BIOENERGETICS

CONCEPT
OF
FREE ENERGY
&
REDOX SYSTEMS

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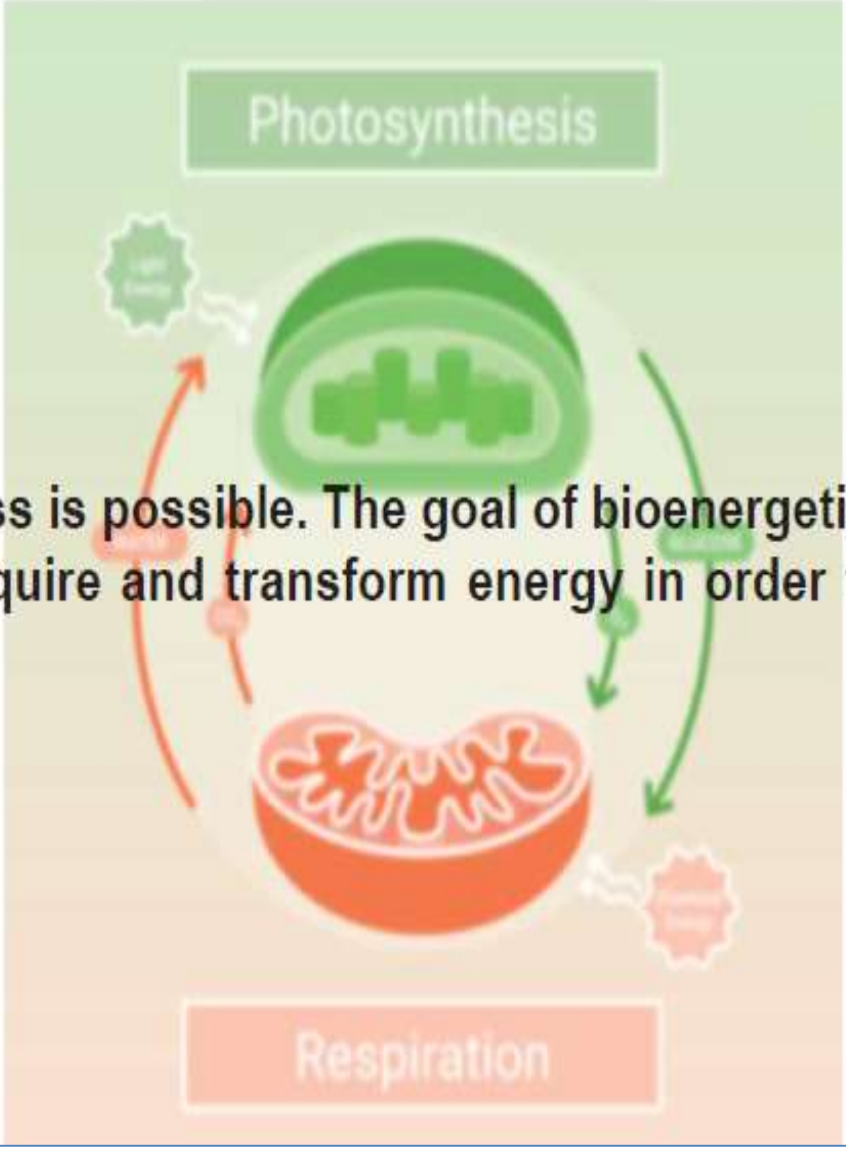
Bioenergetics

Living cells constantly perform work. They require energy for maintaining their highly organized structures, synthesizing cellular components, generating electric currents, and many other processes.

Bioenergetics (biological thermodynamics) **is the quantitative study of the energy transductions (changes of one form of energy into another) that occur in living cells and of the nature and function of the chemical processes underlying these transductions.**

- It deals with the study of energy changes (transfer and utilization) in biochemical reactions
- It concerns only the initial and final energy states of reaction components, not the mechanism or how much time is needed for the chemical change to take place (the rate).

