# Nitrogen

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**Nitrogen** is a chemical element with symbol **N** and atomic number 7. It was first discovered and isolated by Scottish physician Daniel Rutherford in 1772. Although Carl Wilhelm Scheele and Henry Cavendish had independently done so at about the same time, Rutherford is generally accorded the credit because his work was published first. The name *nitrogen* was suggested by Jean-Antoine-Claude Chaptal in 1790, when it was found that nitrogen was present in nitric acid and nitrates; this name derives from the Greek roots v1τρον "nitre" and -γενναν "to form". Antoine Lavoisier suggested instead the name *azote*, from the Greek άζωτικός "no life", as it is an asphyxiant gas; his name is instead used in many languages, such as French, Russian, and Turkish, and appears in the English names of some nitrogen compounds such as hydrazine, azides and azo compounds.

Nitrogen is the lightest member of group 15 of the periodic table, often called the pnictogens. The name comes from the Greek  $\pi\nu$ ( $\gamma\epsilon\iota\nu$  "to choke", directly referencing nitrogen's asphyxiating properties. It is a common element in the universe, estimated at about seventh in total abundance in the Milky Way and the Solar System. At standard temperature and pressure, two atoms of the element bind to form dinitrogen, a colourless and odorless diatomic gas with the formula  $N_2$ .

Dinitrogen forms about 78% of Earth's atmosphere, making it the most abundant uncombined element. Nitrogen occurs in all organisms, primarily in amino acids (and thus proteins), in the nucleic acids (DNA and RNA) and in the energy transfer molecule adenosine triphosphate. The human body contains about 3% nitrogen by mass, the fourth most abundant element in the body after oxygen, carbon, and hydrogen. The nitrogen cycle describes movement of the element from the air, into the biosphere and organic compounds, then back into the atmosphere.

Many industrially important compounds, such as ammonia, nitric acid, organic nitrates (propellants and explosives), and cyanides, contain nitrogen. The extremely strong triple bond in elemental nitrogen ( $N\equiv N$ ), the strongest bond in any diatomic molecule, dominates nitrogen chemistry. This causes difficulty for both organisms and industry in converting  $N_2$  into useful compounds, but at the same time means that burning, exploding, or decomposing nitrogen compounds to form nitrogen gas

## Nitrogen, 7N



Liquid nitrogen

## Spectral lines of nitrogen

#### **General properties**

Name, symbol nitrogen, N

Pronunciation / 'naɪtrədʒən/

**NY-**trə-jən

**Appearance** colorless gas, liquid or

solid

#### Nitrogen in the periodic table

Atomic number (Z) 7

**Group, block** group 15 (pnictogens),

p-block

**Period** period 2

**Element category** \( \square\$ diatomic nonmetal

**Standard atomic** 

releases large amounts of often useful energy. Synthetically produced ammonia and nitrates are key industrial fertilisers, and fertiliser nitrates are key pollutants in the eutrophication of water systems.

Apart from its use in fertilisers and energy-stores, nitrogen is a constituent of organic compounds as diverse as Kevlar used in high-strength fabric and cyanoacrylate used in superglue. Nitrogen is a constituent of every major pharmacological drug class, including antibiotics. Many drugs are mimics or prodrugs of natural nitrogen-containing signal molecules: for example, the organic nitrates nitroglycerin and nitroprusside control blood pressure by metabolizing into nitric oxide. Many notable nitrogen-containing drugs, such as the natural caffeine and morphine or the synthetic amphetamines, act on receptors of animal neurotransmitters.

## **Properties**

#### **Atomic**

A nitrogen atom has seven electrons. In the ground state, they are arranged in the electron configuration  $1s^22s^22p_\chi^12p_y^12p_z^1$ . It therefore has five valence electrons in the 2s and 2p orbitals, three of which (the p-electrons) are unpaired. It has one of the highest electronegativities among the elements (3.04 on the Pauling scale), exceeded only by chlorine (3.16), oxygen (3.44), and fluorine (3.98). Following periodic trends, its single-bond covalent radius of 71 pm is smaller than those of boron (84 pm) and carbon (76 pm), while it is larger than those of oxygen (66 pm) and fluorine (57 pm). The nitride anion, N³-, is much larger at 146 pm, similar to that of the oxide ( $O^{2-}$ : 140 pm) and fluoride ( $F^{-}$ : 133 pm) anions. The first three ionisation energies of nitrogen are 1.402, 2.856, and 4.577 MJ·mol<sup>-1</sup>, and the sum of the fourth and fifth is 16.920 MJ·mol<sup>-1</sup>. Due to these very high figures, nitrogen has no simple cationic chemistry.

