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Mr. Gil Schoener
President
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November 18, 2004

Dear Gil:

This is in response to your request for a review of scientific principles relating to the use of nitrogen as a gas for tire inflation.

- 1. Why does oxygen migrate out of tires quicker than nitrogen?**
- 2. Why does nitrogen not expand and contract as much as air?**

Answers:

1. Oxygen migrates out quicker than nitrogen, because:
 - a. Permeability coefficients measured for oxygen, P_{O_2} , are higher than the values for nitrogen, P_{N_2} , in all known rubbers (elastomers), including those typical of tires. The ratio of the permeability coefficients, P_{O_2} divided by P_{N_2} , is between 3 and 4 depending on the particular rubber. This means that oxygen permeates 3 to 4 times faster through rubber than does nitrogen, other conditions being equal;
 - b. oxygen is a smaller molecule than nitrogen (as determined by a wide variety of measurements of molecular size); this is true despite the fact that molecular weight of O_2 (32) is greater than that of N_2 (28), which might suggest that oxygen is larger than nitrogen;
 - c. relative permeabilities for oxygen and nitrogen are dominated by the difference in size of the molecules.
2. There is no significant difference in expansion and contraction characteristics of nitrogen, compared to air, when moisture is absent.
 - a. Expansion or contraction of either air or nitrogen occurs to very similar extent, in response to changes in temperature, in the commonly encountered range of temperatures and pressures relevant to discussion of tire inflation.

- b. There is no practical difference as long as the gases are dry, with respect to the effect of temperature on pressure in an essentially fixed volume container, such as in a tire.
- c. Water is usually present in the case for conventional compressed air. At lower temperatures, as a liquid, water occupies very little volume. However, as temperature increases, liquid water vaporizes to become a gas and its volume expands, causing total pressure to be higher in the tire, than would be the case with dry gas. Thus, the presence of water in a tire contributes to pressure variations as temperatures change.

Please find attached several pages of more detailed information. I provide a Summary, explaining in plain language several factors at play in tires, comparing using Nitrogen to using conventional compressed air. In Appendix, I provide more detailed technical information drawn from credible literature sources.

If I may be of further assistance, please contact me or our Sales/Marketing Specialists, Bill Phelps and Phil Powell in St. Louis.

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Summary - Nitrogen compared to conventional compressed air for tire inflation

Benefits:

1. Maintain proper tire pressure longer with Nitrogen than with compressed air
2. Reduced degradation of rubber's mechanical properties caused by oxidation, in the absence of oxygen, using Nitrogen

Composition differences between membrane-generated Nitrogen and conventional compressed air:

Oxygen and moisture are almost completely removed from air by the membrane.

Explanations for the benefits of using membrane-generated Nitrogen compared to compressed air for tire inflation

1. Better inflation pressure maintenance using Nitrogen:

Nitrogen permeation through the rubber is much slower than oxygen permeation.

Measured permeability in all known rubbers is faster for O₂ compared to N₂, by factors ranging from 2.4 to 4.7, depending on the rubber.

Permeability of gases is generally faster in some rubbers than in other rubbers, but all rubbers permeate O₂ faster than N₂ by a ratio of about 3 to 4.

Oxygen permeates faster because it is a smaller molecule than is nitrogen.

Thus, any tire filled to proper pressure will hold that pressure longer, if the higher permeability component (O₂) is not in the tire in the first place.

2. Reduced oxidative degradation of rubber, because oxygen is absent, using Nitrogen: according to J. D. Baldwin, et.al., (Ford Motor Co.), in "Passenger tires inflated with nitrogen age slower", Rubber & Plastics News, pp. 14-19, Sept. 20, 2004

Oxygen chemically reacts with rubber,

causing the rubber's mechanical properties to degrade.

Nitrogen does not react with rubber.

If oxygen is absent or present at much lower concentration, rubber mechanical properties are more stable over time.

Do tires run cooler ?:

Tire run temperature is influenced by many factors, including:

Proper inflation

Rolling resistance

Road conditions

Speed

Outside environment temperature

Vehicle load

Temperature influences gas pressure.

