

The compressibility and the capacitance coefficient of helium-oxygen atmospheres

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Imbert G, Dejourns P, Hildwein G. The compressibility and the capacitance coefficient of helium-oxygen atmospheres. *Undersea Biomed Res* 1982; 9(4):305-314.—The capacitance coefficient β of an ideal gas mixture depends only on its temperature T , and its value is derived from the ideal gas law (i.e., $\beta = 1/RT$, R being the ideal gas constant). But real gases behave as ideal gases only at low pressures, and this would not be the case in deep diving. High pressures of helium-oxygen are used in human and animal experimental dives (up to 7 or 12 MPa or more, respectively). At such pressures deviations from the ideal gas law cannot be neglected in hyperbaric atmospheres with respect to current accuracy of measuring instruments. As shown both theoretically and experimentally by this study, the non-ideal nature of helium-oxygen has a significant effect on the capacitance coefficient of hyperbaric atmospheres. The theoretical study is based on interaction energy in either homogeneous (He-He and O_2 - O_2) or heterogeneous (He- O_2) molecular pairs, and on the virial equation of state for gas mixtures. The experimental study is based on weight determination of samples of known volume of binary helium-oxygen mixtures, which are prepared in well-controlled pressure and temperature conditions. Our experimental results are in good agreement with theoretical predictions. 1) The helium compressibility factor Z_{He} increases linearly with pressure [$Z_{He} = 1 + 0.0045 P$ (in MPa) at 30°C]; and 2) in same temperature and pressure conditions ($T = 303$ K and $P = 0.1$ to 15 MPa), the same value for Z is valid for a helium-oxygen binary mixture and for pure helium. As derived from the equation of state of real gases, the capacitance coefficient is inversely related to Z ($\beta = 1/ZRT$); therefore, for helium-oxygen mixtures, this coefficient would decrease with increasing pressure. A table is given for theoretical values of helium-oxygen capacitance coefficient, at pressures ranging from 0.1 to 15.0 MPa and at temperatures ranging from 25°C to 37°C.

hyperbaric atmospheres
helium compressibility
helium-oxygen mixtures
real gases

deep diving
factor of compressibility
capacitance coefficient
virial equation of state

In ambient media, as in body fluids, respiratory physiologists use the general concept of capacitance to study the relation between the amount of gases (mol) present per unit volume and their partial pressures (1, 2). The capacitance coefficient, β , of a milieu for a gas species is defined as the increment of gas molar concentration, ΔC_x , per increment of its partial pressure, ΔP_x .

$$\beta = \frac{\Delta C_x}{\Delta P_x} \quad (1)$$

In gaseous environments β can be easily derived from the ideal gas law:

$$P V = n R T \quad (2)$$

in which P is the gas pressure, V the volume, n the number of moles of gas (that is, the quantity of substance), T the absolute temperature and R the gas constant (see Table 1). As the gas concentration is $C = n/V$:

$$\beta = \frac{1}{RT} \quad (3)$$

β would be the same for all gases and depends only on temperature. The capacitance relationship is used in any evaluation involving quantities of gas as related to pressure, such as evaluations of absolute density, concentration of atmospheric constituents, respiratory gas exchange, or heat transfer by convection.

Equation 3 will be verified as far as the gaseous environment complies with the ideal gas law, i.e., can be assumed an ideal gas mixture. This assumption is correct for the earthly atmosphere and for most respiratory mixtures used under normal or moderately raised pressures (1). However, gases usually deviate from the ideal gas law at high pressure, and high pressures of helium-oxygen are used in experimental chamber dives: up to 7 MPa with human subjects, up to 12 MPa and more with animals.

With respect to the accuracy of instruments that are used in hyperbaric research, the deviation of helium from the ideal gas law is not to be neglected at such pressures. Therefore, compared to ideal gas mixtures, some correction is needed for the capacitance coefficient of helium-oxygen hyperbaric atmospheres. The aim of this paper is to infer this correction from a study of pure helium and of compressibility of binary helium-oxygen mixtures.

