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► **To cite this version:**

Andriniaina Harry Solo, Malyk Benmouffok, Pierre Freton, Jean Jacques Gonzalez. STOICHIOMETRY AIR – CH₄ MIXTURE: COMPOSITION, THERMODYNAMIC PROPERTIES AND TRANSPORT COEFFICIENTS. Plasma Physics and Technology, 2020, 7 (1), pp.21-29. 10.14311/ppt.2020.1.21 . hal-02900589

HAL Id: hal-02900589

<https://hal.science/hal-02900589>

Submitted on 13 Nov 2020

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STOICHIOMETRY $AIR - CH_4$ MIXTURE: COMPOSITION, THERMODYNAMIC PROPERTIES AND TRANSPORT COEFFICIENTS

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Abstract. This work is related to the determination of the local thermodynamic equilibrium (LTE) data of 90.5% air and 9.5% CH_4 mixture. The results of chemical composition, thermodynamic properties and transport coefficients are presented according to temperature (300K to 30kK) and pressure (1 and 10 bars) or mass density (0.1481 and 1.111 $kg.m^{-3}$). The chemical composition is determined using the mass action law. Input data come from the NIST and JANAF sites. For pressure equation, Debye-Huckel's first order and virial's second order corrections are used in the equation system to take account the different particle interactions. For the considered mixture (90.5% air and 9.5% CH_4) the properties are compared to those of pure air.

Keywords: *air- CH_4* , plasma composition, constant pressure, constant mass density, thermodynamic properties, transports coefficients..

1. Introduction

The $CH_4 - air$ gas mixture is generally used in the ignition studies of thermal engines [1–3]. The used mixture proportions change according to the literature works, and are sometimes subject of parametric studies [1, 3]. However, it is difficult to find the data for the desired conditions (temperature range, pressure, or mixture proportions). So mixing laws are sometimes used, whereas they are inappropriate for reactive gases. Other authors consider the proportion of methane in the mixture to be small (5-10%) and use air data [2, 4]. These assumptions may lead to erroneous results, or at least far from real behavior. Our goal in this paper consists to determine a database for a mixture of 90.5% air and 9.5% CH_4 in order to be able to implement in the future a plasma modelling after the spark phase of an ignition process. We present our calculation methods and the equation system under the hypothesis of local thermodynamic equilibrium (LTE). The results of the air-methane mixture will be compared with those of air, and with results from the literature.

2. Theory

2.1. Partition function

The determination of the data need generally the internal partition functions Q_{int} of species and their derivatives. They are calculated from equations (1 or 2). The input parameters used come from the NIST [5] and JANAF [6] sites. These equations are solved for a temperature step of 1K and the derivatives passed in a spline to avoid oscillations in thermodynamic properties as well as transport coefficients.

□ Atomic Species

$$Q_{int}(T) = \sum_i^{i_{max}} g_i \cdot e^{-\frac{E_i}{k_B \cdot T}} \quad (1)$$

with g_i the degeneration of the electronic level i given by $g_i = 2J + 1$, where J is the quantum number of angular moment, k_B the Boltzmann constant, T the temperature, E_i the energy of electronic level, and i_{max} the limit of the summation such as:

$$E_{imax} \leq E_{ion} - \Delta E \quad (2)$$

E_{ion} is the ionization energy and ΔE the lowering of ionization potential [7].

□ Molecular Species

o

Laws	Equations
Mass action	$\prod_{i=1}^N n_i^{v_i} = \prod_{i=1}^N Q_{tot,i}^{v_i} \quad (4)$
Conservation of atomic nucleus	$\epsilon_j \sum_i n_i \cdot C_{i,k} = \epsilon_k \sum_i n_i \cdot C_{i,j} \quad (5)$
Conservation of electrical neutrality	$\sum_i Z_i \cdot n_i = 0 \quad (6)$
Dalton	$P = \sum_i n_i \cdot k_B \cdot T \quad (7)$
Conservation of mass density	$\rho = \sum_i n_i \cdot m_i \quad (8)$

Table 1. Basis equations used to determine the chemical composition.

$$Q_{int}(T) = \frac{P_r}{k_B \cdot T} \left(\frac{h^2}{2 \cdot \pi \cdot m \cdot k_B \cdot T} \right)^{\frac{3}{2}} \exp \left[\frac{1}{N_a \cdot k_B} \left(\frac{[H(0) - H(T_r)]_{JANAF}}{T} - \left[\frac{G - H(T_r)}{T} \right]_{JANAF} \right) \right] \quad (3)$$

with P_r and T_r respectively the pressure and reference temperature in the JANAF table [6], h the Planck constant, m the mass of the species, N_a the Avogadro number, $H(0) - H(T_r)$ the enthalpy evaluated at zero kelvin, and $[G - H(T_r)]/T$ the Gibbs energy dependent of the temperature.

