

1		2																		3	4	5	6	7	8	9	10							
	H	He																		B	C	N	O	F	Ne									
11	Li	Be																	13	Al	Si	15	P	16	S	17	Cl	18	Ar					
19	K	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr
37	Rb	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe
55	Cs	Ba	57	La	58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu		
87	Fr	Ra	89	Ac	90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr		

11

Nitrogen

11.1 Introduction

Nitrogen is the most abundant uncombined element accessible to man. It comprises 78.1% by volume of the atmosphere (i.e. 78.3 atom% or 75.5 wt%) and is produced industrially from this source on the multimegatonne scale annually. In combined form it is essential to all forms of life, and constitutes, on average, about 15% by weight of proteins. The industrial fixation of nitrogen for agricultural fertilizers and other chemical products is now carried out on a vast scale in many countries, and the number of moles of anhydrous ammonia manufactured exceeds that of any other compound. Indeed, of the top fifteen "high-volume" industrial chemicals produced in the USA, five contain nitrogen (Fig. 11.1).⁽¹⁾ This has important consequences, predominantly beneficial but occasionally detrimental, since of all man's recent interventions in the cycles of nature the industrial fixation of nitrogen is by far the most extensive. These aspects will be discussed further in later sections.

The "discovery" of nitrogen in 1772 is generally credited to Daniel Rutherford, though the gas was also isolated independently about the same time by both C. W. Scheele and H. Cavendish.⁽²⁾ Rutherford (at the suggestion of his teacher Joseph Black who had earlier discovered CO₂, p. 269) was studying the properties of the residual "air" left after carbonaceous substances were burned in a limited supply of air; he removed the CO₂ by means of KOH and so obtained nitrogen which he thought was ordinary air that had taken up phlogiston from the combusted material. The elementary nature of nitrogen was disputed by some even as late as 1840 despite the work of A. L. Lavoisier. The name "nitrogen" was suggested by Jean-Antoine-Claude Chaptal in 1790 when it was realized that the element was a constituent of nitric acid and nitrates (Greek *νίτρον*, nitron; *γεννᾶν*, to form). Lavoisier preferred *azote* (Greek *ἄζωτικός*, no life) because

² M. E. WEEKS, in H. M. LEICESTER (ed.), *Discovery of the Elements*, 6th edn., Journal of Chemical Education Publication, 1956: Nitrogen, pp. 205-8; Rutherford, discoverer of nitrogen, pp. 235-51; Old compounds of nitrogen, pp. 188-95.

¹ Facts and Figures, *Chem. & Eng. News*, 23 June, 1997, pp. 40-1.

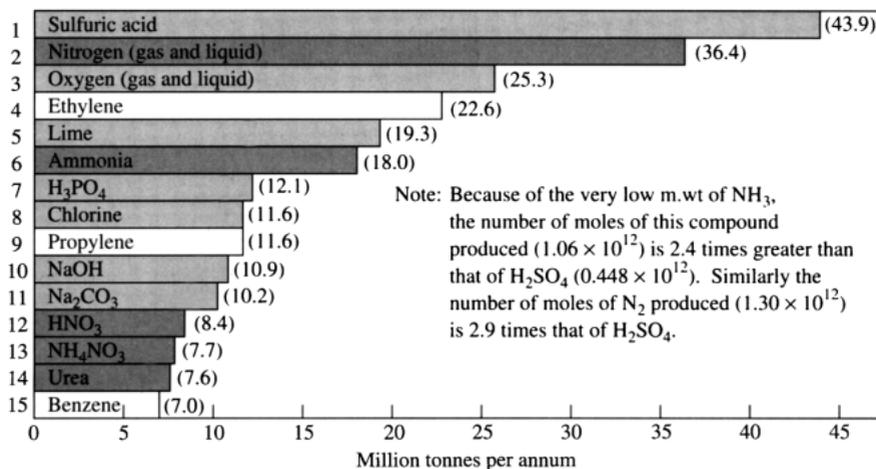


Figure 11.1 US production of the top 15 industrial chemicals (1996).

of the asphyxiating properties of the gas, and this name is still used in the French language and in such forms as azo, diazo, azide, etc. The German name *Stickstoff* refers to the same property (*sticken*, to choke or suffocate).

Compounds of nitrogen have an impressive history. Ammonium chloride was first mentioned in the *Historia* of Herodotus (fifth century BC)[†] and ammonium salts, together with nitrates, nitric acid and aqua regia, were well known to the early alchemists.⁽²⁾ Some important dates in the subsequent development of the chemistry of nitrogen are given in the Panel on p. 408. Exciting discoveries are still being made at the present time and, indeed, the detailed mechanisms by which bacteria fix nitrogen at

ambient temperatures and pressures is still an active area of research. Several recent reviews, monographs, and proceedings of symposia have been published.⁽³⁻⁶⁾

11.2 The Element

11.2.1 Abundance and distribution

Despite its ready availability in the atmosphere, nitrogen is relatively un abundant in the crustal rocks and soils of the earth. At 19 ppm it is equal 33rd with Ga in the order of abundance, and similar to Nb (20 ppm) and Li (18 ppm). The only major minerals are KNO₃ (nitre, saltpetre) and NaNO₃ (sodanitre, Chile saltpetre). Both occur widespread, usually in small amounts as evaporites in arid regions, often as an efflorescence on soils or in caverns. NaNO₃ is isomorphous with calcite (p. 109) whereas KNO₃ is isomorphous with aragonite (p. 109), thus reflecting the similar size of NO₃⁻ and CO₃²⁻, and the fact that K⁺ is considerably larger than Na⁺ and Ca²⁺. Major deposits of KNO₃ occur in India and there are smaller amounts in Bolivia, Italy, Spain and the former Soviet Union. There are vast deposits of NaNO₃ in the desert regions of northern Chile where it occurs with other evaporites such as NaCl, Na₂SO₄ and

[†] "There are pieces of salt in large lumps on the hills of Libya and the Ammonians who live there worship the god Ammon in a temple resembling that of the Theban Jupiter." (Greek Ἀμμων, the name of the Egyptian diety Amun, whence *sal ammoniac* from ἄμμωνιακόν, belonging to Ammon.)

