Nitrogen

Contents :

1 . Introduction :

Nitrogen is a chemical element that has the symbol **N** and atomic number 7 and atomic mass 14. U . Elemental nitrogen is a colorless, odorless, tasteless and mostly inert diatomic gas at standard conditions, constituting 78 % by volume of Earth's atmosphere.

Many industrially important compounds, such as ammonia, nitric acid, organic nitrates (propellants and explosives), and cyanides, contain nitrogen. The extremely strong bond in elemental nitrogen dominates nitrogen chemistry, causing difficulty for both organisms and industry in converting the N_2 into useful compounds, and releasing large amounts of energy when these compounds burn or decay back into nitrogen gas.

The element nitrogen was discovered by Daniel Rutherford, a Scottish physician, in 1772. Nitrogen occurs in all living organisms. It is a constituent element of amino acids and thus of proteins, and of nucleic acids (DNA and RNA). It resides in the chemical structure of almost all neurotransmitters, and is a defining component of alkaloids, biological molecules produced by many organisms.

Name , Symbol , Number	Nitrogen , N , 7
Element category	Non metal
Group , period , block	15 , 2 , p
Standard atomic weight	14.0067 g · mol^{-1}
Electron configuration	$1s^2$ $2s^2$ $2p^3$
Electrons per shell	2 , 5
Physical properties	
Density	(0 °C) 1.251 g / L
Melting Point	- 210.00 ° C
boiling Point	- 195.79 ° C
Triple Point	- 210°C ,
Critical Point	126.19 K, 3.3978 MPa
Heat of Fusion	(N_2) 0.72 kJ · mol^{-1}
Heat of Vaporization	(N_2) 5.56 kJ · mol^{-1}
Specific heat capacity	(25 °C) (N_2) 29.124 J · mol^{-1} · K^{-1}
Oxidation states	5 , 4 , 3 , 2 , 1 , -1 , -2 , -3 (strongly acidic oxide)
Electro negativity	3.04 (Pauling scale)
Ionization energies (more)	1st : 1402.3 kJ·mol^{-1} 2nd : 2856 kJ·mol^{-1} 3rd : 4578.1 kJ·mol^{-1}
Covalent radius	71 ± 1 pm
Van der Waals radius	155 pm
Speed of sound	(gas, 27 °C) 353 m/s

Most stable isotopes of nitrogen

iso	**N.A.**	**half - life**	**DM**	**DE** (MeV)	**DP**
^{13}N	syn	9.965 min	ε	2.220	^{13}C
^{14}N	99.634 %	^{14}N is stable with 7 neutrons			
^{15}N	0.366 %	^{15}N is stable with 8 neutrons			

2 . History

Nitrogen (Latin *nitrogenium*, where *nitrum* (from Greek *nitron*) means "saltpetre" and *genes* means "forming") is formally considered to have been discovered by Daniel Rutherford in 1772, who called it *noxious air* or *fixed air*. That there was a fraction of air that did not support combustion was well known to the late 18th century chemist. Nitrogen was also studied at about the same time by Carl Wilhelm Scheele, Henry Cavendish, and Joseph Priestley, who referred to it as *burnt air* or *phlogisticated air*. Nitrogen gas was inert enough that Antoine Lavoisier referred to it as "mephetic air" or *azote*, from the Greek word *άζωτος* (*azotos*) meaning "lifeless". Animals died in it, and it was the principal component of air in which animals had suffocated and flames had burned to extinction. Lavoisier's name for nitrogen is used in many languages (French, Russian, etc.) and still remains in English in the common names of many compounds, such as hydrazine and compounds of the azide ion. Compounds of nitrogen were known in the Middle Ages. The alchemists knew nitric acid as *aqua fortis* (strong water). The mixture of nitric and hydrochloric acids was known as *aqua regia* (royal water), celebrated for its ability to dissolve gold (the *king* of metals). The earliest military, industrial and agricultural applications of nitrogen compounds involved uses of saltpeter (sodium nitrate or potassium nitrate), notably in gunpowder, and much later, as fertilizer.

3 . Properties

Nitrogen is a nonmetal, with an electronegativity of 3.04. It has five electrons in its outer shell and is therefore trivalent in most compounds. The triple bond in molecular nitrogen (N_2) is the strongest in nature. The resulting difficulty of converting N_2 into other compounds, and the ease (and associated high energy release) of converting nitrogen compounds into elemental N_2, have dominated the role of nitrogen in both nature and human economic activities.

At atmospheric pressure molecular nitrogen condenses (liquifies) (− 195.8 °C) and freezes (− 210.0 °C) into the beta hexagonal close-packed crystal allotropic form. Below (− 237.6 °C) nitrogen assumes the alpha cubic crystal allotropic form. Liquid nitrogen, a fluid resembling water, but with 80.8 % of the density (the density of liquid nitrogen at its boiling point is 0.808 g / mL) , is a common cryogen.

Unstable allotropes of nitrogen consisting of more than two nitrogen atoms have been produced in the laboratory, like N_3 and N_4. Under extremely high pressures (1.1 million atm) and high temperatures (2000 K), as produced using a diamond anvil cell, nitrogen polymerizes into the single-bonded cubic gauche crystal structure. This structure is similar to that diamond, and both have extremely strong covalent bonds. N_4 is nicknamed "nitrogen diamond."

3 . 1 . Isotopes

There are two stable isotopes of nitrogen: ^{14}N and ^{15}N. By far the most common is ^{14}N (99.634 %), which is produced in the CNO cycle in stars. Of the ten isotopes produced synthetically, ^{13}N has a half-life of ten minutes and the remaining isotopes have half-lives on the order of seconds or less. Biologically-mediated reactions (e.g., assimilation, nitrification, and denitrification) strongly control nitrogen dynamics in the soil. These reactions typically result in ^{15}N enrichment of the substrate and depletion of the product.

0.73 % of the molecular nitrogen in Earth's atmosphere is comprised of the isotopologue $^{14}N^{15}N$ and almost all the rest is $^{14}N_2$.

Radioisotope ^{16}N is the dominant radionuclide in the coolant of pressurized water reactors during normal operation. It is produced from ^{16}O (in water) via (n,p) reaction. It has a short half-life of about 7.1 s, but during its decay back to ^{16}O produces high-energy gamma radiation (5 to 7 MeV). Because of this, the access to the primary coolant piping must be restricted during reactor power operation[3]. ^{16}N is one of the main means used to immediately detect even small leaks from the primary coolant to the secondary steam cycle.

3 . 2 . Electro magnetic Spectrum

Molecular nitrogen ($^{14}N_2$) is largely transparent to infrared and visible radiation because it is a homonuclear molecule and thus has no dipole moment to couple to electromagnetic radiation at these wavelengths. Significant absorption occurs at extreme ultraviolet wavelengths, beginning around 100 nanometers. This is associated with electronic transitions in the molecule to states in which charge is not distributed evenly between nitrogen atoms. Nitrogen absorption leads to significant absorption of ultraviolet radiation in the Earth's upper atmosphere as well as in the atmospheres of other planetary bodies. For similar reasons, pure molecular nitrogen lasers typically emit light in the ultraviolet range.

Nitrogen also makes a contribution to visible air glow from the Earth's upper atmosphere, through electron impact excitation followed by emission. This visible blue air glow (seen in the polar aurora and in the re-entry glow of returning spacecraft) typically results not from molecular nitrogen, but rather from free nitrogen atoms combining with oxygen to form nitric oxide (NO).

3 . 3 Reactions

Nitrogen is generally unreactive at standard temperature and pressure. N_2 reacts spontaneously with few reagents, being resilient to acids and bases as well as oxidants and most reductants. When nitrogen reacts spontaneously with a reagent, the net transformation is often called nitrogen fixation.

Nitrogen reacts with elemental lithium at STP. Lithium burns in an atmosphere of N_2 to give lithium nitride:

$$6\ Li + N_2 \rightarrow 2\ Li_3N$$

Magnesium also burns in nitrogen, forming magnesium nitride.

$$3\ Mg + N_2 \rightarrow Mg_3N_2$$

N_2 forms a variety of adducts with transition metals. The first example of a dinitrogen complex is $[Ru (NH_3)_5(N_2)]^{2+}$. Such compounds are now numerous , other examples include :

$Ir Cl (N_2) (P Ph_3)_2 b$,

$W (N_2)_2 (Ph_2 CH_2CH_2PPh_2)_2$,

and $[(\eta^5- C_5 Me_4 H)_2 Zr]_2 (\mu_2 ,\eta^2 , \eta^2 - N_2)$.

These complexes illustrate how N_2 might bind to the metal (s) in nitrogenase and the catalyst for the Haber process . A catalytic process to reduce N_2 to ammonia with the use of a molybdenum complex in the presence of a proton source was published in 2005.

The starting point for industrial production of nitrogen compounds is the Haber process, in which nitrogen is fixed by reacting N_2 and H_2 over an iron (III) oxide (Fe_3O_4) catalyst at about 500 °C and 200 atmospheres pressure. Biological nitrogen fixation in free-living cyanobacteria and in the root nodules of plants also produces ammonia from molecular nitrogen. The reaction, which is the source of the bulk of nitrogen in the biosphere, is catalyzed by the nitrogenase enzyme complex which contains Fe and Mo atoms, using energy derived from hydrolysis of adenosine triphosphate (ATP) into adenosine diphosphate and inorganic phosphate (−20.5 kJ / mol) .

4 . Occurrence :

Nitrogen is the largest single constituent of the Earth's atmosphere (78.082 % by volume of dry air, 75.3 % by weight in dry air) . It is created by fusion processes in stars, and is estimated to be the 7 th most abundant chemical element by mass in the universe .

Molecular nitrogen and nitrogen compounds have been detected in interstellar space by astronomers using the Far Ultraviolet Spectroscopic Explorer . Molecular nitrogen is a major constituent of the Saturnian moon Titan's thick atmosphere, and occurs in trace amounts in other planetary atmospheres .

Nitrogen is present in all living organisms, in proteins, nucleic acids and other molecules. It typically makes up around 4% of the dry weight of plant matter, and around 3 % of the weight of the human body. It is a large component of animal waste (for example, guano) , usually in the form of urea, uric acid, ammonium compounds and derivatives of these nitrogenous products, which are essential nutrients for all plants that are unable to fix atmospheric nitrogen.

Nitrogen occurs naturally in a number of minerals, such as saltpetre (potassium nitrate) , Chile saltpetre (sodium nitrate) and sal ammoniac (ammonium chloride). Most of these are relatively uncommon, partly because of the minerals' ready solubility in water. See also Nitrate minerals and Ammonium minerals.

5 . Compounds

The main neutral hydride of nitrogen is ammonia (NH_3), although hydrazine (N_2H_4) is also commonly used. Ammonia is more basic than water by 6 orders of magnitude. In solution ammonia forms the ammonium ion (NH_4+). Liquid ammonia (boiling point 240 K) is amphiprotic (displaying either Brønsted-Lowry acidic or basic character) and forms ammonium and the less common amide ions (NH_2-); both amides and nitride (N_{3-}) salts are known, but decompose in water. Singly, doubly, triply and quadruply substituted alkyl compounds of ammonia are called amines (four substitutions, to form commercially and biologically important quaternary amines, results in a positively charged nitrogen, and thus a water-soluble, or at least amphiphilic, compound). Larger chains, rings and structures of nitrogen hydrides are also known, but are generally unstable. $N_2$2+ is another polyatomic cation as in hydrazine.

Other classes of nitrogen anions (negatively charged ions) are the poisonous azides (N_3-), which are linear and isoelectronic to carbon dioxide, but which bind to important iron-containing enzymes in the body in a manner more resembling cyanide. Another molecule of the same structure is the colorless and relatively inert anesthetic gas Nitrous oxide (dinitrogen monoxide, N_2O), also known as laughing gas. This is one of a variety of nitrogen oxides that form a family often abbreviated as **NOx**. Nitric oxide (nitrogen monoxide, NO), is a natural free radical used in signal transduction in both plants and animals, for example in vasodilation by causing the smooth muscle of blood vessels to relax. The reddish and poisonous nitrogen dioxide NO_2 contains an unpaired electron and is an important component of smog. Nitrogen molecules containing unpaired electrons show an understandable tendency to dimerize (thus pairing the electrons), and are generally highly reactive. The corresponding acids are nitrous HNO_2 and nitric acid HNO_3, with the corresponding salts called nitrites and nitrates.