2.2. Chemical composition

The calculation of chemical composition was developed using the mass action law including the chemical base concept [8]. This method allows us to generalize the equations for different types of pure gases and gas mixtures. If calculation is at constant pressure, Dalton's law is used with the corrections of Debye-Hückel δP_{Debye} and virial δP_{virial} [7, 9]. For a calculation at constant density, the mass density equation is used. The basic equations for the determination of chemical composition are summarized in Table 1.

In Table 1, N represents the total number of chemical species, n_i the density of the species i , v_i the stoichiometry coefficients of the reaction, $Q_{(tot,i)}^{vol}$ the total partition function by volume [7], ϵ the atomic proportion of the species j or k , $C_{i,k}$ et $C_{i,j}$ the elements of the composition matrix [7], and Z_i the charge of the species.

2.3. Thermodynamic properties

By knowing the densities of each species, as well as their internal partition functions, the thermodynamic properties can be calculated (such as mass density ρ , enthalpy H or specific heat at constant pressure C_p). These properties are generally presented for a given pressure [9]. Here we will look at internal energy U and specific heat at constant volume C_v . These data are used particularly in variable pressure and constant volume systems. Their equations are illustrated in Table 2 with N_i is the particle density of the i species given by $N_i = \frac{n_i}{\rho}$, and E_i^{ref} the reference energy.

Thermodynamic properties	Equations
Internal energy	$U = \frac{3}{2} \cdot k_B \cdot T \cdot \sum_i N_i + k_B \cdot T^2 \cdot \sum_i N_i \cdot \frac{\delta Q_i^{int}}{\delta T} + \sum_i N_i \cdot E_i^{ref} \quad (9)$
Specific heat at constant volume	$C_v = \left(\frac{\delta U}{\delta T} \right)_V \quad (10)$

Table 2. Equations to calculate thermodynamic properties.

Species(i)/Species(j)	Electron	Neutral	Charged
Electron	Coulomb	Polarity	Coulomb
Neutral	Reciprocity	Lennard Jones	Polarity
Charged	Reciprocity	Reciprocity	Coulomb

Table 3. Used formalism according to the species collision type.

2.4. Transport coefficients

The conventional formulations of the literature based on approximation of Chapman-Enskog method are used for the determination of transport coefficients [10, 11]. The equations to be solved require the knowledge of additional input data that are the collision integrals. In our code, they are calculated in first approximation from the hard sphere potentials. However, following available data, the appropriate formalism according to the type of collision of the species (Table 3) is considered.