Heating a gas in a fixed volume container increases gas pressure ($P_1/T_1 = nR/V = P_2/T_2$) and cooling decreases gas pressure. For example,

a truck tire filled to 100 psig at 60F, increases in pressure to ~118 psig at 140F;

a car tire filled to 30 psig at 60F will increase in pressure to ~ 37 psig at 140F.

For temperatures and pressures near common experience,

air, or O₂ or N₂, all behave very similarly in this respect.

Thus, there is no significant difference in pressure changes, comparing air and N₂, due to gas temperature effects alone (that is, as long as either gas is “dry”).

Water, however, can exist as liquid or as vapor (i.e., a gas) and

water changes from liquid to vapor over the relevant range of temperatures.

The “vapor pressure” of water is very sensitive to temperature,

increasing from 0.26 psi at 60F to 2.89 psi at 140F.

If there is liquid water in the tire at 60F, as does occur with conventional compressed air,

water’s vapor pressure contributes a small additional amount to pressure at 140F.

If dry air or dry N₂ is used to fill the tire, the effect of water on pressure is eliminated.

Tire heating will be greater, if proper inflation pressure is not maintained.

Over time, a tire filled with air, will loose pressure faster, due to faster permeation of O₂.

This will contribute to under-inflation of the tire, absent frequent pressure checks.

Under-inflation may contribute to excessive mechanical flexing of the tire,

which will contribute to additional road resistance and frictional heating.

Thus, improper inflation is a principle contributor to excessive tire heating.

Nitrogen helps better maintain proper tire inflation pressure, compared to compressed air.

Do tires wear longer?

Tire wear is influenced by many factors:

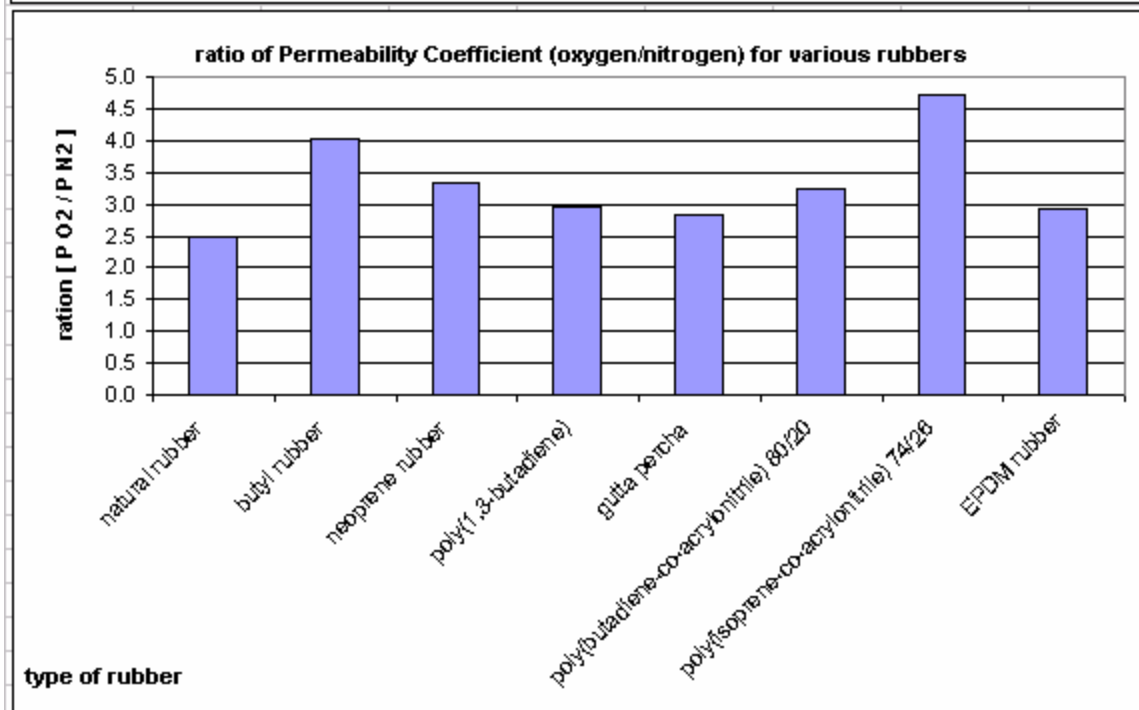
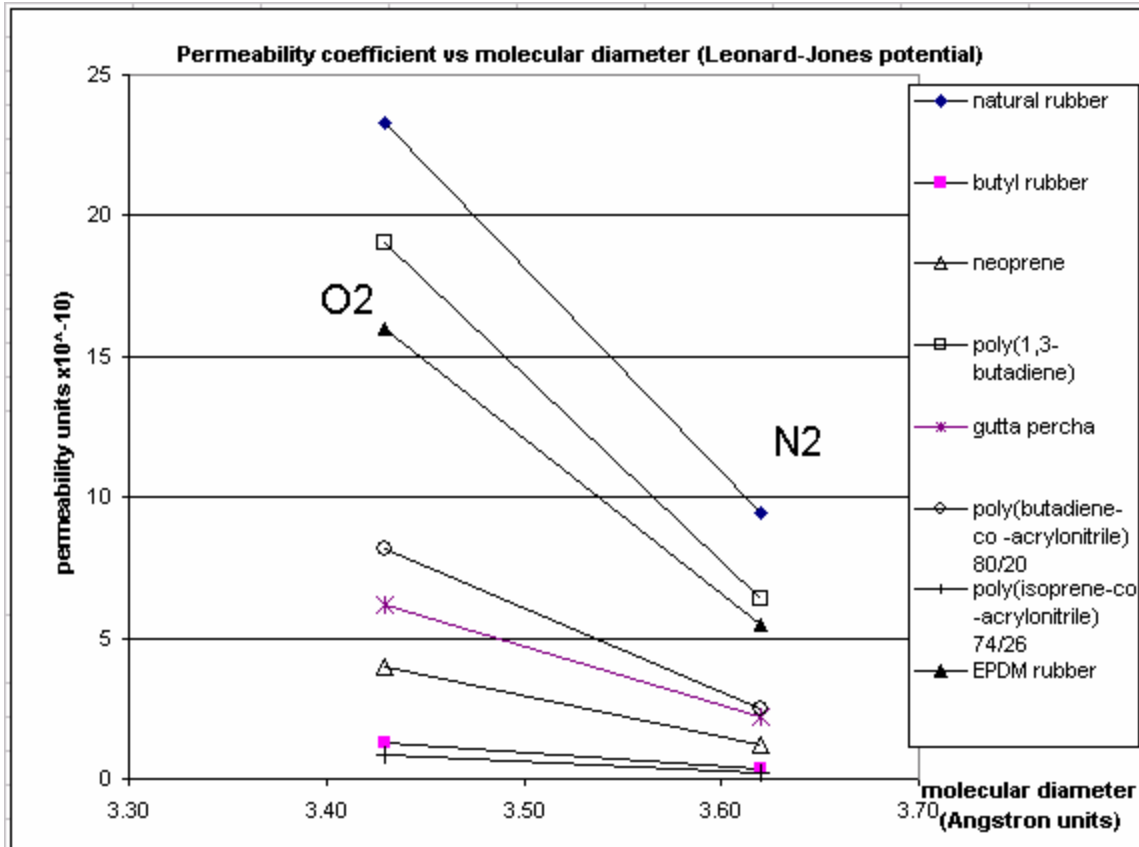
Proper inflation pressure (see above discussion)

Rubber’s mechanical properties are more stable, if oxygen is not present.

