

64. Nitric Oxide
65. Nitrogen Dioxide
66. Nitrous Oxide

CHEMICAL NAME = nitric monoxide	nitrogen dioxide	dinitrogen oxide
CAS NUMBER = 10102-43-9	10102-44-0	10024-97-2
MOLECULAR FORMULA = NO	NO ₂	N ₂ O
MOLAR MASS = 30.0 g/mol	46.0 g/mol	44.0 g/mol
COMPOSITION = N(46.7%) O(53.3%)	N(30.4%) O(69.6%)	N(63.7%)
MELTING POINT = -164°C	-11.2	-90.8°C
BOILING POINT = -152°C	21.1°C	-88.6°C
DENSITY = 1.35 g/L	2.05 g/L	.99 g/L
VAPOR DENSITY = 1.04 (air = 1)	1.58	1.53



Nitrogen oxides refer to several compounds composed of nitrogen and oxygen. This entry focuses on the three most common: nitric oxide, nitrogen dioxide, and nitrous oxide. Other nitrogen oxides not addressed include dinitrogen trioxide (N₂O₃), dinitrogen tetroxide (N₂O₄), nitrogen trioxide (NO₃), and dinitrogen pentoxide (N₂O₅). As air pollutants, nitrogen oxides generally refer to the compounds nitric oxide and nitrogen dioxide. Nitrogen oxides exist as gaseous compounds under normal conditions, although nitrogen dioxide changes phases between liquid and gas near room temperature (its liquid density at 20°C is 1.45 g/cm³). Nitrogen monoxide (NO) is commonly called nitric oxide, and dinitrogen monoxide's (N₂O) common name is nitrous oxide. Nitric oxide and nitrogen dioxide are nonflammable, toxic gases. Nitric oxide is colorless and has a sharp sweet odor; nitrogen dioxide is a reddish-brown gas (or yellow liquid) with a strong, acrid odor. Nitrogen dioxide readily dimerizes to produce N₂O₄. Dinitrogen tetroxide production is favored as temperature decreases. As N₂O₄ increases in the NO₂ \rightleftharpoons N₂O₄ equilibrium, the color of the gas fades from brown toward colorless.

Nitric oxide is a free radical that quickly reacts in air to produce nitrogen dioxide. It is also an important biological messenger and transmitter. Nitrous oxide is a colorless, nonflammable, nontoxic gas with a slightly sweet odor and taste. Nitrous oxide is called laughing gas and has been used as a recreational inhalant, anesthetic, oxidizer, and propellant.

Nitric oxide, nitrogen dioxide, and nitrous oxide were prepared in 1772 by Joseph Priestley (1733–1804) and described in his volumes *Experiments and Observations of Different Kinds of Air* published between 1774 and 1786. Priestley called nitric oxide *nitrous air*, nitrogen dioxide *nitrous acid vapor*, and nitrous oxide *phlogisticated nitrous air*, but also referred to the latter as *diminished nitrous air*. He observed the change of clear nitric oxide to red nitrogen dioxide. Priestley prepared nitric oxide by reacting nitric acid with a metal such as copper: $3\text{Cu}_{(s)} + 8\text{HNO}_{3(aq)} \rightarrow 2\text{NO}_{(g)} + 3\text{Cu}(\text{NO}_3)_{2(aq)} + 4\text{H}_2\text{O}_{(l)}$. He prepared nitrous oxide by reducing nitric oxide using iron: $2\text{NO}_{(g)} + \text{H}_2\text{O}_{(l)} + \text{Fe}_{(s)} \rightarrow \text{N}_2\text{O}_{(g)} + \text{Fe}(\text{OH})_{2(aq)}$. Confusion existed involving the numerous gases prepared by scientists during Priestley's era because chemical reactions produced gas mixtures. Scientists attempted to separate these mixtures into the pure components to characterize their behavior. Thus dates of discovery of gases are often ambiguous, with multiple dates being cited in the literature. For example, the year of discovery for nitrous oxide ranges between 1772 and 1793. Humphrey Davy (1778–1829) examined the physiological effects of nitrous oxide and in 1799 wrote *Researches Chemical and Philosophical, Chiefly Concerning Nitrous Oxide*. Davy noted that it had the ability to reduce pain in medical procedures and discovered that it created a temporary state of intoxicated euphoria; symptoms in people who inhaled it included disorientation, loss of motor coordination, and hysterical laughter. Thus the name laughing gas was adopted. Although Davy observed that nitrous oxide had potential as an anesthetic, its main use was as a recreational substance for several decades before it was first used as an anesthetic in 1844 (see Ether, Chloroform). Parties in which people became intoxicated on nitrous oxide, called frolics, were quite common in the early 19th century (Figure 66.1)

Nitrogen oxides are produced both naturally and by human activity. The main natural sources are volcanoes, oceans, lightning, forest fires, and biological decay. Human activities produce approximately 25 million tons of nitrogen oxides annually, which are a form of air pollution that is regulated by the federal government. Nitrogen oxides are produced when fuels are burned at high temperatures. The primary human sources of nitrogen oxides are motor vehicles, power utilities, industrial combustion, and residential combustion. Motor vehicles account for about half of the human output of nitrogen oxides, with utility plants accounting for another 30–35%. Most nitrogen oxides are emitted as NO but are quickly converted to NO₂ in the atmosphere. The federal government has established air quality standards for nitrogen dioxide at 0.053 parts per million (ppm), which equals 100 μg (micrograms) per cubic meter.