THEORY

The most general form for the equation of state for real gases is

$$P V = Z_{P,T} n R T \quad (4)$$

TABLE 1
CONSTANTS FOR GASEOUS STUDIES

Symbol	Definition	Value (SI)
R	Ideal gas constant Limit of $P\bar{V}/T$ when $P \rightarrow 0$ (real gases)	8.312 J/(K · mol)
N_A	Avogadro number Number of molecules in a mole for $\theta = 16$	$6.002 \cdot 10^{23}/\text{mol}$
k	Boltzmann constant $k = R/N$	$1.380 \cdot 10^{-23}$ J/K
\bar{V}_n	Molar volume of an ideal gas Volume of a mole measured in standard temperature and pressure (STP) conditions (273.2 K and 101, 300 Pa).	0.02241 m ³
$\bar{V}_{n_{\text{He}}}$	Molar volume for helium (STP)	0.02243 m ³
$\bar{V}_{n_{\text{O}_2}}$	Molar volume for oxygen (STP)	0.02239 m ³

R , N_A , and k , from Allard (6); \bar{V}_n , $\bar{V}_{n_{\text{He}}}$, and $\bar{V}_{n_{\text{O}_2}}$ from Radford (7).

in which $Z_{p,T}$ is the compressibility factor—that is, a dimensionless quantity that measures the deviation from the ideal gas law at this pressure and this temperature. The compressibility depends on the nature of the gas; for an ideal gas $Z_{p,T}$ would be equal to unity, even at highest pressures. For real gases it only tends to unity at low pressure.

For a given gas at a given temperature $Z_{p,T}$ can be expressed as a series of powers of pressure (3) known as the virial equation of state:

$$Z_{p,T} = 1 + \frac{B_T}{RT} P + \frac{C_T - B_T^2}{(RT)^2} P^2 + \dots \quad (5)$$

in which B_T is the second virial coefficient, C_T the third, and so on. Their values depend only on temperature, and the number of these coefficients to be considered increases with pressure.

The virial equation can be discussed in terms of 1) intermolecular separation r , and 2) of potential energy of interaction between gaseous molecules (3–5):

The first term equals one and would stand for an ideal gas, the molecules of which are assumed to have no volume—never to collide, never to interact. As P decreases V increases, and all gases are able to approach an ideal behavior ($Z_{p,T} = 1$) because mean molecular distances are large compared to molecular dimensions.

The second term accounts for binary interaction. The potential energy of interaction of two molecules U_r is dependant on their separation r . For nonpolar molecules, it can be evaluated using the Lennard-Jones function:

$$U_r = 4 \epsilon_0 \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (6)$$

in which σ is the molecular separation where the middle-range forces of attraction compensate exactly for the short-range forces of repulsion ($U_r = 0$) and ϵ_0 is the maximal energy of attraction (Fig. 1). Values of σ and of ϵ_0 in pure gases are computed from compressibility but can also be derived from viscosities (3, 5). Table 2 gives for helium (1-1) and oxygen (2-2) values of σ and of ϵ_0 matching with their second virial coefficients and gives the values of these parameters in a heterogeneous helium-oxygen pair (1-2). In this case, σ and ϵ_0 are respectively approximated as the arithmetic mean and the geometric mean of their relative values in both of the homogeneous pairs.

The second virial coefficient can be computed (4) from U_r as

$$B_T = 2 \pi N_A \int_0^\infty \left[1 - \exp \left(-\frac{U_r}{kT} \right) \right] r^2 dr \quad (7)$$

in which N_A is the Avogadro number and k the Boltzmann constant (see Table 1).

Values of B_T at 303 K, for pure helium and pure oxygen, either computed from Eqs. 6 and 7 or interpolated from experimental data in the literature (4), are presented in Table 2, lines 1-1 and 2-2.

The third, fourth, or following terms would account for triple, quadruple, or multiple interactions and are not considered here. In other words, we assume, with respect to molecular dimensions, that molecular separation is sufficient at the pressures under consideration for us to neglect the effects of multiple interactions.

Therefore, the virial series is truncated to

$$Z_{p,T} = 1 + \frac{B_T}{RT} \quad (8)$$

The truncated form of the virial equation is the only relevant equation that can be used for real gas mixtures (6). This implies taking into account all possible binary interactions—that is, not

