

Molecular nitrogen: inert but essential

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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 NO_x 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). Isolectronic 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:



depends on the bulk gas M, and if it were Ar instead of N₂ 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.

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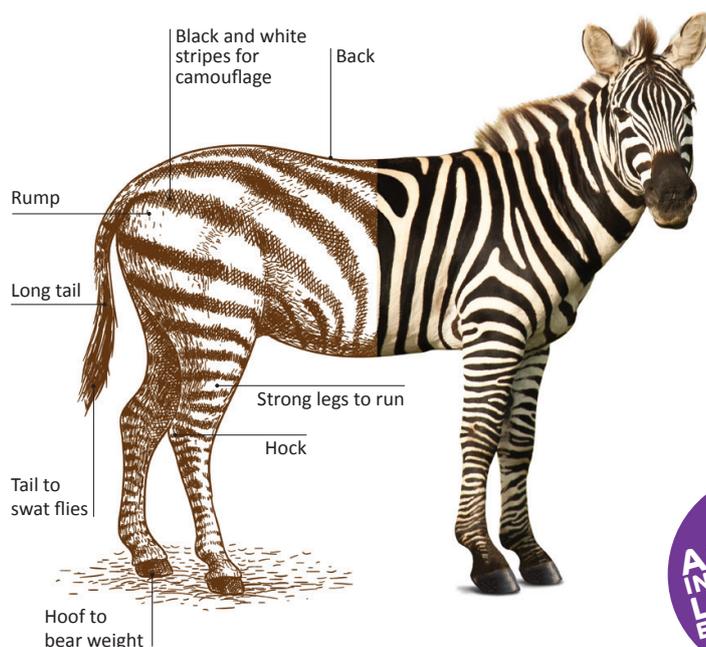
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