³ R. W. F. HARDY, F. BOTTOMLEY and R. C. BURNS (eds.), *A Treatise on Dinitrogen Fixation*, Sections 1 and 2, Wiley, New York 1979, 812 pp.

⁴ J. CHATT, L. M. DA C. PINA and R. L. RICHARDS, *New Trends in the Chemistry of Nitrogen Fixation*, Academic Press, London, 1980, 284 pp.

⁵ J. CHATT, J. R. DILWORTH and R. L. RICHARDS, *Chem. Rev.* **78**, 589-625 (1978).

⁶ A. E. SHILOV, *Pure Appl. Chem.* **64**, 1409-20 (1992).

Time Chart for Nitrogen Chemistry

- 1772 N₂ gas isolated by D. Rutherford (also by C. W. Scheele and H. Cavendish).
 1772 N₂O prepared by J. Priestley who also showed it supported combustion
 1774 NH₃ gas isolated by Priestley using mercury in a pneumatic trough.
 1809 First donor-acceptor adduct (coordination compound) NH₃.BF₃ prepared by J. L. Gay Lussac (A. Werner's theory, 1891-5).
 1811 NCl₃ prepared by P. L. Dulong who lost an eye and three fingers studying its properties.
 1828 Urea made from NH₄CNO by F. Wöhler.
 1832 Phosphonitrilic chloride (NPCl₂)_x prepared by J. von Liebig by heating NH₃ or NH₄Cl with PCl₅.
 1835 S₄N₄ first prepared by M. Gregory.
 1862 Importance of N in soil for agriculture recognized (despite von Liebig having incorrectly maintained, in the face of fierce opposition, that it came from the atmosphere directly).
 1864 Ability of liquid NH₃ to dissolve metals giving coloured solutions reported by W. Weyl.
 1886 Atmospheric N₂ shown to be "fixed" by organisms in certain root nodules.
 1887 Hydrazine, N₂H₄, first isolated by T. Curtius; he also first made HN₃ (from N₂H₄) in 1890.
 1895 First industrial process involving atmospheric N₂ — the Frank-Caro process for calcium cyanamide.
 1900 Birkeland-Eyde industrial oxidation of N₂ to NO and hence HNO₃ (now obsolete).
 1906 Crystalline sulfamic acid, H₃NSO₃, first obtained by F. Raschig.
 1907 Raschig's industrial oxidation of NH₃ to N₂H₄ using hypochlorite.
 1908 Catalytic oxidation of NH₃ to HNO₃ (1901) developed on an industrial scale by W. Ostwald (awarded the 1909 Nobel Prize in Chemistry for his work on catalysis).
 1909 F. Haber's catalytic synthesis of NH₃ developed in collaboration with C. Bosch into a large-scale industrial process by 1913. (Haber was awarded the 1918 Nobel Prize in Chemistry "for the synthesis of ammonia from its elements"; Bosch shared the 1931 Nobel Prize for "contributions to the invention and development of chemical high-pressure methods", the Haber synthesis of NH₃ being the first high-pressure industrial process.)
 1926 Borazine, (HBNH)₃, analogous to benzene prepared by A. Stock and E. Pohland.
 1928 NF₃ first prepared by O. Ruff and E. Hanke, 117 y after NCl₃.
 1925-35 Spectrum of atomic N gradually analysed.
 1929 Discovery of a nitrogen isotope ¹⁵N by S. M. Naudé following the discovery of isotopes of O and C by others earlier in the same year.
 1934 Microwave absorption in NH₃ (due to molecular inversion) first observed — this marks the start of microwave spectroscopy.
 1950 Nuclear magnetic resonance in compounds, containing ¹⁴N and ¹⁵N first observed by W. E. Proctor and F. C. Yu.
 1957 N₂F₄ first made by C. B. Colburn and A. Kennedy and later (1961) shown to be in dissociative equilibrium with paramagnetic NF₂ above 100°C.
 1958 NH₃.BH₃ isoelectronic with ethane prepared by S. G. Shore and R. W. Parry (direct reaction of NH₃ and B₂H₆ gives [BH₂(NH₃)₂]⁺[BH₄]⁻).
 1962 First "bent" NO complex encountered, viz. [Co(NO)(S₂CNMe₂)₂] (P. R. H. Alderman, P. G. Owston and J. M. Rowe).
 1965 First N₂ ligand complex prepared by A. D. Allan and C. V. Senoff.
 1966 ONF₃ (isoelectronic with CF₄) discovered independently by two groups.
 1968 N₂ recognized as a bridging ligand in [(NH₃)₅RuN₂Ru(NH₃)₅]⁴⁺ by D. F. Harrison, E. Weissberger, and H. Taube. (H. Taube, 1983 Nobel Prize for chemistry "for his work on the mechanisms of electron transfer reactions especially in metal complexes").
 1974 First thionitrosyl (NS) complex isolated by J. Chatt and J. R. Dilworth.
 1975 (SN)_x polymer, known since 1910, found to be metallic (and a superconductor at temperatures below 0.33 K).
 1979 Trigonal prismatic 6-fold coordination of N (Table 11.1, p. 413).
 1980-90 Square pyramidal and trigonal bipyramidal 5-fold coordination of N (Table 11.1).

KNO₃ on the eastern slopes of the coastal ranges at an elevation of 1200-2500 m. Because of the development of the synthetic ammonia and nitric acid industries these large deposits are no longer a major source of nitrates, though they played an important role in agriculture until the 1920s (as also did guano, the massive deposits of bird excreta on certain islands).

