

Estimation of gas-phase diffusivities in hyperbaric environments

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Van Liew HD, Paganelli CV, Sponholtz DK. Estimation of gas-phase diffusivities in hyperbaric environments. *Undersea Biomed Res* 1982; 9(2):175-181.—Diffusion of a particular gas in a mixture of three or more gases depends on diffusion characteristics and concentrations of the other gases and also on environmental pressure. 1) Estimates of gas-phase diffusivities in hyperbaric environments can be calculated from binary coefficients by the Wilke equation. Sample calculations show that addition of carbon dioxide and water to inspired gas has very little effect on diffusivity of oxygen but that neglect of lesser components of a mixture, such as the nitrogen in "trimix" or the helium in crude neon, would lead to errors of 10% to 20%. 2) It is not possible to match a compressed air environment with a helium-oxygen or a helium-oxygen-nitrogen environment for both density and diffusivity. Diffusivities of oxygen and carbon dioxide in a helium mixture can be less than half the values in compressed air having the same density. In a plot of diffusivity vs. gas density, most useful mixtures are included in a hyperbolic-shaped band; diffusivity falls to below 25% of the room air value when density is 5 times normal.

binary diffusion coefficients

density-diffusivity relationships

multicomponent diffusion

gas density

gas-phase diffusivity

On theoretical grounds, hindrance to pulmonary ventilation is expected to increase in proportion to the square root of environmental gas density (1), and experimental data are approximately in accordance with the theory. For example, peak expiratory flow decreased from about 11 liters/s at normal density to about 4 liters/s at 10 ATA with breathing of air (1), and data on maximal voluntary ventilation (MVV) and other ventilatory variables follow a similar trend (2, 3). This is not due to viscous effects, since viscosity does not change appreciably with pressure (4).

Hindrance to diffusive gas mixing increases in direct proportion to gas density because diffusivity is inversely proportional to pressure (5-7). Studies with inert insoluble gases inhaled together in a mixture have shown that low diffusivity leads to subnormal mixing of inspired gas in the lung (8). The subnormal mixing operates as though there were increased dead space; it could easily be compensated by increase of ventilation. However, the high gas density that causes the mixing defect also hinders air flow through airways, so poor mixing adds "insult" to the "injury" of reduced ventilation.

A quantitative approach to the problems of diffusive mixing requires estimation of gas-phase diffusivities in various environments. This is complicated by the fact that diffusion flux of each gas in a multigas mixture depends on the diffusivities and concentration gradients of the other gases in the mixture (9, 10). The appropriate effective diffusivity can be calculated from diffusion coefficients determined in binary mixtures. According to Worth et al. (11), binary coefficients can be assumed to be independent of concentration of the two component gases. We present experimentally determined binary diffusivities for O_2 and CO_2 in various other gases in Table 1, along with values calculated by the Chapman-Enskog equation (7). When necessary, coefficients were corrected to $37^\circ C$ from the temperature at which measurements were made. T_m in degrees Celsius, by the formula

$$D^{37} = D^{T_m} \left(\frac{310}{273 + T_m} \right)^{3/2} \quad (1)$$

where D^{T_m} is the coefficient measured at T_m (7).

CALCULATION OF DIFFUSIVITIES

Effective diffusivity of gas x in a mixture, $D'_{x,y}$ can be estimated from its binary diffusivities in each of the components of the mixture, $D_{x,y}$ by the Wilke equation (10, 13):

$$\frac{1}{D'_{x,y}} = \left(\frac{1}{1 - F_x} \right) \sum_{y=1}^n \frac{F_y}{D_{x,y}} \quad (2)$$

where F_x is the fraction of the gas in question and y designates one of the other components in the mixture.

