

Metabolism

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METABOLISM



WHAT IS METABOLISM ??????????

- The term metabolism applies to the assembly of biochemical reactions which are employed by the organisms for the synthesis of cell materials and for the utilization of energy from their environments.
- In other words, metabolism of an organism (or of a cell) may be defined as “the sum total of all enzyme catalyzed reactions that occur in an organism.”



WHAT IS CATABOLISM ????

- Generation of chemical energy in forms suitable for the mechanical and chemical processes of the cells
- It is the degradative metabolism involving the release of energy and resulting in the breakdown of complex materials .

EXAMPLE :

Fuels (Carbohydrates, Fats) \longrightarrow $\text{CO}_2 + \text{H}_2\text{O} +$
useful energy



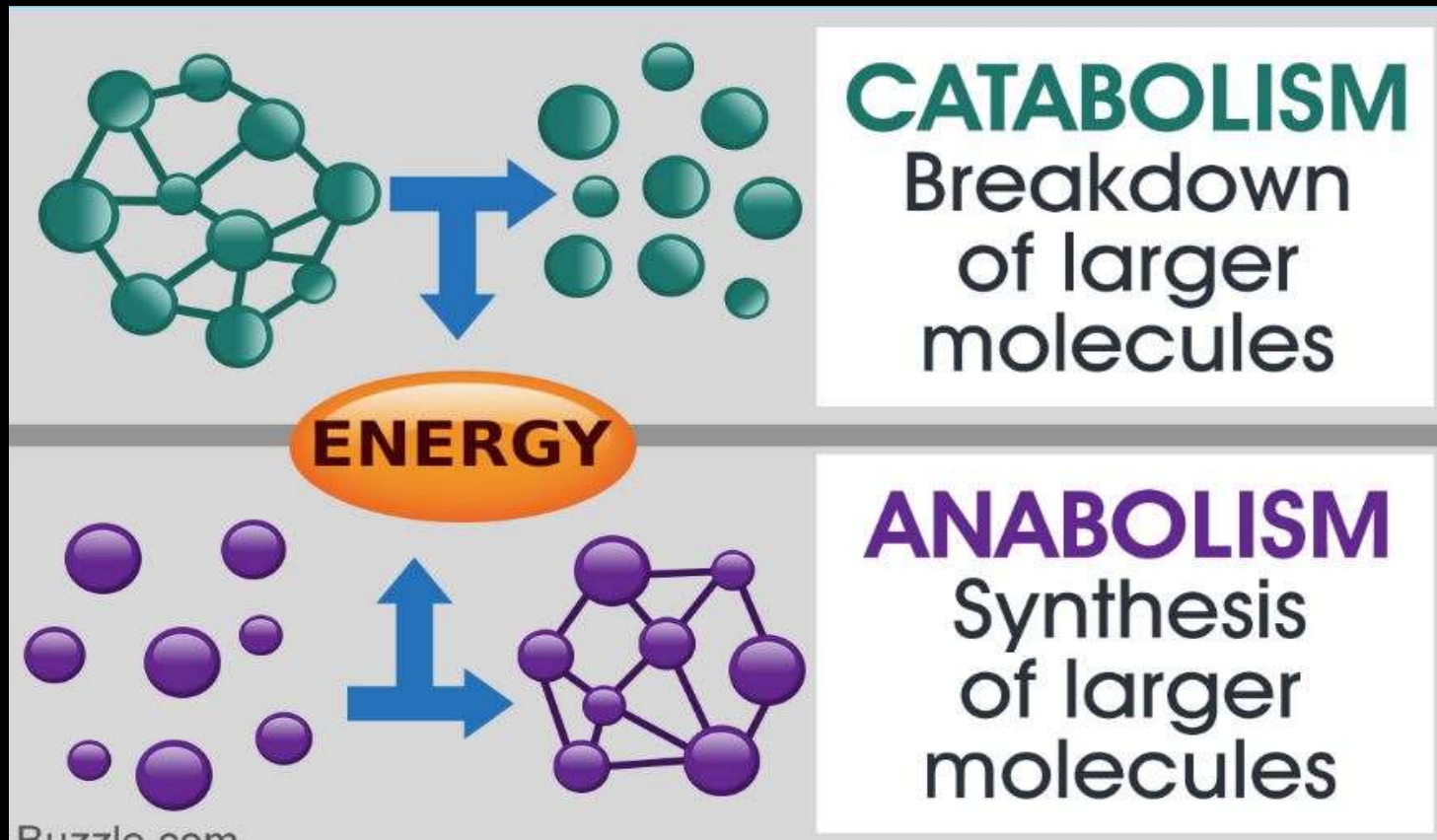
WHAT IS ANABOLISM???????

