

Adenosine Tri-Phosphate

Adenosine triphosphate (ATP) is a small nucleotide molecule used in cells as a coenzyme. It is often referred to as the molecular unit of currency of intracellular energy transfer.

One molecule of ATP contains one adenosine (purine base), a ribose sugar and three phosphate groups. The adenosine remains attached to the 1' carbon of the ribose sugar, while the three phosphate groups remain attached to the 5' carbon of the sugar. It is the addition and removal of the three phosphate groups that interconnect ATP with ATP and AMP. The closest phosphoryl group to the ribose sugar is called the α , the middle one is called β and the farthest is called γ . ATP is highly soluble in water and is quite stable in solutions between pH 6.8 to 7.4, but rapidly hydrolyses in extreme pH.

Structure of ATP

ATP is one of the end products of photophosphorylation, aerobic respiration and fermentation. It is produced by a wide variety of enzymes including ATP synthase. Substrate level phosphorylation, oxidative phosphorylation and photophosphorylation are three major mechanisms of ATP biosynthesis.

ATP is used as a substrate in signal transduction pathways by kinases. It is also used by adenylate cyclase to produce the second messenger molecule cAMP. The ratio between ATP and AMP is used to control the metabolic pathways that produce and/or consume ATP. It is also incorporated to nucleic acid by polymerases in the process of transcription. ATP transports chemical energy within the cell for processes like synthesis of protein, synthesis of membrane, movement of cell, cell division, transport of solutes, etc. When ATP breaks into ADP and P_i , the breakdown of the last covalent link of phosphate liberates energy that is used in reactions where it is needed.

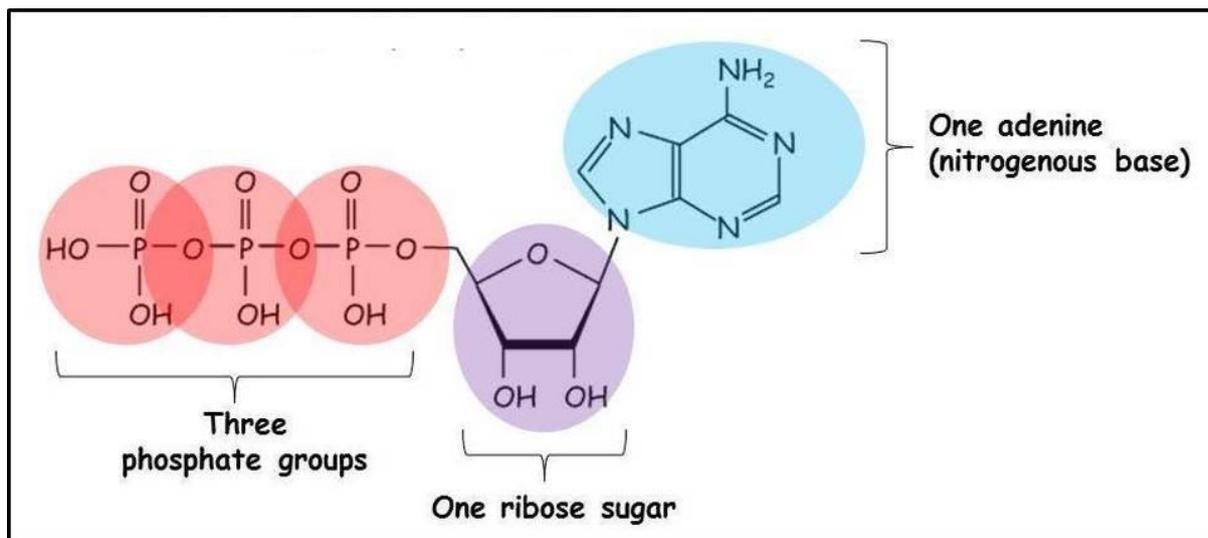
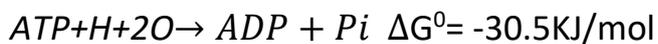
ATP is an energy rich compound that is highly charged and yields a large negative free energy when hydrolysed at physiological pH. The phosphate groups can be removed by hydrolysis in several ways, but the free energy released varies from cell to cell depending upon pH and Mg^{2+} concentration.

