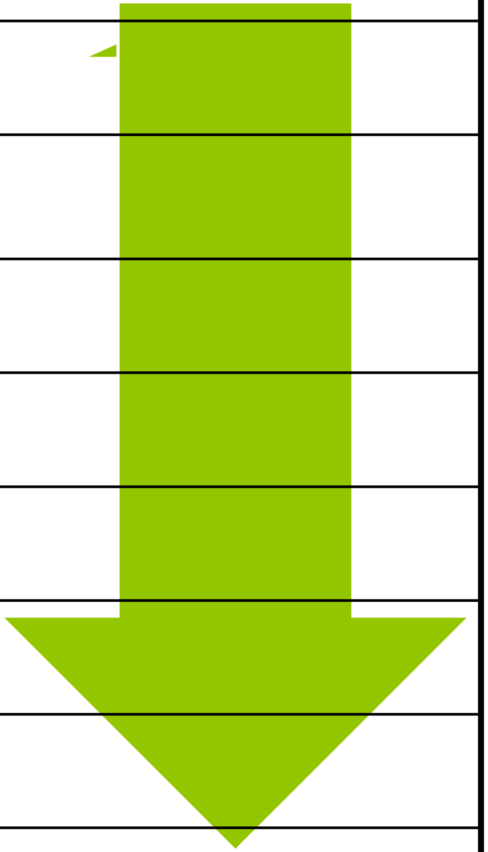
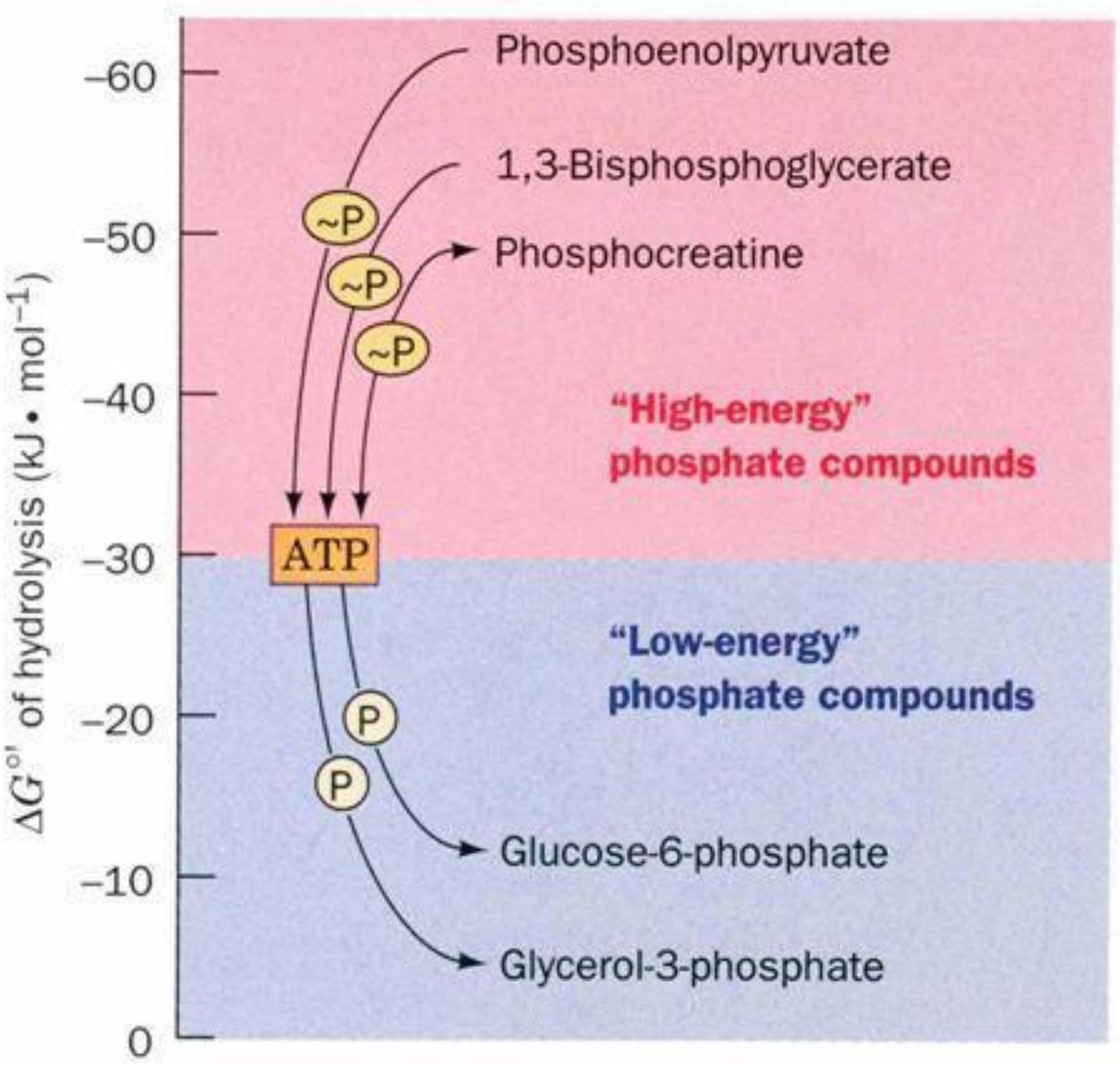


