



Ricerca di Sistema elettrico

Sviluppo di una Nuova Strategia per il Calcolo delle Proprietà di una Miscela ad Alta Pressione

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Il presente documento descrive anche le attività di ricerca svolte all'interno dell'Accordo di collaborazione "Sviluppo di tecniche e modelli numerici per LES nel codice HeaRT per la simulazione di processi di combustione. Obiettivo A: simulazione del mescolamento di due gas in condizioni supercritiche"

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Sommario

Il modello attualmente piú accurato (e validato con dati sperimentali) per il calcolo delle proprietá delle miscele ad alta pressione, da condizioni sub-critiche a super-critiche, é il GERG-2008. Tipicamente, per ridurre l'onere computazionale, in CFD si ricorre ad equazioni di stato per gas reali semplificate: la piú usata é quella cubica di Peng-Robinson. Assunta l'equazione di stato, sviluppando alcune relazioni termodinamiche, si ottengono espressioni per le "departure functions" di alcune grandezze della miscela, come il calore specifico e l'entalpia. Le "departure functions" rappresentano lo scostamento della proprietá dal valore ad una data pressione di riferimento, tipicamente 1 bar. In questo lavoro é stata sviluppata (da parte di ENEA) una nuova strategia per il calcolo delle proprietá di miscele basata sulla tabulazione dei valori esatti (GERG-2008) delle proprietá delle singole specie, e sull'utilizzo di regole di miscelamento opportune per il calcolo delle proprietá di miscela. Questa nuova strategia é stata validata nel caso di miscele binarie metano/ossigeno, ottenendo ottimi risultati in termini di errori percentuali rispetto al GERG-2008. I risultati sono stati buoni anche rispetto agli errori del modello Peng-Robinson per le stesse miscele. Miglioramenti sono previsti per la viscositá dinamica e la conducibilitá termica, e verranno sviluppati nella prossima annualitá, con l'estensione della validazione a miscele ternarie ed a piú componenti. Il presente lavoro si conclude con una simulazione (effettuata in collaborazione con l'Universitá di Roma "Sapienza") relativa al mescolamento di due getti di metano ed ossigeno a 150 bar.

1 Introduction

1.1 Supercritical Fluids

Supercritical fluids are those fluids above critical point (see Fig. 1.1), i.e., critical pressure and temperature. At this state, a fluid is indistinguishable between being gaseous or liquid. For example, CO₂ critical point is around 74 atm and 304 K. The triple point at which the three states coexist is 5.2 atm and 216.6 K. Table 1.1 reports critical thermo-dynamic data of some species. In the last five years, the interest in using supercritical CO₂ as working fluid for power cycles applications has been rapidly growing. In fact, adopting supercritical conditions for CO₂ is very attractive for power cycle applications since its critical temperature is close to the ambient temperature. By cooling CO₂ below its T_{cr} (e.g., 25 °C) but staying above its critical pressure, it can be efficiently pressurized in its liquid state by using pumps, thus reducing the work of compression. Integration of oxy-combustion of natural gas or hydrogen also appear a very promising strategy for further advanced supercritical CO₂ power cycles.

1.2 A Few Remarks on Thermodynamics of Gases

In many branches of science it is convenient to set up model systems to which the behaviour of real systems approximates under limiting conditions. Simple and exact relations may be established for the model (it would be impossible for the real systems) and form a practical standard against which actual phenomena may be compared.