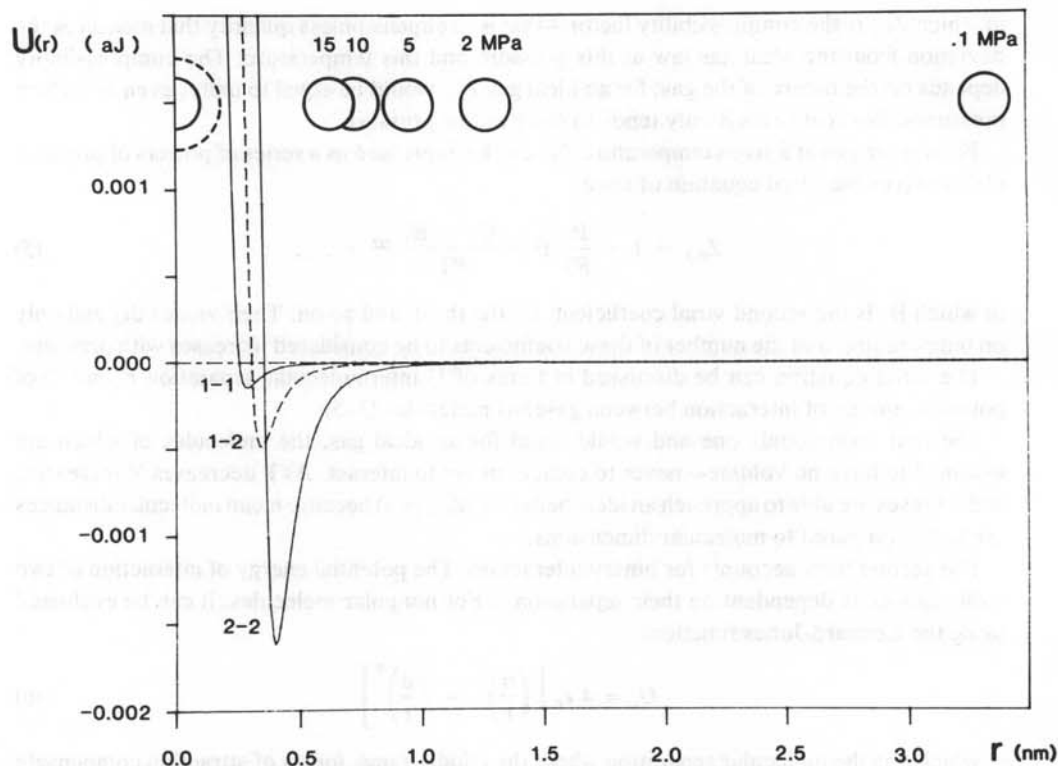


Fig. 1. Lennard-Jones intermolecular potentials U_r in molecule pairs: helium-helium (1-1), oxygen-oxygen (2-2), helium-oxygen (1-2) and mean molecular separation r at high pressures. Potential energy of interaction is given in aJ (10^{-18} J) as a function of molecular distances in nm. Mutual short-range repulsion (positive) or middle-range attraction (negative) depend on molecular separation and are in equilibrium at a distance σ characteristic of the molecular species. When r is 3 times longer than σ , molecular interactions can be neglected, their energy becoming less than 1% of the maximum energy of mutual attraction ϵ_0 . In the heterogeneous 1-2 pair (dashed line) the relevant values for σ and for ϵ_0 are taken as, respectively, the arithmetic mean and the geometric mean of σ and of ϵ_0 in both the homogeneous pairs (1-1) and (2-2). Top, helium molecules are represented with a molecular diameter of 0.22 nm. The distances between the half-molecule at the origin of abscissa and the molecules to the right correspond to an average value of r at a temperature of 30°C for pressures ranging from atmospheric (0.1 MPa) to 15 MPa. This value can be approximated as the cube root of the inverse of the Loschmidt number (the number of molecules per unit volume) in each condition. Dashed half-circle outlines a half-oxygen molecule 0.36 nm in diameter.

only interactions between molecule pairs of the same species but also pairs of different species. The Lennard-Jones potential for the interaction between helium and oxygen molecules, as obtained from Eq. 6, is presented graphically in Fig. 1 (dashed line). Equation 7 is used to compute a value for the second virial coefficient of a hypothetical pure gas, $B_{(1-2)_T}$, the molecules of which would interact with the same energy as oxygen and helium molecules do (Table 2).