The higher oxides dinitrogen trioxide N_2O_3, dinitrogen tetroxide N_2O_4 and dinitrogen pentoxide N_2O_5, are fairly unstable and explosive, a consequence of the chemical stability of N_2. N_2O_4 is one of the most important oxidizers of rocket fuels, used to oxidize hydrazine in the Titan rocket and in the recent NASA MESSENGER probe to Mercury. N_2O_4 is an intermediate in the manufacture of nitric acid HNO_3, one of the few acids stronger than hydronium and a fairly strong oxidizing agent.

Nitrogen is notable for the range of explosively unstable compounds that it can produce. Nitrogen triiodide NI_3 is an extremely sensitive contact explosive. Nitrocellulose, produced by nitration of cellulose with nitric acid, is also known as guncotton. Nitroglycerin, made by nitration of glycerin, is the dangerously unstable explosive ingredient of dynamite. The comparatively stable, but more powerful explosive trinitrotoluene (TNT) is the standard explosive against which the power of nuclear explosions are measured.

Nitrogen can also be found in organic compounds. Common nitrogen functional groups include: amines, amides, nitro groups, imines, and enamines. The amount of nitrogen in a chemical substance can be determined by the Kjeldahl method.

6 . Applications

Nitrogen gas is an industrial gas produced by the fractional distillation of liquid air, or by mechanical means using gaseous air (i.e. pressurized reverse osmosis membrane or Pressure swing adsorption). Commercial nitrogen is often a byproduct of air-processing for industrial concentration of oxygen for steelmaking and other purposes. When supplied compressed in cylinders it is often referred to as OFN (oxygen - free nitrogen) .

Nitrogen gas has a wide variety of applications, including serving as an inert replacement for air where oxidation is undesirable ;

- To preserve the freshness of packaged or bulk foods (by delaying rancidity and other forms of oxidative damage)
- In ordinary incandescent light bulbs as an inexpensive alternative to argon .
- On top of liquid explosives as a safety measure
- The production of electronic parts such as transistors, diodes, and integrated circuits
- Dried and pressurized, as a dielectric gas for high voltage equipment
- The manufacturing of stainless steel .
- Use in military aircraft fuel systems to reduce fire hazard .
- Filling automotive and aircraft tires due to its inertness and lack of moisture or oxidative qualities, as opposed to air, though this is not necessary for consumer automobiles .

Nitrogen molecules are less likely to escape from the inside of a tire compared with the traditional air mixture used . Air consists mostly of nitrogen and oxygen. Nitrogen molecules have a larger effective diameter than oxygen molecules and therefore diffuse through porous substances more slowly .

Nitrogen is commonly used during sample preparation procedures for chemical analysis. Specifically, it is used as a means of concentrating and reducing the volume of liquid samples. Directing a pressurized stream of nitrogen gas perpendicular to the surface of the liquid allows the solvent to evaporate while leaving the solute(s) and un-evaporated solvent behind .

Nitrogen tanks are also replacing carbon dioxide as the main power source for paintball guns. The downside is that nitrogen must be kept at higher pressure than CO_2, making N_2 tanks heavier and more expensive.

6 . 1 . Nitrogenated beer

A further example of its versatility is its use as a preferred alternative to carbon dioxide to pressurize kegs of some beers, particularly stouts and British ales, due to the smaller bubbles it produces, which make the dispensed beer smoother and headier. A modern application of a pressure sensitive nitrogen capsule known commonly as a "widget" now allows nitrogen charged beers to be packaged in cans and bottles.

6 . 2 . Liquid nitrogen

Liquid nitrogen is a cryogenic liquid. At atmospheric pressure, it boils at −195.8 °C. When insulated in proper containers such as Dewar flasks, it can be transported without much evaporative loss.

Like dry ice, the main use of liquid nitrogen is as a refrigerant. Among other things, it is used in the cryopreservation of blood, reproductive cells (sperm and egg), and other biological samples and materials. It is used in cold traps for certain laboratory equipment and to cool x-ray detectors . It has also been used to cool central processing units and other devices in computers which are overclocked, and which produce more heat than during normal operation .

6 . 3 . Applications of nitrogen compounds

Molecular nitrogen (N_2) in the atmosphere is relatively non-reactive due to its strong bond, and N_2 plays an inert role in the human body, being neither produced nor destroyed. In nature, nitrogen is converted into biologically (and industrially) useful compounds by lightning, and by some living organisms, notably certain bacteria (i.e. nitrogen fixing bacteria) . Molecular nitrogen is released into the atmosphere in the process of decay, in dead plant and animal tissues.

The ability to combine or **fix** molecular nitrogen is a key feature of modern industrial chemistry, where nitrogen and natural gas are converted into ammonia via the Haber process. Ammonia, in turn, can be used directly (primarily as a fertilizer, and in the synthesis of nitrated fertilizers), or as a precursor of many other important materials including explosives, largely via the production of nitric acid by the Ostwald process.

The organic and inorganic salts of nitric acid have been important historically as convenient stores of chemical energy. They include important compounds such as potassium nitrate (or saltpeter used in gunpowder) and ammonium nitrate, an important fertilizer and explosive . Various other nitrated organic compounds, such as nitroglycerin and trinitrotoluene, and nitrocellulose, are used as explosives and propellants for modern firearms. Nitric acid is used as an oxidizing agent in liquid fueled rockets. Hydrazine and hydrazine derivatives find use as rocket fuels and monopropellants. In most of these compounds, the basic instability and tendency to burn or explode is derived from the fact that nitrogen is present as an oxide, and not as the far more stable nitrogen molecule (N_2) which is a product of the compounds' thermal decomposition. When nitrates burn or explode, the formation of the powerful triple bond in the N_2 produces most of the energy of the reaction.

Nitrogen is a constituent of molecules in every major drug class in pharmacology and medicine. Nitrous oxide (N_2O) was discovered early in the 19th century to be a partial anesthetic, though it was not used as a surgical anesthetic until later. Called "laughing gas", it was found capable of inducing a state of social disinhibition resembling drunkenness. Other notable nitrogen - containing drugs are drugs derived from plant alkaloids, such as morphine (there exist many alkaloids known to have pharmacological effects; in some cases they appear natural chemical defenses of plants against predation) . Nitrogen containing drugs include all of the major classes of antibiotics, and organic nitrate drugs like nitroglycerin and nitroprusside which regulate blood pressure and heart action by mimicking the action of nitric oxide.

7 . Biological role

Nitrogen is an essential building block of amino and nucleic acids, essential to life on Earth.

Elemental nitrogen in the atmosphere cannot be used directly by either plants or animals, and must converted to a reduced (or 'fixed') state in order to be useful for higher plants and animals. Precipitation often contains substantial quantities of ammonium and nitrate, thought to result from nitrogen fixation by lightning and other atmospheric electric phenomena. This was first proposed by Liebig in 1827 and later confirmed . However, because ammonium is preferentially retained by the forest canopy relative to atmospheric nitrate, most fixed nitrogen that reaches the soil surface under trees as nitrate. Soil nitrate is preferentially assimilated by these tree roots relative to soil ammonium .

Specific bacteria (e.g. *Rhizobium trifolium*) possess nitrogenase enzymes which can fix atmospheric nitrogen (see nitrogen fixation) into a form (ammonium ion) that is chemically useful to higher organisms. This process requires a large amount of energy and anoxic conditions . Such bacteria may live freely in soil (e.g. *Azotobacter*) but normally exist in a symbiotic relationship in the root nodules of leguminous plants (e.g. clover, *Trifolium*, or soybean plant, *Glycine max*). Nitrogen-fixing bacteria are also symbiotic with a number of unrelated plant species such as alders (*Alnus*) spp., lichens (*Casuarina*), *Myrica*, liverworts, and *Gunnera*.

As part of the symbiotic relationship, the plant converts the 'fixed' ammonium ion to nitrogen oxides and amino acids to form proteins and other molecules, (e.g. alkaloids) . In return for the 'fixed' nitrogen, the plant secretes sugars to the symbiotic bacteria .

Some plants are able to assimilate nitrogen directly in the form of nitrates which may be present in soil from natural mineral deposits, artificial fertilizers, animal waste, or organic decay (as the product of bacteria, but not bacteria specifically associated with the plant) . Nitrates absorbed in this fashion are converted to nitrites by the enzyme *nitrate* reductase, and then converted to ammonia by another enzyme called *nitrite* reductase.

Nitrogen compounds are basic building blocks in animal biology as well. Animals use nitrogen-containing amino acids from plant sources, as starting materials for all nitrogen - compound animal biochemistry, including the manufacture of proteins and nucleic acids. Plant-feeding insects are dependent on nitrogen in their diet, such that varying the amount of nitrogen fertilizer applied to a plant can affect the reproduction rate of insects feeding on fertilized plants .

Soluble nitrate is an important limiting factor in the growth of certain bacteria in ocean waters · In many places in the world, artificial fertilizers applied to crop - lands to increase yields result in run-off delivery of soluble nitrogen to oceans at river mouths[*citation needed*]. This process can result in eutrophication of the water, as nitrogen-driven bacterial growth depletes water oxygen to the point that all higher organisms die. Well-known "dead zone" areas in the U.S. Gulf Coast and the Black Sea are due to this important polluting process .

Many saltwater fish manufacture large amounts of tri methyl amine oxide to protect them from the high osmotic effects of their environment (conversion of this compound to dimethylamine is responsible for the early odor in not fresh salt water fish . In animals, free radical nitric oxide (*NO*) (derived from an amino acid), serves as an important regulatory molecule for circulation .

Animal metabolism of *NO* results in production of nitrite . Animal metabolism of nitrogen in proteins generally results in excretion of urea, while animal metabolism of nucleic acids results in excretion of urea and uric acid. The characteristic odor of animal flesh decay is caused by the creation of long-chain, nitrogen - containing amines, such as putrescine and cadaverine .

Decay of organisms and their waste products may produce small amounts of nitrate , but most decay eventually returns nitrogen content to the atmosphere , as molecular nitrogen . The circulation of nitrogen from atmosphere to organic compounds and back is referred to as the nitrogen cycle.

8 . Safety

Rapid release of nitrogen gas into an enclosed space can displace oxygen, and therefore represents an asphyxiation hazard. This may happen with few warning symptoms, since the human carotid body is a relatively slow and a poor low - oxygen (hypoxia) sensing system . An example occurred shortly before the launch of the first Space Shuttle mission in 1981, when two technicians lost consciousness and died after they walked into a space located in the Shuttle's Mobile Launcher Platform that was pressurized with pure nitrogen as a precaution against fire. The technicians would have been able to exit the room if they had experienced early symptoms from nitrogen-breathing.

When inhaled at high partial pressures (more than about 4 bar, encountered at depths below about 30 m in scuba diving) nitrogen begins to act as an anesthetic agent. It can cause nitrogen narcosis, a temporary semi-anesthetized state of mental impairment similar to that caused by nitrous oxide .

Nitrogen also dissolves in the bloodstream and body fats. Rapid decompression (particularly in the case of divers ascending too quickly, or astronauts decompressing too quickly from cabin pressure to spacesuit pressure) can lead to a potentially fatal condition called decompression sickness (formerly known as caisson sickness or more commonly, the "bends"), when nitrogen bubbles form in the bloodstream, nerves, joints, and other sensitive or vital areas . Other "inert" gases (those gases other than carbon dioxide and oxygen) cause the same effects from bubbles composed of them, so replacement of nitrogen in breathing gases may prevent nitrogen narcosis, but does not prevent decompression sickness .