- Those processes which utilize the energy generated by the catabolism for the synthesis of cell components are termed as anabolism.
- The synthesis of complex molecule from simpler ones together with the storage of energy i.e. it is a constructive metabolism.

EXAMPLE:

Useful energy + small molecules \longrightarrow complex molecule



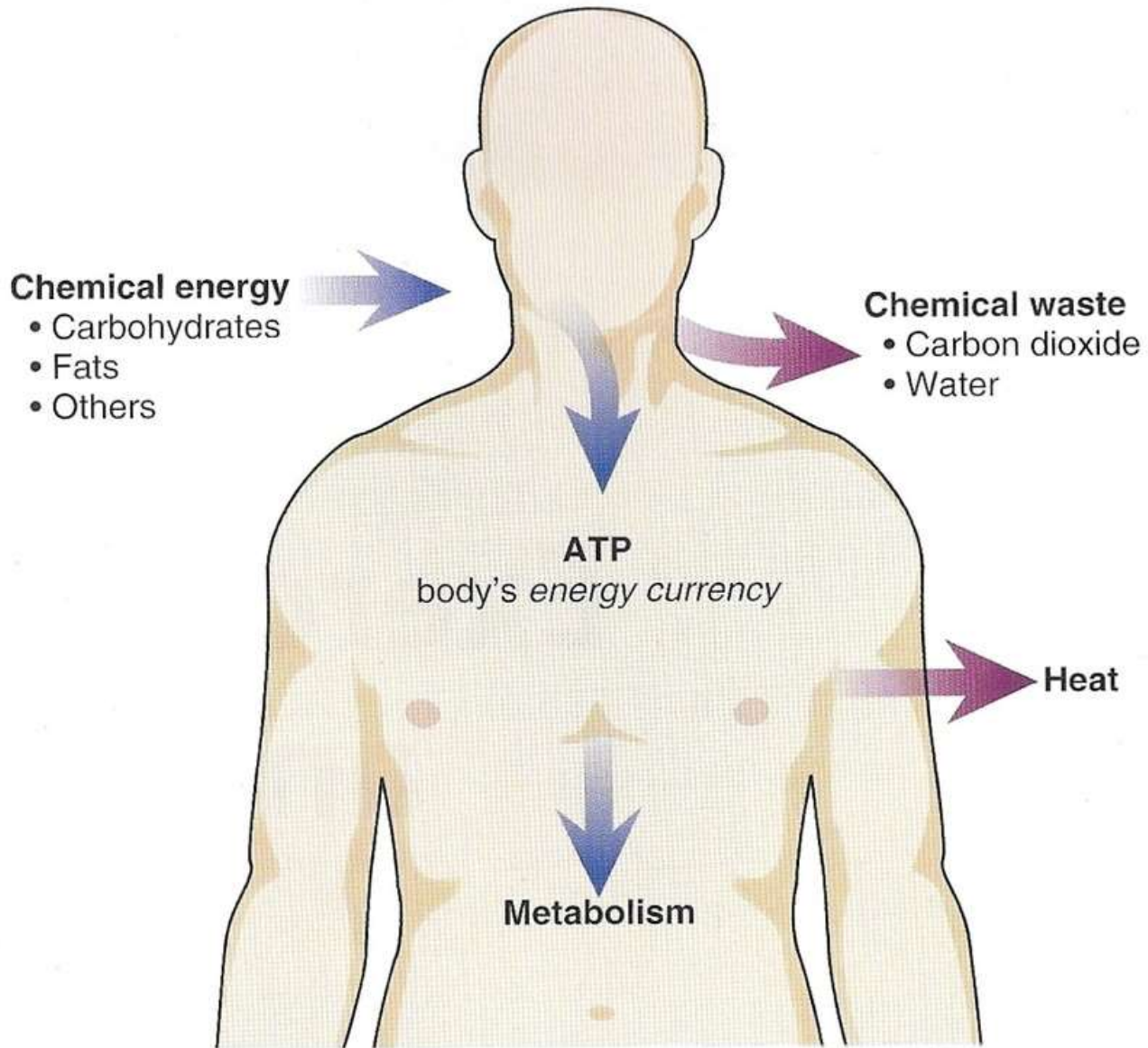


PHOTOSYNTHESIS: Example of anabolism (endergonic)

RESPIRATION: Example of catabolism (exergonic)

BIOENERGETICS

- Bioenergetics is the quantitative study of the energy transductions that occur in living cells and of the nature and functions of the chemical processes underlying these transductions.
- Thermodynamics is the branch of physical chemistry that deals with the energy changes. And biochemical thermodynamics (or biochemical energetics or bioenergetics, as it is also called) is the field of biochemistry concerned with the transformation and use of energy by living cells.
- The chemical reactions occurring in living beings (or biochemical reactions) are associated with the liberation of energy as the reacting system moves from a higher to a lower energy level. Most often, the energy is liberated in the form of heat.