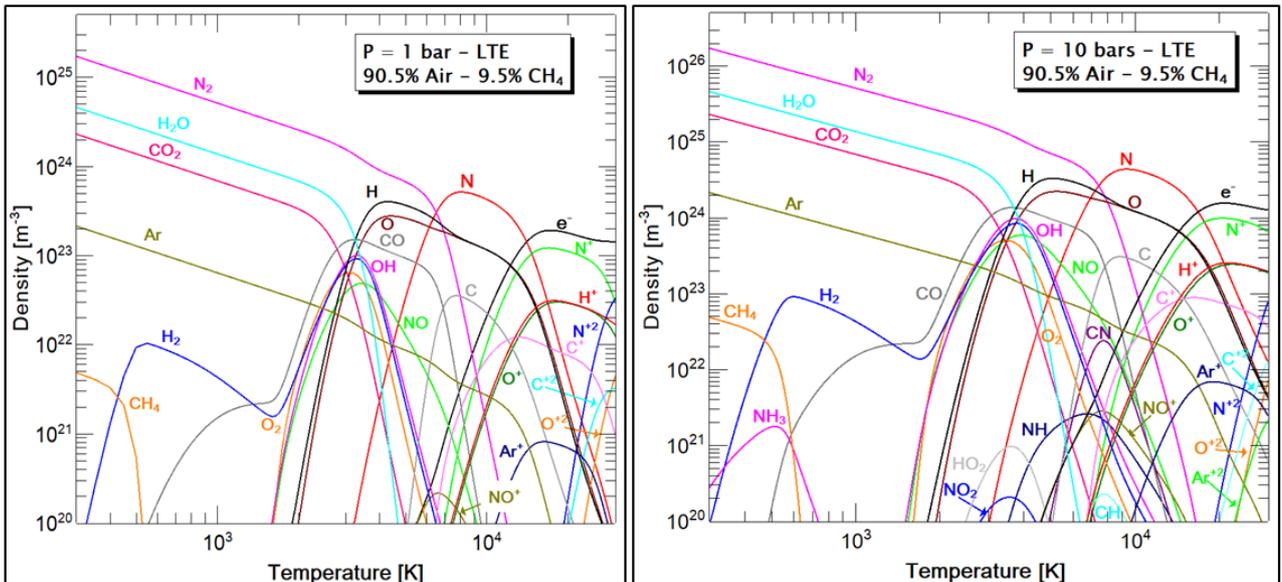
- Case of Charged-Charged interaction: The Coulomb potential limited by the Debye's length is used. It depends of the species charge, its temperature and the Debye's length. The collision integrals are so calculated from Mason [12] and Devoto [13–15] tables.
- Case of Neutral-Neutral interaction: Lennard-Jones potential (atoms or molecules). The reduced temperature $T_{reduced}$ is used. This formalism depends on the maximal energy attraction. Tabulated values for the Lennard-Jones potential (12-6) are used.
- Case of Neutral-Charged: Electron/Neutral and Charged/Neutral (Input: charge, polarity and $T_{reduced}$). The parameters used to calculate the collision integrals come from Capitelli et al [16] for air, and from Bar et al [17] as well as Sanon [18, 19] for methane.

3. Results and Discussion

We present the results obtained for a mixture of 90.5% air and 9.5% CH_4 for a temperature range from 300K to 30kK. 51 species were considered in our calculations: N , N^+ , N^{+2} , N_2 , N_2^+ , NO , NO^+ , N_2O , NH , CN , CNO , O , O^+ , O^{+2} , O^- , O_2 , O_2^+ , O_2^- , OH , OH^+ , CO_2 , HO_2 , NO_2 , C , C^+ , C^{+2} , C_2 , CO , CO^+ , CH , CHN , CHO , C_2H , C_2H_2 , H , H^+ , H^- , H_2 , H_2O , H_2O_2 , HNO , NH_2 , NH_3 , CH_2 , CH_3 , CH_4 , CH_2O , Ar , Ar^+ , Ar^{+2} , e^- . A comparison is made between the thermodynamic properties and the transport coefficients of the air-methane mixture and the pure air. For validation, we compare our results with those available in the literature.

3.1. Chemical composition

The chemical compositions for a pressure of 1 bar and 10 bars and at a density of $0.1481 \text{ kg}\cdot\text{m}^{-3}$ and $1.111 \text{ kg}\cdot\text{m}^{-3}$ are shown respectively in Figure 1 and Figure 2.

Figure 1. Chemical composition: 90.5% air and 9.5% CH_4 - 1 bar and 10 bars - LTE.