Direct skin contact with liquid nitrogen will eventually cause severe frostbite (cryogenic burns). This may happen almost instantly on contact, depending on the form of liquid nitrogen. Bulk liquid nitrogen causes less rapid freezing than a spray of nitrogen mist (such as is used to freeze certain skin growths in the practice of dermatology). The extra surface area provided by nitrogen-soaked materials is also important, with soaked clothing or cotton causing far more rapid damage than a spill of direct liquid to skin. Full "contact" between naked skin and large droplets or pools of undisturbed liquid nitrogen may be prevented for a few seconds by a layer of insulating gas from the Leidenfrost effect. However, liquid nitrogen applied to skin in mists, and on fabrics, bypasses this effect .

Nitrogen oxides

Contents

1 . Introdution :

The term **nitrogen oxide** typically refers to any binary compound of oxygen and nitrogen, or to a mixture of such compounds :

- Nitric oxide (NO) , nitrogen (II) oxide
- Nitrogen dioxide (NO_2) , nitrogen (IV) oxide
- Nitrous oxide (N_2O) , nitrogen (I) oxide
- Dinitrogen trioxide (N_2O_3) , nitrogen (II,IV) oxide
- Dinitrogen tetroxide (N_2O_4) , nitrogen (IV) oxide
- Dinitrogen pentoxide (N_2O_5) , nitrogen (V) oxide

(Note that the last three are unstable.)

Chemical reactions that produce nitrogen oxides often produce several different compounds, the proportions of which depend on the specific reaction and conditions. For this reason, secondary production of N_2O is undesirable, as NO and NO_2 - which are extremely toxic - are liable to be produced as well.

NO_x is a generic term for mono - nitrogen oxides (NO and NO_2) These oxides are produced during combustion, especially combustion at high temperatures.

At ambient temperatures, the oxygen and nitrogen gases in air will not react with each other. In an internal combustion engine, combustion of a mixture of air and fuel produces combustion temperatures high enough to drive endothermic reactions between atmospheric nitrogen and oxygen in the flame, yielding various oxides of nitrogen. In areas of high motor vehicle traffic, such as in large cities, the amount of nitrogen oxides emitted into the atmosphere can be quite significant.

In the presence of excess oxygen (O_2), nitric oxide (NO) will be converted to nitrogen dioxide (NO_2), with the time required dependent on the concentration in air as shown below :

When NO_x and volatile organic compounds (VOCs) react in the presence of sun light, they form photochemical smog, a significant form of air pollution, especially in the summer. Children, people with lung diseases such as asthma, and people who work or exercise outside are susceptible to adverse effects of smog such as damage to lung tissue and reduction in lung function .

Mono - nitrogen oxides eventually form nitric acid when dissolved in atmospheric moisture, forming a component of acid rain. The following chemical reaction occurs when nitrogen dioxide reacts with water:

$$2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

Nitrous acid then decomposes as follows:

$$3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O$$

where nitric oxide will oxidize to form nitrogen dioxide that again reacts with water, ultimately forming nitric acid:

$$4\ NO + 3\ O_2 + 2\ H_2O \rightarrow 4\ HNO_3$$

Mono - nitrogen oxides are also involved in tropospheric production of ozone .

NO_x should not be confused with NOS, a term used to refer to nitrous oxide (N_2O) in the context of its use as a power booster for internal combustion engines.

3 . Definition of NO_x , NO_y , NO_z in atmospheric chemistry :

In atmospheric chemistry the term NO_x is used to mean the total concentration of NO plus NO_2. During daylight NO and NO_2 are in equilibrium with the ratio NO/NO_2 determined by the intensity of sunshine (which converts NO_2 to NO) and the concentration of ozone (which reacts with NO to give back NO_2). NO and NO_2 are also central to the formation of tropospheric ozone. This definition excludes other oxides of nitrogen such as nitrous oxide (N_2O). NO_y (reactive odd nitrogen) is defined as the sum of NO_x plus the compounds produced from the oxidation of NO_x which include nitric acid.

4 . Industrial sources of NO_x

The three primary sources of NO_x in combustion processes :

- thermal NO_x
- fuel NO_x
- prompt NO_x

Thermal NO_x formation, which is highly temperature dependent, is recognized as the most relevant source when combusting natural gas. Fuel NO_x tends to dominate during the combustion of fuels, such as coal, which have a significant nitrogen content, particularly when burned in combustors designed to minimize thermal NO_x. The contribution of prompt NO_x is normally considered negligible. A fourth source, called *feed* NO_x is associated with the combustion of nitrogen present in the feed material of cement rotary kilns, at between 300° and 800°C, where it is also a minor contributor.

4 . 1 . Thermal NO_x

Thermal NO_x refers to NO_x formed through high temperature oxidation of the diatomic nitrogen found in combustion air. The formation rate is primarily a function of temperature and the residence time of nitrogen at that temperature. At high temperatures, usually above 1600 °C , molecular nitrogen (N_2) and oxygen (O_2) in the combustion air disassociate into their atomic states and participate in a series of reactions.

The three principal reactions (the extended Zeldovich mechanism) producing thermal NO_x are:

$$N_2 + O \rightarrow NO + N$$
$$N + O_2 \rightarrow NO + O$$
$$N + OH \rightarrow NO + H$$

All 3 reactions are reversible. Zeldovich was the first to suggest the importance of the first two reactions. The last reaction of atomic nitrogen with the hydroxyl radical, OH, was added by Lavoie, Heywood and Keck to the mechanism and makes a significant contribution to the formation of thermal NO_x.

4 . 2 . Fuel NO_x

The major source of NO_x production from nitrogen - bearing fuels such as certain coals and oil, is the conversion of fuel bound nitrogen to NO_x during combustion. During combustion, the nitrogen bound in the fuel is released as a free radical and ultimately forms free N_2, or NO. Fuel NO_x can contribute as much as 50 % of total emissions when combusting oil and as much as 80 % when combusting coal.

Although the complete mechanism is not fully under stood, there are two primary paths of formation. The first involves the oxidation of volatile nitrogen species during the initial stages of combustion. During the release and prior to the oxidation of the volatiles, nitrogen reacts to form several intermediaries which are then oxidized into NO. If the volatiles evolve into a reducing atmosphere, the nitrogen evolved can readily be made to form nitrogen gas, rather than NO_x. The second path involves the combustion of nitrogen contained in the char matrix during the combustion of the char portion of the fuels. This reaction occurs much more slowly than the volatile phase. Only around 20 % of the char nitrogen is ultimately emitted as NO_x, since much of the NO_x that forms during this process is reduced to nitrogen by the char, which is nearly pure carbon.

4 . 3 . Prompt NO_x

This third source is attributed to the reaction of atmospheric nitrogen, N_2, with radicals such as C, CH, and CH_2 fragments derived from fuel, where this cannot be explained by either the aforementioned thermal or fuel processes. Occurring in the earliest stage of combustion, this results in the formation of fixed species of nitrogen such as NH (nitrogen mono hydride) , HCN (hydrogen cyanide) , H_2CN (di hydrogen cyanide) and CN - (cyano radical) which can oxidize to NO. In fuels that contain nitrogen, the incidence of prompt NO_x is especially minimal and it is generally only of interest for the most exacting emission targets.

5 . Health effects

NO_x react with ammonia, moisture, and other compounds to form nitric acid vapor and related particles. Small particles can penetrate deeply into sensitive lung tissue and damage it, causing premature death in extreme cases. Inhalation of such particles may cause or worsen respiratory diseases such as emphysema, bronchitis it may also aggravate existing heart disease .

NO_x react with volatile organic compounds in the presence of heat and sunlight to form Ozone. Ozone can cause adverse effects such as damage to lung tissue and reduction in lung function mostly in susceptible populations (children, elderly, asthmatics). Ozone can be transported by wind currents and cause health impacts far from the original sources. The American Lung Association estimates that nearly 50 percent of United States inhabitants live in counties that are not in ozone compliance .

NO_x also readily react with common organic chemicals, and even ozone, to form a wide variety of toxic products: nitroarenes, nitrosamines and also the nitrate radical some of which may cause biological mutations .

6 . Regulation and emission control technologies :

The Kyoto Protocol, ratified by 54 nations in 1997, classifies N_2O as a green house gas , and calls for substantial world wide reductions in its emission .

As discussed above, atmospheric NO_x eventually forms nitric acid, which contributes to acid rain. NO_x emissions are regulated in the United States by the Environmental Protection Agency, and in the UK by the Department for Environment, Food and Rural Affairs.

Technologies such as flameless oxidation (FLOX) and staged combustion significantly reduce thermal NO_x in industrial processes. Bowin low NO_x technology is a hybrid of staged-premixed-radiant combustion technology with a major surface combustion preceded by a minor radiant combustion. In the Bowin burner, air and fuel gas are premixed at a ratio greater than or equal to the stoichiometric combustion requirement . Water Injection technology, where by water is introduced into the combustion chamber, is also becoming an important means of NO_x reduction through increased efficiency in the overall combustion process. Alternatively, the water (e.g. 10 to 50%) is emulsified into the fuel oil prior to the injection and combustion. This emulsification can either be made in-line (un stabilized) just before the injection or as a drop-in fuel with chemical additives for long term emulsion stability (stabilized). Other technologies, such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) reduce post combustion NO_x.

The use of exhaust gas recirculation and catalytic converters in motor vehicle engines have significantly reduced emissions.

7 . Biogenic sources

Agricultural fertilization and the use of nitrogen fixing plants also contribute to atmospheric NO_x, by promoting nitrogen fixation by micro organisms .

8 . Derivatives

Oxidized (cationic) and reduced (anionic) derivatives of many of these oxides exist: nitrite (NO_2^-), nitrate (NO_3^-), nitronium or NO_2^+, and nitrosonium or NO^+. NO_2 is intermediate between nitrite and nitronium :

$$NO_2^+ + e^- \rightarrow NO_2$$
$$NO_2 + e^- \rightarrow NO_2^-$$

Nitric oxide (NO)

Contents

1 . Introduction :

Nitric oxide or **nitrogen monoxide** is a chemical compound with chemical formula NO. This gas is an important signaling molecule in the body of mammals, including humans, and is an extremely important intermediate in the chemical industry. It is also an air pollutant produced by cigarette smoke, automobile engines and power plants.

NO is an important messenger molecule involved in many physiological and pathological processes within the mammalian body both beneficial and detrimental . Appropriate levels of NO production are important in protecting an organ such as the liver from ischemic damage. However sustained levels of NO production result in direct tissue toxicity and contribute to the vascular collapse associated with septic shock, whereas chronic expression of NO is associated with various carcinomas and inflammatory conditions including juvenile diabetes, multiple sclerosis, arthritis and ulcerative colitis .

Nitric oxide should not be confused with nitrous oxide (N_2O), a general an aesthetic and greenhouse gas, or with nitrogen dioxide (NO_2) which is another air pollutant. The nitric oxide molecule is a free radical, which is relevant to understanding its high reactivity.

Despite being a simple molecule, NO is a fundamental player in the fields of neuroscience, physiology, and immunology, and was proclaimed “Molecule of the Year” in 1992.

Properties	
Molecular Formula	NO
Molar Mass	30.006 g / mol
Appearance	colourless gas , paramagnetic
Density	1.269 g / cm^3 (liquid) 1.3402 g / l (gas)
Melting Point	− 163.6 ° C
Boiling Point	− 150.8 ° C
Solubility in Water	7.4 ml / 100 ml (STP)
Solubility	Soluble in alcohol , CS_2
Refractive index (n_D)	1.0002697
Flash point	Non - flammable

2 . **Reactions**

- When exposed to oxygen, NO is converted into nitrogen dioxide.

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

This conversion has been speculated as occurring via the ONOONO intermediate. In water, NO reacts with oxygen and water to form HNO_2 or nitrous acid. The reaction is thought to proceed via the following stoichiometry :

$$4\ NO + O_2 + 2\ H_2O \rightarrow 4\ HNO_2$$

- NO will react with fluorine, chlorine, and bromine to form the XNO species, known as the nitrosyl halides, such as nitrosyl chloride. Nitrosyl iodide can form but is an extremely short lived species and tends to reform I_2.

$2 NO + Cl_2 \rightarrow 2 N O Cl$

- Nitroxyl (HNO) is the reduced form of nitric oxide.

