Topic Page: Coenzyme

Definition: **coenzyme** from *The Penguin Dictionary of Science*

A non-protein organic molecule that plays an accessory yet necessary role in the catalytic action of an ➤enzyme. Many ➤vitamins function as coenzymes, particularly those of the B group. ➤➤FAD; NAD+; NADP+; thiamine.

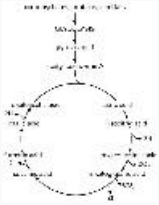

Image from: **Krebs cycle (citric acid cycle or tricarboxylic acid cycle)** in *The Macmillan Encyclopedia*

Summary Article: **coenzyme**
From *The Columbia Encyclopedia*

(kō-ĕn'zīm), any one of a group of relatively small organic molecules required for the catalytic function of certain enzymes. A coenzyme may either be attached by covalent bonds to a particular enzyme or exist freely in solution, but in either case it participates intimately in the chemical reactions catalyzed by the enzyme. Often a coenzyme is structurally altered in the course of these reactions, but it is always restored to its original form in subsequent reactions catalyzed by other enzyme systems.

Adenosine triphosphate (ATP) is a coenzyme of vast importance in the transfer of chemical energy derived from biochemical oxidations. Other nucleotides (formed from uracil, cytosine, guanine, and inosine) have also been found to act as coenzymes. For example, uridine triphosphate—a derivative of uracil—has been demonstrated to be of great importance in the metabolism of carbohydrates, as in the biosynthesis of glycogen and sucrose.

Those coenzymes that have been found to be necessary in the diet are vitamins. One such compound, **biotin**, is a member of the B complex; it was first isolated in 1935 from dried egg yolk, and its structure was established in 1942. Biotin is usually found attached to a lysine residue in certain enzymes, where it participates in reactions involving the transfer of carboxyl (—COOH) groups; one such reaction is essential for the synthesis of fatty acids.

Another group of coenzymes is the **cobalamin** family; one member, cyanocobalamin (vitamin B_{12}) is known to be essential in the diet, although its role in metabolism remains obscure. Closely related cobalamins seem to be involved in the biosynthesis of methionine and methane. The complicated cyanocobalamin molecule was reported in 1973 to have been synthesized; it was first isolated from liver some 25 years prior to that date.

has been shown to participate in a variety of biochemical reactions, all involving acyl groups such as the acetyl unit; it is, for instance, associated with the pivotal first step of the Krebs cycle, in which an acetyl unit (the breakdown product of carbohydrates) is introduced into the cycle to be converted eventually into carbon dioxide, water, and chemical energy. Coenzyme A is derived from adenine, ribose, and pantothenic acid (a vitamin of the B complex).

The two **flavin** coenzymes, riboflavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD), occur universally in living organisms and play important roles in biochemical oxidations and reductions. They are usually found tightly bound to certain enzymes (flavoproteins) and are derived from riboflavin (vitamin B_2).

a tripeptide consisting of residues of glutamic acid, cysteine, and glycine, is known to act as a coenzyme in a few enzymatic reactions, but its importance may lie in its role as a nonspecific reducing agent within the cell. It is hypothesized that glutathione serves to maintain the biological activity of certain proteins by keeping selected cysteine sidechains in the reduced thiol form, thereby not allowing these residues to oxidize and cross-link with one another to form cystine residues. (Unnecessary cross-links often result in distortions of protein structure.)

a complicated molecule containing iron in the ferrous state, serves as a coenzyme in a variety of biochemical processes. It forms an essential part of the structure of hemoglobin and participates intimately in the uptake and release of oxygen by this protein. (In this case the use of the word coenzyme may be inappropriate in that often hemoglobin is not considered to be an enzyme, since it does not catalyze a chemical reaction.) Heme is an important part of the cytochromes, enzymes that catalyze the biochemical oxidations and reductions involved in the production of chemical energy in the form of ATP; heme is also associated with the various enzymes that catalyze the cleavage of peroxides.

acid seems to be involved in the removal of carboxyl groups from α-keto acids and in the transfer of the remaining acyl groups to various acceptors. Lipoic acid in fact transfers the acetyl group of pyruvic acid to coenzyme A. Like biotin, lipoic acid is commonly found attached to lysine residues within certain enzymes. It was first reported to have been purified and isolated in crystalline form in 1953.

The **nicotinamide nucleotides** were the first coenzymes to be detected (1904) in extracts of a living organism. Nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP) are derived from adenine, ribose, and nicotinic acid or niacin (a vitamin of the B complex) and are important intermediates in the biochemical oxidations and reductions that provide chemical energy within the cell. Both NAD and NADP can be reduced by accepting a hydride ion (H^-, a proton with two electrons) from an appropriate donor; the resulting NADH and NADPH can then be oxidized back to their original states by transferring their hydride ions to various acceptors. In this fashion electron pairs (and protons) are shuttled about in the cell from high-energy donors to lower-energy acceptors. As a general rule, NADPH donates its hydride ions to biosynthetic processes, such as the fixing of carbon dioxide to make carbohydrates during the dark reaction of photosynthesis. NADH, on the other hand, donates its hydride ions to systems such as the cytochromes, which eventually donate them to oxygen to make (with the addition of a proton) water, producing chemical energy in the form of ATP as a byproduct; the process is not yet completely understood.

is a coenzyme that is essential for many enzymatic reactions, almost all of which are associated with amino acid metabolism. It is, for example, involved in the synthesis of tryptophan, a derivative of pyridoxine (another vitamin of the B complex).

The coenzyme **tetrahydrofolic acid** is derived in humans from the B-complex vitamin folic acid. This coenzyme and its close relatives participate in the transfer of various carbon fragments from one molecule to another; they are, for instance, involved in the synthesis of methionine and thymine.

is derived from another B-complex vitamin, thiamine. This coenzyme often plays a role in the removal of carboxyl (—COOH) groups from organic acids, releasing the carbon and oxygen atoms as carbon dioxide (CO_2). This coenzyme, for example, helps to remove a carboxyl group from pyruvic acid, leaving behind an acetyl group, which it donates to lipoic acid; the lipoic acid then transfers the acetyl group to coenzyme A, which finally inserts it into the beginning of the Krebs cycle. This important three-step

enzymatic process requires the participation of three coenzymes; hundreds of other biochemical reactions require coenzymes as well, and this serves to explain the great significance of those molecules in the functioning of living organisms. In the case of human beings, it also serves to explain the importance of proper dietary intake of vitamins, which provide the only source of certain “building blocks” for several of these coenzymes.


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