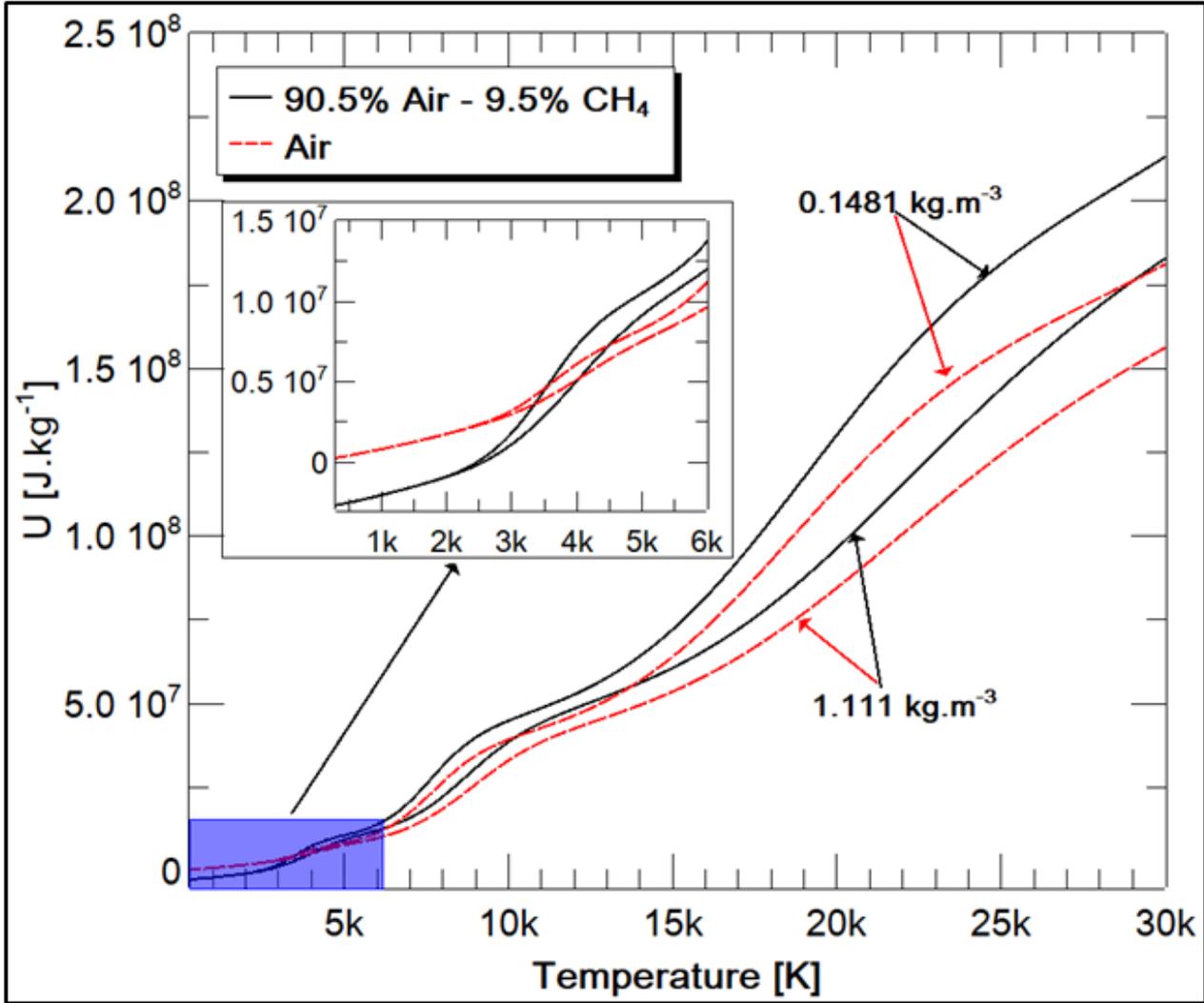


Figure 3. Internal energy: 90.5% air and 9.5% CH_4 for 0.1481 and 1.111 kg.m^{-3} at LTE.

when the pressure increases. However, when the electronic translation component becomes dominant, the phenomenon reverses and the thermal conductivity increases with the pressure. In comparison with air, the *air* – CH_4 mixture allows overall a better ability to drive heat. For electrical conductivity, Figure 6 compares our work with two literature results. There is a strong increase for temperatures up to 10kK, followed by a quasi-linear variation and finished with a constant profile where the electron density begins to stabilize as can be seen in the case at 1 bar above 25kK (Figure 6 left). The electrical conductivity depends heavily on the electronic density, the differences observed between the two gases studied are in principle at the level of the strong gradient ($T < 10\text{kK}$). In this area of temperature, electrons vary as a result of ionization phenomena such as molecule NO. In the case of the *air*– CH_4 mixture, the formation of this molecule results from several species, and as the proportion of air is reduced in the mixture, its quantity in the medium also decreases. As a result, the ionization of NO is delayed compared to that of air, hence a relatively low electronic density.

In Figure 7 the viscosities of 90.5% air and 9.5% CH_4 mixture, as well as the air at a pressure of 1 and 10 bars are confronted with the literature. We find the typical bell shape, with a maximum who reflects the transition from neutral or weakly ionized plasma to a fully ionized medium. As the molar fraction of the species is involved in the viscosity equation, it also depends on the pressure. We then see an increase values and the movement of the maximum toward higher temperatures when the pressure increases. For the gap observed between the two gases presented here, they can be explained by the difference in the values of molar masses and the number of collisions between particles, especially neutrals. For the transport coefficients compared with the literature presented in this work, we find generally a good agreement. The differences may be due to the lack of consideration of some species or the choice of collision integrals.

