

Are Nitrogen Molecules Really Larger Than Oxygen Molecules?

The correct answer, with respect to “permeation”, is yes.

Graham’s Law Explained: The Difference between Effusion and Permeation

There's often confusion associated with the molecular size, molecular weight and permeation properties of oxygen and nitrogen molecules, and GNI is often called to task to explain why nitrogen actually migrates (permeates) out through the rubber of a tire slower than does oxygen. We felt it best to leave it to the expertise of Dr. Keith Murphy to elaborate on the scientific principles:

"Effusion" calculations are not appropriate for "permeation" of gas molecules through materials, such as the rubber of tire walls. There is a fundamental difference in transport occurring through “effusion”, and transport occurring through “permeation”.

Effusion would be appropriate, if the O₂ and N₂ molecules were passing through a relatively large passage way through the tire wall, such as a leak. Graham's Law for "effusion" applies ONLY if the exit through which the molecules pass is relatively large compared to the size of the molecules and does NOT obstruct or constrain one molecule from passing through relative to the other molecule. O₂ and N₂ molecules are only slightly different in molecular size but both are very small. Thus, to constrain one molecule's (e.g., molecule of type A) passage relative to the other's (e.g., molecule of type B) passage, that passage way size must be fairly close in dimension to the sizes of the molecules themselves.

Graham's Law does not apply, if the passage way is very small, as occurs for dimensions of passage ways in-between the polymer chains in a solid rubber, where the dimensions between the polymer chains do indeed constrain passage of the larger size molecule, which is actually N₂, compared to less constraint on the smaller size molecule, which is actually O₂.

It is often mistakenly assumed that "molecular size" correlates directly with "molecular weight". O₂ does have a greater molecular weight (32) than N₂ (28), but O₂ is actually smaller in size. Thus, O₂ fits through the relatively tight passage ways between polymer chains in the rubber more easily than does N₂. The difference in size between O₂ and N₂ is very small, only about 0.3 times 10 to the -10th meters (0.00000000003 meters).

Among the various descriptions of the sizes of molecules, that most applicable to transport phenomena is called the "kinetic diameter" of molecules. The kinetic diameter is a reflection of the smallest effective dimension of a given molecule. It is easy to visualize that a given molecule can have more than one dimension, which characterizes its size, if the molecule is not spherical. O₂ and N₂ are diatomic molecules (two atoms joined by a chemical bond or bonds), not spheres in shape but rather cylindrical in shape, akin to the shape of a tiny jelly bean. Thus, a "length" dimension of the cylindrical shape is a larger dimension than the smaller "waistline" diameter of the cylindrical shape. In transport phenomena, the molecule with the smallest effective waistline diameter is that which behaves as the smallest molecule, i.e., has the smallest kinetic diameter.

Literature reports of kinetic diameters for O₂ and N₂ molecules, derived from several different types of experimental measurements, give slightly different values, but all show that O₂ has a slightly smaller diameter than N₂. The following examples expressed in Angstrom units demonstrate this (one Angstrom unit is 10 to the -10th power meters, i.e., one-ten-billionth of a meter): from gas viscosity data, O₂ 2.96 and N₂ 3.16 (difference 0.20); from van der Waal's interaction data, O₂ 2.90 and N₂ 3.14 (difference 0.24); from molecular refraction data, O₂ 2.34 and N₂ 2.40 (difference 0.06). Other experiments, less applicable to transport situations, such as from closest packing, when the two molecules exist in a frozen solid state at very low temperatures, still show O₂ to be a smaller size than N₂ (O₂ 3.75 and N₂ 4.00, difference 0.25).

The reason that O₂, despite a larger MW 32, has a smaller diameter than N₂ MW 28, lies in the electronic structure of the molecules. As indicated by quantum mechanical theory of molecules, the electrons of a molecule form a diffuse "cloud" surrounding the nuclei of the atoms in the molecule. The electron cloud around the oxygen nuclei in the O₂ molecule is smaller, more compact in size, due to attractive electrostatic interactions between the electrons in the cloud and the greater positive charge of the nuclei of the O atoms in the O₂ molecule. Each oxygen atom has 8 protons in its nucleus, while each nitrogen atom has only 7 protons in its nucleus. Thus, the overall size of the electron cloud of the O₂ molecule is smaller than for N₂, in part because its electron cloud is drawn in closer to the O nuclei by the greater positive charge on the O nuclei.

The dimension of the molecule's electron cloud defines the size and shape for a given type of molecule. When one molecule bumps into another molecule, the outer-most extent of the electron clouds of each molecule repel each other in that local vicinity of the contact between the molecules. Each colliding molecule's electron cloud experiences a repulsion, due to the proximity to the like electrical charge of electrons around the other molecule in the collision. Since like electrical charges repel each other (like-repels-like), the electrostatic interaction between the electron clouds of the colliding molecules is repulsive. That repulsion effectively defines the size of the molecules.

O₂ "permeates" approximately 3-4 times faster than does N₂ through a typical rubber, as is used in tires, primarily because O₂ has a slightly smaller effective molecular size than does N₂.

