Bulgarian Chemical Communications, Volume 50, Special Issue B (pp. 99 - 103) 2018

Thermodynamic properties of helium – oxygen mixtures

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Received July 10, 2017; Accepted November 16, 2017

The paper reports regression functions describing thermodynamic properties of helium-oxygen mixtures covering the pressure range p=0.1-1.8 MPa, temperature T=273.15-333K and helium molar fraction x_{He}=0.65-0.98. Regression equations that have been derived enable to determine specific heat, specific enthalpy, density, dynamic viscosity and thermal conductivity as the function of pressure, temperature and helium molar fraction in helium-oxygen (HELIOX) breathing mixtures.

Keywords*:* Thermodynamic properties, Helium-oxygen mixtures

INTRODUCTION

Development of off-shore industry and submarine rescue contributed to increasing importance of underwater operations at a great depth. The diving operations where the divers are exposed to the ambient water pressure can be classified in two groups: bounce (nonsaturation) dives for short jobs and saturation diving for long ones. The saturation diving theoretically enables the divers to stay on the bottom for a long time but the divers must be supported by a hyperbaric complex on the surface, where the divers live in a dry hyperbaric environment at a pressure equal to the ambient pressure existing at their work site [1].

The tissues of a diver's body absorb the inert gases as a function of the duration of the diving operation and the type of the breathing mixture used. In long duration dives, the body tissues become saturated with the inert gases. The techniques of saturation diving make use of the fact that once the body reaches this equilibrium, it can safely remain saturated for long periods, and the diver's obligation of decompression does not increase with further exposure. Decompression is performed during return of the divers at the sea level [1,2].

Saturation diving enables improving of the effectiveness of the diving operation. Two crews of the divers rotate; one crew works on the bottom while the other one rests in the living compartment of DDC (2).

Helium causes certain problems related to dangerous cooling of the divers. This is due to the high thermal conductivity of helium, six times that of air [1-7]. One of the major tasks for the life support systems of the hyperbaric facilities is to create the environment which maintains the safe level of oxygen partial pressure, contaminants, temperature, relative humidity, velocity of the breathing gas and consequently the thermal comfort for the divers. In saturation diving, the partial pressure of oxygen should be maintained between p_{O2}=0.02-0.05 MPa [1-3].

The comfort temperature in the hyperbaric environment increases with the total pressure of gas and should be maintained at a level higher (t≈ 20-36°C) than that in normobaric air environment [1-3,8,9] while relative humidity should be kept within φ = 0.4-0.7.

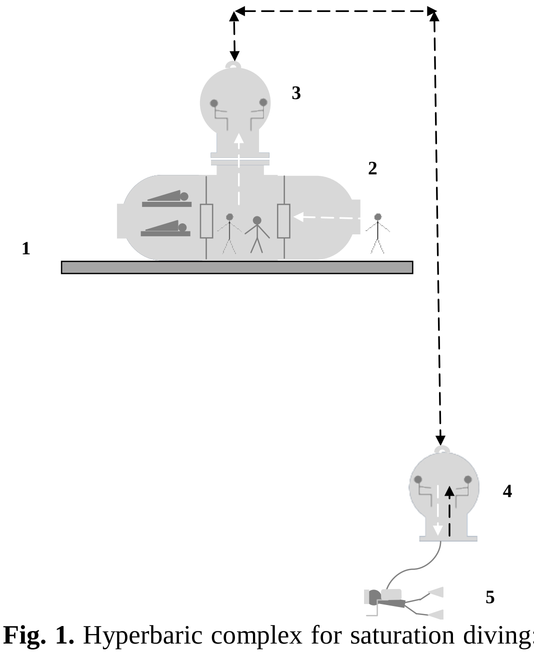

Fig. 1. Hyperbaric complex for saturation diving: 1 - deck of a vessel or drilling platform, 2 - deck decompression chamber (DDC), 3 - personnel transfer capsule (PTC) mated to DDC, 4 - personnel transfer capsule (PTC) in the sea, 5 - the diver performing work at the operational depth.