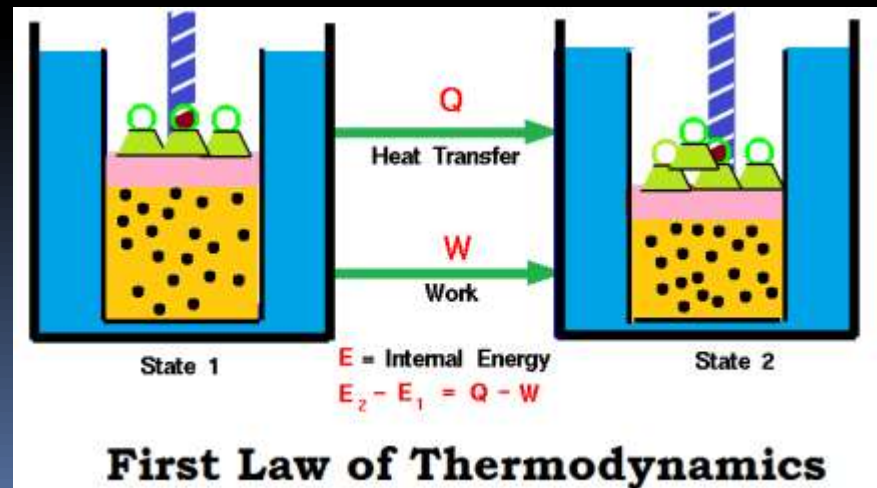


- Biological energy transductions obey the laws of thermodynamics.
- Many quantitative observations made on the interconversion of various forms of energy have led scientists to the formulation of two fundamental laws of thermodynamics, the first and second.

1) First law of thermodynamics (principle of conservation of energy) –

For any physical or chemical energy change, the total amount of energy in the universe remains constant, energy may be transported from one form to another, but it cannot be destroyed or created.

$$\Delta E = \Delta q + \Delta W$$



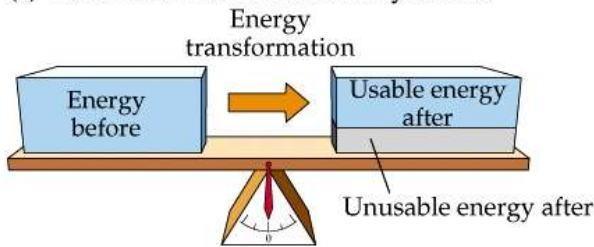
2) Second law of thermodynamics –

The law states that the total entropy of a system must increase if a process is to occur spontaneously.

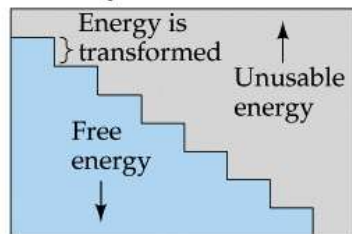
$$\Delta S \geq \Delta q/T$$

- It is unavailable, useless energy. In other words, entropy is a measure of the degree of randomness or disorder of a system. The entropy of a system increases (i.e., ΔS is positive) when it becomes more disordered.
- According to the second law, at each transfer or transformation of energy, part of that energy assumes a form that cannot be passed on any further because it is randomly dispersed, often as heat. And it is this randomly dispersed energy which is called entropy.
- For example, suppose a full gas cylinder is connected to an empty cylinder by a tube with valve. If the valve is opened, gas flows from the full to the empty cylinder until the gas pressure is equal on both sides. Energy has not only been redistributed but also conserved.
- The expansion of gas is explained by the second law of thermodynamics and a condition of matter called entropy which, as already stated, is a measure of the randomness or disorder of a system.

(b) The Second Law of Thermodynamics



Closed system



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➤ The greater the disorder of a system, the greater is its entropy.

➤ The second law states that physical and chemical processes proceed in such a way that the randomness or disorder of the universe (the system and its surroundings) increases to the maximum possible. Gas will always expand into an empty cylinder.