Appendix

Gas permeability data for various rubbers (elastomers)

| 1. textbook Physical Chemistry by W. J. Moore 3rd Ed., 1962, Prentiss-Hall publ., NJ pp. 228-228, and Table 7.5 in Chapter 7, Kinetic Theory of Gases | | | | | | | 2. Polymer Handbook by J. Brandrup, E. H. Immergut, editors 2nd Ed., 1975, Wiley-Interscience publ., NY pp. III-229-239, Ch. 3, Permeability Coefficients | | | | 3. Permeability Properties of Plastics and Elastomers by L. K. Massey 2nd Ed., 2003, Plastics Design Library publ., NY pp. 543-549, Appendix II, Permeation Rates | | | | |
|---|-------------------------|----------------------------|---|--|--|---|---|--------------|-----------------|---------------------|--|--|---------------------------------------|-------------|------------|
| molecular dimensions (in Angstrom units, 10 ⁻¹⁰ meters) obtained from various experimental methods and from potential calculations | | | | | | | Permeability coefficient, at standard T = 25C measured gas flux (volume/time) across a sample of known thickness and area at known pressure differential units = x10 ⁻¹⁰ [(cm ³)/(cm)/(cm ²)*(sec)*(cmHg)] | | | | | | | | |
| gas molecule | from gas viscosity data | from refractive index data | from density data, closest packing in solid state | from van der Waal's radii calculations | from Leonard-Jones potential calculation | molecular weight of the gas (grams /mole) | natural rubber cis-poly(isoprene) | butyl rubber | neoprene rubber | poly(1,3-butadiene) | gutta percha trans-poly(isoprene) | poly(butadiene-co-acrylonitrile) 80/20 | poly(isoprene-co-acrylonitrile) 74/26 | EPDM rubber | |
| helium | 2.00 | 1.48 | | 2.48 | 2.37 | 4.00 | | 8.4 | | | | 16.9 | 7.8 | | |
| O2 | 2.96 | 2.34 | 3.75 | 2.34 | 3.43 | 32.00 | 23.3 | 1.3 | 4.0 | 19 | 6.2 | 8.2 | 0.85 | 16.0 | |
| N2 | 3.16 | 2.40 | 4.00 | 2.40 | 3.62 | 28.00 | 9.4 | 0.32 | 1.2 | 6.4 | 2.2 | 2.5 | 0.18 | 5.5 | |
| argon | 2.86 | 2.96 | 3.83 | 2.86 | 3.35 | 40.00 | 22.8 | | 3.8 | | | | | | |
| water vapor | | | | | | | 2290 | 37.5 | 910 | | 510 | | | | |
| | | | | | | | ratio (P O2/P N2) | 2.5 | 4.0 | 3.3 | 3.0 | 2.8 | 3.2 | 4.7 | 2.9 |
| | | | | | | | Oxygen is higher permeability than nitrogen through all rubbers | | | | | | | | |
| | | | | | | | Absolute value of the permeability depends on the type of rubber | | | | | | | | |
| | | | | | | | Higher permeability reflects "tighter packing of rubber polymer chains", molecular structure in the solid | | | | | | | | |

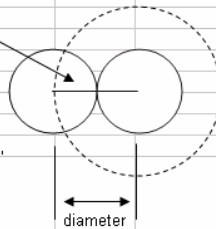


1. van der Waal's correction due to molecules being a "finite" real size, rather than an "idealized" points of zero size applied to correct the "Ideal Gas Law" from Kinetic Theory of Gases

Ideal Gas Law $P*V = n*R*T$
 correction from van der Waal $P*(V - n*b) = n*R*T$

radius

two molecules
"hard spheres"



"b" is called the "excluded volume" per molecule
 "R" is a constant of proportionality, called the Gas Constant
 Two molecules cannot approach each other more closely than a distance, "d".
 This assumes a simple but unrealistic "hard sphere" model of molecules.
 The excluded volume per pair is a sphere of radius = d, of volume = $8(4/3)(\pi)(r^3)$,

which has a volume per molecule = $4(4/3)(\pi)(r^3)$.

Thus, molecular radius (r) and diameter (d=2*r) can be calculated.