Finally, with respect to all kinds of bimolecular interactions, the second virial coefficient of a multicomponent mixture of real gases, $B_{mix,T}$, would be computed as (2, 7)

$$B_{mix,T} = \sum_i \sum_j F_i F_j B_{ij,T} \quad (9)$$

in which F_i , F_j are the molar fractions of components i to j , and $B_{ij,T}$ are the second virial coefficients computed from molecular interactions. Hence the compressibility factor for this mixture would be

TABLE 2
LENNARD-JONES PARAMETERS AND SECOND VIRIAL COEFFICIENTS FOR HELIUM AND OXYGEN

Molecular Species	σ^* m	ϵ_0/k^{**} K	B_{303K}^\dagger m ³ /mol	B_{303K}^\ddagger m ³ /mol
1-1 He	$0.257 \cdot 10^8$	10.8^{\S}	$11.3 \cdot 10$	$(11.6 + 0.5) \cdot 10$
2-2 O ₂	$0.358 \cdot 10^8$	117.5^{\S}	$-15.4 \cdot 10$	$(-15.5 + 1) \cdot 10$
1-2 He-O ₂	$0.308 \cdot 10^8$	35.6^{\S}	$15.8 \cdot 10$	unknown

* σ , Intermolecular distance in a pair of molecules at which the middle-range attractive forces are in equilibrium with the short-range repulsive forces; therefore, at that distance the Lennard-Jones function equals zero (see Fig. 1). ** ϵ_0 , Maximum energy of attraction here related to the Boltzmann constant k (see Table 1) and expressed as a temperature. † Second virial coefficient at 303 K resulting from theoretical evaluations by numerical integration of Eqs. 6 and 7. ‡ Second virial coefficient linearly interpolated at 303 K from data compiled and averaged (smoothed values at different temperatures) according to Dymond and Smith (4). § Theoretical values for helium (1-1) and oxygen (2-2) homogeneous pairs [close values are obtained from study of viscosities; see Reid et al. (5)] estimated from averaging for the helium-oxygen (1-2) heterogeneous pair (see text).

$$Z_{\text{mix},p,T} = 1 + B_{\text{mix},T} \cdot \frac{P}{RT} \quad (10)$$

EXPERIMENTAL PROCEDURE

Gas products (helium > 0.9995 and oxygen > 0.9998) and most materials and instruments that were used in this study are in current use in diving and in hyperbaric technology.

1. All operations on gas were carried out in a temperature-controlled room ($30.0^\circ\text{C} \pm 0.1^\circ\text{C}$).
2. Pure or mixed gases were prepared and weighed in three light-alloy Gerzat cylinders weighing 2.5 to 3.0 kg, containing approximately 2.0 liters of gas and previously tested for their maximal working pressure (15 MPa) and for their cubic expansion coefficient ($+0.0002 \text{ MPa}^{-1}$). The cylinders contained some stainless steel balls to improve gas mixing by manual agitation.
3. For gas-filling and pressure measurements the cylinders were connected by flexible tubing in parallel to the high pressure circuitry and were immersed in a 2000-liter water tank at room temperature (Fig. 2). Gas was slowly injected at a constant rate of approximately 1 MPa/min—first oxygen, then helium. For each gas, pressure was measured after agitation and temperature equilibration (thermal equilibrium was considered as complete when no more appreciable change was observed between two pressure readings at 10-min intervals). Oxygen pressure was read on a mercury column in the low pressure circuitry. Pure helium or helium-oxygen pressures after helium injection were read on two Heise-Bourdon (Dresser Industries, Newtown, CT) precision manometers in the high pressure circuitry (0–5.00 and 0–15.00 MPa, respectively, and 0.001 of full scale in accuracy). Correction was made for instrument readings at 30°C .
4. The cylinders were then sealed and secured from circuitry; they were wiped, dried, and weighed for their whole gas content. The cylinders were weighed one at a time in a precision two-pan balance of 5-kg range and 1-cg sensitivity. In fact, since they were evacuated and weighed before and after any utilization, each cylinder was weighed three times: before, during, and after being gas filled. This allowed correction for the metal loss due to cylinder corrosion that accompanied each cycle of utilization; a correction was also made for air buoyancy of weight standards manipulated in counterbalance weighing operations.