To illustrate the method of calculation, we have used, where possible, the experimentally derived coefficients of Table 1 to perform calculations for diffusivities of O_2 and CO_2 in three mixtures that have been used in specific hyperbaric exposures; to do so, we calculated the diffusivity in the mixture at 1 ATA, then divided by total pressure. Note that we assume a simple inverse relationship between diffusivity and pressure. Although there is evidence of deviations from this relationship even at pressures below 100 ATA, they are not large, and no satisfactory way of predicting the deviations is known (7). Results are presented in Table 2. For a specific example, the diffusivity of O_2 in the 5% trimix mixture used by Salzano et al. (14) (top line in Table 2) was calculated from Table 1 values as follows:

$$X = [1/(1 - 0.0107)] [(0.0501/0.252) + (0.939/0.795)] = 1.3949$$

$$D'_{O_2} = 1/46.74X = 0.0153$$

In Table 2, two different conditions are presented for each of the gas mixtures: the first one shows effective diffusivity of O_2 in the dry mixture at $37^\circ C$, and the second estimates effective diffusivities of O_2 and CO_2 in humidified lung gas at $37^\circ C$. Comparison of D'_{O_2} in the two lines shows that addition of small amounts of H_2O and CO_2 to lung gas has little effect on D'_{O_2} . Substitution of binary coefficients (O_2 or CO_2 in the major component of the mixture) would lead to errors of 10% to 20%. For example, $D_{O_2,He}$ at 46.74 ATA is $0.0170 \text{ cm}^2/\text{s}$ instead of the 0.0153 value of the table, and $D_{O_2,Ne}$ at 37.5 ATA is $0.0092 \text{ cm}^2/\text{s}$ instead of 0.0106 .

TABLE 1
 BINARY DIFFUSION COEFFICIENTS* OF O₂ AND CO₂ IN VARIOUS GASES AT 37°C AND 1 ATA

Gas y	$D_{O_2,y}$		$D_{CO_2,y}$	
	measured	calculated	measured	calculated
H ₂	0.878 **	0.834	0.661 **	0.664
He	0.795 †	0.791	0.651 **	0.635
Ne	0.345 †	0.349	—	0.268
H ₂ O	0.291 ‡	0.229	0.201 ‡	0.160
N ₂	0.252 **	0.219	0.178 **	0.166
O ₂	—	0.220	0.167 **	0.164
CO ₂	0.167 **	0.164	0.123 ‡	0.119
SF ₆	0.0971**	0.100	0.0751**	0.0707

Calculated values obtained from Chapman-Enskog equation Worth et al. (11); corrected to 1 ATA (760 torr, 101.3 kPa).
 †Cited by Reid et al. (7); corrected to 37°C.

*Values in cm²/s. **Measured by

‡Cited by Marrero and Mason (12);

RELATIONSHIPS AMONG DIFFUSIVITY, DENSITY, AND PRESSURE

Figure 1 shows the diffusivity of O₂ in a normoxic He-O₂ mixture and in compressed air at various pressures (*upper*) and the density of He-O₂ and air at various pressures (*lower*). Two dashed horizontal arrows in each panel illustrate how the total pressures of the He-O₂ environments that match 1.5 and 3 ATA of compressed air for density are considerably higher than the pressures that match for diffusivity. This issue is illustrated in another way in Fig. 2, which shows the pressure of an He-O₂ mixture that matches a given pressure of compressed air for density and diffusivity.

As shown in Figs. 1 and 2, it is not possible to match both the density and gas-phase diffusivity of O₂ of an air environment with He-O₂, so air-flow parameters and diffusivity parameters cannot both be matched in a pair of environments. Diffusivity of a gas in a mixture