The lack of radial nodes in the 2p subshell is directly responsible for many of the anomalous properties of the first row of the p-block, especially in nitrogen, oxygen, and fluorine. The 2p subshell is very small and has a very similar radius to the 2s shell, facilitating orbital hybridisation. It also results in very large electrostatic forces of attraction between the nucleus and the valence electrons in the 2s and 2p shells,

**weight**  $(A_r)$  14.007<sup>[1]</sup> (14.00643-

 $14.00728)^{[2]}$ 

Electron configuration

[He]  $2s^2 2p^3$ 

per shell 2, 5

**Physical properties** 

**Phase** gas

**Melting point** 63.15 K (-210.00 °C,

-346.00 °F)

**Boiling point** 77.355 K (-195.795 °C,

-320.431 °F)

**Density** at stp (0 °C 1.251 g/L

and 101.325 kPa)

when liquid, at b.p.  $0.808 \text{ g/cm}^3$ 

**Triple point** 63.151 K, 12.52 kPa

**Critical point** 126.192 K, 3.3958 MPa

**Heat of fusion**  $(N_2) 0.72 \text{ kJ/mol}$ 

Heat of vaporisation

(N<sub>2</sub>) 5.56 kJ/mol

Molar heat capacity

 $(N_2)$  29.124 J/(mol·K)

#### Vapour pressure

<b>P</b> (Pa)	1	10	100	1 k	<b>10</b> k	100 k
at T (K)	37	41	46	53	62	77

#### **Atomic properties**

**Oxidation states 5**, 4, **3**, 2, 1, -1, -2, **-3** 

(a strongly acidic oxide)

**Electronegativity** Pauling scale: 3.04

lonisation energies

1st: 1402.3 kJ/mol 2nd: 2856 kJ/mol 3rd: 4578.1 kJ/mol

(more)

resulting in very high electronegativities. Hypervalency is almost unknown in these elements for the same reason, because the high electronegativity makes it difficult for a small nitrogen atom to be a central atom in an electron-rich three-center four-electron bond since it would tend to attract the electrons strongly to itself. Thus, despite nitrogen's position at the head of group 15 in the periodic table, its chemistry shows huge differences from that of its heavier congeners phosphorus, arsenic, antimony, and bismuth.<sup>[20]</sup>

Nitrogen may be usefully compared to its horizontal neighbours carbon and oxygen as well as its vertical neighbours in the pnictogen column (phosphorus, arsenic, antimony, and bismuth). Although each period 2 element from lithium to nitrogen shows some similarities to the period 3 element in the next group from magnesium to sulfur (known as the diagonal relationships), their degree drops off guite abruptly past the boron-silicon pair, so that the similarities of nitrogen to sulfur are mostly limited to sulfur nitride ring compounds when both elements are the only ones present. Nitrogen resembles oxygen far more than it does carbon with its high electronegativity and concomitant capability for hydrogen bonding and the ability to form coordination complexes by donating its lone pairs of electrons. It does not share carbon's proclivity for catenation, with the longest chain of nitrogen yet discovered being composed of only eight nitrogen atoms (PhN=N-N(Ph)-N=N-N(Ph)-N=NPh). One property nitrogen does share with both its horizontal neighbours is its preferentially forming multiple bonds, typically with carbon, nitrogen, or oxygen atoms, through  $p_{\pi}$ - $p_{\pi}$  interactions. This is not possible for its vertical neighbours; thus, the nitrogen oxides, nitrites, nitrates, nitro-, nitroso-, azo-, and diazocompounds, azides, cyanates, thiocyanates, and imino-derivatives find no echo with phosphorus, arsenic, antimony, or bismuth. By the same token, however, the complexity of the phosphorus oxoacids finds no echo with nitrogen. [21]

Covalent radius71±1 pmVan der Waals155 pm

radius

Miscellanea

Crystal structure hexagonal



**Speed of sound** 353 m/s (gas, at 27 °C)

Thermal conductivity

 $25.83 \times 10^{-3} \text{ W/(m·K)}$ 

Magnetic ordering diamagnetic CAS Number 7727-37-9

History

**Discovery** Daniel Rutherford

(1772)

Named by Jean-Antoine Chaptal

(1790)

Most stable isotopes of nitrogen

iso	NA	half-life	DM	<b>DE</b> (MeV)	DP		
13N	syn	9.965 min	ε	2.220	<sup>13</sup> C		
<sup>14</sup> N	99.6%	is stable with 7 neutrons					
<sup>15</sup> N	0.4%	is stable with 8 neutrons					