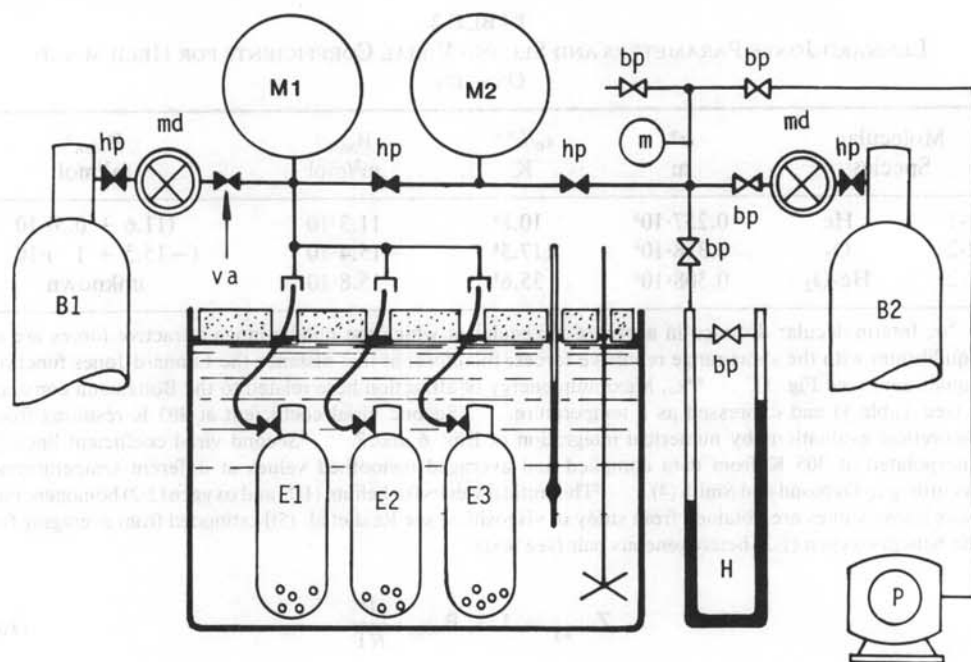


Fig. 2. Apparatus for preparation of helium-oxygen binary mixture and for pressure measurements. Apparatus is located in a temperature-controlled room ($30.0^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$) and is set up above a 2000-liter water tank at the same temperature. B1, high pressure helium (20 MPa); B2, high pressure oxygen (15 MPa); md, pressure reducing valves; va, needle valve; hp, high pressure section valves; bp, low pressure valves; M1 and M2, two high pressure manometers, 0.1–15.0 and 0.1–5.0 MPa, respectively; m, low pressure manometer; H, mercury column; P, vacuum pump. E1, E2, E3: three light-alloy test cylinders connected in parallel to the high pressure circuitry by flexible tubing and immersed in water tank for gas filling (first oxygen, then helium) and for pressure measurements. Helium or oxygen and helium-oxygen pressures are measured just after agitation and temperature equilibration. Then cylinders are sealed and secured from circuitry; they are wiped, dried, and weighed to determinate their whole gas content.

5. Binary gas mixtures of roughly constant oxygen molar concentration ($\text{CO}_2 \approx 40 \text{ mmol/l}$) were obtained by filling the evacuated cylinders with 0.1 MPa of oxygen before pressurizing them with helium. Oxygen fractions were controlled in mixtures using a paramagnetic analyzer.

RESULTS AND DISCUSSION

Table 3 presents the pressure-volume-temperature data obtained with pure helium and with mixtures of helium and low amounts of oxygen studied in well-controlled conditions (30.0°C and 0.1 to 15.0 MPa).

The main results were that 1) Pure helium was less compressible than an ideal gas. The compressibility factor of helium at 30°C increased linearly with P , following the approximate relationship: $Z_{\text{He}_{303\text{K}}} = 1.000 + 0.0045 P$ (in MPa). 2) There was no significant difference in behavior of pure helium and of low-oxygen binary helium-oxygen mixtures ($F_{\text{O}_2} < 1\%$) as shown by a paired Student t test (same pressure, same cylinder with or without oxygen) of values presented in Table 3.

This study was carried out in temperature and pressure conditions that approximated temperature and pressure conditions of hyperbaric atmospheres for human and animal studies in

TABLE 3
EXPERIMENTAL RESULTS: PRESSURE-VOLUME-TEMPERATURE DATA AND VALUES OF
COMPRESSIBILITY FOR PURE HELIUM AND FOR HELIUM-OXYGEN MIXTURES