Entropy Change in the Universe

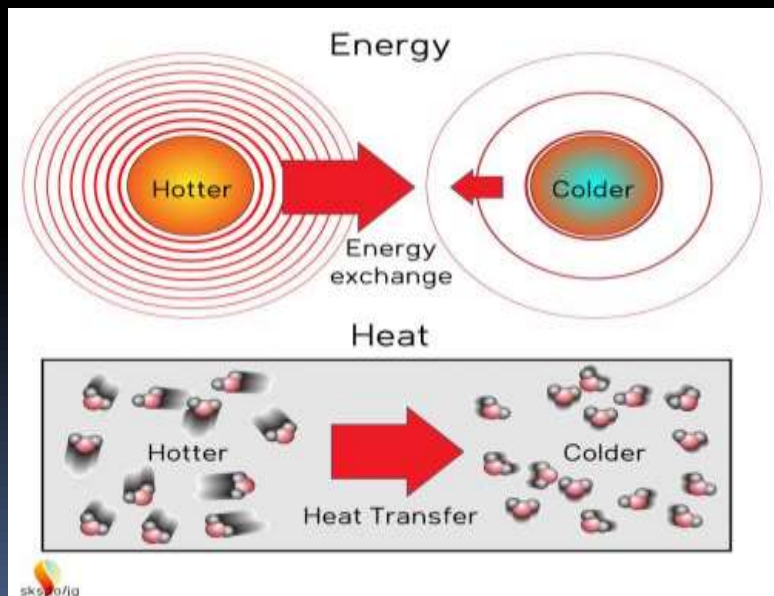
- The universe is composed of the system and the surroundings.
- Therefore,

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

- For spontaneous processes

$$\Delta S_{\text{universe}} > 0$$

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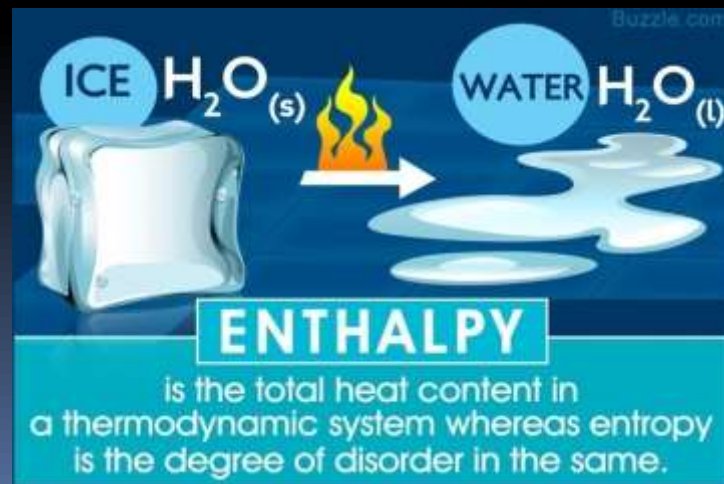


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What is enthalpy?

- Enthalpy denoted by H, is the heat content of the reacting system. It reflects the number and kinds of chemical bonds in the reactants and products. OR
- A thermodynamic quantity equivalent to the total heat content of a system.
- When a reaction releases heat, it is said to be exothermic, the heat content of product is said to be less than reactants. $\Delta H = -$
- When a reaction absorbs heat, it is said to be endothermic, the heat content of products is more than reactants. $\Delta H = +$
- It is equal to the internal energy of the system plus the product of pressure and volume.

$$\Delta H = \Delta E + P\Delta V$$



CONCEPT OF FREE ENERGY

Cells require sources of free energy :

- Cells are isothermal systems – they function at essentially constant temperature.
- Heat flow is not a source of energy for cells, because heat can do work only as it passes to a zone or object of low temperature.
- The energy that cells can and must use is free energy, described by the Gibbs free-energy function G , which allows prediction of the direction of chemical reactions, their exact equilibrium position, and the amount of work they can (in theory) perform at constant temperature and pressure.
- Heterotrophic cells acquire free energy from nutrient molecules, and photosynthetic cells acquire it from absorbed solar radiation. Both kinds of cells transform this free energy into ATP and other energy-rich compounds capable of providing energy for biological work at constant temperature.

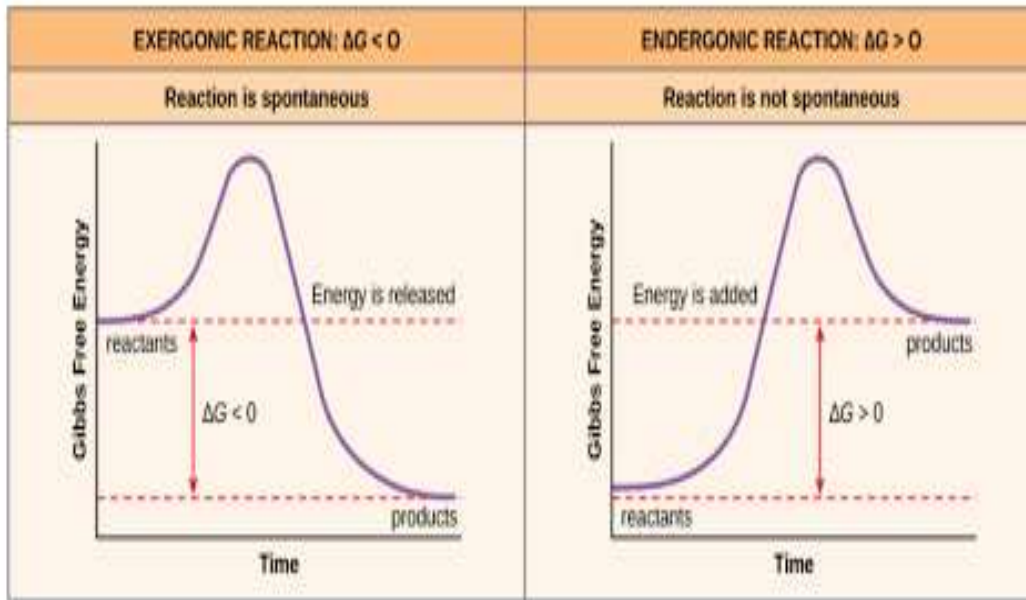
➤ Gibbs free energy, G , expresses the amount of energy capable of doing work during a reaction at constant temperature and pressure.