2. Leonard-Jones potential calculation

More rigorous analysis of interaction between real molecules includes effects of energy fields around molecules. A useful "potential" function, was developed by J. E. Leonard-Jones, to describe these interactions
 From viscosity data, diameters of molecules can be obtained, using the Leonard-Jones potential, (**sigma**)

"sigma" is a distance at which the potential energy of interaction between nearest neighbor molecules vanishes.

viscosity is proportional to $[\text{square root } (MW)*T] / (\text{sigma})^2$

"sigma" is "effective molecular radius", analogous to "excluded volume" van der Waal's description (above)
 Rather than assuming the molecules are "hard spheres", having a discrete outer surface, the molecule's outer extent is defined as a distance where its potential energy for interaction with another molecule is so small as fall to essentially zero.

3. Density of solidied gases, measured at very low temperatures

density of the solid = mass/volume or grams/volume
 Assuming hard sphere molecules, simple geometry shows
 that closest packing leaves void space between spheres of 26% of the total volume.
 Thus only 74% of total volume is actually space occupied by the molecules in the solid.

Molecular weight (MW) of a molecule is a number equal to a weight in grams of 1 mole of that type of molecule.
 MW (O2) = 32 grams/mole, MW (N2) = 28 grams/mole
 1 mole is a very large number of molecules $6.022*10^{23}$ molecules per mole

volume occupied by 1 mole of the molecules = MW / density of the solid

Volume occupied by only the molecules can be used to calculate the volume, and thus diameters (d), of individual molecules

$[(\pi) / 6]*6.022*10^{23}*(d^3) = (0.74)*(MW)*(density)$
 $d = \text{cube root } [(0.74)*(MW)*(density) / ((\pi)/6)*6.022*10^{23}]$

4. Gas viscosity is a reflection of momentum transfer during collisions between molecules in a gas.

How frequently collisions occur is influenced by the size of the molecules, i.e., larger molecules collide with other molecules more often.
 Molecule diameters (d) can be estimated from measured gas viscosity data.

$d = (3/2)*(\text{square root } [(\pi) / R*T*(MW)])*(viscosity/b)$

5. Refractive index is one measure of the interaction of light, electromagnetic radiation, passing through (but not absorbed by) matter.

When the electric field component of light interacts with molecules in a material, the electric field induces a magnetic moment in the material, and this effect responsible for the refraction of the light passing through the material.
 We see visually the refraction as an apparent bending of the light leaving, relative to entering, the material.

Magnetic moment (m) is related to both the size of the molecule and strength (F) of the electric field of light:
 $m = (r^3)*F$

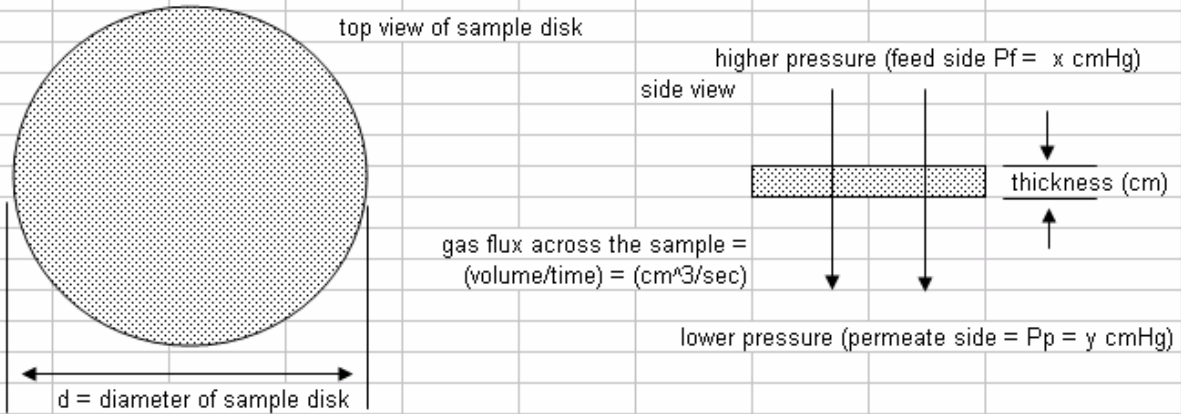
An estimate of the radius of the molecule, and thus its diameter (d = 2*r), can be obtained.