V, ^a liter	T, ^b K	P, ^c MPa	M _{O₂} , ^d g	M _{He} , ^e g	F _{O₂} , ^f %	Z _{303K} , ^g dimensionless
2.000	303.2	0.10	0.00	0.32	0.00	1.00
2.000	303.2	0.10	2.54	0.00	100.00	1.00
1.990	303.2	0.10	0.00	0.32	0.00	1.00
1.990	303.2	0.10	2.53	0.00	100.00	1.00
2.017	303.2	0.10	0.00	0.32	0.00	1.00
2.017	303.2	0.10	2.56	0.32	100.00	1.00
2.003	303.2	4.98	0.00	15.46	0.00	1.025
2.003	303.2	5.01	2.54	15.26	2.04	1.023
1.992	303.2	4.98	0.00	15.43	0.00	1.021
1.992	303.2	5.01	2.53	15.19	2.04	1.022
2.019	303.2	4.98	0.00	15.59	0.00	1.024
2.019	303.2	5.01	2.56	15.40	2.04	1.022
2.005	303.2	9.97	0.00	30.41	0.00	1.044
2.005	303.2	9.95	2.54	30.02	1.05	1.045
1.994	303.2	9.97	0.00	30.25	0.00	1.044
1.994	303.2	9.95	2.53	29.87	1.05	1.044
2.021	303.2	9.97	0.00	30.62	0.00	1.045
2.021	303.2	9.95	2.56	30.26	1.05	1.043
2.008	303.2	14.94	0.00	44.64	0.00	1.067
2.008	303.2	14.96	2.54	44.36	0.71	1.066
1.996	303.2	14.94	0.00	44.34	0.00	1.068
1.996	303.2	14.96	2.53	44.18	0.71	1.064
2.023	303.2	14.94	0.00	44.91	0.00	1.069
2.023	303.2	14.96	2.56	44.64	0.71	1.067

^aV, cylinder volume. ^bT, temperature. ^cP, final pressure. ^dM_{O₂}, oxygen mass. ^eM_{He}, helium mass. ^fF_{O₂}, fractional concentration of oxygen. ^gZ_{303K}, compressibility computed from M_{O₂} and M_{He} with respect to molecular mass. The deviations from ideal gas law in pure helium are in good agreement with values reported in literature. In controlled pressure and temperature conditions, deviations from ideal gas law in binary helium-oxygen mixtures with low oxygen fractional concentrations are not significantly different from those of pure helium.

diving experiments in dry pressure chambers. Results are not discussed as a contribution to fundamental physics; basically, they are analyzed for their practical significance regarding the control of hyperbaric atmospheres.

For helium compressibility, the experimental findings are in good agreement with values predicted from well-established theory. Linear increase in Z_{He303K} with P was predicted by the truncated form of the virial equation of state (Eq. 8). Accordingly, a slope of +0.0045/MPa corresponds to a second virial coefficient B_{303K} = +11.4 cm³/mol, close to values given in Table 2. Furthermore, similarity in behavior of pure helium and mixtures of low oxygen with helium was also predictable from theory. With reference to Table 2, Eq. 9 would be written for a binary helium-oxygen mixture at 30°C:

$$B_{\text{mix}303K} = F_{\text{He}}^2 B_{(1-1)303K} + 2 F_{\text{He}} F_{\text{O}_2} B_{(1-2)303K} + F_{\text{O}_2}^2 B_{(2-2)303K} \quad (11)$$

in which F_{He} and F_{O_2} are the respective fractions of helium and of oxygen in the mixture. As F_{O_2} is very low, the last term would be neglected in this expression. Moreover, $B_{(1-2)303\text{K}}$ is not very different from $B_{(1-1)303\text{K}}$ (Table 2). For these reasons the compressibility of mixtures of low oxygen with helium is very similar to compressibility of pure helium. At 10 MPa, the predicted difference in the compressibility factors is less than 1/1000, that is, less than the normal uncertainty in accurate pressure measurements.

From a practical point of view—that is, with respect to the accuracy of measurements that are to be performed in hyperbaric technology—the most important conclusions are as follows: 1) the deviation from ideal gas law of pressurized helium-oxygen atmospheres used in deep diving may not be neglected; 2) since at great depths the oxygen fractional concentration is low, the relevant corrections can be done with sufficient accuracy and very simply—by using for these atmospheres the compressibility factor of pure helium in the same temperature and pressure conditions (Z_{He}).

The capacitance coefficient of these atmospheres is a function of helium compressibility and can be deduced from the general equation of state of real gases (Eq. 4). This coefficient is related to temperature and to compressibility:

$$\beta = \frac{1}{Z_{p,T}RT} \quad (12)$$

As $Z_{p,T}$ of helium increases with pressure, the capacitance coefficient of helium-oxygen hyperbaric atmospheres is inversely proportionate to depth.