- Nitric oxide reacts with acetone and an alkoxide to a *diazenium diolate* or *nitroso hydroxylamine* and Methyl acetate : Nitric oxide can also react directly with sodium methoxide, forming sodium formate and nitrous oxide .

2 . 1 . Preparation

- Commercially, NO is produced by the oxidation of ammonia at 750°C to 900°C (normally at 850 ° C) in the presence of platinum as catalyst:

$4 NH_3 + 5 O_2 \rightarrow 4 NO + 6 H_2O$

The un catalyzed endothermic reaction of O_2 and N_2 which is performed at high temperature (> 2000°C) with lightning has not been developed into a practical commercial synthesis .

$N_2 + O_2 \rightarrow 2 NO$

- In the laboratory, it is conveniently generated by reduction of nitric acid with copper:

$8 HNO_3 + 3 Cu \rightarrow 3 Cu(NO_3)_2 + 4 H_2O + 2 NO$

- or by the reduction of nitrous acid in the form of sodium nitrite or potassium nitrite :

$2 NaNO_2 + 2 Na I + 2 H_2SO_4 \rightarrow I_2 + 4 NaHSO_4 + 2 NO$

$2 NaNO_2 + 2 FeSO_4 + 3 H_2SO_4 \rightarrow$

$Fe_2(SO_4)_3 + 2 NaHSO_4 + 2 H_2O + 2 NO$

$3 KNO_2 (l) + KNO_3 (l) + Cr_2O_3 (s) \rightarrow 2 K_2CrO_4 (s) + 4 NO (g)$

The iron(II) sulfate route is simple and has been used in undergraduate laboratory experiments.

- So - called NONO ate compounds are also used for NO generation.

2 . 2 . Coordination chemistry (metal nitrosyl) :

NO forms complexes with all transition metals to give complexes called metal nitrosyls . The most common bonding mode of NO is the terminal linear type (M – NO) . The angle of the M - N - O group can vary from 160° to 180° but are still termed as " linear ". In this case the NO group is formally considered a 3 - electron donor. In the case of a bent M - N - O conformation the NO group can be considered a one electron donor. Alternatively, one can view such complexes as derived from NO^+, which is iso electronic with CO.

Nitric oxide can serve as a one-electron pseudo halide . In such complexes, the M - N - O group is characterized by an angle between 120° and 140°.

The NO group can also bridge between metal centers through the nitrogen atom in a variety of geometries.

2 . 3 . Measurement of nitric oxide concentration

Nitric oxide (white) in conifer cells, visualized using DAF-2 DA (di amino fluorescein di acetate)

The concentration of nitric oxide can be determined using a simple chemi luminescent reaction involving ozone : A sample containing nitric oxide is mixed with a large quantity of ozone. The nitric oxide reacts with the ozone to produce oxygen and nitrogen dioxide. This reaction also produces light (chemi luminescence) , which can be measured with a photo detector. The amount of light produced is proportional to the amount of nitric oxide in the sample.

$$NO + O_3 \rightarrow NO_2 + O_2 + \text{light}$$

Other methods of testing include electroanalysis(amperometric approach), where NO reacts with an electrode to induce a current or voltage change. The detection of NO radicals in biological tissues is particularly difficult due to the short lifetime and concentration of these radicals in tissues. One of the few practical methods is spin trapping of nitric oxide with iron - dithio carbamate complexes and subsequent detection of the mono-nitrosyl-iron complex with Electron Paramagnetic Resonance (EPR) .

A group of fluorescent dye indicators exist that are also available in acetylated form for intracellular measurements. The most common compound is 4,5-diaminofluorescein (DAF-2).

3 . Production environmental effects :

From a thermodynamic perspective, NO is unstable with respect to O_2 and N_2, although this conversion is very slow at ambient temperatures in the absence of a catalyst. Because the heat of formation of NO is endothermic, its synthesis from molecular nitrogen and oxygen requires elevated temperatures, >1000°C. A major natural source is lightning. The use of internal combustion engines has drastically increased the presence of nitric oxide in the environment. One purpose of catalytic converters in cars is to minimize NO emission by catalytic reversion to O_2 and N_2.

Nitric oxide in the air may convert to nitric acid, which has been implicated in acid rain. Furthermore, both NO and NO_2 participate in ozone layer depletion. Nitric oxide is a small highly diffusible gas and a ubiquitous bioactive molecule.

4 . Technical applications :

Although NO has relatively few direct uses, it is produced on a massive scale as an intermediate in the Ostwald process for the synthesis of nitric acid from ammonia. In 2005, the US alone produced 6M metric tons of nitric acid. It finds use in the semiconductor industry for various processes. In one of its applications it is used along with nitrous oxide to form oxy nitride gates in CMOS devices.

4 . 1 . Miscellaneous applications :

Nitric oxide can be used for detecting surface radicals on polymers. Quenching of surface radicals with nitric oxide results in incorporation of nitrogen, which can be quantified by means of X-ray photoelectron spectroscopy .

5 . Biological functions of nitric oxide

NO is one of the few gaseous signaling molecules known. It is a key vertebrate biological messenger, playing a role in a variety of biological processes. Nitric oxide, known as the 'endothelium-derived relaxing factor', or 'EDRF', is bio synthesized endogenously from arginine and oxygen by various nitric oxide synthase (NOS) enzymes and by reduction of inorganic nitrate. The endothelium (inner lining) of blood vessels use nitric oxide to signal the surrounding smooth muscle to relax, thus resulting in vasodilatation and increasing blood flow. Nitric oxide is highly reactive (having a lifetime of a few seconds), yet diffuses freely across membranes. These attributes make nitric oxide ideal for a transient paracrine (between adjacent cells) and autocrine (within a single cell) signaling molecule. The production of nitric oxide is elevated in populations living at high-altitudes, which helps these people avoid hypoxia by aiding in pulmonary vasculature vasodilatation. Effects include vasodilatation, neurotransmission (see Gas transmitters), modulation of the hair cycle, production of reactive nitrogen intermediates and penile erections (through its ability to vasodilate). Nitroglycerin and amyl nitrite serve as vasodilators because they are converted to nitric oxide in the body. Sildenafil, popularly known by the trade name Viagra, stimulates erections primarily by enhancing signaling through the nitric oxide pathway in the penis.

Nitric oxide (NO) contributes to vessel homeostasis by inhibiting vascular smooth muscle contraction and growth, platelet aggregation, and leukocyte adhesion to the endothelium. Humans with atherosclerosis, diabetes or hypertension often show impaired NO pathways. A high - salt intake was demonstrated to attenuate NO production, although bioavailability remains unregulated.

Nitric oxide is also generated by phagocytes (mono cytes, macrophages, and neutrophils) as part of the human immune response. Phagocytes are armed with inducible nitric oxide synthase (iNOS) which is activated by interferon-gamma (IFN-γ) as a single signal or by tumor necrosis factor (TNF) along with a second signal . Conversely, transforming growth factor-beta (TGF - β) provides a strong inhibitory signal to iNOS where as interleukin - 4 (IL- 4) and IL - 10 provide weak inhibitory signals. In this way the immune system may regulate the armamentarium of phagocytes that play a role in inflammation and immune responses. Nitric oxide secreted as an immune response is as free radicals and is toxic to bacteria; the mechanism for this include DNA damage and degradation of iron sulfur centers into iron ions and iron-nitrosyl compounds . In response, however, many bacterial pathogens have evolved mechanisms for nitric oxide resistance. Because nitric oxide might serve as an *inflammo meter* in conditions like asthma, there has been increasing interest in the use of exhaled nitric oxide as a breath test in diseases with airway inflammation.

Nitric oxide can contribute to reperfusion injury when an excessive amount produced during reperfusion (following a period of ischemia) reacts with superoxide to produce the damaging oxidant peroxynitrite. In contrast, inhaled nitric oxide has been shown to help survival and recovery from paraquat poisoning, which produces lung tissue damaging superoxide and hinders NOS metabolism.

In plants, nitric oxide can be produced by any of four routes :

(i) L- arginine - dependent nitric oxide synthase , (although the existence of animal NOS homologs in plants is debated) .

(ii) by plasma membrane-bound nitrate reductase .

(iii) by mitochondrial electron transport chain .

or (iv) by non - enzymatic reactions. It is a signaling molecule, acts mainly against oxidative stress and also plays a role in plant pathogen interactions. Treating cut flowers and other plants with nitric oxide has been shown to lengthen the time before wilting .

A biologically important reaction of nitric oxide is S - nitrosylation , the conversion of thiol groups, including cysteine residues in proteins, to form S - nitrosothiols (RSNOs). S - Nitrosylation is a mechanism for dynamic, post-translational regulation of most or all major classes of protein.

5 . 1 Mechanism of action

There are several mechanisms by which NO has been demonstrated to affect the biology of living cells. These include oxidation of iron containing proteins such as ribo nucleotide reductase and aconitase, activation of the soluble guanylate cyclase, ADP ribosylation of proteins, protein sulphhydryl group nitrosylation, and iron regulatory factor activation. NO has been demonstrated to activate NF - κB in peripheral blood mononuclear cells, an important transcription factor in iNOS gene expression in response to inflammation. It was found that NO acts through the stimulation of the soluble guanylate cyclase which is a hetero dimeric enzyme with subsequent formation of cyclic GMP. Cyclic GMP activates protein kinase G, which caused phosphorylation of myosin light chain phosphatase (and therefore inactivation) of myosin light-chain kinase and leads ultimately to the de phosphorylation of the myosin light chain, causing smooth muscle relaxation.

5 . 2 . Use in pediatric intensive care

Nitric oxide/oxygen blends are used in critical care to promote capillary and pulmonary dilation to treat primary pulmonary hypertension in neonatal patients post meconium aspiration and related to birth defects. These are often a last - resort gas mixture before the use of extracorporeal membrane oxygenation (ECMO). Nitric oxide therapy has the potential to significantly increase the quality of life and in some cases save the lives of infants at risk for pulmonary vascular disease .

5 . 3 . Nutraceutical marketing

GNC has begun to sell an oral "nitric oxide" product targeted for bodybuilders, with the claim that it dramatically increases muscle growth. The claim is grounded in an understanding of NO as being a vasodilator, and when taken prior to and after workouts, it enables muscles to receive more blood and therefore, more oxygen and nutrients. This is critical to maximal muscle exertion during training and recovery afterward. However, there are currently no valid studies supporting the hypothesis that orally ingested NO actually will cause vasodilation; additionally, while users of some supplements have claimed to experience results , these results are generally attributable to ingredients besides NO itself (proteins, creatine etc) .

Nitrogen dioxide (NO_2)

Contents

1 . Introduction :

Nitrogen dioxide is the chemical compound with the formula NO_2. It exists as a radical in nature. One of several nitrogen oxides, NO_2 is an intermediate in the industrial synthesis of nitric acid, millions of tons of which are produced each year. This reddish-brown toxic gas has a characteristic sharp, biting odor and is a prominent air pollutant. Nitrogen dioxide is a paramagnetic bent molecule with C_{2v} point group symmetry.

Molecular Formula	NO_2
Molar Mass	46.0055 g / mol
Appearance	Brown gas
Density	1449 kg / m^3 (liquid , 20 ºC) 3.4 kg / m^3 (gas, 22 ºC)
Melting point	- 11.2 ° C , 262 K, 12 ° F
Boiling point	21.1 ° C , 294 K , 70 ° F
Solubility in Water	Reacts
Refractive index (*n*$_D$)	1.449 (20 ° C)
Flash point	Non-flammable

2 . Preparation and reactions

Nitrogen dioxide typically arises via the oxidation of nitric oxide by oxygen in air :

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

In the laboratory, NO_2 can be prepared in a two step procedure by thermal decomposition of dinitrogen pentoxide , which is obtained by dehydration of nitric acid :

$$2\ HNO_3 \rightarrow N_2O_5 + H_2O$$
$$2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$$

The thermal decomposition of some metal nitrates also affords NO_2 :

$$2\ Pb\ (\ NO_3\ )_2 \rightarrow 2\ PbO + 4\ NO_2 + O_2$$

2 . 1 . Monomer - dimer equilibrium

NO_2 exists in equilibrium with $N_2\ O_4$:

$$2\ NO_2\ N_2O_4$$

The equilibrium is characterized by ΔH = -57.23 kJ / mol. Resulting from an endothermic reaction, the paramagnetic monomer is favored at higher temperatures. Colourless diamagnetic N_2O_4 can be obtained as a solid melting at m.p. –11.2 ° C .