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

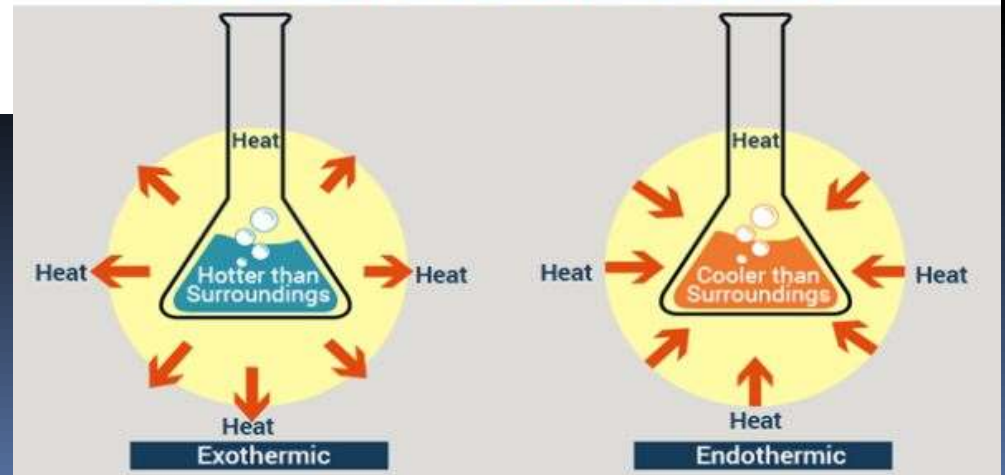
➤ Spontaneous reactions are reactions that are energetically favorable and occur without outside energy.

➤ Systems in general move from a high energy state to low energy state. In general exothermic reactions are spontaneous - but not always.

SPONTANEOUS REACTON	NON-SPONTANEOUS REACTON
<ul style="list-style-type: none">➤ Mostly reactions are exothermic➤ Enthalpy of the reaction is $\Delta H = -$➤ Entropy is $\Delta S = +$➤ There fore, $\Delta G = -$➤ Hence, the reaction must be spontaneous and product is favored.	<ul style="list-style-type: none">➤ Mostly reactions are endothermic.➤ Enthalpy of the reaction is $\Delta H = +$➤ Entropy is $\Delta S = -$➤ Therefore, $\Delta G = +$➤ Hence , the reaction must be non-spontaneous and reactant is favored.



Exothermic Vs. Endothermic



Standard free energy change

- The actual change in free energy ΔG during a reaction is influenced by temperature, pressure and the initial concentrations of reactants and products, and usually differs from standard free energy change, ΔG°
- The chemical reaction has a characteristic standard free energy change and it is constant for a given reaction.
- It can be calculated from the equilibrium constant of the reaction under standard conditions i.e. at a solute concentration of 1.0M, at temperature of 25°C and at 1.0 atm pressure. The free energy change that corresponds to the standard state is known as standard free energy change, ΔG°
- If a reaction is allowed to go to equilibrium at constant temperature and pressure, then at equilibrium the overall free energy change is zero.

$$\text{So, } \Delta G^\circ = -RT \ln K_{\text{eq}}$$

- A relationship has been worked out by which a distinction can be made between ΔG° and ΔG

$$\Delta G = \Delta G^\circ + RT \ln K_{\text{eq}}$$

So standard free energy change is the change in free energy when products and reactants are present in unit concentration.