The continuous interchange of nitrogen between the atmosphere and the biosphere is called the nitrogen cycle. Global estimates are difficult to obtain and there are frequently regional and local impacts which vary greatly from the mean. However, some indication of the size of the various "reservoirs" of nitrogen in the atmosphere, on land, and in the seas is

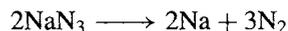
given in Fig. 11.2 together with the estimated annual rate of transfer between these various pools.^(7,8) Estimates frequently vary by a factor of 3 or more. Atmospheric nitrogen is fixed by biological action (p. 1035), industrial processes (p. 421), and to a significant extent by fires, lightning and other atmospheric discharges which produce NO_x . There is also a minute production (on the global scale) of NO_x from internal combustion engines and from coal-burning, though the local concentration in some urban environments can be very high and extremely unpleasant.⁽⁹⁻¹¹⁾ Absorption of fixed nitrogen by both terrestrial and aquatic plants leads to protein synthesis followed by death, decay, oxidation and denitrification by bacterial and other action which eventually returns the nitrogen to the seas and the atmosphere as N_2 . An alternative sequence involves the digestion of plants by animals, the synthesis of animal proteins, excretion of nitrogenous material, and, again, ultimate death, decay and denitrification. Figure 11.2 indicates that the greatest anthropogenic impact on the cycle arises from the industrial fixation of nitrogen by the Haber and other processes. Much of this is used beneficially as fertilizers but the leaching of excess nitrogenous material can lead to eutrophication in freshwater systems, and the increased nitrate concentration in waters used for human consumption can pose a health hazard. Nevertheless, there is no doubt that the high yields of agriculture necessary to maintain even the present human population of the world cannot be achieved without the judicious application of manufactured nitrogenous fertilizers. Concern has also been expressed that increasing levels

of N_2O following denitrification may eventually impoverish the ozone layer in the stratosphere. Much more data are required and the subject is being actively pursued by several international agencies as well as by national and local governments and individual scientists.

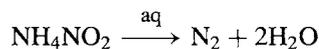
11.2.2 Production and uses of nitrogen

The only important large-scale process for producing N_2 is the liquefaction and fractional distillation of air⁽¹²⁾ (see Panel on p. 411). Production has grown remarkably during the past few years, partly as a result of the increasing demand for its coproduct O_2 for steelmaking. For example, US domestic production has increased 250-fold in the past 25 y from 0.12 million tonnes in 1955 to 30 million tonnes in 1980. In 1991 world production was 56 million tonnes (USA 47%; Europe 35%; Asia 15%). Commercial N_2 is a highly purified product, typically containing less than 20 ppm O_2 . Specially purified "oxygen-free" N_2 , containing less than 2 ppm, is available commercially, and "ultrapure" N_2 (99.999%) containing less than 10 ppm Ar is also produced on the multitonne per day scale.

Laboratory routes to highly purified N_2 are seldom required. Thermal decomposition of sodium azide at 300°C under carefully controlled conditions is one possibility:



Hot aqueous solutions of ammonium nitrite also decompose to give nitrogen though small amounts of NO and HNO_3 are also formed (p. 434) and must be removed by suitable absorbents such as dichromate in aqueous sulfuric acid:



Other routes are the thermal decomposition of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, the reaction of NH_3 with bromine water, or the high-temperature reaction of NH_3

⁷ C. C. DELWICHE, The nitrogen cycle, Chap. 5 in C. L. HAMILTON (ed.), *Chemistry in the Environment*, Readings from Scientific American, W. H. Freeman, San Francisco, 1973.

⁸ SCOPE Report No. 10, *Environmental Issues*, Wiley, New York, 1977, 220 pp.

⁹ J. HEICKLEN, *Atmospheric Chemistry*, Academic Press, 1976, 406 pp.

¹⁰ I. M. CAMPBELL, *Energy and the Atmosphere*, 2nd edn. Wiley, London, 1986, Nitrogen cycles, pp 169-81.

¹¹ U. S. OZKAN, S. K. AGARWAL and G. MARCELIN (eds.), *Reduction of Nitrogen Oxide Emissions*, ACS Symposium Series No. 587, 1995, 260 pp.

¹² W. J. GRANT and S. L. REDFEARN, Industrial gases, in R. THOMPSON (ed.), *The Modern Inorganic Chemicals Industry*, Chem. Soc. Special Publ. 31, 273-301 (1977).