2 . 2 . Main reactions

The chemistry of nitrogen dioxide has been investigated extensively. At 150 °C , NO_2 decomposes with release of oxygen via an endothermic process (ΔH = 114 kJ/mol) :

$$2\ NO_2 \rightarrow 2\ NO + O_2$$

As suggested by the weakness of the N - O bond, NO_2 is a good oxidizer and will sustain the combustion, sometimes explosively, with many compounds, such as hydrocarbons.

It hydrolyzes with disproportionation to give nitric acid:

$$3\ NO_2 + H_2O \rightarrow NO + 2\ HNO_3$$

This reaction is one step in the Ostwald process for the industrial production of nitric acid from ammonia . Nitric acid decomposes slowly to nitrogen dioxide, which confers the characteristic yellow color of most samples of this acid:

$$4\ HNO_3 \rightarrow 4\ NO_2 + 2\ H_2O + O_2$$

NO_2 is used to generate anhydrous metal nitrates from the oxides :

$$MO + 3\ NO_2 \rightarrow 2\ M(NO_3)_2 + NO$$

Similarly, alkyl and metal iodides give the corresponding nitrates :

$$2\ CH_3I + 3\ NO_2 \rightarrow 2\ CH_3NO_3 + NO + I_2$$
$$TiI_4 + 8\ NO_2 \rightarrow Ti(NO_3)_4 + 4\ NO + 2\ I_2$$

3 . Safety and pollution considerations

Nitrogen dioxide is toxic by inhalation, but this could be avoided as the material is acrid and easily detected by our sense of smell. One potential source of exposure is fuming nitric acid, which is often contaminated with NO_2. Symptoms of poisoning (lung edema) tend to appear several hours after one has inhaled a low but potentially fatal dose. Also , low concentrations (4 ppm) will anesthetize the nose, thus creating a potential for overexposure.

Long - term exposure to NO_2 at concentrations above 40–100 $\mu g/m^3$ causes adverse health effects.

Nitrogen dioxide is formed in most combustion processes using air as the oxidant. At elevated temperatures nitrogen combines with oxygen to form nitrogen dioxide:

$$2\ O_2 + N_2 \rightarrow 2\ NO_2$$

The most important sources of NO_2 are internal combustion engines , thermal power stations and, to a lesser extent, pulp mills. Atmospheric nuclear tests are also a source of nitrogen dioxide, which is responsible for the reddish colour of mushroom clouds[6] The excess air required for complete combustion of fuels in these processes introduces nitrogen into the combustion reactions at high temperatures and produces nitrogen oxides .

Nitrous oxide (N_2 O)

Contents

1 . Introdution :

Nitrous oxide, commonly known as **happy gas** or **laughing gas**, is a chemical compound with the chemical formula N_2O. At room temperature, it is a colorless non-flammable gas, with a pleasant, slightly sweet odor and taste. It is used in surgery and dentistry for its anesthetic and analgesic effects. It is known as "laughing gas" due to the euphoric effects of inhaling it, a property that has led to its recreational use as an inhalant drug. It is also used as an oxidizer in rocketry and in motor racing to increase the power output of engines. It is often created in bushfires .

Nitrous oxide reacts with ozone and is the main naturally occurring regulator of stratospheric ozone. Nitrous oxide is also a major greenhouse gas. Considered over a 100 year period, it has 298 times more impact per unit weight than carbon dioxide .

Other names	Laughing Gas
Molecular Formula	N_2O
Molar mass	44.013 g / mol
Appearance	Colorless gas
Density	1.977 g / L (gas)
Melting point	− 90.86 °C
Boiling point	− 88.48 ° C
Solubility in water	0.15 g / 100 ml (15 ° C)
Solubility	soluble in alcohol, ether, sulfuric acid
log P	0.35
Vapor pressure	5150 kPa (20 °C)
Flash point	Non-flammable

2 . Manufacture

Nitrous oxide is most commonly prepared by careful heating of ammonium nitrate, which decomposes into nitrous oxide and water vapor. The addition of various phosphates favors formation of a purer gas at slightly lower temperatures..

$$NH_4NO_3 \text{ (s)} \rightarrow 2\ H_2O \text{ (g)} + N_2O \text{ (g)}$$

This reaction occurs between 170 - 240°C, temperatures where ammonium nitrate is a moderately sensitive explosive and a very powerful oxidizer. Above 240 ° C the exothermic reaction may accelerate to the point of detonation, so the mixture must be cooled to avoid such a disaster. Superheated steam is used to reach reaction temperature in some turnkey production plants .

Down stream, the hot, corrosive mixture of gases must be cooled to condense the steam, and filtered to remove higher oxides of nitrogen. Ammonium nitrate smoke, as an extremely persistent colloid, will also have to be removed. The cleanup is often done in a train of 3 gas washes; namely base, acid and base again. Any significant amounts of nitric oxide (NO) may not necessarily be absorbed directly by the base (sodium hydroxide) washes.

The nitric oxide impurity is some times chelated out with ferrous sulfate, reduced with iron metal, or oxidized and absorbed in base as a higher oxide. The first base wash may (or may not) react out much of the ammonium nitrate smoke, however this reaction generates ammonia gas, which may have to be absorbed in the acid wash.

2 . 1 . Other routes

The direct oxidation of ammonia may someday rival the ammonium nitrate pyrolysis synthesis of nitrous oxide mentioned above. This capital-intensive process, which originates in Japan, uses a manganese dioxide-bismuth oxide catalyst :

$$2\ NH_3 + 2\ O_2 \rightarrow N_2O + 3\ H_2O$$

Higher oxides of nitrogen are formed as impurities. In comparison, uncatalyzed ammonia oxidation (i.e. combustion or explosion) goes primarily to N_2 and H_2O.

Nitrous oxide can be made by heating a solution of sulfamic acid and nitric acid. Many gases are made this way in Bulgaria .

$$HNO_3 + NH_2SO_3H \rightarrow N_2O + H_2SO_4 + H_2O$$

There is no explosive hazard in this reaction if the mixing rate is controlled. However, as usual, toxic higher oxides of nitrogen form.

Nitrous oxide is produced in large volumes as a by-product in the synthesis of adipic acid; one of the two reactants used in nylon manufacture. This might become a major commercial source, but will require the removal of higher oxides of nitrogen and organic impurities. Currently much of the gas is decomposed before release for environmental protection. Greener processes may prevail that substitute hydrogen peroxide for nitric acid oxidation; hence no generation of oxide of nitrogen by - products.

Hydroxyl ammonium chloride can react with sodium nitrite to produce N_2O as well :

$$NH_3\,OH^+\,Cl^- + NaNO_2 \rightarrow N_2O + Na\,Cl + 2\,H_2O$$

If the nitrite is added to the hydroxylamine solution, the only remaining byproduct is salt water. However, if the hydroxylamine solution is added to the nitrite solution (nitrite is in excess), then toxic higher oxides of nitrogen are also formed.

3 . Uses

3 . 1 . Rocket motors

Nitrous oxide can be used as an oxidizer in a rocket motor. This has the advantages over other oxidizers that it is non - toxic and, due to its stability at room temperature, easy to store and relatively safe to carry on a flight. As a secondary benefit it can be readily decomposed to form breathing air. Its high density and low storage pressure enable it to be highly competitive with stored high-pressure gas systems.

In a 1914 patent, American rocket pioneer Robert Goddard suggested nitrous oxide and gasoline as possible propellants for a liquid - fueled rocket. Nitrous oxide has been the oxidizer of choice in several hybrid rocket designs (using solid fuel with a liquid or gaseous oxidizer). The combination of nitrous oxide with hydroxyl-terminated poly butadiene fuel has been used by Space Ship One and others. It is also notably used in amateur and high power rocketry with various plastics as the fuel.

Nitrous oxide can also be used in a monopropellant rocket. In the presence of a heated catalyst, N_2O will decompose exothermically into nitrogen and oxygen, at a temperature of approximately 1300 °C. Because of the large heat release the catalytic action rapidly becomes secondary as thermal auto decomposition becomes dominant. In a vacuum thruster, this can provide a monopropellant specific impulse (I_{sp}) of as much as 180s. While noticeably less than the I_{sp} available from hydrazine thrusters (monopropellant or bipropellant with nitrogen tetroxide), the decreased toxicity makes nitrous oxide an option worth investigating. Because of its release of very high temperature oxygen as a monopropellant the addition of even small amounts of a fuel such as hydrogen rapidly increases the specific impulse and the high oxygen temperatures simplify ignition of the fuel. I_{sp} greater than 340 seconds can be readily achieved . Its low freezing point also eases thermal management as compared to hydrazine - a valuable property on a spacecraft which may contain quantities of cryogenic propellant.

3 . 2 . Internal combustion engine

In vehicle racing, nitrous oxide (often referred to as just "nitrous" in this context to differ from the acronym NOS which is the brand Nitrous Oxide Systems) allows the engine to burn more fuel and air, resulting in a more powerful combustion. The gas itself is not flammable, but it delivers more oxygen than atmospheric air by breaking down at elevated temperatures.

Nitrous oxide is stored as a compressed liquid; the evaporation and expansion of liquid nitrous oxide in the intake manifold causes a large drop in intake charge temperature, resulting in a denser charge, further allowing more air/fuel mixture to enter the cylinder. Nitrous oxide is sometimes injected into (or prior to) the intake manifold, whereas other systems directly inject right before the cylinder (direct port injection) to increase power.

The technique was used during World War II by *Luftwaffe* aircraft with the GM - 1 system to boost the power output of aircraft engines. Originally meant to provide the *Luftwaffe* standard aircraft with superior high-altitude performance, technological considerations limited its use to extremely high altitudes. Accordingly, it was only used by specialized planes like high-altitude reconnaissance aircraft, high - speed bombers and high-altitude interceptor aircraft.

One of the major problems of using nitrous oxide in a reciprocating engine is that it can produce enough power to damage or destroy the engine. Very large power increases are possible, and if the mechanical structure of the engine is not properly reinforced, the engine may be severely damaged or destroyed during this kind of operation. It is very important with nitrous oxide augmentation of internal combustion engines to maintain proper operating temperatures and fuel levels to prevent "preignition", or "detonation" (sometimes referred to as "knocking" or "pinging"). Most problems that are associated with nitrous do not come from mechanical failure due to the power increases. Since nitrous allows a much denser charge into the cylinder it dramatically increases cylinder pressures. The increased pressure results in heat, and heat will cause many problems from melting the piston, cylinder head or valves, to predetonation.

3 . 3 . Aerosol propellant

The gas is approved for use as a food additive (also known as E942) , specifically as an aerosol spray propellant. Its most common uses in this context are in aerosol whipped cream canisters, cooking sprays, and as an inert gas used to displace bacteria-inducing oxygen when filling packages of potato chips and other similar snack foods.

The gas is extremely soluble in fatty compounds. In aerosol whipped cream, it is dissolved in the fatty cream until it leaves the can, when it becomes gaseous and thus creates foam. Used in this way, it produces whipped cream four times the volume of the liquid, whereas whipping air into cream only produces twice the volume. If air were used as a propellant, oxygen would accelerate rancidification of the butterfat ; nitrous oxide inhibits such degradation. Carbon dioxide cannot be used for whipped cream because it is acidic in water, which would curdle the cream and give it a seltzer - like 'sparkling' sensation.

However, the whipped cream produced with nitrous oxide is unstable, and will return to a more or less liquid state within half an hour to one hour. Thus, the method is not suitable for decorating food that will not be immediately served. Similarly, cooking spray, which is made from various types of oils combined with lecithin (an emulsifier), may use nitrous oxide as a propellant; other propellants used in cooking spray include food-grade alcohol and propane.

Users of nitrous oxide often obtain it from whipped cream dispensers that use nitrous oxide as a propellant (see above section), for recreational use as a euphoria-inducing inhalant drug. It is non - harmful in small doses, but risks due to lack of oxygen do exist .