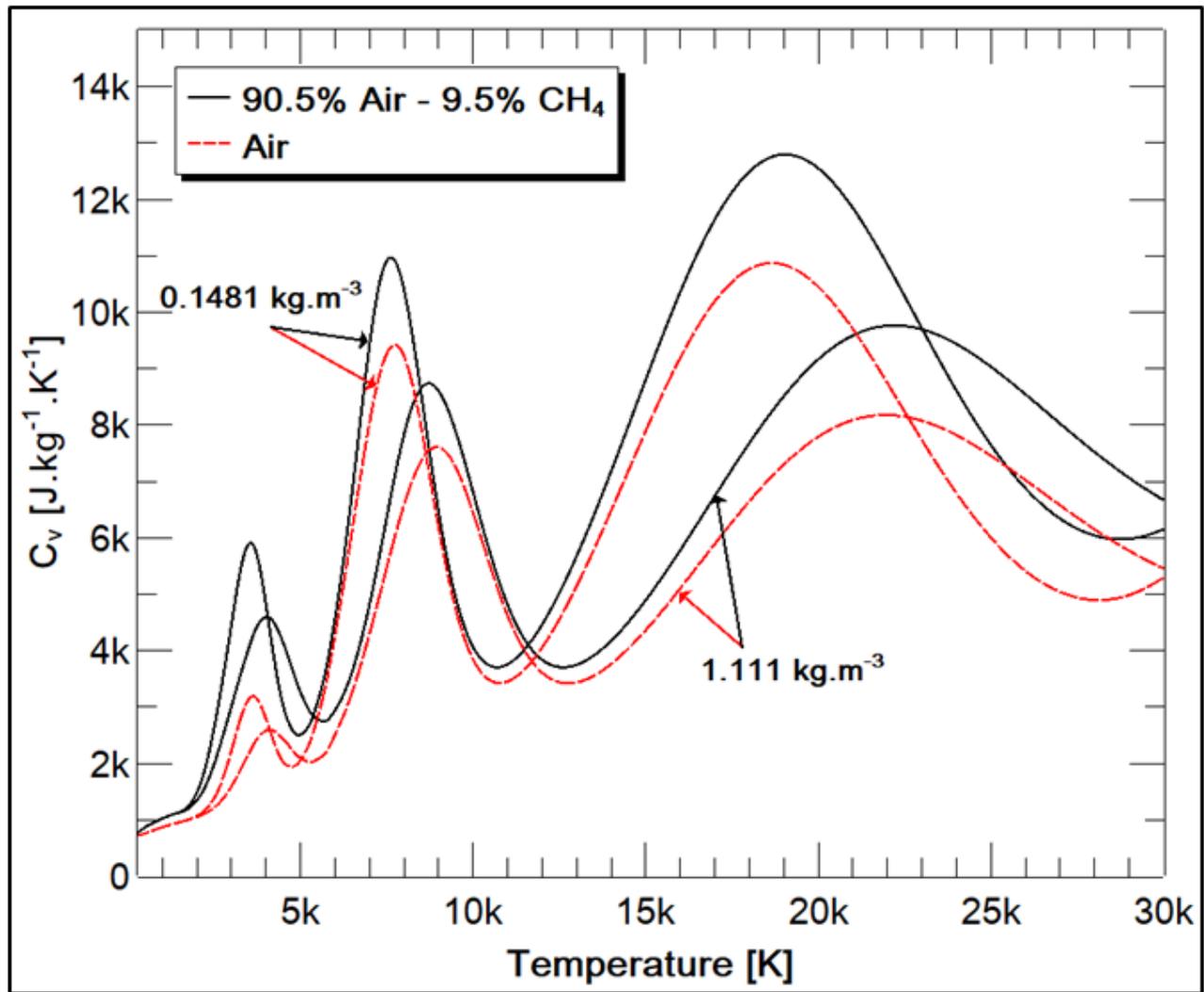


Figure 4. LTE Specific heat capacity at constant volume: 90.5% air and 9.5% CH₄ for 0.1481 and 1.111 kg.m⁻³ at LTE.