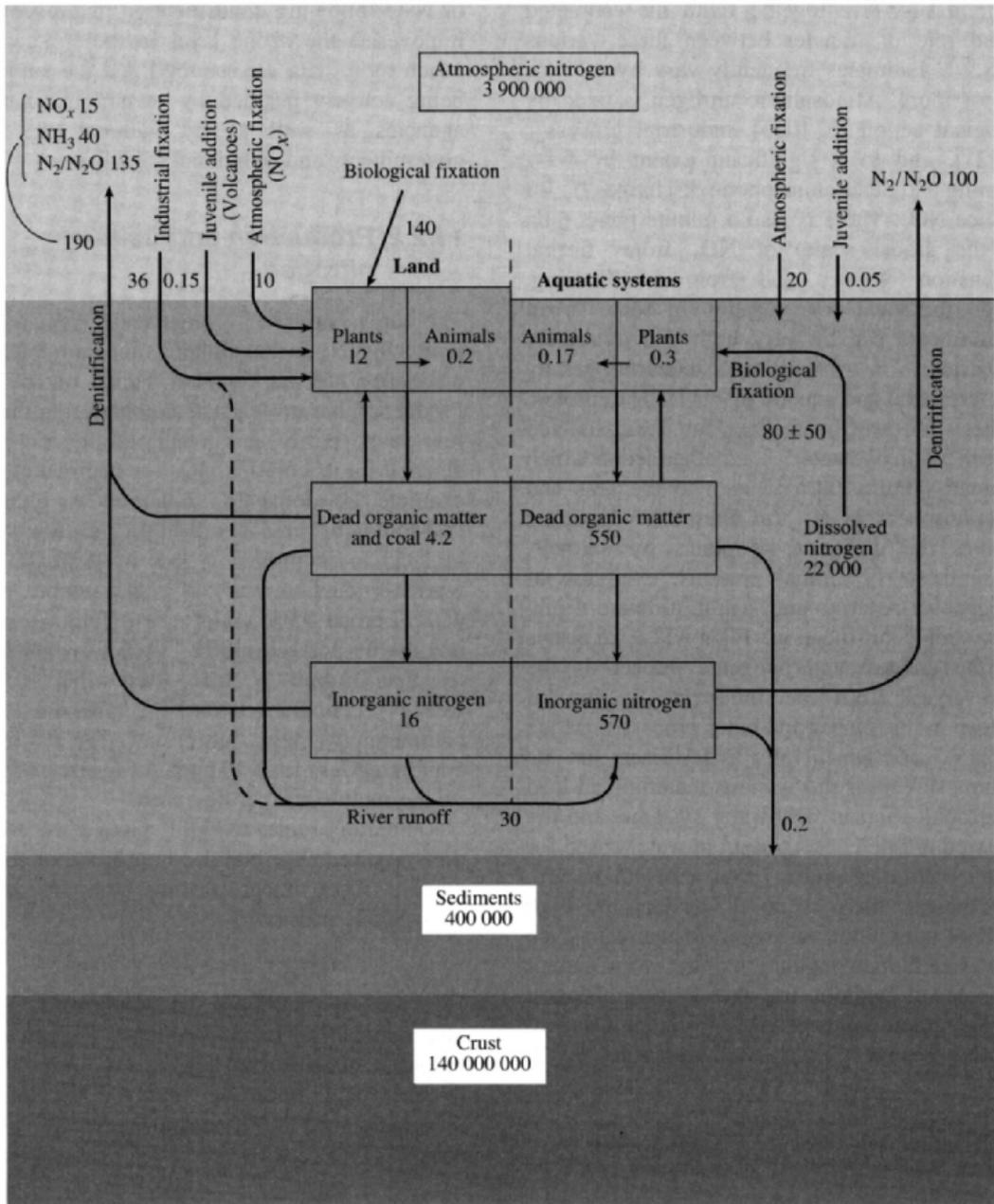


Figure 11.2 Distribution of nitrogen in the biosphere and annual transfer rates can be estimated only within broad limits. The two quantities known with high confidence are the amount of nitrogen in the atmosphere and the rate of industrial fixation. The inventories (within the boxes) are expressed in terms of 10^9 tonnes of N; the transfers (indicated by arrows) are in 10^6 tonnes of N. Taken from ref. 7 with some adjustments for more recent data.

Industrial Gases from Air

Air is the source of six industrial gases, N₂, O₂, Ne, Ar, Kr and Xe. As the mass of the earth's atmosphere is approximately 5×10^9 million tonnes, the supply is unlimited and the annual industrial production, though vast, is insignificant by comparison. The composition of air at low altitudes is remarkably constant, the main variable component being water vapour which ranges from ~4% by volume in tropical jungles to very low values in cold or arid climates. Other minor local variations result from volcanism or human activity. The main invariant part of the air has the following composition (% by volume, bp in parentheses):

N ₂	78.03 (77.2 K)	CO ₂	0.033 (194.7 K)	He	0.0005 (4.2 K)
O ₂	20.99 (90.1 K)	Ne	0.0015 (27.2 K)	Kr	0.0001 (119.6 K)
Ar	0.93 (87.2 K)	H ₂	0.0010 (20.2 K)	Xe	0.000008 (165.1 K)

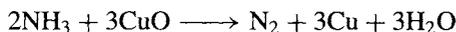
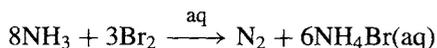
Details of the production and uses of O₂ (p. 604) and the noble gases (p. 889) are in later chapters.

About two-thirds of the N₂ produced industrially is supplied as a gas, mainly in pipes but also in cylinders under pressure. The remaining one-third is supplied as liquid N₂ since this is also a very convenient source of the dry gas. The main use is as an inert atmosphere in the iron and steel industry and in many other metallurgical and chemical processes where the presence of air would involve fire or explosion hazards or unacceptable oxidation of products. Thus, it is extensively used as a purge in petrochemical reactors and other chemical equipment, as an inert diluent for chemicals, and in the float glass process to prevent oxidation of the molten tin (p. 370). It is also used as a blanketing gas in the electronics industry, in the packaging of processed foods and pharmaceuticals, and to pressurize electric cables, telephone wires, and inflatable rubber tyres, etc.

About 10% of the N₂ produced is used as a refrigerant. Typical of such applications are (a) freeze grinding of normally soft or rubbery materials, (b) low-temperature machining of rubbers, (c) shrink fitting and assembly of engineering components, (d) the preservation of biological specimens such as blood, semen, etc., and (e) as a constant low-temperature bath (−196°C). Liquid N₂ is also frequently used for convenience in applications where a very low temperature is not essential such as (a) food freezing (and hamburger meat grinding), (b) in-transit refrigeration, (c) freeze branding of cattle, (d) pipe-freezing for stopping flow in the absence of valves, and (e) soil-freezing for consolidating unstable ground in tunnelling or excavation.