3 . 4 . In medicine

Nitrous oxide has been used for anesthesia in dentistry since the 1800s. The most common use is as a 50 : 50 mix with oxygen, commonly known as Entonox or Nitronox delivered through a demand valve, and frequently used to relieve pain associated with childbirth, trauma and heart attacks.

Professional use can involve constant supply flowmeters which allow the proportion of nitrous oxide and the combined gas flow rate to be individually adjusted. Nitrous oxide is typically administered by dentists through a demand-valve inhaler over the nose that only releases gas when the patient inhales through the nose.

Because nitrous oxide is minimally metabolized, it retains its potency when exhaled into the room by the patient and can pose an intoxicating and prolonged-exposure hazard to the clinic staff if the room is poorly ventilated. Where nitrous oxide is administered, a continuous- flow fresh - air ventilation system or nitrous-scavenging system is used to prevent waste gas buildup .

Nitrous oxide is a weak general anesthetic, and so is generally not used alone in general anesthesia. In general anesthesia it is used as a carrier gas in a 2 : 1 ratio with oxygen for more powerful general anesthetic agents such as sevo flurane or des flurane . It has a MAC (minimum alveolar concentration) of 105 % and a blood : gas partition coefficient of 0.46. Less than 0.004 % is metabolized in humans.

3 . 5 . Recreational use

Nitrous oxide (N_2O) is a dissociative drug that can cause analgesia, depersonalization, derealization, dizziness, euphoria, and some sound distortion.

Since the earliest uses of nitrous oxide for medical or dental purposes, it has also been used recreationally as an inhalant, because it causes euphoria and slight hallucinations. Only a small number of recreational users (such as dental office workers or medical gas technicians) have legal access to pure nitrous oxide canisters that are intended for medical or dental use. Most recreational users obtain nitrous oxide from compressed gas containers which use nitrous oxide as a propellant for whipped cream or from automotive nitrous systems. Automotive nitrous available to the public sometimes has ~100 ppm sulfur dioxide and/or elemental sulfur added to prevent recreational use/abuse ; (not hydrogen sulfide as suggested by). Inhalation of such a mixture is nearly impossible after one breath due to gagging and sooner or later, involuntary clamping off of the trachea; (some with "sulfite" allergies could even die due to allergic reaction) .

Users typically inflate a balloon or a plastic bag with nitrous oxide from a tank or a one - use 'charger' (often referred to as a cracker, as it 'cracks' open the nitrous canister) , and then inhale the gas for its effects. Highly compressed liquid expelled from a tank or canister is extremely cold, and should not be inhaled directly, thus for medical and recreational use it is decompressed into something else, such as a balloon, first. Mis-cracked canisters can cause skin damage due to freezing temperatures.

Recreational users typically do not mix it with air or oxygen and thus may risk injury or death from anoxia if they tie plastic bags around their heads or otherwise obstruct their breathing.

Nitrous oxide can be habit - forming because of its short-lived effect (generally from 0.1 – 1 minutes in recreational doses). Long - term use in excessive quantities has been associated with vitamin B12 deficiency anemia due to reduced hemopoiesis, neuropathy, tinnitus, and numbness in extremities, unless vitamin B12 supplements are taken to counteract this. Pregnant women should not use nitrous oxide as chronic use is teratogenic and foetotoxic. One study in rats found that long term exposure to high doses of nitrous oxide may lead to Olney's lesions that may become persistent.

4 . Neuro pharmacology

Nitrous oxide shares many pharmacological similarities with other inhaled anesthetics, but there are a number of differences. Nitrous oxide is relatively non-polar, has a low molecular weight, and high lipid solubility. As a result it can quickly diffuse into phospholipid cell membranes.

Like many classical anesthetics, the exact mechanism of action is still open to some conjecture. It antagonizes the NMDA receptor at partial pressures similar to those used in general anaesthesia . The evidence on the effect of N_2O on GABA - A currently is mixed, but tends to show a lower potency potentiation . N_2O, like other volatile anesthetics, activates twin-pore potassium channels, albeit weakly. These channels are largely responsible for keeping neurons at the resting (unexcited) potential . Unlike many anesthetics, however, N_2O does not seem to affect calcium channels.

Unlike most general anesthetics, N_2O appears to affect the GABA receptor. In many behavioral tests of anxiety, a low dose of N_2O is a successful anxiolytic . This anti-anxiety effect is partially reversed by benzodiazepine receptor antagonists. Mirroring this, animals which have developed tolerance to the anxiolytic effects of benzo diazepines are partially tolerant to nitrous oxide . Indeed, in humans given 30 % N_2 O , benzo diazepine receptor antagonists reduced the subjective reports of feeling “high”, but did not alter psycho - motor performance .

The effects of N_2O seem linked to the interaction between the endogenous opioid system and the descending noradrenergic system. When animals are given morphine chronically they develop tolerance to its analgesic (pain killing) effects; this also renders the animals tolerant to the analgesic effects of N_2O . Administration of antibodies which bind and block the activity of some endogenous opioids (not beta-endorphin), also block the antinociceptive effects of N_2O. Drugs which inhibit the breakdown of endogenous opioids also potentiate the antinociceptive effects of N_2O. Several experiments have shown that opioid receptor antagonists applied directly to the brain block the antinociceptive effects of N_2O, but these drugs have no effect when injected into the spinal cord.

Conversely, alpha – adreno receptor antagonists block the antinociceptive effects of N_2O when given directly to the spinal cord, but not when applied directly to the brain.[18] Indeed, alpha2B-adrenoreceptor knockout mice or animals depleted in noradrenaline are nearly completely resistant to the antinociceptive effects of N_2O. It seems N_2O-induced release of endogenous opioids causes disinhibition of brain stem noradrenergic neurons, which release nor epinephrine into the spinal cord and inhibit pain signaling (Maze, M. and M. Fujinaga, 2000). Exactly how N_2O causes the release of opioids is still uncertain.

5 . Safety

The major safety hazards of nitrous oxide come from the fact that it is a compressed liquefied gas, an asphyxiation risk, and a dissociative anaesthetic. Exposure to nitrous oxide causes short-term decreases in mental performance, audiovisual ability, and manual dexterity .

A study of workers and several experimental animal studies indicate that adverse reproductive effects for pregnant females may also result from chronic exposure to nitrous oxide.

The National Institute for Occupational Safety and Health recommends that workers' exposure to nitrous oxide should be controlled during the administration of anesthetic gas in medical, dental, and veterinary operatories.

5 . 1 . Chemical / physical

At room temperature (20° C) the saturated vapour pressure is 58.5 bar, rising up to 72.45 bar at 36.4° C — the critical temperature. The pressure curve is thus unusually sensitive to temperature . Liquid nitrous oxide acts as a good solvent for many organic compounds; liquid mixtures may form shock sensitive explosives .

As with many strong oxidisers, contamination of parts with fuels have been implicated in rocketry accidents, where small quantities of nitrous / fuel mixtures explode due to 'water hammer' like effects (sometimes called ' dieseling ' — heating due to adiabatic compression of gases can reach decomposition temperatures) . Some common building materials such as stainless steel and aluminum can act as fuels with strong oxidizers such as nitrous oxide, as can contaminants, which can ignite due to adiabatic compression . There have also been accidents where nitrous oxide decomposition in plumbing has led to the explosion of large tanks.

5 . 2 . Biological

Nitrous oxide inactivates the cobalamin form of vitamin B_{12} by oxidation. Symptoms of vitamin B_{12} deficiency, including sensory neuropathy, myelopathy, and encephalopathy, can occur within days or weeks of exposure to nitrous oxide anesthesia in people with subclinical vitamin B_{12} deficiency. Symptoms are treated with high doses of vitamin B_{12}, but recovery can be slow and incomplete . People with normal vitamin B_{12} levels have stores to make the effects of nitrous oxide insignificant, unless exposure is repeated and prolonged (nitrous oxide abuse) . Vitamin B_{12} levels should be checked in people with risk factors for vitamin B_{12} deficiency prior to using nitrous oxide anesthesia.

Nitrous oxide has also been shown to induce early stages of Olney's lesions in the brains of rats. However none of the lesions found were irreversible .

5 . 3 . Environmental

Nitrous oxide is also a green house gas. According to 2006 data from the United States Environmental Protection Agency, industrial sources make up only about 20 % of all anthropogenic sources, and include the production of nylon, and the burning of fossil fuel in internal combustion engines. Human activity is thought to account for 30 %; tropical soils and oceanic release account for 70 %. However, a 2008 study by Nobel Laureatte Paul Crutzen suggests that the amount of nitrous oxide release attributable to agricultural nitrate fertilizers has been seriously underestimated, most of which would presumably come under soil and oceanic release in the Environmental Protection Agency data. Atmospheric levels have risen by more than 15% since 1750. Each year we add 7 - 13 million tons into the atmosphere by using nitrogen based fertilizers, disposing of human and animal waste in sewage treatment plants, automobile exhaust, and other sources not yet identified .

6 . Legality

In the United States, possession of nitrous oxide is legal under federal law and is not subject to DEA purview. It is, however, regulated by the Food and Drug Administration under the Food Drug and Cosmetics Act; prosecution is possible under its "misbranding" clauses, prohibiting the sale or distribution of nitrous oxide for the purpose of human consumption.

Many states have laws regulating the possession, sale, and distribution of nitrous oxide. Such laws usually ban distribution to minors or limit the amount of nitrous oxide that may be sold without special license. In most jurisdictions, such as at the federal level, sale or distribution for the purpose of recreational consumption is illegal.

In some countries, it is illegal to have nitrous oxide systems plumbed into an engine's intake manifold. These laws are ostensibly used to prevent street racing and meet emission standards.

Nitrous oxide is entirely legal to possess and inhale in the United Kingdom, although supplying it to others to inhale, especially minors, is more likely to end up with a prosecution under the Medicines act.

In New Zealand, the Ministry of Health has warned that nitrous oxide is a prescription medicine, and its sale or possession without a prescription is an offense under the Medicines Act . This statement would seemingly prohibit all non-medicinal uses of the chemical, though it is implied that only recreational use will be legally targeted.

In India, for general anaesthesia purposes, nitrous oxide is available as Nitrous Oxide IP. India's gas cylinder rules (1985) permit the transfer of gas from one cylinder to another for breathing purposes. This law benefits remote hospitals, which would otherwise suffer as a result of India's geographic immensity. Nitrous Oxide IP is transferred from bulk cylinders (17,000 liters capacity gas) to smaller pin-indexed valve cylinders (1,800 liters of gas), which are then connected to the yoke assembly of Boyle's machines. Because India's Food & Drug Authority (FDA - India) rules state that transferring a drug from one container to another (refilling) is equivalent to manufacturing, anyone found doing so must possess a drug manufacturing license.

7 . History

The gas was first synthesized by English chemist and natural philosopher Joseph Priestley in 1775, who called it *phlogisticated nitrous air* (see phlogiston). Priestley describes the preparation of "nitrous air diminished" by heating iron filings dampened with nitric acid in *Experiments and Observations on Different Kinds of Air* (1775). Priestley was delighted with his discovery: "I have now discovered an air five or six times as good as common air... nothing I ever did has surprised me more, or is more satisfactory."

Humphry Davy in the 1790s tested the gas on himself and some of his friends, including the poet Samuel Taylor Coleridge. They realized that nitrous oxide considerably dulled the sensation of pain, even if the inhaler were still semi - conscious. After it was publicized extensively by Gardner Quincy Colton in the United States in the 1840s, it came into use as an anaesthetic , particularly by dentists, who do not typically have access to the services of an anesthesiologist and who may benefit from a patient who can respond to verbal commands.

Dinitrogen trioxide (N_2 O_3)

1 . Introduction :

Dinitrogen trioxide is the chemical compound with the formula N_2O_3. This deep blue liquid is one of binary nitrogen oxides. It forms upon mixing equal parts of nitric oxide and nitrogen dioxide and cooling the mixture below −21 °C :

$$NO + NO_2 \; N_2O_3$$

Dinitrogen trioxide is only isolable at low temperatures, i.e. in the liquid and solid phases. At higher temperatures the equilibrium favors the constituent gases, with K_{diss} = 193 kPa (25 °C) .