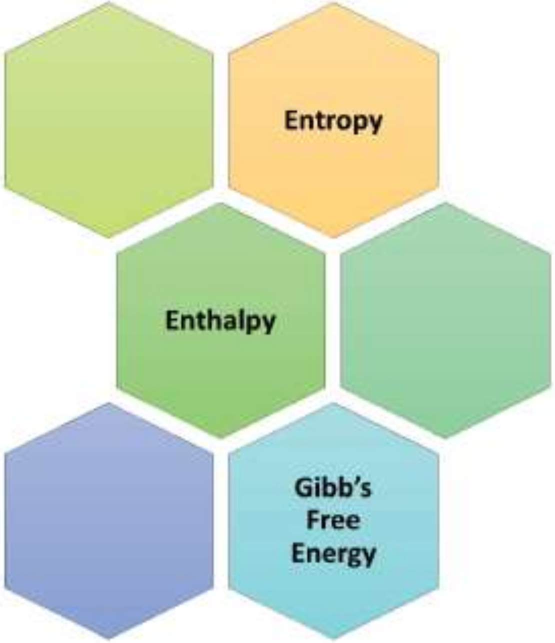
Bioenergetics



It predicts if a process is possible. The goal of bioenergetics is to describe how living organisms acquire and transform energy in order to perform biological work.

Bioenergetics

Biological Energy Transformations Obey the Laws of Thermodynamics



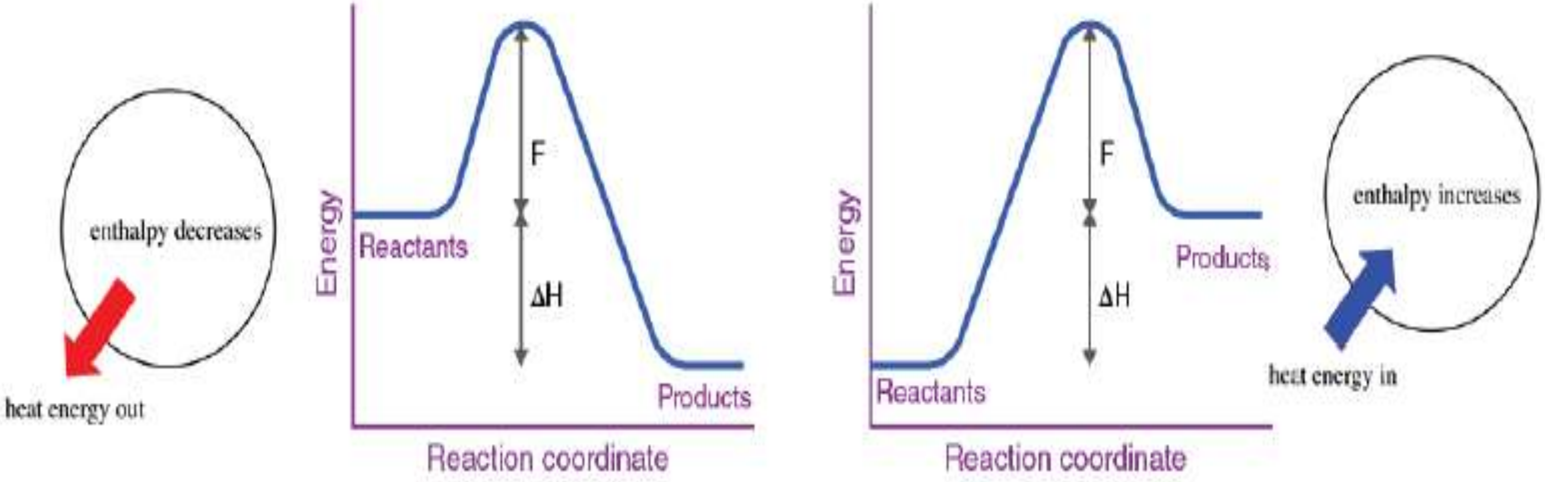
- **First Law of Thermodynamics**
- The total energy of a system, including its surroundings, remains constant.
- This is also called the law of conservation of energy.

- **Second Law of Thermodynamics**
- The total entropy of a system must increase if a process is to occur spontaneously.

Thermodynamic Concepts

Enthalpy (H) : is the heat content of the reacting system and reflects the number and kinds of chemical bonds in the reactants and products.