This statement has many practical consequences. For example, it implies that the density of diving respiratory mixtures is not linearly related to depth, even at constant temperature and without change in composition. For a constituent in a mixture, it implies also that even at the same temperature a constant molar concentration does not correspond at any depth to the same value computed for its partial pressure. Thus, a normoxic helium-oxygen mixture is defined as a mixture with 21 kPa of oxygen partial pressure; this corresponds at 30°C to 8.33 mol/m³ O₂ at sea level, but to only 7.95 mol/m³ O₂ at 1000 m.

What the foregoing means can be clearly illustrated by a numerical example. Let us consider a pressure vessel filled with pure oxygen at sea level, the initial conditions being a temperature of 27.6°C and a pressure of 10⁵ Pa. In these conditions, oxygen is reasonably assumed to be an ideal gas; the capacitance coefficient would depend on temperature (Eq. 3) and equal exactly 0.4000 mmol/(m³·Pa). This gives us the molar concentration of the gas and its absolute density with respect to molecular mass of oxygen ($M \approx 32$) as, respectively, 40 mol/m³ and 1.28 kg/m³. Then helium is slowly injected in the vessel without change in temperature, up to a pressure 100 times higher, i.e., 10⁷ Pa. Such a procedure is very close to the procedure used in this study and to procedures used in practical diving operations. As there is no change in temperature during the compression, the capacitance coefficient would remain unchanged if helium behaved as an ideal gas. Thereafter, the final concentration would reach a value 100 times higher, i.e., 4000 mol/m³. Since 40 mol/m³ of oxygen were previously introduced in the vessel, the helium concentration would be 3960 mol/m³ and the absolute density of the mixture would be 17.1 kg/m³ with respect to the molecular mass of helium ($M \approx 4$). In fact, because helium is less compressible than an ideal gas, fewer molecules are needed to achieve the final pressure. In the final conditions (i.e., 10⁷ Pa at 27.6°C) $Z = 1.053$. Because this is not changed by the presence of a small amount of oxygen, the capacitance coefficient of this gas mixture is easily computed (Eq. 12) as $\beta = 0.4000/1.053 = 0.3800$ mmol/(m³·Pa). Therefore, the mixture will reach a final concentration of 3800 mol/m³, that is, more than 5% less than expected from an ideal gas behavior; the helium concentration will be 3760 mol/m³ and the absolute density 16.3

TABLE 4
CAPACITANCE COEFFICIENT OF HELIUM-OXYGEN MIXTURES (mmol/m³·Pa) AS A FUNCTION OF TEMPERATURE AND PRESSURE

Pressure, MPa	Temperature, °C						
	25	27	29	31	33	35	37
0.1	0.4034	0.4007	0.3980	0.3954	0.3928	0.3903	0.3878
1.0	0.4014	0.3988	0.3962	0.3936	0.3910	0.3885	0.3860
2.0	0.3995	0.3969	0.3943	0.3917	0.3892	0.3867	0.3842
3.0	0.3976	0.3950	0.3925	0.3899	0.3874	0.3849	0.3825
4.0	0.3958	0.3932	0.3906	0.3881	0.3856	0.3832	0.3808
5.0	0.3939	0.3913	0.3888	0.3863	0.3839	0.3815	0.3791
6.0	0.3920	0.3895	0.3870	0.3846	0.3821	0.3797	0.3773
7.0	0.3902	0.3877	0.3853	0.3828	0.3804	0.3780	0.3757
8.0	0.3884	0.3859	0.3835	0.3811	0.3787	0.3764	0.3740
9.0	0.3866	0.3842	0.3817	0.3794	0.3770	0.3747	0.3724
10.0	0.3848	0.3824	0.3800	0.3776	0.3753	0.3730	0.3707
11.0	0.3831	0.3807	0.3783	0.3760	0.3737	0.3714	0.3691
12.0	0.3813	0.3790	0.3766	0.3743	0.3720	0.3697	0.3675
13.0	0.3796	0.3772	0.3749	0.3726	0.3704	0.3681	0.3659
14.0	0.3779	0.3756	0.3733	0.3710	0.3687	0.3665	0.3643
15.0	0.3762	0.3739	0.3716	0.3694	0.3671	0.3649	0.3628

Theoretical values of capacitance coefficient of binary helium-oxygen mixtures are computed according to Eq. 12 and assuming a compressibility factor equal to the compressibility factor of pure helium Z_{He} in the same pressure and temperature conditions. Values of Z_{He} are interpolated from thermodynamic tables for pure helium (Ref. 8).

kg/m³. We have also to point out that any variable related to absolute density, such as heat capacity, would be modified in the same direction.