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It must be noted that also toxic effects of contaminants are increased in the hyperbaric environment [10]. Helium-oxygen breathing mixtures are used at depths down to 200 m [1-3]. The use of helium as an inert component of the breathing mixture enables elimination of nitrogen narcosis when diving to less than 50 m and reduces the diver's effort while breathing. The pressure and composition of the helium-oxygen (HELIOX) breathing mixture depend on the depth of bottom operation and duration of the diver's exposure. The thermodynamic properties of the breathing mixture that depend on composition, pressure and temperature are as follows: specific heat at constant pressure, specific heat at constant volume, specific enthalpy, specific volume, density, dynamic viscosity, thermal conductivity.

Thermodynamic properties of the breathing mixtures have impact on the diver and the parameters to be maintained by environmental life support systems in hyperbaric objects. As the depth of the diving operation increases, the pressure of the breathing mixture increases and it contributes to significant increase of the breathing mixture density. Increased density of the breathing mixture causes increased physical effort of the diver while breathing. It may result in improper lung ventilation, hypoxia, chest tightness, etc. [1,3]. Viscosity of the breathing mixture also has an impact on the respiratory resistance of the diver and the heat exchange during respiration.

Thermal properties of the inert gases (helium, hydrogen) cause certain problems related to dangerous cooling of the divers. This is due to the high thermal conductivity and specific heat of inert gases, however, the other thermodynamic properties also influence thermal sensations of the divers and finally the effective work.

Maintenance of the diver's thermal homeostasis requires creation of a microclimate in a hyperbaric facility of the parameters compensating heat loss from the diver's body.

The most important variables which influence the condition of thermal comfort in hyperbaric environment are as follows: composition, temperature, pressure, humidity and relative velocity of the breathing gas, mean radiant temperature, activity level and thermal resistance of the diver's clothing. Thermal comfort in the hyperbaric facilities can be achieved by many different combinations of the above mentioned variables. It should be noted that thermal sensations of the divers can be different. Microclimate parameters should provide thermal comfort to the divers who stay in the hyperbaric facility. Creation of a hyperbaric microclimate of comfort parameters is a complex issue of great ergonomic importance.

Calculation of gas mixture thermodynamic properties as the function of gas composition, pressure and temperature is essential for solving the comfort equation for hyperbaric environment [8,9]. It makes also possible to determine contributions of heat loss to the overall diver's thermal balance in the hyperbaric environment.

Based on experimental data of oxygen and helium, gaseous components of HELIOX (helium-oxygen) breathing mixture given by Bretsznajder [4], Golubiev [5, 6] Varhaftik [7] and methods of calculation of thermodynamic properties of real gas mixtures published by Bretsznajder [4] and Sobański [11], the correlations describing thermodynamic properties of HELIOX will be derived. Specific heat at constant pressure, specific enthalpy, specific volume, density and thermal conductivity of the HELIOX mixture will be given as functions of pressure, absolute temperature and molar fraction of helium. When designing hyperbaric systems, it is required to know the thermodynamic properties of the breathing mixtures as the function of pressure, temperature and its composition. Methods of gas mixture thermodynamic properties calculation published by Bretsznajder [4] and Sobański [11] are very accurate but very laborious, as they require calculation of many auxiliary parameters. In order to simplify the further calculations, while maintaining a sufficient engineering accuracy, the regression equations for calculating the thermodynamic properties of helium-oxygen mixtures as a function of pressure, temperature and molar fraction of helium in the mixture will be derived.

THERMODYNAMIC PROPERTIES OF HELIUM- OXYGEN MIXTURES

In order to determine the thermodynamic properties of helium-oxygen (HELIOX) mixtures experimental data of oxygen and helium thermodynamic properties published by Bretsznajder [4], Gołubiev [5] Varhaftik [7] were applied. Regression correlations describing the thermodynamic properties of oxygen and helium as the functions of pressure and absolute temperature were developed in a numerical experiment in which experimental data published in the above mentioned works were used. Regression correlations were developed with the use of Statistics software.