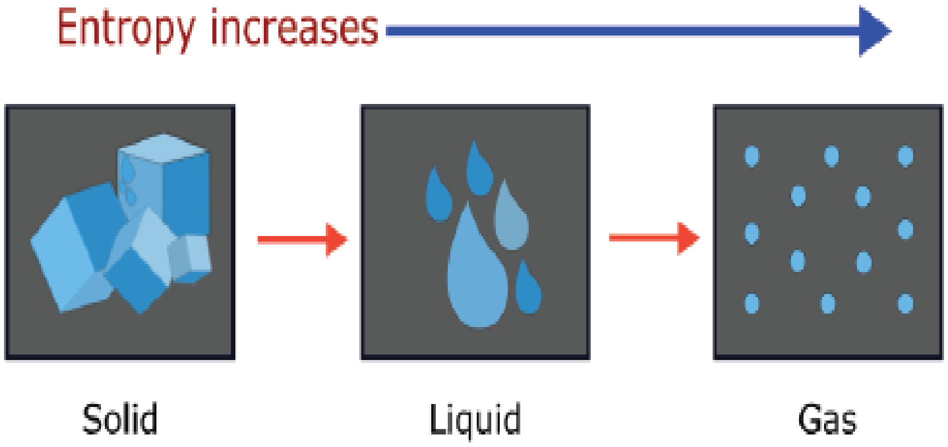
- When a chemical reaction releases heat, it is said to be exothermic (-H): the heat content of the products is less than that of the reactants;
- Reacting systems that take up heat from their surroundings are endothermic (+H): the heat content of the products is more than that of the reactants.



Entropy (S) : is a quantitative expression for the randomness or disorder in a system

- Measures the amount of heat dispersed or transferred during a chemical process
- The entropy of the system and surroundings are opposite to each other
- The entropy of the universe is always increasing (2nd Law of thermodynamics)

When the products of a reaction are less complex and more disordered than the reactants, the reaction is said to proceed with a gain in entropy.


Entropy increases

Solid

Liquid

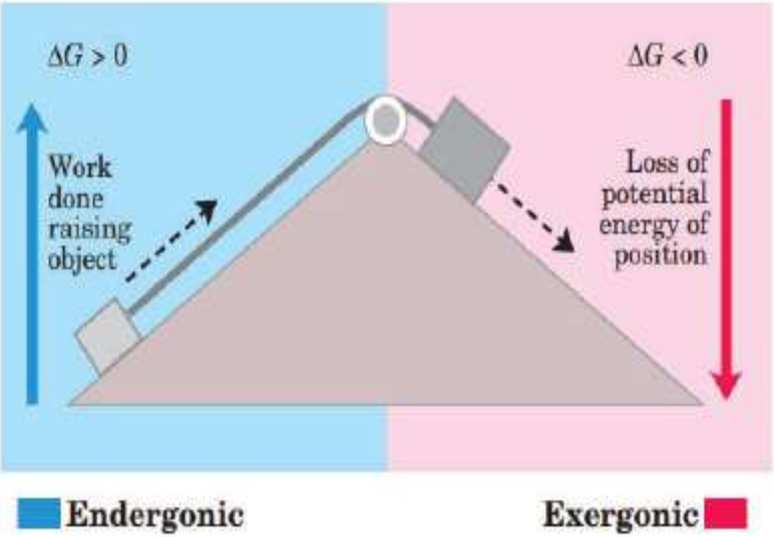
Gas

Gibbs free energy, (G)

The amount of energy capable of doing work during a reaction at constant temperature and pressure.

- In endergonic reactions, the system gains free energy and G is positive.
- In exergonic reactions, the system releases free energy and G is negative.

Reaction will not occur spontaneously



Reaction will occur spontaneously

G=0, the system is at equilibrium.

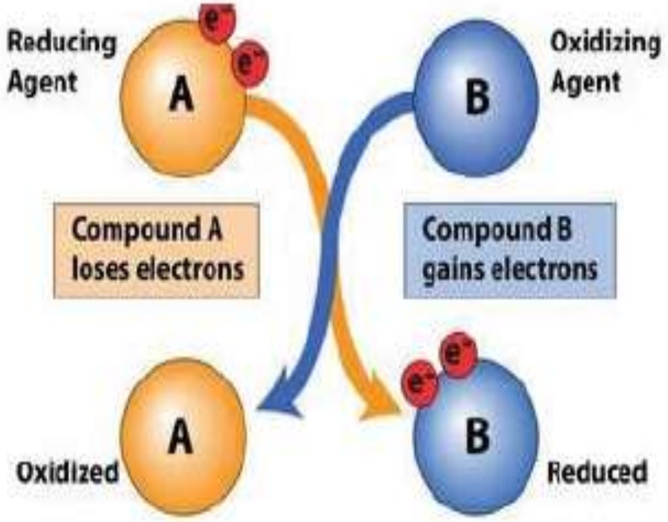
Relationship between free energy, enthalpy and entropy