1.2.1 Ideal Gas

Considering the chemical potentials μ_{ch} and μ_{ch}^o at the pressures p and p^o , respectively, and the same temperature T , a gas is said to be perfect if [2][p. 111]

$$\mu_{ch} = \mu_{ch}^o + \mathcal{R}_u T \ln(p/p^o), \quad (1.1)$$

where \mathcal{R}_u is the universal gas constant. It is convenient to choose p^o as unity, in the same system of units of p . It is observed that μ_{ch}^o is a function of temperature only, and hence it is called the standard chemical potential (or Gibbs free energy per mole) at the temperature T . The molecular conditions associated to the perfect gas are that the gas must consist of freely moving particles of negligible volume and having negligible forces of interaction. Reminding that [2][p. 99-104], for any single component fluid, the molar volume $v = V/n$ (where $n = m/W$ is the amount of substance, i.e., moles, in the total volume V of the gas, with mass m and molecular weight W) is equal to the partial molar volume given by $(\partial V/\partial n)|_{T,p} = (\partial \mu_{ch}/\partial p)|_T$, and calculating this derivative from Eqn. (1.1), the equation of state for ideal gases is found: $v = \mathcal{R}_u T/p$ or $pV = n\mathcal{R}_u T$. Hence, the definition of the perfect gas in terms of its chemical potential entails the gas law. Similarly, relations for internal energy and enthalpy can be derived as well [2][p. 113]. It is reminded that the internal energy and enthalpy of a perfect gas depend only on the temperature.

1.2.2 Ideal Mixture

Analogously to the ideal gas, it is possible to define an ideal gaseous mixture with the same molecular properties and respecting the simple behaviour provided by the ideal gas equation of state. Hence, a gaseous mixture will

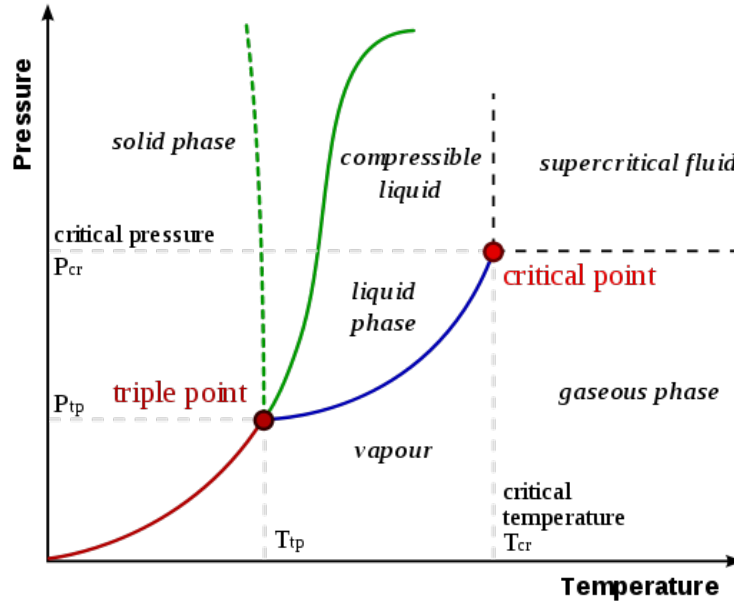


Figura 1.1: Typical fluid composition, in the pressure-temperature space.

Species	T_c [K]	P_c [bar]	ρ_c [mol/l]
CH ₄	190.60 ± 0.3000	46.100 ± 0.3000	10.10 ± 0.200
CO	134.45 ± 0.4000	34.980 ± 0.3000	11.10 ± 0.040
CO ₂	304.18 ± 0.0400	73.800 ± 0.1500	10.60 ± 0.050
H ₂	33.180 ± 0.2000	13.000 ± 0.0119	15.40 ± 2.000
H ₂ O	647.00 ± 2.0000	220.64 ± 0.0500	17.90 ± 0.200
N ₂	126.19 ± 0.0100	33.978 ± 0.0070	11.18 ± 0.020
O ₂	154.58 ± 0.0015	50.430 ± 0.0050	13.60 ± 0.014

Tabella 1.1: Critical thermodynamic data of some species from NIST database [1].