Nitrogen oxides have a number of detrimental health and environmental effects. Nitric oxide is a main ingredient in forming other pollutants such as ground-level ozone and photochemical smog. At low levels, nitrogen oxides irritate the eyes, nose, and throat, causing coughing, fatigue, and shortness of breath. Chronic exposure can lead to respiratory infections or lung damage, leading to emphysema. Breathing high concentrations of nitrogen oxides can cause spasms, burns, swelling of respiratory tissues, and fluid in the lungs. Nitrogen oxides combine with water in the atmosphere to form acids, contributing to acid precipitation. Nitrogen dioxide is highly soluble in water and forms nitric acid (HNO₃), and nitric oxide is slightly soluble and forms nitrous acid (HNO₂). Nitrogen oxides are detrimental to plants,



Laughing Gas.

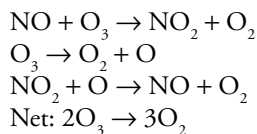
"Some jumped over the tables and chairs; some were bent upon making speeches; some were very much inclined to fight; and one young gentleman persisted in an attempt to kiss the ladies."

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Figure 66.1 Nitrous oxide frolic by George Cruikshank, 1839. From *Chemistry No Mystery*, by J. Scoffern. Caption reads: "Some jumped over the tables and chairs; some were bent upon making speeches; some were very much inclined to fight; and one young gentleman persisted in an attempt to kiss the ladies."

Source: Edgar Fahs Smith Collection, University of Pennsylvania.

causing bleaching, loss of leaves, and reduced growth rates. Nitrate particles produce haze, which impairs visibility. Nitrogen oxides react with other chemicals to form a variety of toxic products such as nitroarenes (nitro substituted benzene) and nitrosamines. Nitrogen dioxide is a strong oxidizing agent and causes corrosion. Nitrous oxide is an important greenhouse gas. Its atmospheric residence time is 120 years. A molecule of N_2O has 310 times the potential for absorbing heat compared to a molecule of CO_2 . Nitrous oxide is stable and unreactive on the earth's surface, but it can be transported to the stratosphere where it absorbs energy and is converted into reactive forms of nitrogen such as nitric oxide and the nitrate radical contributing to ozone destruction. A simple model is given in the following series of reactions:



Nitrogen oxides play a key role in ozone chemistry. Paul Crutzen (1933–) received the 1995 Nobel Prize in chemistry for research that helped define the role of nitrogen oxides in ozone depletion.

Nitric oxides have relatively few industrial uses. Nitric oxide is produced as an intermediate using the Ostwald method to make nitric acid (see Nitric Acid). Nitrogen compounds produced from nitric acid are used to manufacture fertilizers, explosives, and other chemicals. Nitrogen dioxide is used as an oxidizing agent, a catalyst in oxidation reactions, an inhibitor, as a nitrating agent for organic reactions, as a flour bleaching agent, and in increasing the wet strength of paper. Nitrous oxide is widely used as an anesthetic in dental surgery, which accounts for approximately 90% of its use. It is used by the dairy industry as a foaming agent for canned whipping creams. Pressurized nitrous oxide dissolves in the fats in the cream. When the trigger on a whipped cream can is pressed, releasing the pressure, N_2O comes out of solution producing bubbles, which instantly whips the cream into foam. Nitrous oxide is injected into fuel systems to increase the horsepower of internal combustion engines by increasing oxygen in the combustion chamber. Oxygen comes from the thermal decomposition of N_2O in the engine: $N_2O(g) \rightarrow N_2(g) + 0.5O_2(g)$. The decomposition takes place at temperatures above 297°C. Nitrous oxide used to increase engine performance, called nitrous, is stored as a liquid in a pressurized bottle at roughly 1,000 psi. An additional benefit of N_2O as a horsepower booster comes during delivery when it changes phases from a liquid to a gas. The phase change cools the intake air temperature, providing several more horsepower.

Nitric oxide is commercially produced by the catalytic oxidation of ammonia using a platinum catalyst: $4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$. Nitrous oxide is produced by the thermal decomposition of ammonium nitrate at approximately 240°C: $NH_4NO_{3(g)} \rightarrow N_2O_{(g)} + 2H_2O_{(g)}$.

During the last three decades, appreciable knowledge has been acquired on the biological importance of nitric oxide. It is synthesized in the body from the amino acid L-arginine by the action of NO synthase (NOS) enzymes. Three similar versions (isoforms) of NOS are endothelial NOS, neuronal NOS, and inducible NOS. Nitric oxide is a gaseous free radical that serves multiple functions in human physiology. Nitric oxide causes vasodilation when it is secreted from endothelial cells (the endothelium is a single layer of cells lining the interior surface of a blood vessel). As blood flow increases through an artery, nitric oxide produced

by the endothelial cells relaxes the artery walls, causing it to dilate. In this role, nitric oxide is called the endothelium-derived relaxing factor. Nitric oxide also inhibits platelet aggregation. Nitric oxide plays an important role in immune systems. Macrophages produce nitric oxide using inducible NOS to directly combat bacteria and to also signal other immune responses. Nitric oxide functions as a neurotransmitter that functions by diffusing into surrounding cells rather than activating receptors like other neurotransmitters. Transmission of nitric oxide by diffusion means it can activate several surrounding neurons and does not require a presynaptic-postsynaptic pathway for nerve signal transmission. Nitric oxide also plays a role in reproduction. It functions as a vasodilator during penis erection. Nitric oxide plays a role in fertilization in some animal species, and its role in human reproduction is currently being explored.