Moreover, an important and obvious consequence is to be emphasized regarding fractional concentrations: F_{O_2} , i.e., the number of oxygen molecules related to the total number of molecules, would not be 1% as in an ideal gas mixture, but more than 1.05%. This leads us to compute an oxygen partial pressure in the final conditions that would be higher than the pressure of pure oxygen alone in the vessel in the initial conditions. The reasons are simple: the definition of partial pressure bears upon the concept of mixtures of ideal (noninteracting) gases and is not quite correct in other conditions. It is clearly evident that in real gas mixtures such as hyperbaric atmospheres a constituent cannot be quantitatively evaluated without taking into consideration the presence of other constituents.

Theoretical values for β of low oxygen binary helium-oxygen mixtures are given in Table 4 for pressures ranging from 0.1 to 15 MPa and for temperatures ranging from 25°C to 37°C.

The authors are grateful to M.M. V. Bianco, G. Ricca, and O. Leandri (Comex Industries, Marseille) for their friendly and skilled technical assistance in preparing the experimental setup, and to Drs. L. Homer, P. K. Weathersby, M. J. Ackerman (Naval Medical Research Institute, Bethesda) for their helpful criticism and to Ms. Rosemary Balenger for the preparation of the manuscript.—*Manuscript received for publication May 1982; revision received September 1982.*

Imbert G, Dejours P, Hildwein G. La compressibilité des mélanges binaires hélium-oxygène et le coefficient de capacitance des atmosphères hyperbares. *Undersea Biomed Res* 1982; 9(4):305–314.—Le coefficient de capacitance d'un mélange de gaz parfaits ne dépend que de sa température T et sa valeur se calcule à partir de la loi des gaz parfaits (avec $\beta = 1/RT$; R étant la constante des

gaz parfaits). Mais les gaz réels ne se comportent comme des gaz parfaits qu'à des pressions peu élevées, ce qui ne devrait plus être le cas en plongée profonde. On utilise des pressions d'hélium-oxygène élevées au cours des expériences de plongées en caisson hyperbare humaines ou animales (respectivement jusqu'à 7 MPa et 15 MPa ou davantage). A de telles pressions, les écarts à la loi des gaz parfaits des atmosphères hyperbares ne sont plus négligeables devant la précision des instruments de mesure en usage. Comme le montre le présent travail, à la fois par la théorie et par l'expérience, les écarts à la loi des gaz parfaits de l'hélium-oxygène ont une influence sensible sur le coefficient de capacitance des atmosphères hyperbares. L'étude théorique s'appuie sur l'énergie des interactions dans des paires de molécules homogènes (He-He et O₂-O₂) ou hétérogènes (He-O₂) et sur l'application de l'équation du viriel aux mélanges de gaz réels. L'étude expérimentale repose sur la pesée d'échantillons de volumes connus de mélanges hélium-oxygène que l'on prépare dans des conditions de pression et de température bien contrôlées. Les résultats obtenus sont en bon accord avec les prédictions théoriques: 1) Le facteur de compressibilité de l'hélium Z_{He} croît linéairement avec la pression P ($Z_{He} = 1 + 0.0045 P(\text{MPa})$ à 30°C); et 2) dans les mêmes conditions de température et de pression ($T = 303 \text{ K}$ et $P = 0.1$ à 15 MPa), on peut prendre la même valeur de Z pour un mélange binaire hélium-oxygène à faible teneur en oxygène et pour l'hélium. Le coefficient de capacitance, déduit de l'équation d'état des gaz réels, est inversement proportionnel à Z ($\beta = 1/ZRT$); donc celui des atmosphères hélium-oxygène sera d'autant plus faible que leur pression sera plus élevée. Une table des valeurs théoriques de β des mélanges binaires hélium-oxygène à faible teneur en oxygène a été calculée pour des pressions de 0.1 à 15.0 MPa et des températures de 25°C à 37°C.

atmosphères hyperbares
plongée profonde
compressibilité de l'hélium
facteur de compressibilité

mélanges hélium-oxygène
coefficient de capacitance
gaz réels
équation d'état du viriel

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