CONCEPT OF HIGH ENERGY BOND

A) STRUCTURE OF ATP

- ATP is the chemical link between catabolism and anabolism.
- Heterotrophic cells obtain free energy in a chemical form by the catabolism of nutrient molecules, and they use that energy to make ATP from ADP and Pi.
- It acts as a donor of high energy phosphate. It is the energy currency of living cells.
- ATP then donates some of its chemical energy to endergonic processes such as the synthesis of metabolic intermediates and macromolecules from smaller precursors, the transport of substances across membranes against concentration gradients, and mechanical motion.
- This donation of energy from ATP generally involves the covalent participation of ATP in the reaction that is to be driven, with the eventual result that ATP is converted to ADP and Pi or, in some reactions, to AMP and 2Pi.
- The chemical basis for the large free-energy changes that accompany hydrolysis of ATP and other high-energy phosphate compounds, and we show that most cases of energy donation by ATP involve group transfer, not simple hydrolysis of ATP.

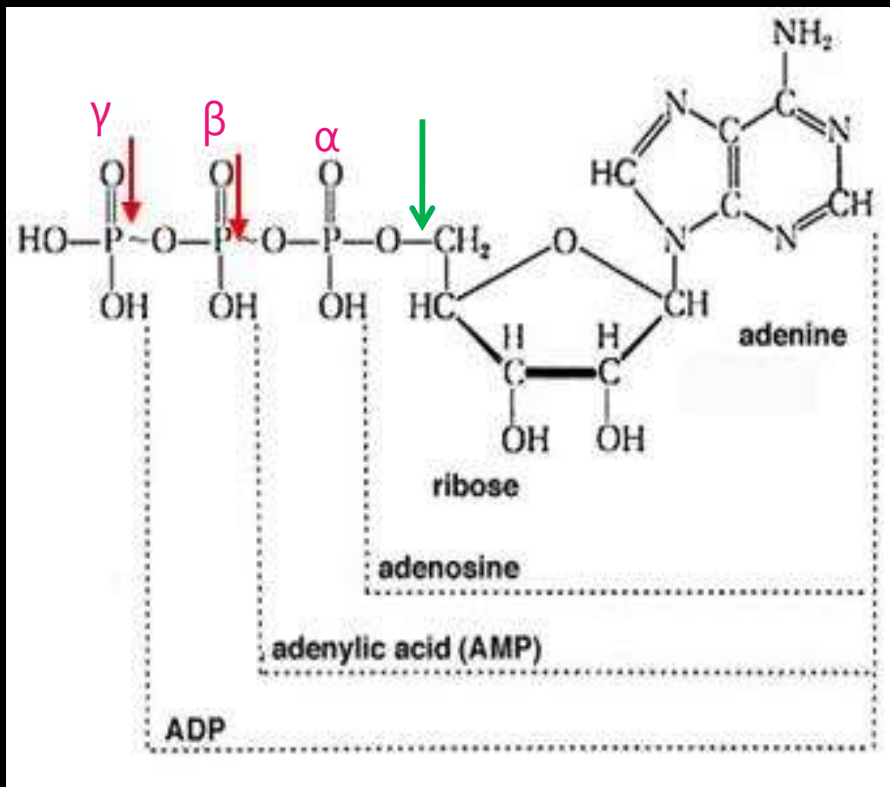
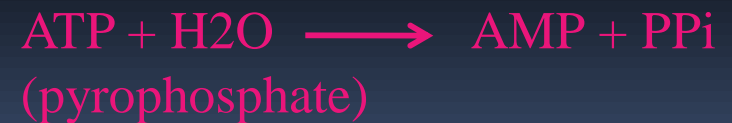


fig : structure of ATP

ATP contains two phosphoanhydride bonds , ADP contains 1 phosphoanhydride bond whereas AMP contains simply an ester link.

- The two red arrows indicate phosphoanhydride bond.
- The green arrow indicates phosphoester bond.
- Phosphoanhydride bonds are high energy bonds whereas, the phosphoester bond is not of as high energy as them because it is simply an ester bond.
- In aqueous solution, the two phosphoanhydride bonds cleave with the incorporation of water.



Chemical basis for large free energy change associated with ATP :

A large amount of free energy is released when ATP is hydrolyzed to ADP + Pi or AMP + Pi.

- 1) The charge separation that results from hydrolysis relieves electrostatic repulsion among the four negative charges on ATP
- 2) The product inorganic phosphate (Pi) is stabilized by formation of a resonance hybrid, in which each of the four phosphorus-oxygen bonds has the same degree of double-bond character and the hydrogen ion is not permanently associated with any one of the oxygen.
- 3) The product ADP^{2-} immediately ionizes, releasing a proton into a medium of very low (H^+) i.e. $\text{pH} = 7$.
- 4) The free-energy change for ATP hydrolysis is -30.5 kJ/mol under standard conditions, but the actual free energy of hydrolysis (ΔG) of ATP in living cells is very different: the cellular concentrations of ATP, ADP, and P, are not identical and are much lower than the 1.0 M of standard condition.