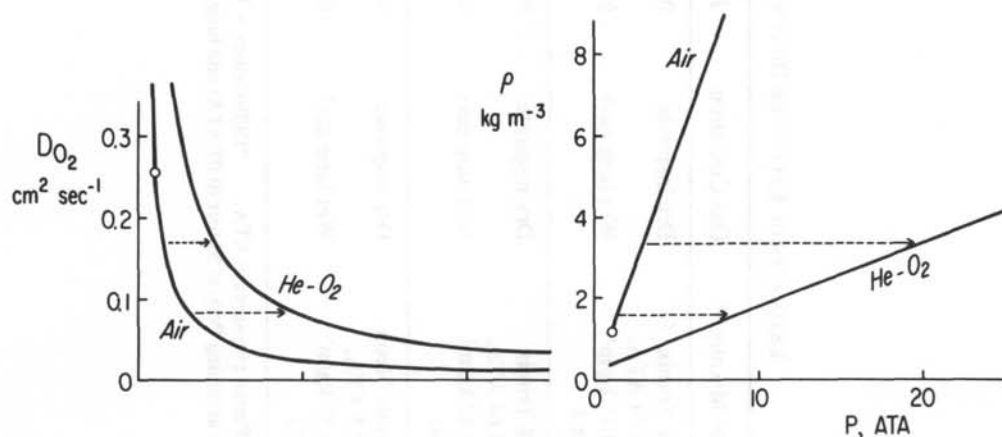


Fig. 1. Relations of O₂ diffusivity (*upper*) and density (*lower*) to pressure for a He-O₂ mixture in which PO₂ = 150 torr (0.1974 ATA) and for compressed air. Open circles, room air points. Dashed arrows, He-O₂ equivalents to air at 1.5 and 3 ATA.

TABLE 2
ESTIMATES OF EFFECTIVE DIFFUSIVITIES* OF O₂ AND CO₂ IN THREE MULTICOMPONENT GAS MIXTURES AT PRESSURE

Gas Mixture**	Gas Condition	PO ₂	PCO ₂	PN ₂	PHe	PNe	PH ₂ O	D'O ₂	D'CO ₂
5% Trimix 46.74 ATA, 10.11 kg/m ³ (14)†	Dry inspire	0.50	0	2.34	43.90	0	0	0.0153	—
	Wet lung gas†	0.43	0.07	2.34	43.84	0	0.062	0.0152	0.0120
8% Trimix 65.64 ATA, 16.12 kg/m ³ (14)	Dry inspire	0.67	0	5.37	59.60	0	0	0.0103	—
	Wet lung gas†	0.60	0.07	5.36	59.54	0	0.062	0.0102	0.00796
Crude Neon 37.5 ATA, 24.51 kg/m ³ (15)	Dry inspire	0.50	0	0	8.58	28.42	0	0.0106	—
	Wet lung gas†	0.43	0.07	0	8.57	28.37	0.062	0.0106	0.00819

Partial pressures in ATA. *Diffusivities = D' in cm²/s. **Designation, total pressure, density, and reference. †Lung gas pressures calculated by assuming PCO₂ is 50 torr (0.07 ATA) and lung PO₂ is 50 torr less than inspired PO₂. ‡Numbers in parentheses refer to number of reference cited.

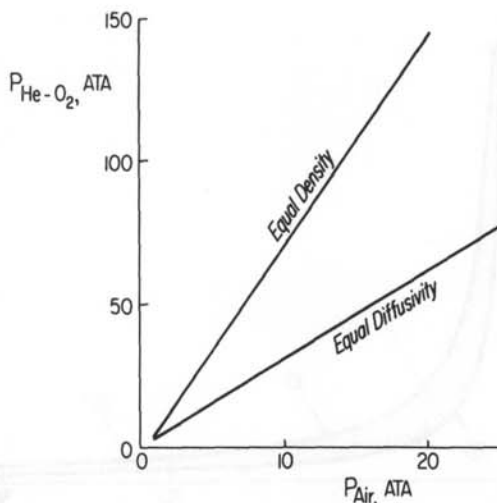


Fig. 2. Environmental pressures of normoxic He-O₂ mixtures ($P_{O_2} = 0.1974$ ATA) that are equivalent to a given pressure of compressed air for density and diffusivity. Consider an air environment of 10 ATA; for density, it can be matched by 70 ATA of the He-O₂ mixture, but for diffusivity, it can be matched by 31 ATA. It follows that diffusive mixing should be considerably poorer in the 70 ATA He-O₂ environment than in the 10 ATA air environment; diffusivity in 70 ATA He-O₂ is equivalent to that in 22.5 ATA of air.

is inversely proportional to atmospheric pressure, and density of a mixture is directly proportional to pressure. From these simple facts it can be shown that the ratio of diffusivities of a given gas, such as O₂, in two gas mixtures having the same density equals the ratio of its diffusivities in the two mixtures under 1 ATA conditions multiplied by the ratio of densities of the two mixtures under 1 ATA conditions:

$$\frac{D'_{O_2, y_1}}{D'_{O_2, y_2}} = \frac{D^0_{O_2, y_1}}{D^0_{O_2, y_2}} \cdot \frac{\rho^0_{y_1}}{\rho^0_{y_2}} \quad (3)$$

where y_1 and y_2 are two different gas mixtures, ρ is density, and zero as a superscript is the value at 1 ATA. If y_1 is taken to be an He-O₂ mixture and y_2 is air, the ratio of diffusivities at 1 ATA is about 3.1 and the ratio of densities at 1 ATA can be as low as 0.14, so the ratio of diffusivities at pressures that are matched for density can be as low as 0.43.

