# Molecular nitrogen: inert but essential

*Tim G. Harrison, M. Anwar H. Khan, Beth M. A. Shallcross, Esther D. G. Shallcross and Dudley E. Shallcross*

**Abstract** Nitrogen gas dominates the Earth's atmosphere but is largely ignored. Molecular nitrogen is extremely stable and so nitrogen is termed inert. What would happen if another 'inert' gas were the dominant species instead of molecular nitrogen? Here we show how unique nitrogen is and how important it has been to life on planet Earth.

## Nitrogen cycle

Molecular nitrogen ($N_2$) consists of two nitrogen atoms bound by a triple bond with an interatomic distance of 1.095 Å and dissociation energy of 941 kJ mol$^{-1}$ (Shilov, 2003). The large energy difference between the highest occupied and lowest unoccupied molecular orbitals (10.82 eV) makes electron transfer reactions for $N_2$ unfavourable. The non-polar nature of $N_2$, its high ionisation potential, low proton affinity and negative electron affinity can confirm its inertness (Zhan, Nichols and Dixon, 2003). The atmospheric lifetime of $N_2$ is of the order of millions of years.

Breaking the triple bond of $N_2$ and releasing the nitrogen atoms, an essential element for living organisms, requires a large amount of energy (942 kJ mol$^{-1}$). It is strange to imagine that plants grow in an $N_2$-rich atmosphere but cannot use this nitrogen as a nutrient. Nitrogen-fixing bacteria are required to break the N–N bond, producing species such as ammonia ($NH_3$/$NH_4^+$) that plants can utilise (Preininger and Gyurján, 2001). Lightning discharges also break the N–N bond and lead to NO production, which can be further oxidised and also lead to a source of nitrogen that is accessible to organisms. Industrially, $N_2$ is converted to $NH_3$ and nitrogen-rich fertilisers through the Haber–Bosch process to supplement the natural nitrogen fixation. $N_2$ is also fixed unintentionally through the formation of NOx by different man-made activities, for example during the combustion of fossil fuels by internal combustion engines and industrial activity, including electricity production.

## What would happen if the Earth's atmosphere were made up mainly of another gas?

It is interesting to speculate what would happen if the Earth's atmosphere were predominantly another 'inert' gas in place of nitrogen. How would biological systems access nitrogen if it were a minor constituent of the atmosphere? The organisms would probably be very different. Some gases that are quite inert, carbon dioxide ($CO_2$) and nitrous oxide ($N_2O$) for example, would be ruled out because they would be potent greenhouse gases, leading to a runaway greenhouse effect, which in the case of $CO_2$ is observed on the planet Venus (Rasool and de Bergh, 1970). If the atmosphere were mainly $N_2O$, apart from making the surface too warm to live on, humans would be laughing all the time, as $N_2O$ is also known as laughing gas and is used as a painkiller in both dental and medical applications (Emmanouil and Quock, 2007). It would also cause severe depletion of the stratospheric ozone layer, being a natural precursor to the catalytic removal species NO (Ravishankara, Daniel and Portmann, 2009). Isoelectronic with $N_2$, CO would be a much weaker greenhouse gas than $CO_2$ and $N_2O$ but would combine with haemoglobin in the blood more efficiently than $O_2$ (Ganong, 1995) and would therefore be a bad substitute.

Several noble gases would be suitable substitutes, in terms of being inert, for example helium (He), neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe). Whereas $N_2$ and $O_2$ have similar densities, He and Ne have a much lower density than $O_2$ and so the atmosphere would separate over time, with $O_2$ concentrated at the surface and the noble gas He or Ne in the upper atmosphere (without considering loss of He or Ne from the atmosphere). In a similar way, Kr and Xe would dominate in the lower atmosphere as they are denser than $O_2$, leading to low levels of $O_2$ at the surface. Ar has a similar density to $O_2$ and so the 'new' atmosphere would be reasonably well mixed.

Many reactions in the atmosphere are called association reactions, meaning that two species (often involving free radicals) come together to form a new molecule. One of the most important reactions leads to the formation of ozone in the stratosphere (10–50 km in altitude). It is well known that the 'ozone layer' is essential to protect the surface of the Earth, and organisms that live there, from harmful radiation from the Sun. However, the rate of the formation reaction:

$$O + O_2 + M \rightarrow O_3 + M$$

depends on the bulk gas M, and if it were Ar instead of $N_2$ then the ozone layer would form at a lower altitude. This would change the atmospheric circulation, the radiation budget of the lower atmosphere and much more. Therefore, although it is inert, nitrogen shapes life on Earth and is an essential ingredient of the current diversity observed.

## References


Emmanouil, D.E. and Quock, R.M. (2007) Advances in understanding the actions of nitrous oxide. *Anesthesia Progress*, **54**(1), 9–18.

Ganong, W.F. (1995) *Review of Medical Physiology*. 17th edn. Norwalk: Appleton & Lange.

Preininger, É. and Gyurján, I. (2001) Trials to create artificial nitrogen-fixing symbioses and associations using in vitro methods: an outlook. *In Vitro Cellular & Developmental Biology – Plant*, **37**(2), 139–148.

Rasool, S.I. and de Bergh, C. (1970) The runaway greenhouse and the accumulation of $CO_2$ in the Venus atmosphere. *Nature*, **226**, 1037–1039.

Ravishankara, A.R., Daniel, J.S. and Portmann, R.W. (2009) Nitrous oxide ($N_2O$): the dominant ozone depleting substance emitted in the 21st century. *Science*, **326**(5949), 123–125.

Shilov, A.E. (2003) Catalytic reduction of molecular nitrogen in solutions. *Russian Chemical Bulletin, International Edition*, **52**(12), 2555–2562.

Zhan, C.-G., Nichols, J.A. and Dixon, D.A. (2003) Ionization potential, electron affinity, electronegativity, hardness, and electron excitation energy: molecular properties from density functional theory orbital energies. *The Journal of Physical Chemistry A*, **107**(20), 4184–4195.



**Tim Harrison** is Director of Outreach, School Teacher Fellow and Science Communicator in Residence at the School of Chemistry, University of Bristol.
**Anwar Khan** is a Senior Research Fellow at the School of Chemistry, University of Bristol.
**Beth Shallcross** is a pharmacist at the Bristol Royal Infirmary.
**Esther Shallcross** studies pharmacy at the University of Manchester.
**Dudley Shallcross** is a Professor of Atmospheric Chemistry at the School of Chemistry, University of Bristol. Email: D.E.Shallcross@bristol.ac.uk