Therefore, these chemical properties make it suitable form of energy currency of living cells.

Phosphoryl group transfers and ATP

The free energy change for ATP hydrolysis is large negative

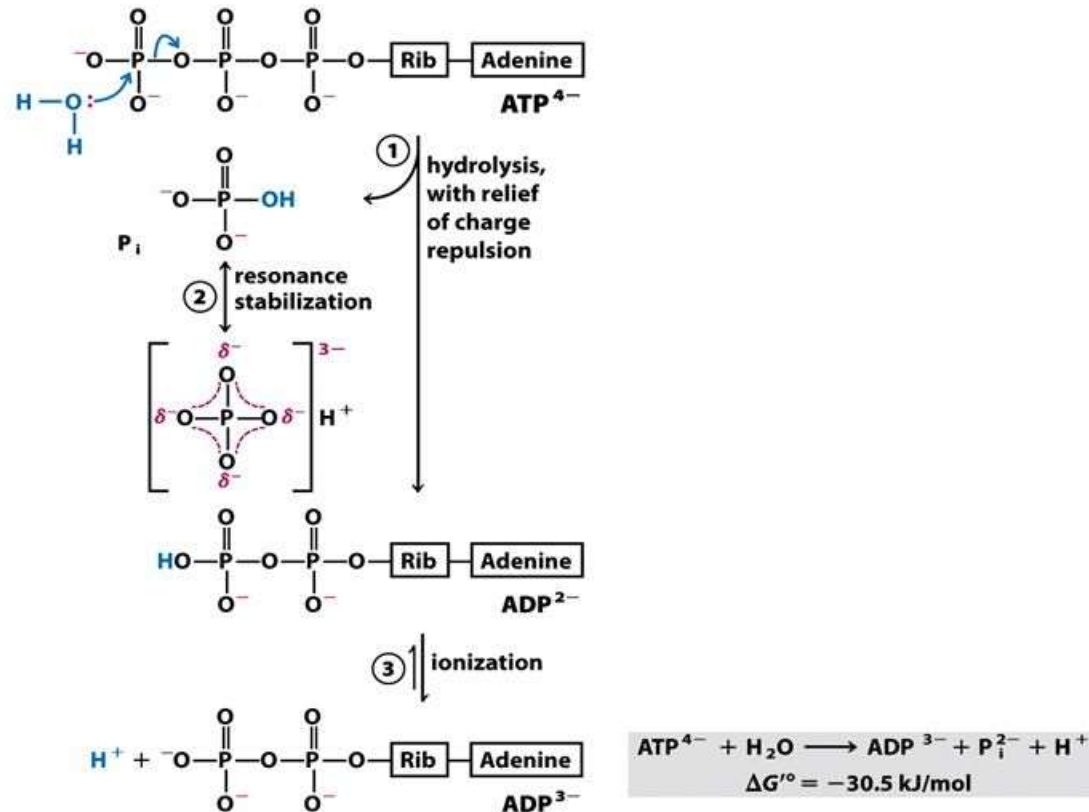
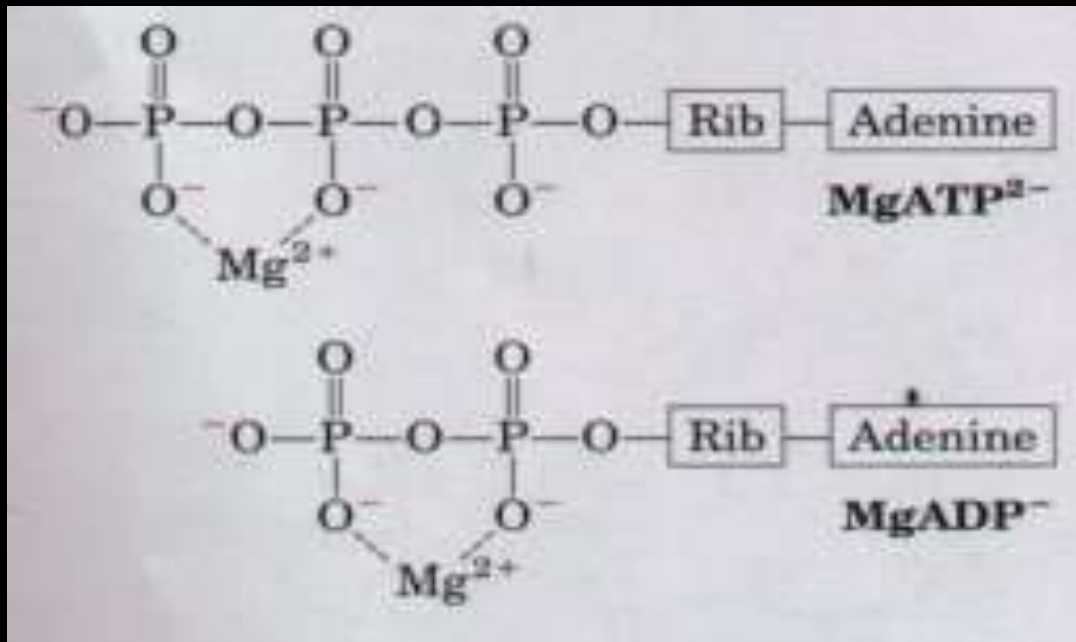