Figure 13-7 Essential Cell Biology, 2/e. (© 2004 Garland Science)

Phosphate compounds	**ΔG^o Kcal/mole**	**Direction of phosphate group**
Phosphoenolpyruvate	-14.8	
1,3-di-p-glycerate	-11.8	
Phosphocreatine	-10.3	
ATP	-7.3	
Glucose-1-p	-5.0	
Fructose-6-p	-3.8	
Glucose-6-p	-3.3	
3-p-glycerate	-2.4	
Glycerol-3-p	-2.2	



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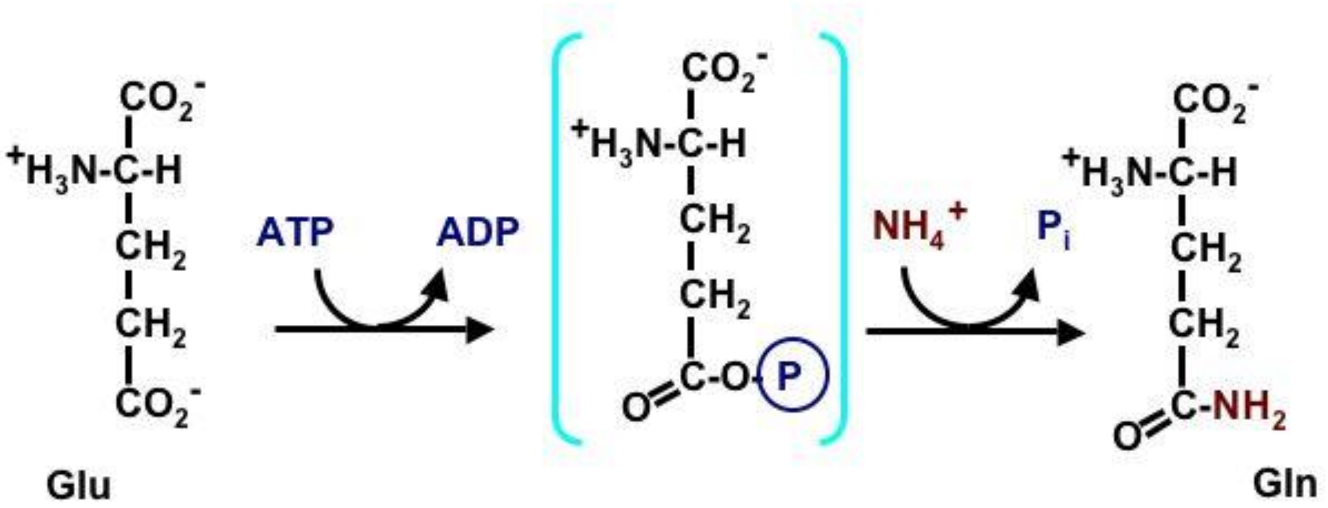
Glutamine synthetase catalyzes formation of glutamine from glutamate and NH_4^+



The reaction proceeds through an enzyme-bound γ-glutamylphosphate intermediate

Linkage of energy-yielding oxidation to energy-requiring reaction

R-CHO + Pi → 2[H] + R-COO-PO3H2
R-COO-PO3H2 +ADP → R-COOH + ATP

ATP + Glutamate →ADP + Glutamyl phosphate
Glutamyl Phosphate + NH3 → Glutamine + Pi

R-CHO + Glutamate + NH3 → 2[H] + R-COOH + Glutamine