In unbuffered water ATP hydrolyses to ADP and phosphate because the strength of the bonds between the phosphate groups in ATP is less than the strength of the hydrogen bonds between ADP + P_i and water. Thus, if ATP and ADP are in chemical equilibrium in water, almost all the ATP will eventually be

converted to ADP. Living cells maintain at least fivefold higher concentration of ATP to ADP so that this displacement from equilibrium leads to hydrolysis of ATP in the cell, thus releasing a large amount of free energy.

The phosphodiester bonds in an ATP molecule are responsible for its high energy content. γ -phosphate group of ATP molecule is hydrolysed primarily. It has a higher energy of hydrolysis than either the α or β phosphate, as it is located the farthest from the ribose sugar. At pH 7.0 ATP has 3.8 negative charges that are closely placed. They repel each other and as a consequence the terminal phosphate group is removed.

The net change in heat energy (enthalpy) and standard temperature and pressure of the decomposition of ATP into ADP and P_i is -30.5KJ/mol with a change in free energy of 3.4KJ/mol



Nicotinamide Nucleotides

Nicotinamide nucleotides comprises of coenzymes involved in hydrogen transfer reactions and form essential components of dehydrogenase enzymes taking part in fermentation and glycolysis. The coenzymes are known as nicotinamide adenine dinucleotide (NAD^+), formerly known as coenzyme I isolated by H. von Euler(1931); nicotinamide adenine dinucleotide phosphate

(NADP⁺), also known as coenzyme II discovered by Warburg and Christian. Collectively these coenzymes are known as Triphospho pyridine nucleotide (TPN).

Pyridine nucleotides are derived from Vitamin B, nicotinic acid or niacin, which is widely distributed in plants and animal tissues. The amide of nicotinic acid, called nicotinamide is the most active form present in pyridine nucleotide coenzymes. The pyridine ring of coenzyme is attached to the ribose molecule through glycosidic linkage while the phosphate group provides a link between adenosine and nicotinamide ribose. In NADP, there is an additional phosphate group in C-2 position of the ribose sugar of adenosine component, hence it is called nicotinamide dinucleotide phosphate.

Biochemical functions

The physiological function and the behaviour of these coenzymes as vitamins has been known for a long time. The pyridine ring of the coenzyme is positively charged and undergoes a change during oxidation-reduction reactions. The hydrogen can reversibly bind with the pyridine ring. The uptake of hydrogen causes reduction retaining two double bonds, accompanied by a loss of positive charge on the nitrogen.