be said to be perfect if the chemical potential of each single component respect [2][p. 115]

$$\mu_{ch_i} = \mu_{ch_i}^o + \mathcal{R}_u T \ln(p/p^o) + \mathcal{R}_u T \ln X_i, \quad (1.2)$$

where p is the total gas pressure and $X_i = n_i/n$ is the mole fraction of the i -th component. Equation (1.2) can be rewritten in terms of partial pressure $p_i = X_i p$ as

$$\mu_{ch_i} = \mu_{ch_i}^o + \mathcal{R}_u T \ln(p_i/p^o). \quad (1.3)$$

It is observed that the choice of definition of the partial pressure makes the sum of all the partial pressures equal to the total pressure, i.e., $\sum_i p_i = p$, even if the mixture is not perfect. Reminding [2][p. 99-104] that the partial molar volume $V_{i,n_i} := (\partial V / \partial n_i)_{T,p,n_j} = (\partial \mu_{ch} / \partial n_i)_{T,p,n_j} = (\partial \mu_{ch} / \partial p)_{T,n_i,n_j}$, and using Eqn. (1.2), it is found $V_{i,n_i} = \mathcal{R}_u T / p$. Considering that the total volume of the mixture is $V = \sum_i n_i V_{i,n_i}$, it is finally found $V = n \mathcal{R}_u T / p$. It is noted that the single species partial molar volume V_{i,n_i} is the same for all components and it is equal to $V/n = v_i$, n being the total number of moles. This implies that there is no volume change when the separate gases, each at pressure p , are put together to form a mixture at total pressure p and same temperature. Like the volume change, also the enthalpy and internal energy changes at constant temperature and pressure mixing conditions are zero ($H_{i,n_i} = h_i$ and $U_{i,n_i} = u_i$, the lower letters referring to the molar quantities, and the

capital ones to their partial molar counterpart), and hence the heat of mixing is zero. Thus, each component behaves as if no other gases were present: this because the molecules all move independently in the whole volume.

1.2.3 Imperfect Gases

Imperfect gases or mixtures are those gases that do not obey Eqns. (1.1) or (1.2), and consequently do not have an equation of state of simple form. Several equations of state have been modeled for real gases and mixtures. Large deviations from the perfect gas law may be represented by means of a power series

$$p = \frac{\mathcal{R}_u T}{v} (1 + B/v + C/v^2 + \dots), \quad (1.4)$$

where B and C are called the second and third virial coefficients respectively and are in general functions of the temperature. Alternatively, the volume of the gas may be expressed as a power series in the pressure [2][p. 120]. In a compact form, the equation of state for a real gas may be written in terms of the so called compressibility factor, Z , that includes the whole non-linear behaviour of the gas, i.e.,

$$p = \frac{\mathcal{R}_u T}{v} Z = \frac{n \mathcal{R}_u T}{V} Z = \frac{m \mathcal{R}_u T}{WV} Z = \rho \mathcal{R}_g T Z, \quad (1.5)$$

where $\mathcal{R}_g = \mathcal{R}_u/W$ is the gas constant.

As stated by Eqn. (1.1), a perfect gas is one, whose chemical potential, at constant temperature, is a linear function of the logarithm of its pressure. For imperfect gases, it is convenient to define a fictitious pressure f , called fugacity, to which the chemical potential of the gas bears the same linear relationship:

$$\begin{cases} \mu_{ch} = \mu_{ch}^o + \mathcal{R}_u T \ln(f/p^o) \\ \text{with } f/p \rightarrow 1 \text{ as } p \rightarrow 0. \end{cases} \quad (1.6)$$

It is observed that the fugacity depends on both temperature and pressure, and that the limiting relation makes the fugacity equal to the pressure when the gas obeys the perfect gas law. The fugacity is a useful quantity in the study of phase and reaction equilibrium, and it may also be used to compute the work of expansion or compression of real gases in a flow process [2][p. 123]. The fugacity for any single species can be calculated at pressure p' and temperature T from experimental data using the following relation [2][p. 124]:

$$\ln\left(\frac{f}{p'}\right) = \int_0^{p'} \left(\frac{v}{\mathcal{R}_u T} - \frac{1}{p} \right) dp = \int_0^{p'} \frac{Z-1}{p} dp. \quad (1.7)$$

For a perfect gas, $v = \mathcal{R}_u T/p$ or, equivalently, $Z = 1$, hence, $f = p'$.

