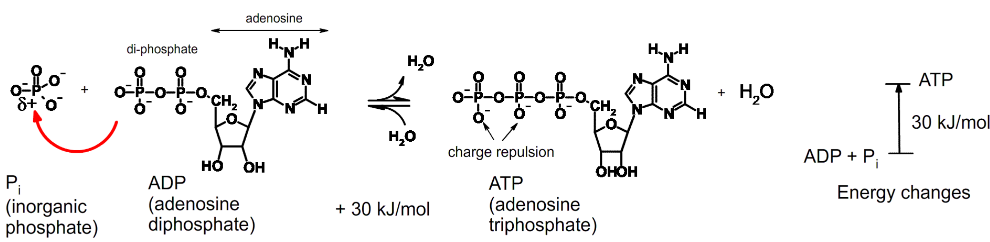
Module 14 / Energy Storage in Metabolism

Explain the major energy storage methods in metabolism - phosphorylated compounds, redox carriers, and proton gradient.	Identify and describe the source of "high-energy" phosphate bonds in ATP.	Tell how the energy stored in a thioester can be used for ATP synthesis or organic addition reactions.

The operation of a metabolic pathway produces (catabolic) or consumes (anabolic) energy. There are a number of different forms of energy storage that are found in metabolic pathways. These include:

1. **Phosphorylated Compounds** Nucleoside triphosphates, such as adenosine triphosphate (ATP) are commonly used to store energy. The addition of an inorganic phosphate group to a nucleotide diphosphate to form the triphosphate requires approximately 30 kJ/mol of energy. The reaction showing the synthesis of ATP from ADP and phosphate is pictured below.



Phosphorylation of adenosine diphosphate (ADP) produces adenosine triphosphate (ATP). This reaction requires the input of approximately 30 kJ/mol. Formation of ATP occurs when the negatively charged phosphate group on ADP attacks the electropositive phosphate in inorganic phosphate, forming a phosphate anhydride bond with the release of water (red arrow).

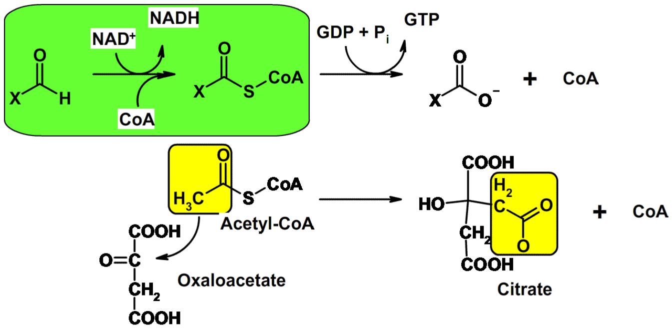
ATP can be used to phosphorylate other nucleoside diphosphates with essentially no input of energy, for example:

$$\text{GDP} + \text{ATP} \rightleftharpoons \text{ADP} + \text{GTP} \qquad \Delta E \sim 0 \text{ kJ/mol}$$

The myth of high-energy phosphate bonds. When a phosphate is released from ATP to form ADP, about 30 kJ/mol of energy is released. It is often stated, incorrectly, that the bond that is broken is "high-energy". In fact, its energy is no different than any other phosphate bond of the same type. The release of energy is due to the fact that the products, ADP and inorganic phosphate, are lower in energy than ATP by 30 kJ/mol. One reason that ATP is higher in energy is due to charge repulsion between the negatively charged phosphate groups. Once the phosphate group is removed, the unfavorable repulsion disappears.

2. **Reduced redox carriers.**The oxidation of metabolytes usually produces energy, If this energy was not captured in some way, it would be lost as heat. The reduced form of redox carriers, such as NADH and $FADH_2$, are higher in energy than their corresponding oxidized forms, capturing the energy that would otherwise be lost as heat. For example, the oxidation of isocitrate to ketoglutarate releases approximately 70 kJ/mol, 60 of which is captured by converting NAD^+ to NADH.
3. **High energy thioesters** are often produced by oxidative steps. For example, the energy released by the oxidation of an aldehyde is stored in both the reduced form of NAD^+ as well in a thioester. The

hydrolysis of the thioester can be used to synthesize nucleoside triphosphates or to facilitate the hydrolysis of the thioester can be used to synthesize nucleoside triphosphates or to facilitate the formation of carbon-carbon bonds, as shown below.



The oxidation of the aldehyde to the thioester is highlighted in green. CoA is coenzyme A, a nucleotide containing cofactor that is an essential co-substrate for many reactions. Part of the energy of this oxidation, 60 kJ/mol, is captured by the formation of NADH. The energy stored in the thioester can be used to either phosphorylate GDP to form GTP, capturing another 30 kJ/mol. In the case of acetyl-CoA (lower diagram) the thioester facilitates the attachment of the acetyl group to oxaloacetate to form citrate, the first compound in the TCA cycle.

4. **Proton gradient** The transfer of electrons from NADH and $FADH_2$ to oxygen to form water during the electron transport chain, provides energy for the pumping of protons across the inner mitochondrial membrane. This is equivalent to pumping water up hill to fill a reservoir. As the protons flow back through the membrane, the energy released is used to generate ATP, in much the same way water generates electricity in a hydroelectric plant.

did I get this

The products of ATP hydrolysis, ADP and inorganic phosphate, are more stable because

- The bond that is broken is higher in energy than other phosphate-phosphate bonds.
- Additional hydrogen bonds can be formed to the new phosphate.
- Electrostatic repulsion between the phosphates is relieved.

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