Under the conditions existing in biological systems (including constant temperature and pressure), changes in free energy, enthalpy, and entropy are related to each other quantitatively by the equation:

$$\Delta G = \Delta H - T \Delta S$$

ΔG – change in Gibbs free energy ($\mathrm{kJ\ mol^{-1}}$)
ΔH – change in enthalpy ($\mathrm{kJ\ mol^{-1}}$)
T – temperature in kelvin, K
ΔS – change in entropy ($\mathrm{J\ K^{-1}\ mol^{-1}}$)

Oxidation-Reduction (Redox) Reactions



Oxidation	**Reduction**
Addition of "O"	Addition of "H"
Loss of "H"	Loss of "O"
Loss of electrons	Gain of electrons

The general principle of oxidation-reduction is applicable to biological systems also

Biological Oxidation-Reduction Reactions

Electrons are transferred from one molecule (electron donor) to another (electron acceptor) in one of four different ways:

1. **Direct combination with O_2**: with an organic reductant and is covalently incorporated in the product.
2. **Directly as electrons**: Fe^{+2}/Fe^{+3} redox pair can transfer an electron to the Cu^{+}/Cu^{+2} redox pair

$$Fe^{2+} + Cu^{2+} \rightleftharpoons Fe^{3+} + Cu^{+}$$

3. **As hydrogen atoms:** H-atom consists of a proton (H^+) with single electron (e^-)

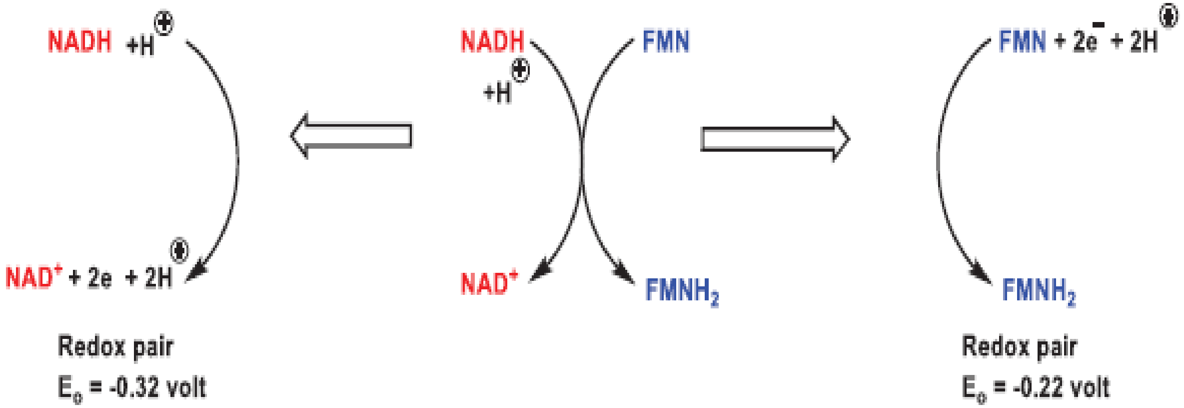
$$AH_2 \rightleftharpoons A + 2e^- + 2H^+$$

4. **As a hydride ion (:H^-):** which has two electrons. This occurs in the case of NAD-linked dehydrogenase. Many redox reactions are dehydrogenations in which one or two hydrogen atoms (H) are transferred from a substrate to a hydrogen acceptor. Redox reactions in living cells involve specialized electron carriers like:
    - **NAD and NADP** are the freely diffusible coenzymes of many dehydrogenases. Both NAD and NADP accept two electrons
    - **FAD and FMN**, the flavin nucleotides, serve as tightly bound prosthetic groups of flavoproteins. They can accept either one or two electrons

Redox pairs: Oxidation (loss of electrons) of one substance is always accompanied by reduction (gain of electrons) of a second. Such oxidation-reduction reactions can be written as the sum of two separate half-reactions, one an oxidation and the other a reduction.