The cost of N₂, like that of O₂, is particularly dependent on electricity costs, though plant maintenance and transport costs also obtrude. Typical prices in 1992 for N₂ in the USA were about \$32 per tonne for bulk liquid (exclusive of transportation and handling charges). Costs for small-scale users of N₂ from gas cylinders are proportionately much higher.

with CuO; overall equations can be written as:



11.2.3 Atomic and physical properties

Nitrogen has two stable isotopes ¹⁴N (relative atomic mass 14.003 07, abundance 99.634%) and ¹⁵N (15.000 11, 0.366%); their relative abundance (272:1) is almost invariant in terrestrial sources and corresponds to an atomic weight of 14.006 74(7). Both isotopes have a nuclear spin and can be used in nmr experiments.⁽¹³⁾ though

the sensitivity at constant field is only one-thousandth that of ¹H. The ¹⁴N nucleus has a spin quantum number of 1 and, in consequence, the spectra are broadened by quadrupole effects. The ¹⁵N nucleus with spin $\frac{1}{2}$ does not have this difficulty though its low abundance poses problems.⁽¹⁴⁾ Interestingly, the first chemical shift ever to be observed in nmr spectroscopy ("as an annoying ambiguity in the magnetic moment of ¹⁴N") was in 1950 in an aqueous solution of NH₄NO₃.⁽¹⁵⁾ Nowadays ¹⁴N and ¹⁵N nmr chemical shifts are widely used to probe the

1981, 382 pp. J. MASON, Nitrogen, in J. MASON (ed.), *Multinuclear NMR*, Plenum Press, New York, pp. 335–67 (1987).

¹⁴ G. C. LEVY and R. L. LICHTER, *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*, Wiley, New York, 1979, 221 pp. W. VON PHILIPSBORN and R. MÜLLER, *Angew. Chem. Int. Edn. Engl.* **25**, 383–413 (1986).

¹⁵ W. G. PROCTOR and F. C. YU, *Phys. Rev.* **77**, 717 (1950).

¹³ G. J. MARTIN, M. L. MARTIN and J.-P. GOUESNARD, *NMR Volume 18: ¹⁵N NMR Spectroscopy*, Springer-Verlag, Berlin,

nature of bonding in N-containing compounds, to study structural features (e.g. linear, bent, encapsulated N), to determine the site of coordination or protonation, to follow kinetically the course of chemical reactions and to detect new species.

Isotopic enrichment of ^{15}N is usually effected by chemical exchange, and samples containing up to 99.5% ^{15}N have been obtained from the 2-phase equilibrium



Other exchange reactions that have been used are:



Fractional distillation of NO provides another effective route and, as the heavier isotope of oxygen is simultaneously enriched, the product has a high concentration of $^{15}\text{N}^{18}\text{O}$. Many key nitrogen compounds are now commercially available with ^{15}N enriched to 5%, 30% or 95%, e.g. N_2 , NO, NO_2 , NH_3 , HNO_3 and several ammonium salts and nitrates. Fortunately the use of these compounds in tracer experiments is simplified by the absence of exchange with atmospheric N_2 under normal conditions, in marked contrast with labelled H, C and O compounds where contact with atmospheric moisture and CO_2 must be avoided.

The ground state electronic configuration of the N atom is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ with three unpaired electrons (4S). The electronegativity of N (~ 3.0) is exceeded only by those of F and O. Its "single-bond" covalent radius (~ 70 pm) is slightly smaller than those of B and C, as expected; the nitride ion, N^{3-} , is much larger and has been assigned a radius in the range 140–170 pm. Ionization energies and other properties are compared with those of the other Group 15 elements (P, As, Sb and Bi) on p. 550.

Molecular N_2 , i.e. dinitrogen (see p. 34), (mp -210°C , bp -195.8°C) is a colourless, odourless, tasteless, diamagnetic gas. The short interatomic distance (109.76 pm) and very high dissociation energy ($945.41 \text{ kJ mol}^{-1}$) are both

consistent with multiple bonding. The free-energy change for the equilibrium $\text{N}_2 \rightleftharpoons 2\text{N}$ is $\Delta G = 911.13 \text{ kJ mol}^{-1}$ from which it is clear that the dissociation constant $K_p = [\text{N}]^2/[\text{N}_2]$ atm is negligible under normal conditions; it is 1.6×10^{-24} atm at 2000 K and still only 1.3×10^{-12} atm at 4000 K. Detailed tabulations of other physical properties of nitrogen are available.⁽¹⁶⁾

11.2.4 Chemical reactivity

Gaseous N_2 is rather inert at room temperature presumably because of the great strength of the $\text{N}\equiv\text{N}$ bond and the large energy gap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO). Further contributory factors are the very symmetrical electron distribution in the molecule and the absence of bond polarity — when these are modified, as in the isoelectronic analogues CO, CN^- and NO^+ , the reactivity is considerably enhanced. Nitrogen reacts readily with Li at room temperature (p. 76) and with several transition-element complexes (p. 414).

Reactivity increases rapidly with rising temperature and the element combines directly with Be, the alkaline earth metals, and B, Al, Si and Ge to give nitrides (p. 417); hydrogen yields ammonia (p. 421), and coke yields cyanogen, $(\text{CN})_2$, when heated to incandescence (p. 320). Many finely divided transition metals also react directly at elevated temperatures to give nitrides of general formula MN ($\text{M} = \text{Sc}, \text{Y}, \text{lanthanoids}; \text{Zr}, \text{Hf}; \text{V}; \text{Cr}, \text{Mo}, \text{W}; \text{Th}, \text{U}, \text{Pu}$). Although not always directly preparable from $\text{N}_2(\text{g})$, many other nitrides are known (p. 417) and, indeed, nitrides as a class include some of the most stable compounds in the whole of chemistry. Nitrogen forms bonds with almost all elements in the periodic table, the only exceptions apparently being the noble gases (other than Xe and Kr, pp. 902, 904). A wide range of stereochemistries is observed and

¹⁶ B. R. BROWN, Physical properties of nitrogen, in *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 8, Suppl. 1, *Nitrogen*, Part 1, pp. 27–149, Longmans, London, 1964.