Specific heat of oxygen at constant pressure in the range of pressure p= 0.1-5.0 MPa, absolute temperature T= 280-330 K is expressed by equation (1), where the correlation coefficient R=0.976:

$$c_p = 0.8858 + \exp(-2.3169 + 0.1881 \cdot p - 0.0027 \cdot T) \quad (1)$$

Specific enthalpy of oxygen in the range of p = 0.1-5.0 MPa, T= 280-330 K is expressed by equation (2), where the correlation coefficient R=0.988:

$$i = 0.7239 + 0.9069 \cdot T - 7.887 \cdot p + 0.0185 \cdot p \cdot T \quad (2)$$

Specific volume of oxygen in the range of p= 0.1-5.0 MPa, T= 280-330 K is expressed by equation (3), where the correlation coefficient R=0.999:

$$v = 0.0776 \cdot p^{-1.0086} + 5.1000 \cdot 10^{-6} \cdot T \quad (3)$$

Dynamic viscosity of oxygen in the range of p = 0.1-5.0 MPa, T= 280-330 K is expressed by equation (4), where the correlation coefficient R=0.999:

$$\eta = (0.7142 \cdot p^{1.5075} + 28.4129 \cdot T^{0.4441} + -149.2896) \cdot 10^{-7} \quad (4)$$

Thermal conductivity of oxygen in the range of p= 0.1- 6.0 MPa, T= 280-350 K is expressed by equation (5), where the correlation coefficient R=0.997:

$$\lambda = (0.4282 \cdot p^{1.0758} + 51.8641 \cdot T^{0.1609} + -103.3646) \cdot 10^{-3} \quad (5)$$

Specific heat of helium at constant pressure in the range of p= 0.1-5.0 MPa, T= 273-323 K is expressed by equation (6), where the correlation coefficient R=0.900:

$$c_p = 1.5642 \cdot p^{6.77 \cdot 10^{-5}} + 3.6654 \cdot T^{-0.0017} + +4.4 \cdot 10^{-6} \cdot p \cdot T \quad (6)$$

Specific enthalpy of helium in the range of p= 0.1-6.0 MPa, T= 273-330 K is expressed by equation (7), where the correlation coefficient R=0.999:

$$i = -1418.467 + 5.19300 \cdot T + 3.36408 \cdot p + -0.00035 \cdot p \cdot T \quad (7)$$

Specific volume of helium in the range of p= 0.1-5.0 MPa, T= 273-323 K is expressed by equation (8), where the correlation coefficient R=0.997:

$$v = 0.6259 \cdot p^{-0.9980} + 0.2167 \cdot T^{-4.8881} \quad (8)$$

Dynamic viscosity of helium in the range of p= 0.1-5.0 MPa, T= 273-473 K is expressed by equation (9), where the correlation coefficient R=0.999:

$$\eta_i = [1.8503 \cdot p^{0.0009} + A] \cdot 10^{-5}$$
where
$$A = 0.0086 \cdot (T - 273)^{0.8693} \quad (9)$$

Thermal conductivity of helium in the range of p= 0.1-5.0 MPa, T= 270-350 K is expressed by equation (10), where the correlation coefficient R=0.999:

$$\lambda = 4.273 \cdot 10^{-4} \cdot p^{1.0491} + +6.2322 \cdot 10^{-3} \cdot T^{0.5593} \quad (10)$$

Thermodynamic properties of helium - oxygen mixtures were calculated from correlations published by Bretsznajder [4] and Sobański [11]. Calculations were performed at the following assumptions: pressure p = 0.1÷1.8 MPa, absolute temperature T = 273.15÷333.15 K. Oxygen partial pressure was assumed to be constant p_{o2}=35 kPa in the range of assumed pressure. Molar fraction of helium x_{He}=0.65÷0.98.