Eg. The oxidation of NADH to NAD^+ is coupled with the reduction of FMN to $FMNH_2$

Overall oxidation-reduction reaction



Redox pairs differ in their tendency to lose electrons

- This tendency is a characteristic of a particular redox pair and can be quantitatively specified by a constant, E_o (the standard reduction potential), with units in volts

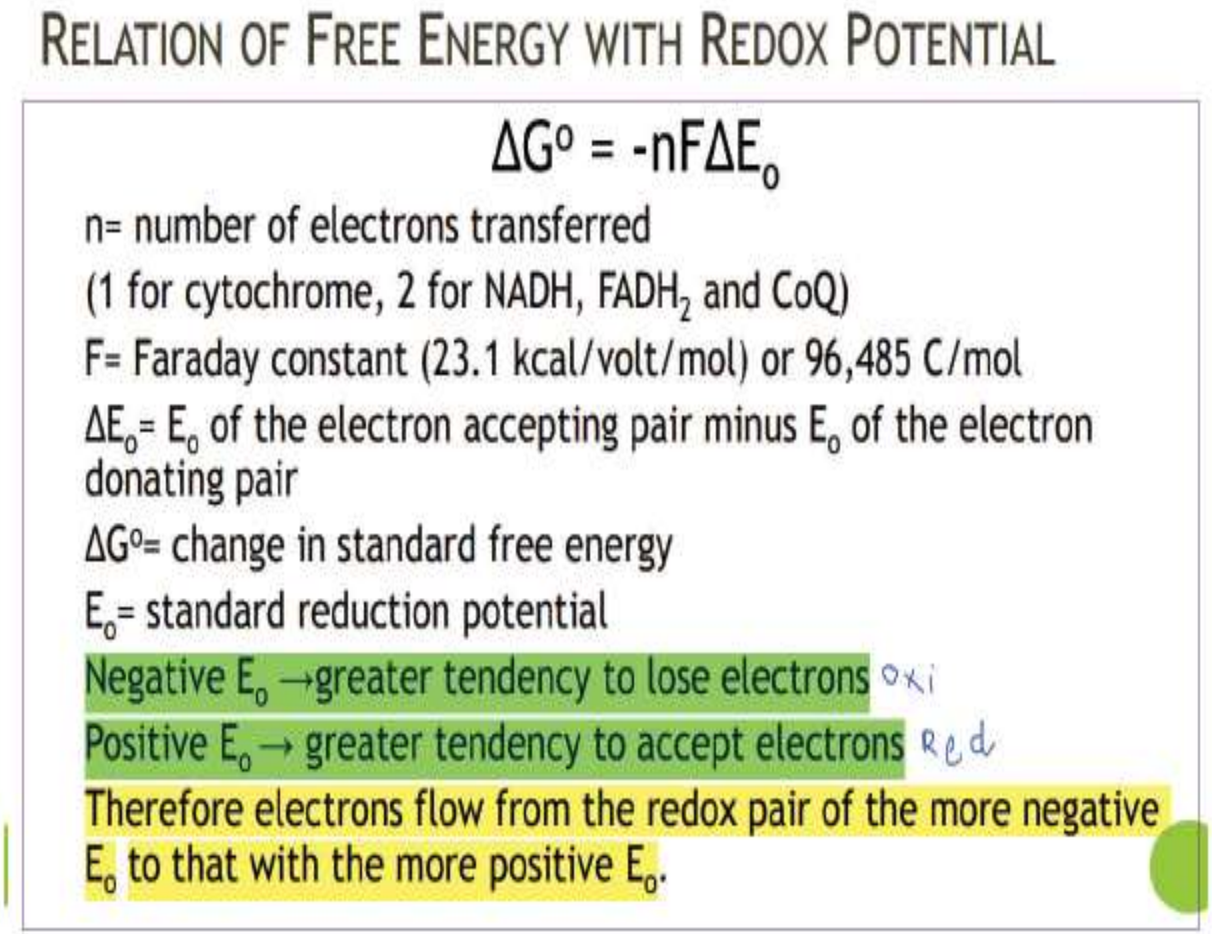
Redox Potential

Oxidation-reduction potential (redox potential): is a quantitative measure of the tendency of a redox pair to lose or gain electrons. The redox pairs are assigned specific standard redox potential (E_0 volts) at pH 7.0 and 25 ^{o}C.

- Hydrogen has the lowest redox potential (-0.42 volt) while oxygen has the highest redox potential (+0.82 volt). The redox potentials of all other substances lie between that of hydrogen and oxygen
- Electrons are transferred from substances with low redox potential to substances with higher redox potential
- Transfer of electrons is an energy yielding process and the amount of energy liberated depends on the redox potential difference between the electron donor and acceptor

Standard reduction potential: The E_0 of various redox pairs can be ordered from the most negative E_0 to the most positive.