Table 11.1 Stereochemistry of nitrogen^(a)

CN	Examples
0	N(g) in "active nitrogen"
1	N ₂ , NO, NNO, [N ₃ N] ⁻ , HN ₃ , RC≡N, XC≡N (X = Hal), [OsO ₃ N] ⁻
2	<i>Linear:</i> [NO ₂] ⁺ , NNO, [N ₃ N] ⁻ , HN ₃ ; η ¹ -N ₂ complexes, e.g. [Ru(N ₂)(NH ₃) ₅] ²⁺ ; η ¹ -NO complexes, e.g. [Fe(CN) ₅ (NO)] ²⁻ ; μ ₂ -N complexes, e.g. [(H ₂ O)Cl ₄ RuNRuCl ₄ (OH ₂)] ³⁻ and [Cl ₅ WNWCl ₅] ²⁻ (ref. 18)
	<i>Bent:</i> NO ₂ , [NO ₂] ⁻ , [NH ₂] ⁻ , HN ₃ , HNCO, RNCO, XNCO, N ₂ F ₂ , <i>cyclo</i> - $\overline{\text{CH}_2\text{NN}}$, <i>cyclo</i> -[NSF(O)] ₃ [W(CO) ₅ OPPh ₂ NPPPh ₃] (ref. 19)
3	<i>Planar:</i> [NO ₃] ⁻ , N ₂ O ₄ , XNO ₂ , (HO)NO ₂ , K[ON(NO)(SO ₃)], K ₂ [ON(SO ₃) ₂] (Fremy's salt), N(SiH ₃) ₃ , NMe(SiMe ₃) ₂ (ref. 20), N(GeH ₃) ₃ , N(PF ₂) ₃ , Si ₃ N ₄ , and Ge ₃ N ₄ (Be ₂ SiO ₄ structure, p. 347), μ ₃ -N complexes, e.g. [(H ₂ O(SO ₄) ₂ Ir) ₃ N] ⁴⁻
	<i>Pyramidal:</i> NH ₃ , NF ₃ , NH ₂ F, NHF ₂ , (HO)NH ₂ , N ₂ H ₄ , N ₂ F ₄ , [N ₄ (CH ₂) ₆]
	<i>T-shaped:</i> [Mo ₃ (μ ₃ -N)O(η ⁵ -C ₅ H ₅) ₃ (CO) ₄] (ref. 21)
4	<i>Tetrahedral:</i> [NH ₄] ⁺ , [NH ₃ (OH)] ⁺ , [NF ₄] ⁺ , H ₃ NBF ₃ and innumerable other coordination complexes of NH ₃ , NR ₃ , en, edta, etc., including Me ₃ NO and sulfamic acid (H ₃ NSO ₃). BN (layer structure and Zn blende-type), AlN (wurtzite-type), [PhAlNPh] ₄ (cubane-type)
	<i>See-saw:</i> [Fe(CO) ₃] ₄ (μ ₄ -N) ⁻ (refs. 22, 23)
5	<i>Square-pyramidal:</i> [Fe ₅ (CO) ₁₄ H(μ ₅ -N)] (ref. 23), [(η ⁵ -C ₅ Me ₅) ₂ Mo ₂ Co ₃ (CO) ₁₀ (μ ₅ -N)] (ref. 24), <i>closo</i> -NB ₉ H ₁₀ (p. 211)
	<i>Trig. bipyramidal:</i> [N(AuPPh ₃) ₅] ²⁺ (ref. 25)
6	<i>Octahedral:</i> MN (interstitial nitrides with NaCl or hcp structure, e.g. M = Sc, La; Ce, Pr, Nd; Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Th, U), Ti ₂ N (anti-rutile TiO ₂ -type), Cu ₃ N (ReO ₃ -type), Ca ₃ N ₂ (anti-Mn ₂ O ₃)
	<i>Trigonal prism:</i> [NC ₆ (CO) ₁₅] ⁻ (ref. 26), [Rh ₁₂ H(N) ₂ (CO) ₂₃] ³⁻ (ref. 27)
	<i>Pentagonal prism:</i> <i>closo</i> -NB ₁₁ H ₁₂ (p. 211)
8	<i>Cubic:</i> Ternary nitrides with anti-CaF ₂ structure, e.g. BeLiN, AlLi ₃ N ₂ , TiLi ₅ N ₃ , NbLi ₇ N ₄ , and CrLi ₉ N ₅
	<i>Square antiprism:</i> [Rh ₁₂ H(N) ₂ (CO) ₂₃] ³⁻ (ref. 27)

^(a)For coordination numbers 1, 2, and 3 the CN is sometimes increased in the condensed phase as a result of H bonding (p. 52), e.g. HCN, NH₂⁻, NH₃, N₂H₄, NH₂(OH), NO₂(OH).

typical examples of coordination numbers 0, 1, 2, 3, 4, 5, 6, and 8 are given in Table 11.1.

A particularly reactive form of nitrogen can be obtained by passing an electric discharge through N₂(g) at a pressure of 0.1–2 mmHg.^(16,17) Atomic

N is formed, and the process is accompanied by a peach-yellow emission which persists as an after-glow, often for several minutes after the discharge

²¹ N. D. FEASEY, S. A. R. KNOX and A. G. ORPEN, *J. Chem. Soc., Chem. Commun.*, 75–6 (1982).

²² D. FJARE and W. L. GLADFELTER, *J. Am. Chem. Soc.* **103**, 1572–4 (1981); **106**, 4799–4810 (1984).

²³ M. TACHIKAWA, J. STEIN, E. L. MUEHTERTIES, R. G. TELLER, M. A. BENO, E. GEBERT and J. M. WILLIAMS, *J. Am. Chem. Soc.* **102**, 6648–9 (1980).

