

# Nitrogenase

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Nitrogenase is the enzyme used by some organisms to fix atmospheric nitrogen gas . It is the only known family of enzymes which accomplishes this process. Dinitrogen is relatively inert, this is because each atom of nitrogen has three open orbitals in its outer electron shell to bond with another atom, and that means that if two nitrogen atoms bond to each other, they do so in all three of these orbitals. To break a nitrogen atom away from another means breaking all three of these chemical bonds. This is referred to as having a triple bond. Nitrogenase is a catalyst for the reaction:  $N_2 + 6H + \text{energy} \rightarrow 2NH_3$ . Since this reaction does not occur very often, and in fact goes the other way more easily, with ammonia breaking down into nitrogen and hydrogen, without nitrogenase, there would be much less life than presently exists. Nitrogenase thus breaks the triple bond by getting electron donors for each of the three bonds, and then bonds the nitrogen to hydrogen atoms. The process is complex because each bond is broken individually, and is not completely understood. Nitrogenase requires both the MoFe protein and ATP, which supplies the energy. Nitrogenase bonds each atom of nitrogen to three atoms of hydrogen to form ammonia or  $NH_3$ , and then ammonia is bonded to glutamate and becomes glutamine. Nitrogenase associates with a second protein, and each cycle transfers one electron from an electron donor which is enough to break one of the nitrogen chemical bonds. However, it has not been proven that exactly three cycles are sufficient to fix an atom of nitrogen. The enzyme therefore requires a great deal of chemical energy, released from the hydrolysis of ATP, and reducing agents, such as dithionite in vitro or ferredoxin in vivo. The enzyme is composed of the heterotetrameric MoFe protein that is transiently associated with the homodimeric Fe protein. Nitrogenase is supplied reducing power when it associates with the reduced, nucleotide-bound homodimeric Fe protein. The heterocomplex undergoes cycles of association and disassociation to transfer one electron, which is the limiting step in the process. ATP supplies the reducing power. The exact mechanism of catalysis is unknown due to the difficulty in obtaining crystals of nitrogen bound to nitrogenase. This is because the resting state of MoFe protein does not bind nitrogen and also requires at least three electron transfers to perform catalysis. Nitrogenase is able to bind acetylene and carbon monoxide, which are noncompetitive substrates and inhibitors, respectively. Dinitrogen, however, is a competitive substrate for acetylene. This is because binding of dinitrogen prevents acetylene binding, and acetylene requires only one electron to be reduced, and it does not inhibit. All nitrogenases have an iron- and sulfur-containing cofactor that includes heterometal atom in the active site . In most, this heterometal is molybdenum, though in some species it is replaced by vanadium or iron. Due to the oxidative properties of oxygen, most nitrogenases are irreversibly inhibited by dioxygen, which degradatively oxidizes the Fe-S cofactors. This requires mechanisms for nitrogen fixers to avoid oxygen in vivo. Despite this problem, many use oxygen as a terminal electron acceptor for respiration. One known exception, a recently-discovered nitrogenase of *Streptomyces thermoautotrophicus*, is unaffected by the presence of oxygen [<http://www.jbc.org/cgi/reprint/272/42/26627.pdf>]. The Azotobacteraceae are unique in their ability to employ an oxygen-labile nitrogenase under aerobic conditions. This ability has been attributed to a high metabolic rate allowing oxygen reduction at the membrane, but this idea has been shown to be unfounded and impossible at oxygen concentrations above 70  $\mu M$  , as well as during additional nutrient limitations. The reaction that this enzyme performs is:  $N_2 + 8H^+ + 8e^- + 16 ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16 Pi$  ( [From the Wikipedia article Nitrogenase](#) .)

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## Nitrogenase Patents:



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- 7273614- [Nucleic acids encoding DP-178 and other viral fusion inhibitor peptides useful for treating aids](#)
- 7285635- [Modified proteins, designer toxins, and methods of making thereof](#)
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- 7338590- [Water-splitting using photocatalytic porphyrin-nanotube composite devices](#)
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- 7226761- [Manufacture of five-carbon sugars and sugar alcohols](#)
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- 7122190- [Fusion proteins comprising DP-178 and other viral fusion inhibitor peptides useful for treating aids](#)
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- 7544782- [Tumour necrosis factor binding ligands](#)
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- 7534595- [Compositions of prokaryotic phenylalanine ammonia-lyase and methods of using compositions thereof](#)
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- 7439050- [Corynebacterium glutamicum genes encoding diaminopimelate epimerase](#)
- 7445894- [Compositions and methods for detection and isolation of phosphorylated molecules](#)
- 7449178- [Attenuated gram negative bacteria](#)
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- 7497901- [Tungstate and molybdate wood preservatives](#)
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