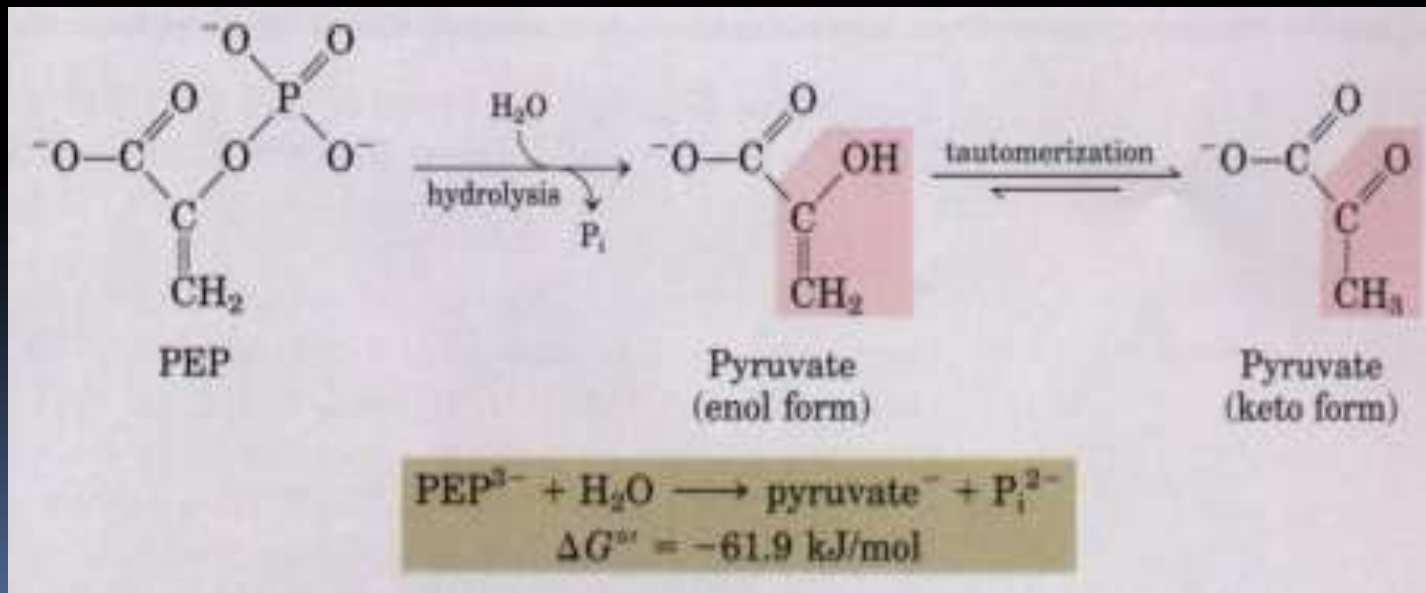
Figure 13-11
Lehninger Principles of Biochemistry, Fifth Edition
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Furthermore, Mg²⁺ in the cytosol binds to ATP and ADP (and for most enzymatic reactions that involve ATP as phosphoryl group donor, the true substrate is MgATP²⁻. The relevant $\Delta G'^{\circ}$ is therefore that for MgATP²⁻ hydrolysis.

B) Phosphoenolpyruvate as high energy bond:

- Phosphoenolpyruvate contains a phosphoester bond that undergoes hydrolysis to yield the enol form of pyruvate, and this direct product can immediately tautomerize to the more stable keto form.
- Because the reactant (PEP) has only one form (enol) and the product (pyruvate) has two possible forms, the product is stabilized relative to the reactant.
- This is the greatest contributing factor to the high standard free energy change of hydrolysis of phosphoenolpyruvate: $\Delta G'^{\circ} = -61.9 \text{ kJ/mol}$



C) PHOSPHOCREATINE AS HIGH ENERGY BOND:

- In phosphocreatine the P-N bond can be hydrolyzed to generate free creatine and P_i.
- The release of P_i and the resonance stabilization of creatine favor the forward reaction. The standard free-energy change of phosphocreatine hydrolysis is again large, -43.0 kJ/mol.
- In all these phosphate-releasing reactions, the several resonance forms available to stabilize this product relative to the reactant, contributing to an already negative free energy change