Figure 3, a plot of diffusivity as a function of density, provides an overview of the problem of gas-phase diffusivity in hyperbaric environments. The shaded band in Fig. 3 includes almost all reasonable values for gases used in hyperbaric exposures, since helium mixtures with O₂ of less than 150 torr and N₂ mixtures with O₂ more than 21% would seldom be used. Therapeutic exposures of pure O₂ or O₂-enriched mixtures with N₂ are close to the upper boundary on the graph, since O₂ and N₂ diffusivities are close to each other. A band for CO₂ diffusivity would be essentially the same as that for O₂, since CO₂ diffusivity is close to that of O₂ in any given medium (Tables 1 and 2). Ambient pressure variations within the band of Fig. 3 are very large, as can be seen by the few pressure notations. For a specific example, the pressure of He-O₂ mixtures associated with 5 ATA of compressed air (dashed arrows) are 15.5 ATA for diffusivity matching and 35 ATA for density matching.

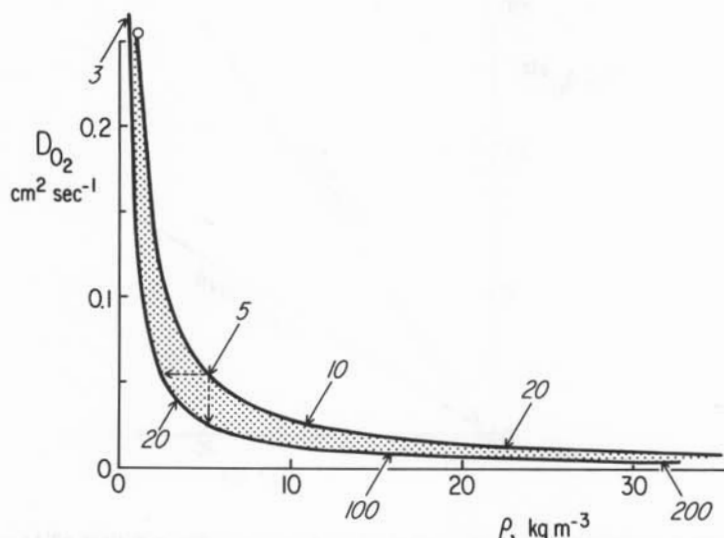


Fig. 3. Band of diffusivity vs. density for most gases used in hyperbaric exposures. Upper boundary of band is for compressed air, lower boundary is for a helium-oxygen mixture containing 150 torr of O_2 at all densities. Open circle, point for 1 ATA air; a few indications of total pressure in ATA of either air or He- O_2 are given on the two boundaries. Dashed arrows, diffusivity matching (horizontal) and density matching (vertical) for compressed air at 5 ATA.

It is seen in Fig. 3 that diffusivity of O_2 falls drastically as density increases up to about 5 kg/m^3 ; the fall is to between 10% to 25% of the diffusivity in air at 1 ATA. At greater densities, the diffusivity falls less steeply. It can be inferred, therefore, that diffusivity-dependent physiological functions will be changed most strongly in the range of densities from 1 to about 5 kg/m^3 . The perspective gained from Fig. 3 indicates that air-vs.-helium differences of diffusivities are relatively small in the greater context of the inverse relation between diffusivity and gas density.