Discrepancies among in the calculated values of molecular diameters,

based on the different experimental and theoretical methods, arise from several factors, including errors associated with experimental measurements of viscosity, refractive index and density, and with theoretical models used, such as whether molecules are "hard spheres" or with particular mathematical forms used to describe "energy potentials".

Experimental measurements of gas Permeability Coefficients for different rubbers (elastomers)

are not dependant on choice of a theoretical model of molecular shape and suffer from few experimental errors.



area = $(\pi)(d/2)^2$
(cm²)

pressure difference across sample = [P_{feed} - P_{permeate}] = (x-y) cmHg
pressure difference across sample = driving force for permeation

gas flux = [(permeability coefficient)*(area)*(pressure difference)] / (thickness)

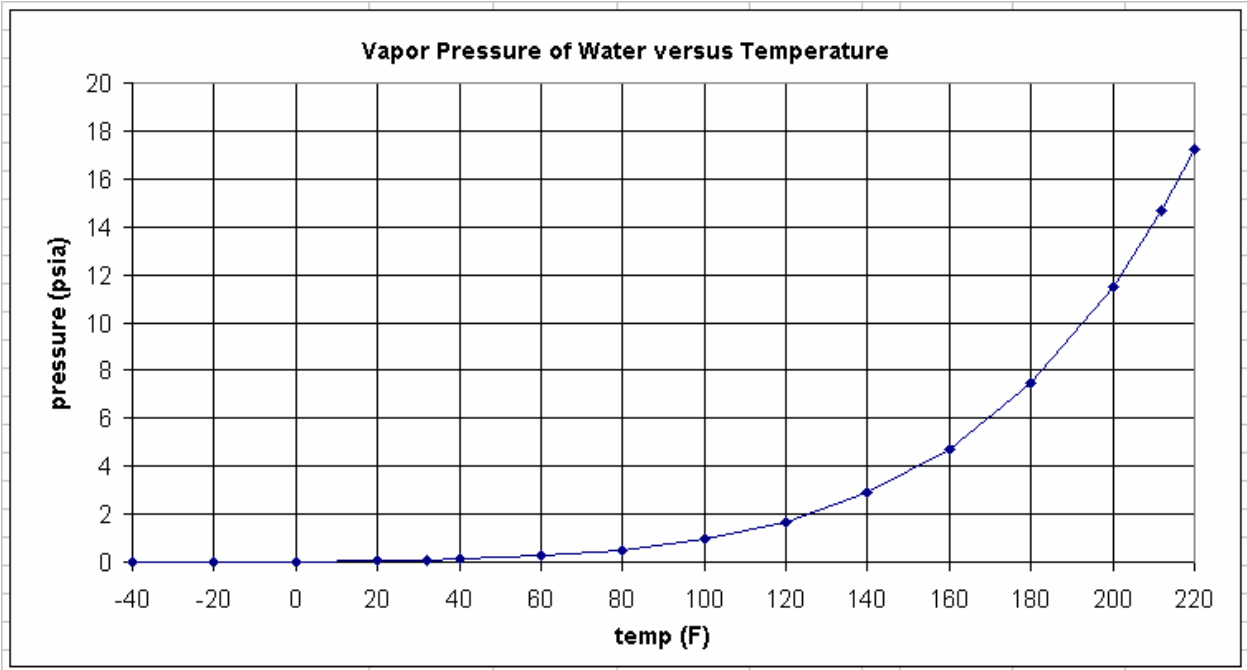
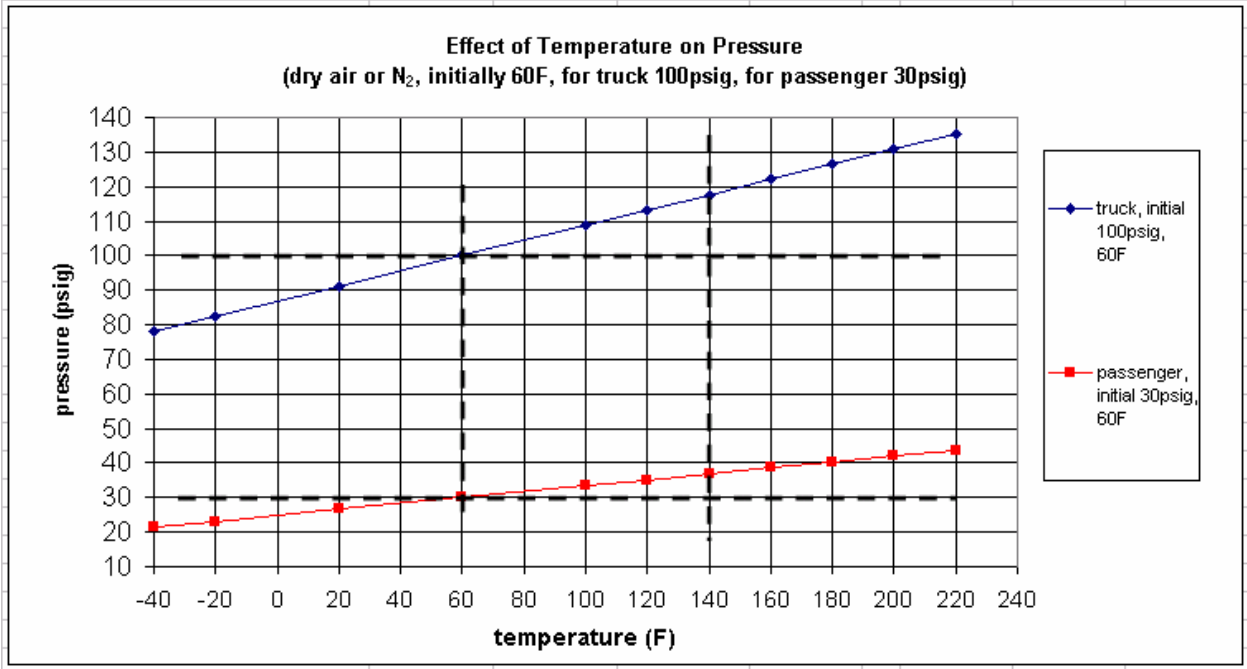
permeability coefficient = [(flux)*(thickness)] / [(area)*(pressure difference)]