4. Conclusions

The objective of this study was to determine the LTE data for the mixture of 90.5% air and 9.5% CH₄ (chemical composition, thermodynamic properties and transport coefficients). For this purpose, tools have been developed allowing access to these quantities for a large temperature range. We first showed the ability of our developments to calculate the chemical composition for a given pressure or density value. The results illustrate fairly similar behavior on the different species transformation processes between the case at P=1 or 10 bars and at $\rho=0.1481$ or 1.111 kg.m⁻³. However, for a given mass density, species evolve differently with the particularity of keeping a linear variation up to their respective dissociation or ionization temperatures. We then presented the thermodynamic properties and transport coefficients of the air – CH₄ mixture compared with those of air. For a proportion of 9.5% of CH₄ in air, the results show an important difference in the properties of these two gases. If we want a better prediction of the real plasma behavior in the models, these differences cannot be ignored and the data of 90.5% of air and 9.5% of CH₄ mixture must be used.

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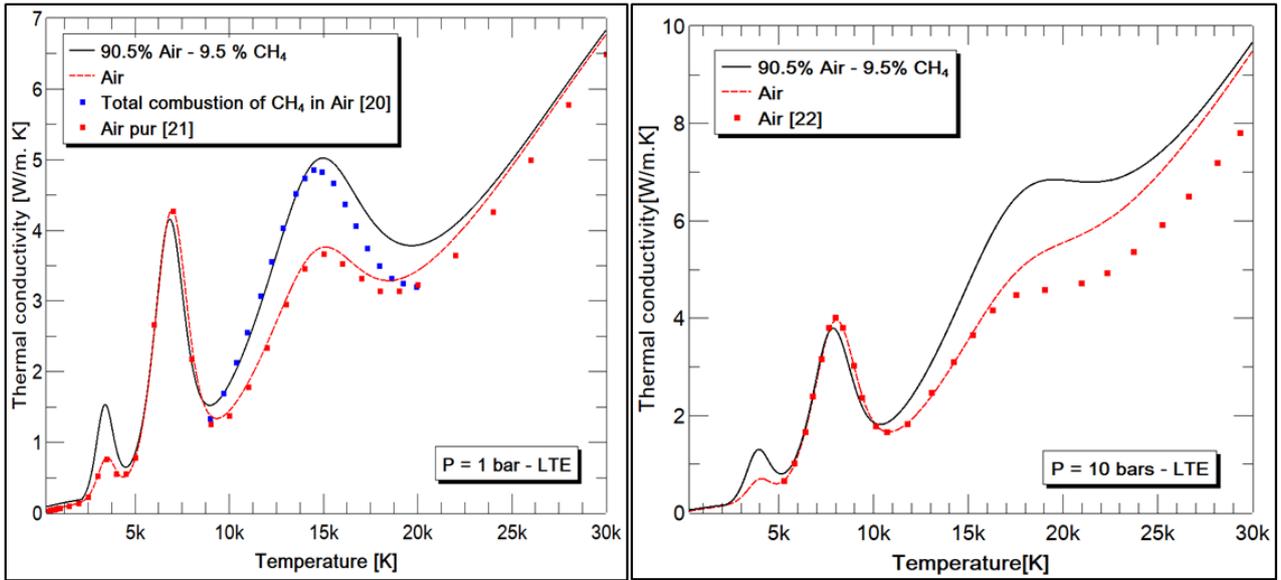


Figure 5. Thermal conductivity: 90.5% air and 9.5% CH_4 and Air for 1 and 10 bars at LTE. Comparison with literature [20–22]