- The redox potential (E_0) is directly related to the change in the free energy.



RELATION OF FREE ENERGY WITH REDOX POTENTIAL

$$\Delta G^o = -nF\Delta E_0$$

n= number of electrons transferred

(1 for cytochrome, 2 for NADH, $FADH_2$ and CoQ)

F= Faraday constant (23.1 kcal/volt/mol) or 96,485 C/mol

ΔE_0= E_0 of the electron accepting pair minus E_0 of the electron donating pair

ΔG^o= change in standard free energy

E_0= standard reduction potential

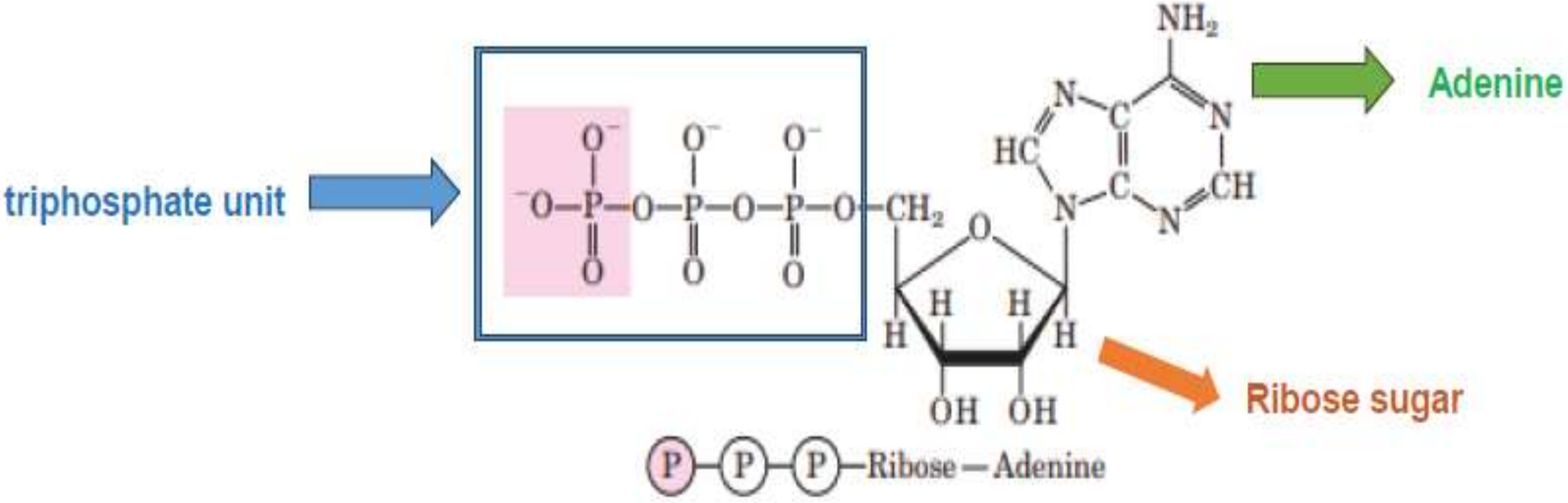
Negative E_0 →greater tendency to lose electrons oxi

Positive E_0 → greater tendency to accept electrons Red

Therefore electrons flow from the redox pair of the more negative E_0 to that with the more positive E_0.

Adenosine triphosphate (ATP)

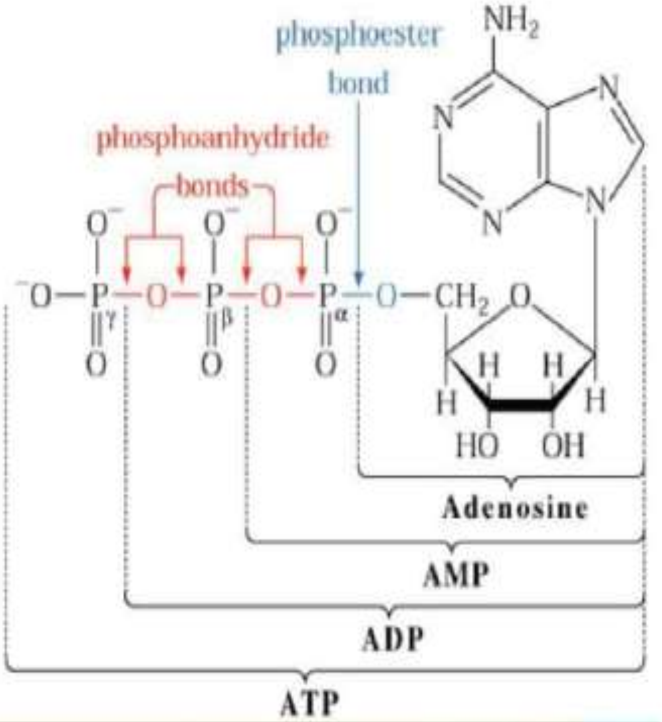
- Serves as the energy currency of the cell
- Consists of an **adenine, a ribose and a triphosphate moiety**
- The active form of ATP is usually a complex of ATP with Mg^{+2} or Mn^{+2}