Other names	Nitrous anhydride
Molecular Formula	N_2O_3
Molar Mass	76.01 g / mol
Appearance	deep blue liquid
Density	1.4 g / cm^3, liquid 1.783 g / cm^3 (gas)
Melting Point	− 100.1 ° C (173.05 K)
Boiling Point	3 °C (276 K)
Solubility in Water	very soluble
Flash Point	Non - flammable

2 . **Structure and bonding**

Dinitrogen trioxide has an unusually long N–N bond at 186 pm. Whereas N – N bonds are more often similar to that in hydrazine (145 pm) , some other oxides of nitrogen do possess long N– N bonds, including dinitrogen tetroxide (175 pm). The N_2 O_3 molecule is planar and exhibits C_s symmetry. The dimensions displayed below come from microwave spectroscopy of low-temperature, gaseous N_2O_3 :

It is the anhydride of the unstable nitrous acid (HNO_2), and produces it when mixed into water. An alternative structure might be anticipated for the true anhydride, i.e. O=N–O–N=O, but this isomer is not observed. If the nitrous acid is not then used up quickly, it decomposes into nitric oxide and nitric acid. Nitrite salts are sometimes produced by adding N_2O_3 to solutions of bases:

$$N_2O_3 + 2\ Na\ OH \rightarrow 2\ NaNO_2 + H2O$$

Dinitrogen tetroxide ($N_2 O_4$)

Contents

1 . Introduction :

Dinitrogen tetroxide (**nitrogen tetroxide** or **nitrogen peroxide**) is the chemical compound N_2O_4. It forms an equilibrium mixture with nitrogen dioxide; some call this mixture dinitrogen tetroxide, some call it nitrogen dioxide. Dinitrogen tetroxide is a powerful oxidizer, highly toxic and corrosive. N_2O_4 is hypergolic with various forms of hydrazine, i.e., they burn on contact without a separate ignition source, making them popular bipropellant rocket fuels. It is a useful reagent in chemical synthesis.

Molecular Formula	N_2O_4
Molar mass	92.011 g / mol
Appearance	Colourless gas
Density	1.443 g / cm^3 (liquid, 21 º C)
Melting Point	−11.2 º C
Boiling Point	21.1 º C
Solubility in Water	reacts
Vapor Pressure	96 kPa (20 °C)
Refractive index (n_D)	1.00112
Flash point	Non - flammable

2 . **Structure and properties**

The molecule is planar with an N-N bond distance of 1.78 Å and N - O distances of 1.19 Å. Unlike NO_2 , N_2O_4 is diamagnetic.[2] It is also colorless but can appear brownish yellow liquid due to the presence of NO_2 according to the following equilibrium:

$$N_2O_4 \rightleftharpoons 2\ NO_2$$

Higher temperatures push the equilibrium towards nitrogen dioxide. Inevitably, some nitrogen tetroxide is a component of smog containing nitrogen dioxide.

3 . Production

Nitrogen dioxide is made by the catalytic oxidation of ammonia: steam is used as a diluent to reduce the combustion temperature. Most of the water is condensed out, and the gases are further cooled; the nitric oxide that was produced is oxidized to nitrogen dioxide, and the remainder of the water is removed as nitric acid. The gas is essentially pure nitrogen tetroxide, which is condensed in a brine - cooled liquefier.

4 . Use as a rocket propellant

Dinitrogen tetroxide is one of the most important rocket propellants ever developed, much like the German developed hydrogen peroxide-based T - Stoff oxidizer used in their World War II rocket propelled combat aircraft designs such as the Messerschmitt Me 163 *Komet*, and by the late 1950s it became the storable oxidizer of choice for rockets in both the USA and USSR. It is a hypergolic propellant often used in combination with a hydrazine - based rocket fuel. One of the earliest uses of this combination was on the Titan rockets used originally as ICBMs and then as launch vehicles for many spacecraft. Used on the U.S. Gemini and Apollo spacecraft, it continues to be used on the Space Shuttle, most geo - stationary satellites, and many deep-space probes. It now seems likely that NASA will continue to use this oxidizer in the next - generation 'crew-vehicles' which will replace the shuttle. It is also the primary oxidizer for Russia's Proton rocket and China's Long March rockets.

When used as a propellant, dinitrogen tetroxide is usually referred to simply as 'Nitrogen Tetroxide' and the abbreviation 'NTO' is extensively used. Additionally, NTO is often used with the addition of a small percentage of nitric oxide, which inhibits stress - corrosion cracking of titanium alloys, and in this form, propellant - grade NTO is referred to as "Mixed Oxides of Nitrogen" or "MON". Most spacecraft now use MON instead of NTO, for example, the Space Shuttle reaction control system uses MON3 (NTO containing 3wt % NO) .

On 24 July 1975, NTO poisoning nearly killed the three astronauts on board the Apollo - Soyuz Test Project during its final descent. This was due to a switch left in the wrong position, which allowed NTO fumes to vent into the spacecraft from a cabin air intake. Upon landing, the crew was hospitalized 14 days for chemical - induced pneumonia and edema.

5 . Power generation using N_2O_4

The tendency of N_2O_4 to reversibly break into NO_2 has led to research into its use in advanced power generation systems as a so - called dissociating gas. "Cool" nitrogen tetroxide is compressed and heated, causing it to dissociate into nitrogen dioxide at half the molecular weight. This hot nitrogen dioxide is expanded through a turbine, cooling it and lowering the pressure, and then cooled further in a heat sink, causing it to recombine into nitrogen tetroxide at the original molecular weight. It is then much easier to compress to start the entire cycle again. Such dissociative gas Brayton cycles have the potential to considerably increase efficiencies of power conversion equipment.

6 . Chemical reactions

N_2O_4 has a very rich chemistry .

6 . 1 . Intermediate in the manufacture of nitric acid

Nitric acid is manufactured on a large scale via N_2O_{4b} . This species reacts with water to give both nitrous acid and nitric acid

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$$

The co product HNO_2 upon heating disproportionates to NO and more nitric acid.

6 . 1 . Synthesis of metal nitrates

N_2O_4 behaves as the salt $[NO^+][NO_3^-]$, the former being a strong oxidant :

$$2\ N_2O_4 + M \rightarrow 2\ NO + M(NO_3)_2$$

where M = Cu , Zn , or Sn .

Dinitrogen pent oxide ($N_2\ O_5$)

Contents

1 . Introduction ;

Dinitrogen pent oxide is the chemical compound with the formula N_2O_5. Also known as nitrogen pent oxide , N_2O_5 is one of the binary nitrogen oxides, a family of compounds that only contain nitrogen and oxygen. It is an unstable and potentially dangerous oxidizer that once was used as a reagent for nitrations but has largely been superseded by NO_2BF_4 (nitronium tetra fluoro borate) .

N_2O_5 is a rare example of a compound that adopts two structures depending on the conditions: most commonly it is a salt, but under some conditions it is a nonpolar molecule:

$$N_2O_5 \rightleftharpoons [NO_2^+]\ [NO_3^-]$$

Other Names	- Nitric anhydride - dnpo
Molecular Formula	$N_2\ O_5$
Molar Mass	108 g / mol
Appearance	White solid
Density	1.642 g / cm3 (18 °C)
Melting Point	30
Boiling Point	47 ºC subl.
Solubility in Water	Reacts to give HNO3

Solubility	Soluble in Chloroform
Flash point	Non - flammable

2 . Syntheses and properties

N_2O_5 was first reported by Deville in 1840, who prepared it by treating $AgNO_3$ with Cl_2. A recommended laboratory synthesis entails dehydrating nitric acid (HNO_3) with phosphorus (V) oxide :

$$P_4O_{10} + 12\ HNO_3 \rightarrow 4\ H_3PO_4 + 6\ N_2O_5$$

In the reverse process, N_2O_5 reacts with water (hydrolyses) to produce nitric acid. Thus, nitrogen pentoxide is the anhydride of nitric acid : $N_2O_5 + H_2O \rightarrow 2\ HNO_3$

N_2O_5 exists as colourless crystals that sublime slightly above room temperature. The salt eventually decomposes at room temperature into NO_2 and O_2.

3 . Structure

Solid N_2O_5 is a salt, consisting of separated anions and cations. The cation is the linear nitronium ion NO_2^+ and the anion is the planar NO_3^- ion. Thus, the solid could be called nitronium nitrate. Both nitrogen centers have oxidation states V.

The intact molecule $O_2N – O - NO_2$ exists in the gas phase (obtained by subliming N_2O_5) and when the solid is extracted into nonpolar solvents such as $C\ Cl_4$. In the gas phase , the O – N - O angle is 133° and the N - O - N angle is 114°. When gaseous N_2O_5 is cooled rapidly ("quenched"), one can obtain the meta stable molecular form, which exothermically converts to the ionic form above -70 ° C .

4 . Reactions and applications

Dinitrogen pent oxide , for example as a solution in chloroform, has been used as a reagent to introduce the NO_2 functionality. This nitration reaction is represented as follows :

$$N_2O_5 + Ar\text{-}H \rightarrow HNO_3 + Ar\text{-}NO_2$$

N_2O_5 is of interest for the preparation of explosives.

5 . NO_2BF_4

Replacement of the NO_3^- portion of N_2O_5 with BF_4^- gives NO_2BF_4 . This salt retains the high reactivity of NO_2^+, but it is thermally stable, decomposing at ca. 180° C (into NO_2F and BF_3). NO_2BF_4 has been used to nitrate a variety of organic compounds, especially arenes and hetero cycles. Interestingly, the reactivity of the NO_2^+ can be further enhanced with strong acids that generate the "super- electrophile" HNO_2^{2+}.

6 . Hazards

N_2O_5 is a strong oxidizer that forms explosive mixtures with organic compounds and ammonium salts. The decomposition of dinitrogen pent oxide produces the highly toxic nitrogen dioxide gas.

Nitrous acid (HNO_2)

Contents

1 . Introduction :

Nitrous acid (molecular formula HNO_2) is a weak and monobasic acid known only in solution and in the form of nitrite salts.

Nitrous acid is used to make diazides from amines; this occurs by nucleophilic attack of the amine onto the nitrite, reprotonation by the surrounding solvent, and double-elimination of water. The diazide can then be liberated as a carbene.

Molecular formula	HNO_2
Molar mass	47 g / mol
Appearance	Pale blue soution
Density	Approx. 1 g / ml
Melting point	Only known in solution
Acidity (pK_a)	3.398
EU Index	Not listed
Flash point	Non-flammable

2 . **Structure**

In the gas phase, the planar nitrous acid molecule can adopt both a *cis* and a *trans* form. The *trans* form predominates at room temperature, and IR measurements indicate it is more stable by around 2.3 kJ mol^{-1}.

3 . Preparation

Nitrous acid can be prepared by adding any mineral acid to sodium nitrite.

4 . Decomposition

Nitrous acid rapidly decomposes into nitrogen dioxide, nitric oxide, and water when in solution.

$$2\ HNO_2 \rightarrow NO_2 + NO + H_2O$$

It also decomposes into nitric acid and nitrous oxide and water.

$$4\ HNO_2 \rightarrow 2\ HNO_3 + N_2O + H_2O$$

5 . Chemistry

Nitrous acid is used to prepare diazonium salts:

$$HNO_2 + ArNH_2 + H^+ \rightarrow ArN_2^+ + 2\ H_2O$$

where Ar is an aryl group.

Such salts are widely used in organic synthesis, e.g., for the Sandmeyer reaction and in the preparation azo dyes, brightly-colored compounds that are the basis of a qualitative test for anilines. Nitrous acid is used to destroy toxic and potentially-explosive sodium azide. For most purposes, nitrous acid is usually formed *in situ* by the action of mineral acid on sodium nitrite :

$$NaNO_2 + H\ Cl \rightarrow HNO_2 + NaCl$$
$$2\ NaN_3 + 2\ HNO_2 \rightarrow 3\ N_2 + 2\ NO + 2\ NaOH$$

6 . Atmosphere of the earth

Nitrous acid is involved in the ozone budget of the lower atmosphere: the troposphere. The hetero genous reaction of nitrous oxide (NO_2) and water produces nitrous acid. When this reaction takes place on the surface of atmospheric aerosols, product readily photolyses to hydroxyl radicals.