To derive regression correlations with the use of Statistics software, the obtained results of HELIOX thermodynamic properties were used as input data. Regression correlations describing the thermodynamic properties of helium-oxygen (HELIOX) mixtures in the range of p=0.1-1.8 MPa, T=273-333 K, x_{He}=0.65÷0.98 at constant oxygen partial pressure p_{O2} =35 kPa, are as follows:

- specific heat at constant pressure, correlation coefficient R=0.999:

$$c_p = \left[1648.3867 + \exp B\right] \cdot 10^{-3}$$
where
$$B = 0.002472 \cdot 10^{-3} \cdot p + -1.2602 \cdot 10^{-4} \cdot T + +8.2017 \cdot x_{He} \quad (11)$$

- specific enthalpy, correlation coefficient R=0.978:

$$i = -161.1602 + \exp C$$
where
$$C = 0.0124 \cdot p + 0.01153 \cdot T + 2.2312 \cdot x_{He} \quad (12)$$

- density, correlation coefficient R=0.950:

$$\rho = 2543.7189 + 28.1176 \cdot p + \\ + 1.5787 \cdot T + -2878.7407 \cdot x_{He} \tag{13}$$

- dynamic viscosity, correlation coefficient R=0.9947:

$$\eta = 9.8048 \cdot 10^{-6} - 4.5019 \cdot 10^{-7} \cdot p + \\ + 5.1973 \cdot 10^{-8} \cdot T - 4.4600 \cdot 10^{-6} \cdot x_{He} \tag{14}$$

- thermal conductivity, correlation coefficient R=0.9930:

$$\lambda = -0.1300 + 2.1188 \cdot 10^{-3} \cdot p + \\ + 3.1898 \cdot 10^{-4} \cdot T + 0.1849 \cdot x_{He} \tag{15}$$

Regression correlations describing the thermodynamic properties of oxygen, helium and helium-oxygen mixtures were elaborated with the use of Statistica Software - nonlinear and multiple regression. The selection of the nonlinear estimation function was determined by the simplicity of the regression function and the high correlation coefficient. Regression functions that have been derived are simpler to use in practical application than the analytical relationships given in the literature [4,11] because some stages of indirect calculations have been eliminated. It is possible to calculate the thermodynamic properties of helium-oxygen mixtures only as a function of pressure, temperature and molar fraction of helium.

Fig. 2 illustrates the relationship of specific heat at constant pressure of HELIOX calculated from equation (11) pressure and molar fraction of helium at absolute temperature T=273K.

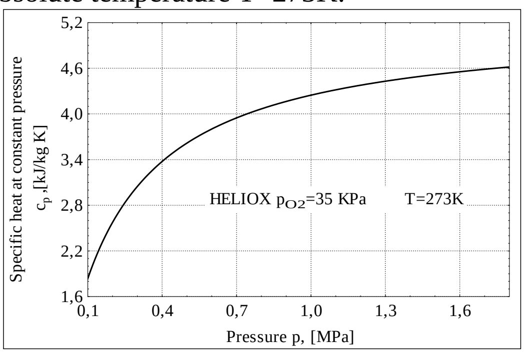

Fig. 2. Relationship between specific heat at constant pressure of HELIOX and pressure at absolute temperature T=273 K.

As it follows from Fig. 2 increasing pressure at constant absolute temperature contributes to a significant increase in specific heat of the oxygen-helium mixture at constant pressure.

Figure 3, based on the regression equation (13), illustrates the relationship between the density of HELIOX mixture pressure and the temperature. As it follows from Figure 3 the density of the HELIOX mixture increases with pressure. Increasing temperature at constant pressure contributes to reduce the density. At a lower pressure of HELIOX the effect of pressure and temperature on density is lower.

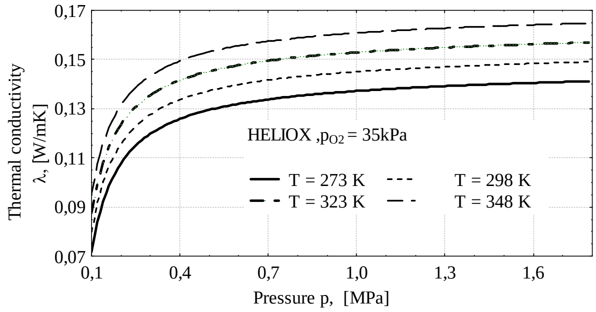

Fig. 3. Relationship between density of HELIOX pressure and temperature

Figure 4 illustrates the relationship between thermal conductivity of Heliox pressure and temperature. As it follows from Fig. 4 increasing pressure and temperature contribute to increase HELIOX thermal conductivity.