A relationship that governs "permeation" is based on Fick's Law of Diffusion and Henry's Law of Solubilities, which takes into account the relative sizes of the molecules and their sizes compared to the very small passage way dimensions in the solid material (such as a rubber) through which the molecules "permeate". Combining Fick's and Henry's Laws yields the overall equation governing permeation of small molecules, such as gases, in material, such as rubbers and other plastics.

Let's call the rate of permeation of gas (i), J_i , J-sub-i, which is simply the volumetric flux of gas permeation per unit of time. Conveniently used units of J_i are cubic centimeters of gas per second, or cm³/s.

Consider a sheet of the rubber, such as a section of the tire wall.

That flux of gas permeating through a material is directly proportional to the first three factors, below, and inversely to the fourth factor, below:

1. the area, call it A (in units of square centimeters, cm²) of the sample of the rubber - More flux of gas would occur, if the area were larger, if everything else were the same; next,
2. the driving force for transport across the wall, which is the difference in concentration of gas (i) across the tire wall - for convenience with gases, a nearly exactly correct measure of this is the difference in partial pressures (p_i) of that gas (i) on the two sides of the tire wall (i.e., p_i inside minus p_i outside) - Obviously, a higher partial pressure (pressure units are cmHg, centimeters of mercury, and remember that 76 cmHg = 1 atmosphere = 14.7 psi) inside versus outside means there is more driving force to promote transport across the tire wall; then next,
3. the intrinsic permeability P, call it P_{ij} , or P-sub-i-sub-j, is the "permeability coefficient" for the particular material (j) for that type of gas (i) - Note that various materials, i.e., different types of rubbers or plastics will permeate O₂ faster or slower depending on the details of solid state structures of the materials, and different types of gases will permeate each material faster or slower depending on the relative sizes of the gas molecules, as well as on how soluble the gas is in the solid material; then lastly,
4. the thickness L (in units of cm) of the material - you can see that if the tire wall were, say, twice as thick, one would expect half the permeation rate (flux, cm³/s), all other things being equal.

Combine these four terms, and you get the permeation equation:

$$J_i = [P_{ij} \times A \times (p_i \text{ inside} - p_i \text{ outside})] / L$$

flux = permeability coefficient of gas (i) in material (j) of the tire wall multiplied by area multiplied by the partial pressure difference for gas (i) across the tire wall divided by the thickness of the tire wall.

Similarly, for the other gas (m), its flux would be:

$$J_m = [P_{mj} \times A \times (p_m \text{ inside} - p_m \text{ outside})] / L$$

since it would have a different permeability coefficient in that same rubber (j) and a different driving force across the tire wall.

So, the fluxes for different gases will be different, depending on the relative magnitudes of the permeability coefficients of the two different types of gas molecules and the relative concentrations (partial pressures) of the two types of molecules on each side of the tire wall (i.e., inside vs outside).

From the early part of this discussion, you will now recognize that P_i , where gas (i) is O₂, is greater than P_m , where gas (m) is N₂, principally because O₂ has a smaller kinetic diameter than N₂ and thus O₂ has a larger permeability coefficient than does N₂ - actually O₂ has a permeability coefficient in a typical tire rubber material, which is about 3-4 times that of N₂ in the same material. Permeation of O₂ and N₂ is primarily determined by size effects, because at normal temperatures and pressures relevant to the discussions of tires, these gases behave almost perfectly as Ideal Gases. As such, the differences in solubilities of O₂ and N₂ in most rubbers and plastics are too small to contribute to differences in their permeability coefficients. The differences observed are essentially solely due to the slight differences in the size of O₂ relative to N₂.

In case you wish to do your own calculations, the units for P (the permeability coefficients) most often used in the technical literature are:

$[\text{cm}^3 \times \text{cm}] / [\text{s} \times \text{cm}^2 \times \text{cmHg}]$ and for convenience, a standard unit of permeability is called the Barrer, after Richard Barrer, one of the early pioneers in studies of permeation in materials, such as rubbers and plastics. One Barrer unit is:

1 times 10 to the minus 10th power $[\text{cm}^3 \times \text{cm}] / [\text{s} \times \text{cm}^2 \times \text{cmHg}]$

In Barrers, for a typical rubber material, the permeability coefficient P, is dependant on temperature, but at 25C (77F) for O₂ is about 10 and for N₂ is about 3.

I hope this helps clarify why O₂ permeates faster through rubber than does N₂ and a major aspect of why it is a good idea to significantly reduce the amount of O₂ used to fill tires by replacing most of the O₂ in air with enriched N₂. Since N₂ permeates through the tire rubber more slowly than would O₂, using enriched nitrogen instead of air for tire filling contributes to better maintenance of the proper inflation pressure for the tire. Better pressure maintenance contributes to reduced tire wear, so that tires last longer and tire replacement costs are reduced.

A simple but approximately correct explanation of this lies in the mechanics of the flexing of tire walls. If proper inflation pressure is maintained, the tire wall most effectively bears the weight of the vehicle. If pressure is allowed to fall too low, extra flexing that occurs as the vehicle bounces somewhat along the road causes excessive mechanical fatigue of the structure of the tire. Similar to flexing a wire coat hanger, this fatigue can weaken the tire faster than would be the case were it kept inflated to a pressure more consistent with that intended in its design.

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