permeability coefficient = (cm³/sec)*(cm) / (cm²)*(cmHg)

or

permeability coefficient = (cm³)*(cm) / (cm²)*(sec)*(cmHg)

Most materials show measured values of permeability coefficients that make it convenient to use a standard unit of 10⁻¹⁰ in the dimensional units of (cm³)*(cm) / (cm²)*(sec)*(cmHg). This unit is named the Barrer, after Professor Richard Barrer, an early pioneer in permeation science.



Calculation of the approximate time required for permeation to result in a significant decrease in tire pressure, assuming case of a typical truck tire inflated with air at 100 psig initially.

This calculation uses “reasonable approximate or typical” values of tire size (volume and sidewall area available for permeation), sidewall thickness, Permeability Coefficients for gases in a “typical” rubber (elastomer), and effects of temperature on permeation rates.

The resulting time is ~11 to 53 days, depending on temperature, for a roughly 1/3rd or 7 psi decrease in partial pressure of Oxygen (initially present as about 21 psi of the 100 psi total pressure, decreasing to 14 psi oxygen partial pressure after calculated number of days). During that time a small additional pressure decrease occurs, due to the slower permeation of some nitrogen.

Thus, a tire initially inflated with compressed air to 100 psig will drop in pressure by about 7-8 psi over a few weeks, due to the oxygen permeation effects alone.

These calculations are approximate. Variations in the resulting times for pressure decreases will occur in a real situation. Actual Permeability Coefficients, area available for permeation and effective thickness of the side wall portion of the tire may differ somewhat, depending on actual tire structure, tire dimensions and the characteristics of the rubber of the tire, including effects of fillers such as carbon black in the rubber composition, and whether the rubber is reinforced with relatively impermeable non-rubber components, such as threads of nylon cord or steel.