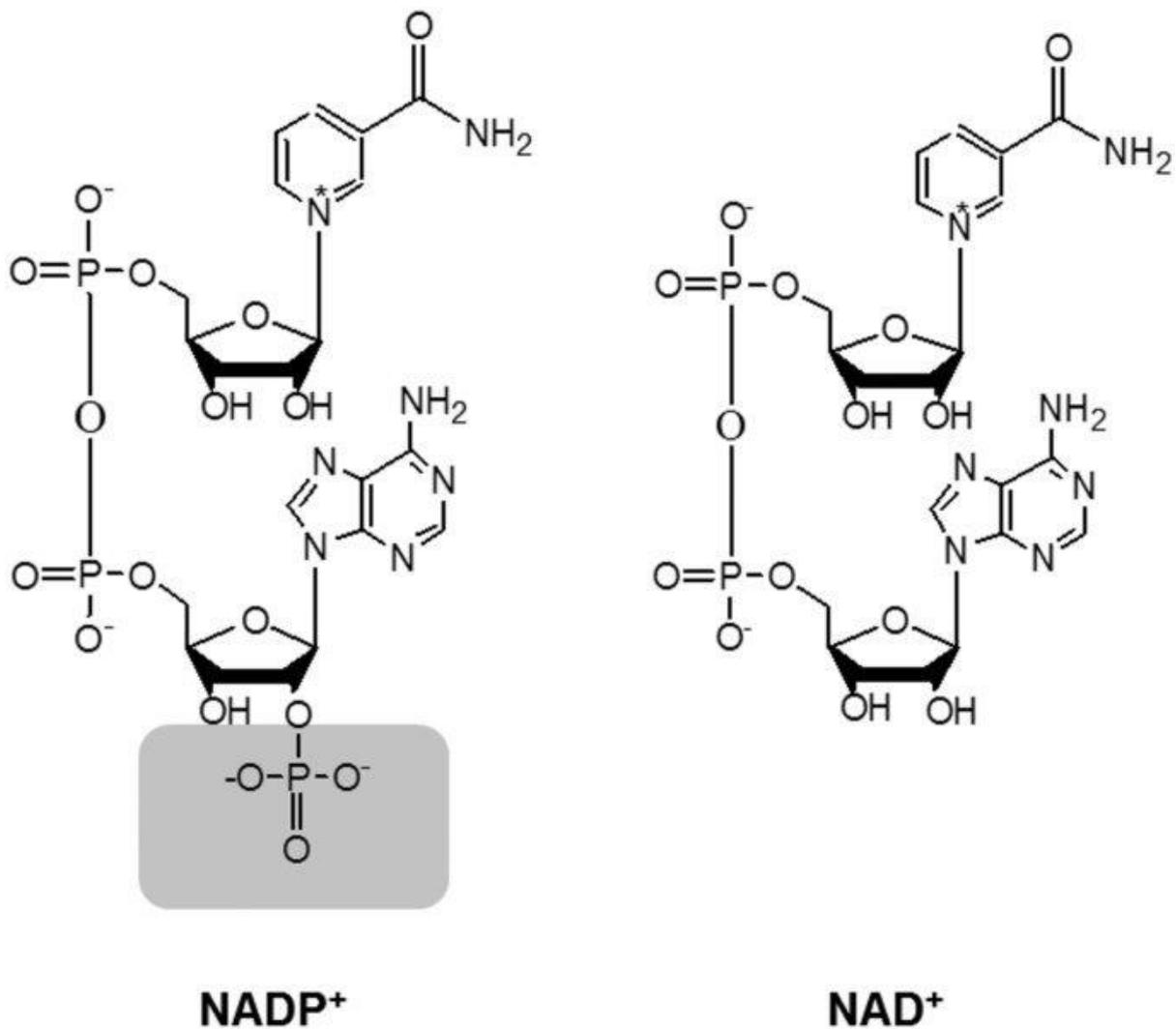
In photosynthetic organisms NADPH is produced by ferredoxine-NADP⁺ reductase in the last step of the electron chain of the light reaction of photosynthesis. It is used as reducing power for the biosynthetic reactions in the Calvin Cycle to assimilate CO₂. It is also needed in the reduction of nitrate into ammonia for plant assimilation in nitrogen cycle.

NADPH provides the reducing equivalents for biosynthetic reactions and the oxidation –reduction involved in protection against the toxicity of reactive oxygen species (ROS), allowing the regeneration of glutathione. It is also used for anabolic pathways, such as lipid synthesis, cholesterol synthesis and fatty acid chain elongation.

The pyridine nucleotides are sometimes called as co-substrates since the enzymes of which they form a prosthetic group are substrate specific. All reactions catalysed by them are reversible.

The reactions involving pyridine nucleotides induces a change in the aromatic nature of the pyridine ring altering the light absorbing quality of the molecule. The reduced form of NAD shows maximum absorption of UV light at 340nm,

while the oxidised form of NAD^+ does not absorb at that wavelength. The two coenzymes (NAD^+ and NADP) have different functions. NADH functions as a coenzyme in such reactions where the ultimate acceptor of hydrogen is molecular oxygen to form water. The transfer of hydrogen and electrons generate ATP through an electron transport mechanism. On the other hand, NADP is used as a coenzyme in reactions where the hydrogen is transferred to an organic compound for biosynthesis.



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