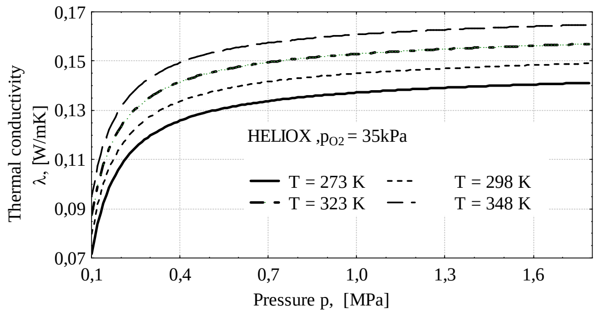

Fig.4. Relationship between thermal conductivity of HELIOX pressure and temperature

Figure 5 illustrates the relationship between thermal conductivity of HELIOX pressure and molar fraction of helium at absolute temperature T=303 K.

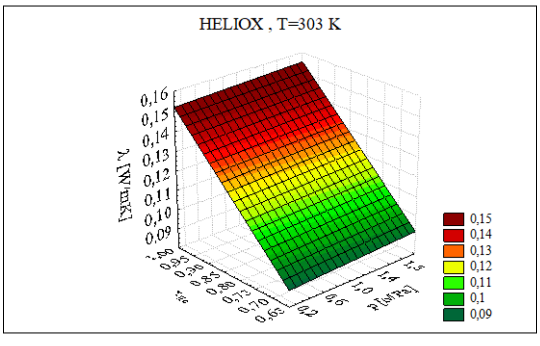

Fig. 5. Relationship between thermal conductivity of HELIOX pressure and molar fraction of helium at absolute temperature of T=303 K.

It is evident from Fig. 5 that increased pressure and molar fraction of helium at the absolute temperature T=303K contribute to increase HELIOX thermal conductivity. It means that at great depth heat losses from the diver's body (respiratory heat loss, heat loss by convection, conduction through the clothing) will also increase, therefore the temperature necessary to maintain the divers in thermal comfort should be increases with the depth of saturation diving.

CONCLUSIONS

- Based on experimental data of oxygen and helium thermodynamic properties published in the literature [4,11] regression correlations describing specific heat at constant pressure, specific enthalpy, specific volume, dynamic viscosity and thermal conductivity as the functions of pressure and temperature have been derived. Correlation coefficients have shown that regression equations are well matched.
- Based on experimental data of oxygen and helium thermodynamic properties published in the literature [4,11] thermodynamic properties of helium-oxygen (HELIOX) mixtures have been calculated in the range of pressure p= 0.1-1.8 MPa, absolute temperature T = 273.15÷333.15 and helium molar fraction x_{He} = 0.65-0.98.
- Regression correlations that enable to determine specific heat at constant pressure, specific enthalpy, specific volume, dynamic viscosity and thermal conductivity of HELIOX as the functions of pressure, temperature and molar fraction of helium have been derived. Correlation coefficients have shown that regression equations are well matched.
- The regression correlations are simple in practical application and allow determining thermodynamic properties of oxygen, helium and HELIOX mixtures with satisfactory engineering accuracy. They eliminate some intermediate, time-consuming computational steps that need to be performed using analytical relationships,
- The regression correlations that have been obtained are very useful in mathematical modelling of thermal comfort in hyperbaric HELIOX atmosphere.

NOMENCLATURE

c_p – specific heat at constant pressure , kJ/kg K,
i – specific enthalpy, kJ/kg,
p – total pressure of the breathing mixture, MPa,
p_{O2} – partial pressure of oxygen, kPa,
R – correlation coefficient,
v – specific volume, m^3/kg,
t – temperature, ^oC,
T – absolute temperature, K,
x_{He} – molar fraction of helium,
λ – thermal conductivity, W/m K,
η – dynamic viscosity, kg/ms
ρ – density, kg/m^3

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