This calculation appears to be of sufficient validity within reasonable confidence limits. It suggests practical implications, regarding the effects of permeation in the case of tire inflation pressure versus time, and supports a case for tire inflation using nitrogen as beneficial compared to using compressed air.

This calculation simply verifies, using reasonable assumptions, that a practically relevant pressure decrease can be expected to occur, due to permeation of oxygen, if compressed air is used. It also demonstrates that if Nitrogen is used instead, it would take a much longer time for a similar significant pressure decrease to occur, due to permeation effects.

Thus, inflating a tire with Nitrogen, instead of compressed air, provides significantly better maintenance of proper tire pressure.

| | | | | | | |
|---|--------------|----------------------|--|----------------|----------------------|------------------------|
| Consider the rubber (elastomer) of a tire's side wall as a membrane, to calculate pressure change due to permeation through the rubber side walls of the tire. | | | | | | |
| inside a truck tire at 100 psig filled with compressed AIR | | | | | | |
| approximate tire total volume ~280 liters = 28000 cm ³ , for a typical truck tire | | | | | | |
| total pressure Pf = 100 psig + 14.7 = 114.7 psia | | | | | | |
| composition = ~20.9% O2 + ~78% N2 + 1.74% H2O (assuming 100% RH at 60F for source of the air) | | | | | | |
| partial pressures of components (psia) | | | | | | |
| O2 | 0.209*114.7 | = | 24.0 | psia | 5852 | cm ³ |
| N2 | 0.78*114.7 | = | 89.5 | psia | 21840 | cm ³ |
| H2O | 0.0174*114.7 | = | 2.0 | psia | 487.2 | cm ³ |
| outside a truck tire is ambient AIR at 1 atm pressure (0 psig = 14.7 psia) | | | | | | |
| composition = ~20.9% O2 + ~78% N2 + 1.74% H2O (assuming 100% RH at 60F) | | | | | | |
| partial pressures of components (psia) | | | | | | |
| O2 | 0.209*14.7 | = | 3.1 | psia | | |
| N2 | 0.78*14.7 | = | 11.5 | psia | | |
| H2O | 0.0174*14.7 | = | 0.3 | psia | | |
| driving force for permeation through the rubber of the tire = (Pf - Pp) for each component; note 1 psia = 5.17 cmHg | | | | | | |
| O2 | 20.9 | psia | = | 108.1 | cmHg | |
| N2 | 78.0 | psia | = | 403.3 | cmHg | |
| H2O | 1.7 | psia | = | 9.0 | cmHg | |
| assume tire rubber is 1/4 inch (0.6 cm) thick | | | | | | |
| assume the area of the tire rubber is ~ 10,000 cm ² for a truck tire (just the two side walls; ignore thick tread or rim area) | | | | | | |
| estimate permeability coefficients for each component, as follows: | | | | | | |
| O2 | 10 | at 25C (77F) | permeation increases at higher temperature | 50 | at 60C (140F) | |
| N2 | 3 | at 25C (77F) | | 15 | at 60C (140F) | |
| H2O | 1000 | at 25C (77F) | | 5000 | at 60C (140F) | |
| calculate initial flux through the rubber area (cm ³ /sec) for each component | | | | | | |
| O2 | 4.22E-04 | cm ³ /sec | | 2.11E-03 | cm ³ /sec | |
| N2 | 3.39E-05 | cm ³ /sec | | 1.70E-04 | cm ³ /sec | |
| H2O | 2.14E-07 | cm ³ /sec | | 1.07E-06 | cm ³ /sec | |
| time required for 1/3rd of each component to permeate across the rubber of the tire | | | | | | |
| O2 | 4.58E+06 | seconds = | 53 | days at 25C or | 9.15E+05 | sec = 11 days at 60C |
| N2 | 2.12E+08 | seconds = | 2459 | days at 25C or | 4.25E+07 | sec = 492 days at 60C |
| H2O | 7.52E+08 | seconds = | 8699 | days at 25C or | 1.50E+08 | sec = 1740 days at 60C |