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Van Liew HD, Paganelli CV, Sponholtz DK. L'Évaluation des diffusibilités en phase gazeuse dans les environnements hyperbares. *Undersea Biomed Res* 1982; 9(2):175-181.—La diffusion d'un gaz donné dans un mélange gazeux à trois ou plus de trois constituants dépend des propriétés de diffusion et des concentrations des autres gaz et elle dépend aussi de la pression de l'environnement. 1) Des estimations des diffusibilités en phase gazeuse en milieux hyperbares peuvent être faites à partir des coefficients de diffusion binaire par l'équation de Wilke. Des applications numériques montrent que l'addition au gaz inspiré de dioxyde de carbone et de vapeur d'eau a très peu d'effet sur la diffusibilité de l'oxygène mais que le fait de négliger des constituants mineurs d'un mélange, tel que l'azote dans le "trimix" ou l'hélium dans le néon brut peut conduire à des erreurs de 10% à 20%. 2) Il n'est pas possible de trouver pour un environnement d'air comprimé donné, un environnement d'hélium-oxygène ou d'hélium-oxygène-azote qui soit équivalent à la fois en densité et en diffusibilité. Sur un diagramme de diffusibilité en fonction de la densité gazeuse, la plupart des mélanges utilisables sont compris dans une bande en forme d'hyperbole; la diffusibilité tombe en dessous de 25% de sa valeur pour l'air dans les conditions ordinaires lorsque la densité est cinq fois plus grande.

coefficients de diffusion binaire
relations densité-diffusibilité

densité gazeuse
diffusibilité en phase gazeuse

diffusion et mélange multiple

REFERENCES

1. Wood LDH, Bryan AC. Effect of increased ambient pressure on flow-volume curve of the lung. *J Appl Physiol* 1969; 27:4-8.
2. Lanphier EH. Pulmonary function. In: Bennett PB, Elliott DH, eds. *The physiology and medicine of diving and compressed air work* (2nd ed.). Baltimore: Williams & Wilkins Co., 1975:102-154.
3. Lambertsen CJ, Gelfand R, Peterson RE, et al. Human tolerance to He, Ne, and N₂ at respiratory gas densities equivalent to He-O₂ breathing at depths to 1200, 2000, 3000, 4000, and 5000 feet of sea water (predictive studies III). *Aviat Space Environ Med* 1977; 48:843-855.
4. Wakeham WA, Kestin J, Mason EA. Viscosity and thermal conductivity of moderately dense gas mixtures. *J Chem Phys* 1972; 57:295-301.
5. Paganelli CV, Ar A, Rahn H, Wangenstein OD. Diffusion in the gas phase: the effects of ambient pressure and gas composition. *Respir Physiol* 1975; 25:247-258.
6. Paganelli CV, Kurata FK. Diffusion of water vapor in binary and ternary gas mixtures at increased pressures. *Respir Physiol* 1977; 30:15-26.
7. Reid RC, Prausnitz JM, Sherwood TK. *The properties of gases and liquids* (3rd ed.). New York: McGraw-Hill, 1977.
8. Van Liew HD, Thalmann ED, Sponholtz DK. Hindrance to diffusive gas mixing in the lung in hyperbaric environments. *J Appl Physiol: Respir Environ Exercise Physiol* 1981; 51:243-247.
9. Chang HK, Tai RC, Farhi LE. Some implications of ternary diffusion in the lung. *Respir Physiol* 1975; 23:109-120.
10. Worth H, Piiper J. Diffusion of helium, carbon monoxide, and sulfur hexafluoride in gas mixtures similar to alveolar gas. *Respir Physiol* 1978; 32:155-166.
11. Worth H, Nüsse W, Piiper J. Determination of binary diffusion coefficients of various gas species used in respiratory physiology. *Respir Physiol* 1978; 32:15-26.
12. Marrero TR, Mason EA. Gaseous diffusion coefficients. *J Phys Chem Ref Data* 1972; 1:3-118.
13. Wilke CR. Diffusional properties of multi-component gases. *Chem Eng Prog* 1950; 46:95-104.
14. Salzano JV, Stolp BW, Moon RE, Camporesi EM. Exercise at 47 and 66 ATA. In: Bachrach AJ, Matzen MM, eds. *Underwater physiology VII. Proceedings of the seventh symposium on underwater physiology*. Bethesda MD: Undersea Medical Society, Inc. 1981:181-196.
15. Gelfand R, Lambertsen CJ, Peterson RE. Human respiratory control at high ambient pressures and inspired gas densities. *J Appl Physiol: Respir Environ Exercise Physiol* 1980; 48:528-539.