Nitric acid

Contents

1 . Introduction :

Nitric acid (HNO_3), also known as ***aqua fortis*** and **spirit of nitre** , is a highly corrosive and toxic strong acid that can cause severe burns.

Colorless when pure, older samples tend to acquire a yellow cast due to the accumulation of oxides of nitrogen. If the solution contains more than 86 % nitric acid , it is referred to as **fuming nitric acid** .

Fuming nitric acid is characterized as white fuming nitric acid and red fuming nitric acid, depending on the amount of nitrogen dioxide present .

Other Names	Aqua fortis Spirit of nitre Salpetre acid Hydrogen Nitrate Azotic acid
Molecular formula	HNO_3
Molar mass	63. g / mol
Appearance	Clear, colorless liquid
Density	1.5129 g / cm^3
Melting Point	- 42 ° C
Boiling Point	83 °C , (bp of pure acid. 68 % solution boils at 120.5 °C)
Solubility in Water	Completely miscible
Acidity (pK_a)	- 1.4
Refractive index (n_D)	1.397 (16.5 ° C)

2 . Properties

Pure anhydrous nitric acid (100 %) is a colorless liquid with a density of 1522 kg/m³ which solidifies at - 42 °C to form white crystals and boils at 83 ° C. When boiling in light, even at room temperature, there is a partial decomposition with the formation of nitrogen dioxide following the reaction:

$$4\ HNO_3 \rightarrow 2\ H_2O + 4\ NO_2 + O_2\ (72°C)$$

which means that anhydrous nitric acid should be stored below 0 °C to avoid decomposition. The nitrogen dioxide (NO_2) remains dissolved in the nitric acid coloring it yellow, or red at higher temperatures. While the pure acid tends to give off white fumes when exposed to air, acid with dissolved nitrogen dioxide gives off reddish-brown vapours, leading to the common name "red fuming acid" or "fuming nitric acid". Fuming nitric acid is also referred to as 16-molar nitric acid — as the most concentrated form of nitric acid at Standard Temperature and Pressure (STP).

Nitric acid is miscible with water and distillation gives an azeotrope with a concentration of 68% HNO_3 and a boiling temperature of 120.5 °C at 1 atm, which is the ordinary concentrated nitric acid of commerce. Two solid hydrates are known; the monohydrate ($HNO_3 \cdot H_2O$) and the tri hydrate ($HNO_3 \cdot 3H_2O$). It is iso electronic with the bicarbonate ion.

Nitrogen oxides (NO_x) are soluble in nitric acid and this property influences more or less all the physical characteristics depending on the concentration of the oxides. These mainly include the vapor pressure above the liquid and the boiling temperature, as well as the color mentioned above.

Nitric acid is subject to thermal or light decomposition with increasing concentration and this may give rise to some non-negligible variations in the vapour pressure above the liquid because the nitrogen oxides produced dissolve partly or completely in the acid.

2 . 1 . Acidic properties

Being a typical acid, nitric acid reacts with alkalis, basic oxides, and carbonates to form salts, such as ammonium nitrate. Due to its oxidizing nature, nitric acid generally does not donate its proton (that is, it does not liberate hydrogen) on reaction with metals and the resulting salts are usually in the higher oxidized states. For this reason, heavy corrosion can be expected and should be guarded against by the appropriate use of corrosion resistant metals or alloys.

Nitric acid has an acid dissociation constant (pK_a) of −1.4: in aqueous solution, it almost completely (93% at 0.1 mol/L) ionizes into the nitrate ion NO −3 and a hydrated proton, known as a hydronium ion, H_3O^+.

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO{-}3$$

2 . 2 . Oxidizing properties

2 . 2 . 1 . Reactions with metals

Being a powerful oxidizing agent, nitric acid reacts violently with many organic materials and the reactions may be explosive. Depending on the acid concentration, temperature and the reducing agent involved, the end products can be variable. Reaction takes place with all metals except the precious metal series and certain alloys. This characteristic has made it a common agent to be used in acid tests. As a general rule, oxidizing reactions occur primarily with the concentrated acid, favouring the formation of nitrogen dioxide (NO_2).

$$Cu + 4\ H^{+} + 2\ NO_3^{-} \rightarrow Cu^{2+} + 2\ NO_2 + 2\ H_2O$$

The acidic properties tend to dominate with dilute acid, coupled with the preferential formation of nitrogen oxide (NO).

$$3\ Cu + 8\ HNO_3 \rightarrow 3\ Cu\ (NO_3)_2 + 2\ NO + 4\ H_2O$$

Since nitric acid is an oxidizing agent, hydrogen (H_2) is rarely formed. Only magnesium (Mg), Manganese (Mn) and calcium (Ca) react with *cold*, *dilute* nitric acid to give hydrogen:

$$Mg\ (s) + 2\ HNO_3\ (aq) \rightarrow Mg(NO_3)_2\ (aq) + H_2\ (g)$$

Nitric acid has the highest distinction (amongst all acids) of attacking and dissolving all metals on the periodic table except Gold and Platinum .

2 . 2 . 2 . Passivation

Although chromium (Cr), iron (Fe) and aluminium (Al) readily dissolve in dilute nitric acid, the concentrated acid forms a metal oxide layer that protects the metal from further oxidation, which is called passivation. Typical passivation concentrations range from 18 % to 22 % by weight.

2 . 2 . 3 . Reactions with non – metals :

Reaction with non - metallic elements, with the exceptions of nitrogen, oxygen, noble gases, silicon and halogens, usually oxidizes them to their highest oxidation states as acids with the formation of nitrogen dioxide for concentrated acid and nitric oxide for dilute acid .

$C + 4\ HNO_3 \rightarrow CO_2 + 4\ NO_2 + 2\ H_2O$ or
$3\ C + 4\ HNO_3 \rightarrow 3\ CO_2 + 4\ NO + 2\ H_2O$

2 . 3 . Xanthoproteic test

Nitric acid reacts with proteins to form yellow nitrated products. This reaction is known as the *xanthoproteic reaction*. This test is carried out by adding concentrated nitric acid to the substance being tested, and then heating the mixture. If proteins are present that contains amino acids with aromatic rings, the mixture turns yellow. Upon adding a strong base such as liquid ammonia, the color turns orange. These color changes are caused by nitrated aromatic rings in the protein .

3 . Grades

White fuming nitric acid, also called 100 % nitric acid or WFNA, is very close to the anhydrous nitric acid product. One specification for white fuming nitric acid is that it has a maximum of 2% water and a maximum of 0.5 % dissolved NO_2.

Red fuming nitric acid, or RFNA, contains substantial quantities of dissolved nitrogen dioxide (NO_2) leaving the solution with a reddish - brown color. One formulation of RFNA specifies a minimum of 17 % NO_2, another specifies 13 % NO_2.

An *inhibited* fuming nitric acid (either IWFNA, or IRFNA) can be made by the addition of 0.6 to 0.7% hydrogen fluoride, HF. This fluoride is added for corrosion resistance in metal tanks (the fluoride creates a metal fluoride layer that protects the metal).

4 . Industrial production

Nitric acid is made by reacting nitrogen dioxide (NO_2) with water.

$$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$$

Normally, the nitric oxide produced by the reaction is reoxidized by the oxygen in air to produce additional nitrogen dioxide.

Dilute nitric acid may be concentrated by distillation up to 68 % acid, which is a maximum boiling azeotrope containing 32 % water. In the laboratory, further concentration involves distillation with sulphuric acid which acts as a dehydrating agent. Such distillations must be done with all - glass apparatus at reduced pressure, to prevent decomposition of the acid. Industrially, strong nitric acid is produced by dissolving additional nitrogen dioxide in 68 % nitric acid in an absorption tower.[3] Dissolved nitrogen oxides are either stripped in the case of white fuming nitric acid, or remain in solution to form red fuming nitric acid.

Commercial grade nitric acid solutions are usually between 52% and 68 % nitric acid. Production of nitric acid is via the Ostwald process, named after German chemist Wilhelm Ostwald. In this process, anhydrous ammonia is oxidized to nitric oxide, which is then reacted with oxygen in air to form nitrogen dioxide. This is subsequently absorbed in water to form nitric acid and nitric oxide.

The nitric oxide is cycled back for reoxidation. By using ammonia derived from the Haber process, the final product can be produced from nitrogen, hydrogen, and oxygen which are derived from air and natural gas as the sole feeds tocks .

5 . Laboratory synthesis

In laboratory, nitric acid can be made from copper(II) nitrate or by reacting approximately equal masses of potassium nitrate (KNO_3) with 96% sulfuric acid (H_2SO_4), and distilling this mixture at nitric acid's boiling point of 83 °C until only a white crystalline mass, potassium hydrogen sulfate ($KHSO_4$), remains in the reaction vessel. The red fuming nitric acid obtained may be converted to the white nitric acid.

$$H_2SO_4 + KNO_3 \rightarrow KHSO_4 + HNO_3$$

The dissolved NO_x are readily removed using reduced pressure at room temperature (10-30 min at 200 mmHg or 27 kPa) to give white fuming nitric acid. This procedure can also be performed under reduced pressure and temperature in one step in order to produce less nitrogen dioxide gas .

Sodium nitrate may be used in place of potassium nitrate.

6 . Uses

A solution of nitric acid and alcohol , Nital , is used for etching of metals to reveal the microstructure.

Commercially available aqueous blends of 5 – 30 % nitric acid and 15 – 40 % phosphoric acid are commonly used for cleaning food and dairy equipment primarily to remove precipitated calcium and magnesium compounds (either deposited from the process stream or resulting from the use of hard water during production and cleaning).

Nitric acid is also used in explosives, and is key to the manufacture of Nitroglycerin and RDX.

6 . 1 . Clog remover

In a high medium concentration nitric acid is used as a cheap clog remover .

6 . 2 . Elemental Analysis

In elemental analysis by ICP - MS, ICP - AES, GFAA, and Flame AA, dilute nitric acid (0.5 to 5.0 %) is used as a matrix compound for determining metal traces in solutions . Ultrapure trace metal grade acid is required for such determination, because small amounts of metal ions could affect the result of the analysis.

It is also typically used in the digestion process of turbid water samples, sludge samples, solid samples as well as other types of unique samples which require elemental analysis via ICP-MS, ICP - OES , ICP - AES , GFAA and FAA . Typically these digestions use a 50 % solution of the purchased HNO_3 mixed with Type 1 DI Water .

6 . 3 . Wood Working

In a low concentration (approximately 10 %) , nitric acid is often used to artificially age pine and maple. The color produced is a grey - gold very much like very old wax or oil finished wood (wood finishing) .

6 . 4 . Other uses

Alone, it is useful in metallurgy and refining as it reacts with most metals, and in organic syntheses. When mixed with hydrochloric acid, nitric acid forms Aqua Regia , one of the few reagents capable of dissolving gold and platinum. The reason for Aqua Regia to be so active is the formation of free chlorine radicals in the statu nascendi when the two acids are mixed. Nitric Acid is also used to make improvised initiator for improvised blasting caps.

A mixture of concentrated nitric and sulphuric acids causes the nitration of aromatic compounds, such as benzene. Examination of the infrared spectrum of the acid mixture using a corrosive resistant diamond cell shows Infrared peaks close to that expected for carbon dioxide. The species responsible for the peaks is the nitronium ion, NO+2, which like CO_2, is a linear molecule. The nitronium ion is the species responsible for nitration: being positive it attacks the negatively charged benzene ring. This is described more fully in organic chemistry books.

7 . Safety

Nitric acid is a powerful oxidizing agent, and the reactions of nitric acid with compounds such as cyanides, carbides, and metallic powders can be explosive. Reactions of nitric acid with many organic compounds, such as turpentine, are violent and hypergolic (i.e., self - igniting).

Concentrated nitric acid dyes human skin yellow due to a reaction with the keratin. These yellow stains turn orange when neutralized .