²⁴ C. P. GIBSON and L. F. DAHL, *Organometallics* **7**, 543–52 (1988).

²⁵ A. GROHMANN, J. RIEDE and H. SCHMIDBAUR, *Nature* **345**, 140–2 (1990).

²⁶ S. MARTINENGO, G. CIANI, A. SIRONI, B. T. HEATON and J. MASON, *J. Am. Chem. Soc.* **101**, 7095–7 (1979).

²⁷ S. MARTINENGO, G. CIANI and A. SIRONI, *J. Chem. Soc., Chem. Commun.*, 1742–4 (1986).

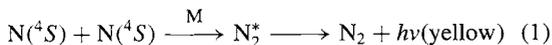
¹⁷ A. N. WRIGHT and C. A. WINKLER, *Active Nitrogen*, Academic Press, New York, 1968.

¹⁸ F. WELLER, W. LIEBELT and K. DEHNICKE, *Angew. Chem. Int. Edn. Engl.* **19**, 220 (1980). [The W–N–W linkage is linear and the interatomic distances are 166 pm (W^{VI}-N) and 207 pm (W^V-N).

¹⁹ D. J. DARENSBOURG, M. PALA, D. SIMMONS and A. L. RHEINGOLD, *Inorg. Chem.* **25**, 2537–41 (1986). See also H. G. ANG, Y. M. CAI, L. L. KOH and W. L. KWIK, *J. Chem. Soc., Chem. Commun.*, 850–2 (1991).

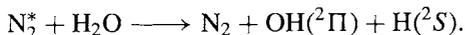
²⁰ D. W. H. RANKIN and H. E. ROBERTSON, *J. Chem. Soc., Dalton Trans.*, 785–8 (1987).

has been stopped. Atoms of N in their ground state (4S) have a relatively long lifetime since recombination involves either a 3-body collision on the surface of the vessel (first-order reaction in N at pressures below ~ 3 mmHg) or a termolecular homogeneous association reaction (second order in N at pressures above ~ 3 mmHg):



The molecules of N_2^* so formed are in an excited state ($B^3\Pi_g$) and give rise to the emission of the first positive band system of the spectrum of molecular N_2 in returning to the ground state ($A^3\Sigma_u^+$).

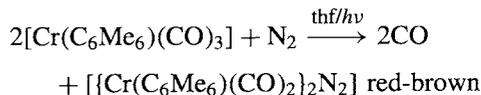
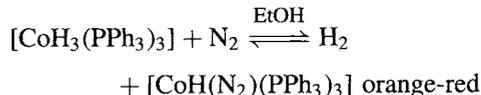
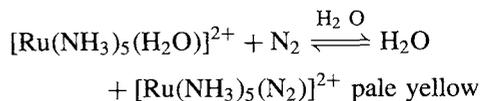
Several elements react with the N atoms in active nitrogen to form nitrides. The excited N_2 molecules are also highly reactive and can cause the dissociation of molecules that are normally stable to attack either by ordinary N_2 or even N atoms, e.g.:



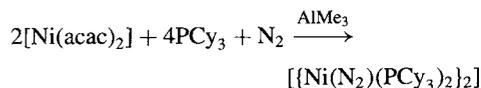
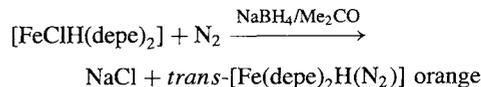
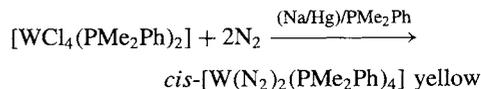
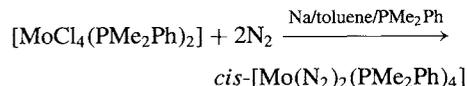
One of the most dramatic developments in the chemistry of N_2 during the past 30 years was the discovery by A. D. Allen and C. V. Senoff in 1965 that dinitrogen complexes such as $[Ru(NH_3)_5(N_2)]^{2+}$ could readily be prepared from aqueous $RuCl_3$ using hydrazine hydrate in aqueous solution.⁽²⁸⁾ Since that time virtually all transition metals have been found to give dinitrogen complexes and several hundred such compounds are now characterized.^(5,29,30) Three general preparative methods are available:

(a) Direct replacement of labile ligands in metal complexes by N_2 : such reactions

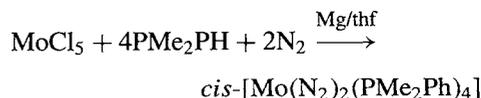
proceed under mild conditions and are often reversible, e.g.:



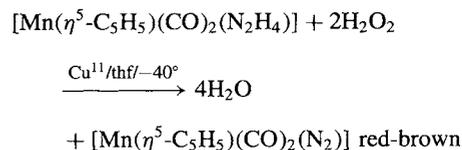
(b) Reduction of a metal complex in the presence of an excess of a suitable coligand under N_2 , e.g.:



where *depe* is $Et_2PCH_2CH_2PET_2$, *acac* is 3,5-pentanedionate, and PCy_3 is tris(cyclohexyl)phosphine. In some systems Mg/thf is a better reducing agent than Na, e.g.:



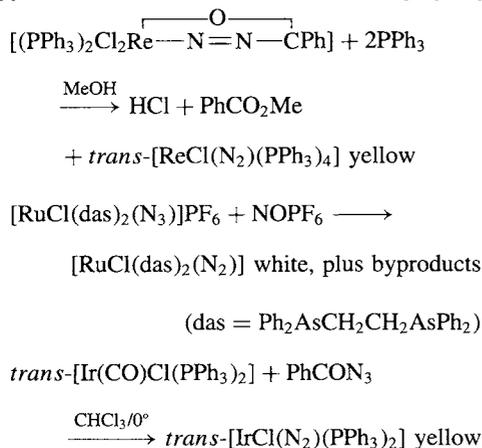
(c) Conversion of a ligand with N–N bonds into N_2 ; in the early development of N_2 complex chemistry this was the most successful and widely used route, e.g.:



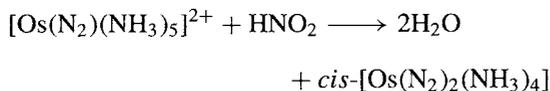
²⁸ A. D. ALLEN and C. V. SENOFF, *Chem. Commun.*, 1965, 621–2. The unprecedented nature of the reaction can be gauged from the fact that this paper was rejected for publication by *J. Am. Chem. Soc.* on the grounds that it was impossible, before being accepted by *Chem. Commun.*. See also H. TAUBE, The researches of A. D. Allen — an appreciation, *Coord. Chem. Rev.* **26**, 1–5 (1978).

²⁹ A. D. ALLEN, R. O. HARRIS, B. R. LOESCHER, J. R. STEVENS and R. N. WHITELEY, *Chem. Revs.* **73**, 11–20 (1973).

³⁰ D. SELLMANN, *Angew. Chem. Int. Edn. Engl.* **13**, 639–49 (1974).

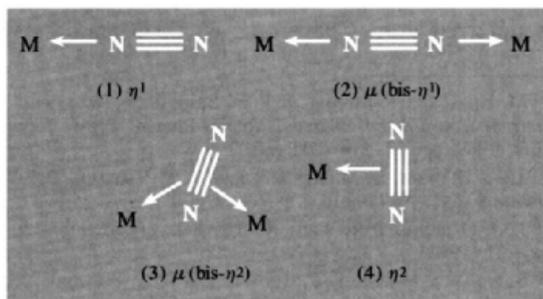


A related example is the reaction of NbCl_5 and thf with $(\text{Me}_3\text{Si})_2\text{NN}(\text{SiMe}_3)_2$ in CH_2Cl_2 to give an 80% yield of $[(\mu\text{-N}_2)\{\text{NbCl}_3(\text{thf})_2\}_2]$.⁽³¹⁾ Occasionally an $\text{N}\equiv\text{N}$ triple bond can be formed within a metal complex, e.g. by reaction of coordinated NH_3 with HNO_2 , but this method is of limited application, e.g.:



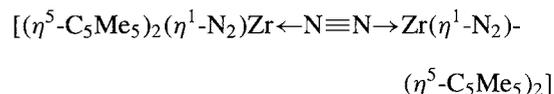
Frequently dinitrogen complexes have colours in the range white-yellow-orange-red-brown but other colours are known, e.g. $[\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\}_2\text{(N}_2)]$ is blue.

Dinitrogen might coordinate to metals in at least 4 ways,⁽³²⁾ but only the end-on modes, structures (1) and (2), are well established as common bonding modes by numerous well-defined examples:



The side-on structure (3) has been established in two dinickel complexes which have very complicated structures involving lithium atoms also in association with the bridging N_2 .⁽³³⁾ It also occurs in the first fully characterized N_2 complex of a lanthanide element, $[(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)\{\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\}_2]$.⁽³⁴⁾ The “side-on” η^2 mode (structure 4) was at one time thought to be exemplified by the rhodium(I) complex $[\text{RhCl(N}_2\text{)(PPr}_3)_2]$ but a reinvestigation of the X-ray structure by another group⁽³⁵⁾ showed conclusively that the N_2 ligand was coordinated in the “end-on” mode (1) — an instructive example of mistaken conclusions that can initially be drawn from this technique. The side on structure (4) has been postulated for the zirconium(III) complex $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2(\text{N}_2)\text{R}]$ on the basis of its ^{15}N nmr spectrum.⁽³⁶⁾ A unique triply-coordinated bridging mode ($\mu_3\text{-N}_2$) has also recently been established by X-ray crystallography.⁽³⁷⁾

Complexes are known which feature more than one N_2 ligand, e.g. $\text{cis-[W(N}_2)_2(\text{PMe}_2\text{Ph)}_4]$ and $\text{trans-[W(N}_2)_2(\text{diphos})_2]$ (where $\text{diphos} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) and some complexes feature more than one bonding mode, e.g.:⁽³⁸⁾



³¹ J. R. DILWORTH, S. J. HARRISON, R. A. HENDERSON and D. R. M. WALTON, *J. Chem. Soc., Chem. Commun.*, 176–7 (1984).

³² K. JONAS, D. J. BRAUER, C. KRÜGER, P. J. ROBERTS and Y.-H. TSAY, *J. Am. Chem. Soc.* **98**, 74–81 (1976). P. R. HOFFMAN, T. YOSHIDA, T. OKANO, S. OTSUKA and J. IBERS, *Inorg. Chem.* **15**, 2462–6 (1976).

³³ K. KRÜGER and Y.-H. TSAY, *Angew. Chem. Int. Edn. Engl.* **12**, 998–9 (1973).

³⁴ W. J. EVANS, T. A. ULIBARRI and J. W. ZILLER, *J. Am. Chem. Soc.* **110**, 6877–9 (1988).

³⁵ D. L. THORN, T. H. TULIP and J. A. IBERS, *J. Chem. Soc., Dalton Trans.*, 2022–5 (1979).

³⁶ M. J. S. GYNANE, J. JEFFREY and M. F. LAPPERT, *J. Chem. Soc., Chem. Commun.*, 34–6 (1978).

³⁷ G. P. PEZ, P. APGAR and R. K. CRISSEY, *J. Am. Chem. Soc.* **104**, 482–90 (1982).

³⁸ R. D. SANNER, J. M. MANRIQUEZ, R. E. MARSH and J. E. BERCAW, *J. Am. Chem. Soc.* **98**, 8351–7 (1976).