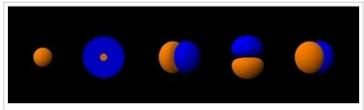
### **Isotopes**

Nitrogen has two stable isotopes:  $^{14}$ N and  $^{15}$ N. The first is much more common, making up 99.634% of natural nitrogen, and the second (which is slightly heavier) makes up the remaining 0.366%. This leads to an atomic weight of around 14.007 u.  $^{[18]}$  Both of these stable isotopes are produced in the CNO cycle in stars, but  $^{14}$ N is more common as its neutron capture is the rate-limiting step.  $^{14}$ N is one of the five stable odd-odd nuclides (a nuclide having an odd number of protons and neutrons); the other four are  $^{2}$ H,  $^{6}$ Li,  $^{10}$ B, and  $^{180}$ mTa.  $^{[22]}$ 

The relative abundance of  $^{14}N$  and  $^{15}N$  is practically constant in the atmosphere but can vary elsewhere, due to natural isotopic fractionation from biological redox reactions and the evaporation of natural ammonia or nitric acid.  $^{[23]}$  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.  $^{[24]}$ 

The heavy isotope  $^{15}$ N was first discovered by S. M. Naudé in 1929, soon after heavy isotopes of the neighbouring elements oxygen and carbon were discovered. [25] It presents one of the lowest thermal neutron capture cross-

sections of all isotopes.<sup>[26]</sup> It is frequently used in nuclear magnetic resonance (NMR) spectroscopy to determine the structures of nitrogen-containing molecules, due to its fractional nuclear spin of one-half, which offers advantages for NMR such as narrower line width. <sup>14</sup>N, though also theoretically usable, has an integer nuclear spin of one and thus has a quadrupole moment that leads to wider and less useful spectra.<sup>[18]</sup> <sup>15</sup>N NMR nevertheless has complications not encountered in the more <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The low natural abundance of <sup>15</sup>N (0.36%) significantly reduces sensitivity, a problem which is only exacerbated by its low gyromagnetic ratio, (only 10.14% that of <sup>1</sup>H). As a result, the signal-to-noise ratio for <sup>1</sup>H is about 300 times as much as that for <sup>15</sup>N at the same magnetic field strength.<sup>[27]</sup> This may be



The shapes of the five orbitals occupied in nitrogen. The two colours show the phase or sign of the wave function in each region. From left to right: 1s, 2s (cutaway to show internal structure),  $2p_x$ ,  $2p_y$ ,  $2p_z$ .



Table of nuclides (Segrè chart) from carbon to fluorine (including nitrogen). Orange indicates proton emission (nuclides outside the proton drip line); pink for positron emission (inverse beta decay); black for stable nuclides; blue for electron emission (beta decay); and violet for neutron emission (nuclides outside the neutron drip line). Proton number increases going up the vertical axis and neutron number going to the right on the horizontal axis.

somewhat alleviated by isotopic enrichment of <sup>15</sup>N by chemical exchange or fractional distillation. <sup>15</sup>N-enriched compounds have the advantage that under standard conditions, they do not undergo chemical exchange of their nitrogen atoms with atmospheric nitrogen, unlike compounds with labelled hydrogen, carbon, and oxygen isotopes that must be kept away from the atmosphere.<sup>[18]</sup>

Of the ten other isotopes produced synthetically, ranging from  $^{12}$ N to  $^{23}$ N,  $^{13}$ N has a half-life of ten minutes and the remaining isotopes have half-lives on the order of seconds ( $^{16}$ N and  $^{17}$ N) or even milliseconds. No other nitrogen isotopes are possible as they would fall outside the nuclear drip lines, leaking out a proton or neutron.  $^{[28]}$  The radioisotope  $^{16}$ N is the dominant radionuclide in the coolant of pressurised water reactors or boiling water reactors during normal operation, and thus it is a

sensitive and immediate indicator of leaks from the primary coolant system to the secondary steam cycle, and is the primary means of detection for such leaks. It is produced from <sup>16</sup>O (in water) via an (n,p) reaction in which the <sup>16</sup>O atom captures a neutron and expels a proton. It has a short half-life of about 7.1 s,<sup>[28]</sup> but during its decay back to <sup>16</sup>O produces high-energy gamma radiation (5 to 7 MeV).<sup>[28][29]</sup> Because of this, access to the primary coolant piping in a pressurised water reactor must be restricted during reactor power operation.<sup>[29]</sup>

### Source

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