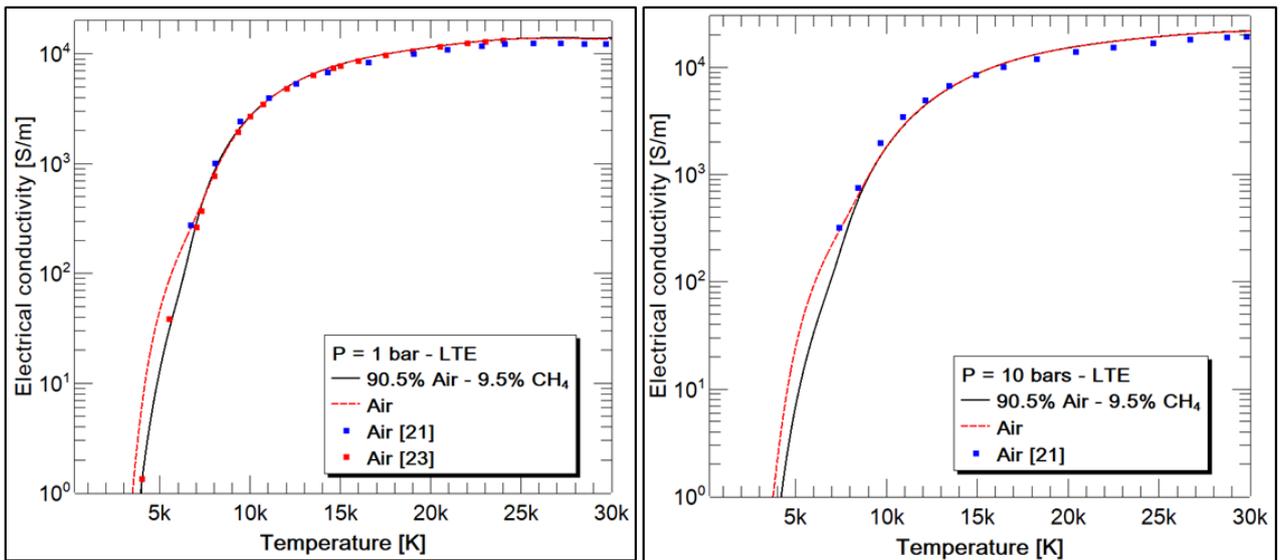


Figure 6. Electrical conductivity: 90.5% air and 9.5% CH_4 and Air for 1 and 10 bars at LTE. Comparison with literature [21, 23]

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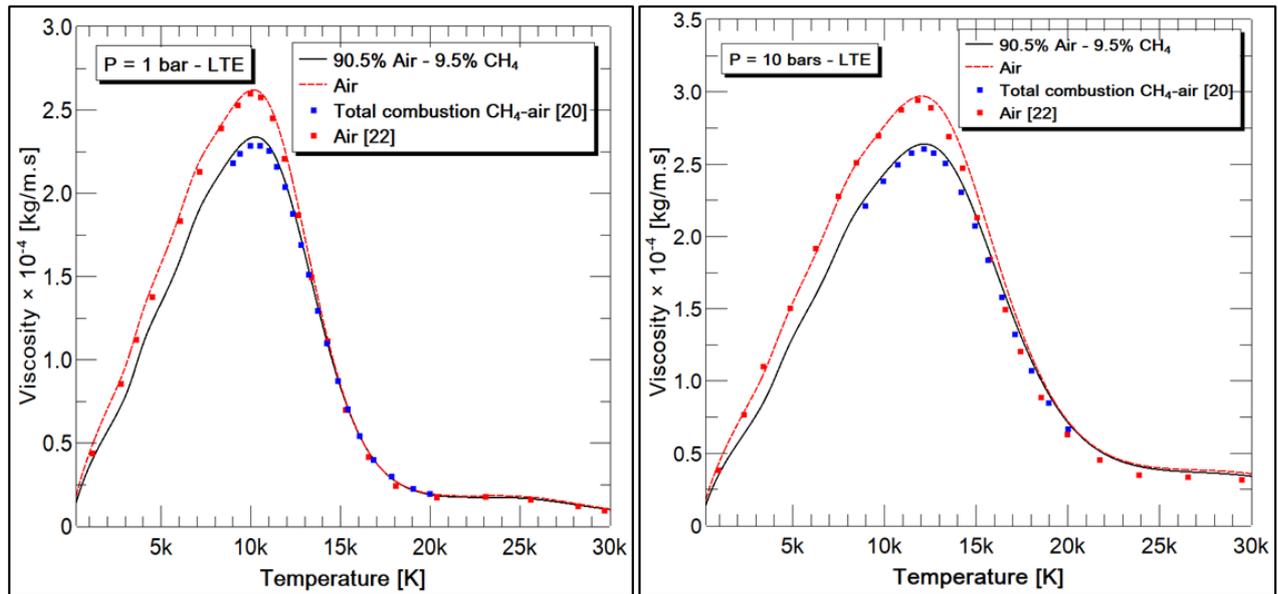


Figure 7. Viscosity : 90.5% air and 9.5% CH₄ and Air for 1 and 10 bars at LTE. Comparison with literature [20, 22]

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