ATP is an energy-rich molecule because **its triphosphate unit** contains **two phosphoanhydride bonds**

Adenosine triphosphate (ATP)

- It is a high-energy compound due to the presence of two phospho-anhydride bonds in the triphosphate unit. **The standard free energy of hydrolysis of ATP, ΔG_o, is approximately –7.3 kcal/mol for each of the two terminal phosphate groups**. Because of this large negative ΔG_o, ATP is called a high-energy phosphate compound.

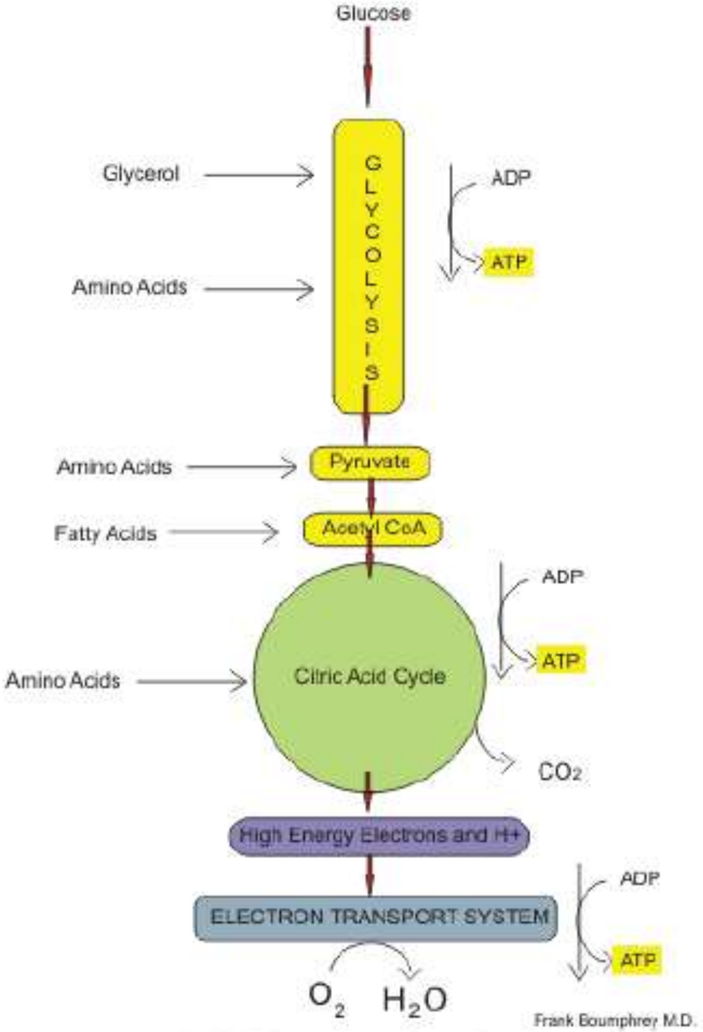


$$ATP + H_2O \rightleftharpoons ADP + P_i$$
$$\Delta G^{\circ\prime} = -30.5\ \text{kJ mol}^{-1}\ (-7.3\ \text{kcal mol}^{-1})$$

$$ATP + H_2O \rightleftharpoons AMP + PP_i$$
$$\Delta G^{\circ\prime} = -45.6\ \text{kJ mol}^{-1}\ (-10.9\ \text{kcal mol}^{-1})$$

Some biosynthetic reactions are driven by the hydrolysis of nucleoside triphosphates that are analogous to ATP—namely:
guanosine triphosphate (GTP),
uridine triphosphate (UTP), and
cytidine triphosphate (CTP)

Major bioenergetics process



Frank Boumphrey M.D.

ATP Production Pathways