1.2.4 Imperfect Mixture

For the i -th component of an imperfect gas mixture, the fugacity is chosen in such a way as to replace the partial pressure in Eqn. (1.6):

$$\begin{cases} \mu_{ch_i} = \mu_{ch_i}^o + \mathcal{R}_u T \ln(f_i/p^o) \\ \text{with } f_i/p_i \rightarrow 1 \text{ as } p \rightarrow 0. \end{cases} \quad (1.8)$$

It is observed that both μ_{ch_i} and f_i depend on the nature and concentrations of all components, and hence they are functions of all the partial pressures, as well as of the temperature. The fugacity of each component may be calculated as at pressure p' and temperature T by means of

$$\ln\left(\frac{f_i}{p_i}\right) \Big|_{p=p'} = \int_0^{p'} \left(\frac{V_{i,n_i}}{\mathcal{R}_u T} - \frac{1}{p} \right) dp. \quad (1.9)$$

It is observed that for a perfect gas mixture $V_{i,n_i} = \mathcal{R}_u T/p$, hence, the fugacity is equal to the partial pressure. Equation (1.9) implies to know experimental values of V_{i,n_i} over the whole range of integration for the specific mixture of chosen composition, temperature and pressure. This procedure requires such a large amount of experimental data that it has been carried out in only a small number of examples. For this reason the fugacities of the components of a mixture are usually estimated by an approximation method based on the definition of a particular mixture named ideal gaseous solution.

1.2.5 Ideal Gaseous Solution

The approximated method to estimate fugacities of the components of an imperfect mixture is based on defining a much less restrictive model of a gas mixture than that defined by Eqn. (1.2), i.e.,

$$\mu_{ch_i} = \mu_{ch_i}^* + \mathcal{R}_u T \ln(p/p^o) + \mathcal{R}_u T \ln X_i, \quad (1.10)$$

where $\mu_{ch_i}^*$ depends on both pressure and temperature, but not on composition, and is not necessarily equal to $\mu_{ch_i}^o + \mathcal{R}_u T \ln(p/p^o)$ in Eqn. (1.2). With this new definition of gas mixture, named ideal gaseous solution, only the dependence on composition is made explicit: the chemical potential of species i depends only on its own mole fraction, at constant total pressure and temperature. Such an ideal gaseous solution has zero volume change of mixing as well as zero enthalpy of mixing at constant pressure and temperature, but do not obey to the gas law $pV = n\mathcal{R}_u T$.

The definition Eqn. (1.10) has important consequences in regard to fugacities in the mixture. In fact, it implies

$$\mathcal{R}_u T \ln \left(\frac{f_i}{X_i} \right) = \mu_{ch_i}^* - \mu_{ch_i}^o, \quad (1.11)$$

where the right hand side does not depend on composition. Hence, the ratio f_i/X_i must remain unchanged as X_i is brought up to unity, i.e.,

$$\frac{f_i}{X_i} = f_i', \quad (1.12)$$

where f_i' is the fugacity of the pure component i at the same temperature and total pressure as the mixture. This law is known as Lewis and Randall's rule: in the ideal gaseous solution the fugacity of each constituent is equal to its molar fraction multiplied by the fugacity which it would exhibit as a pure gas, at the same temperature and the same total pressure. The applicability of the ideal solution model was tested on some mixtures whose true fugacities have been obtained directly from Eqn. (1.9). For example, error in argon-ethylene mixtures was less than 20% up to 50 atm, but the error was larger at 100 atm, up to 100% in certain mixtures. Other studies on nitrogen-hydrogen mixtures reported errors less than 20% up to 1000 atm.

1.3 A First Look at Thermal and Transport Data

Molecular, transport and thermo-dynamic data in this work were taken from the NIST database (REFPROP) [1, 3]. Figures 1.2-1.9 show the temperature dependence of molecular and transport properties of the main species in oxy-combustion processes at different pressures from 1 bar to 300 bar.

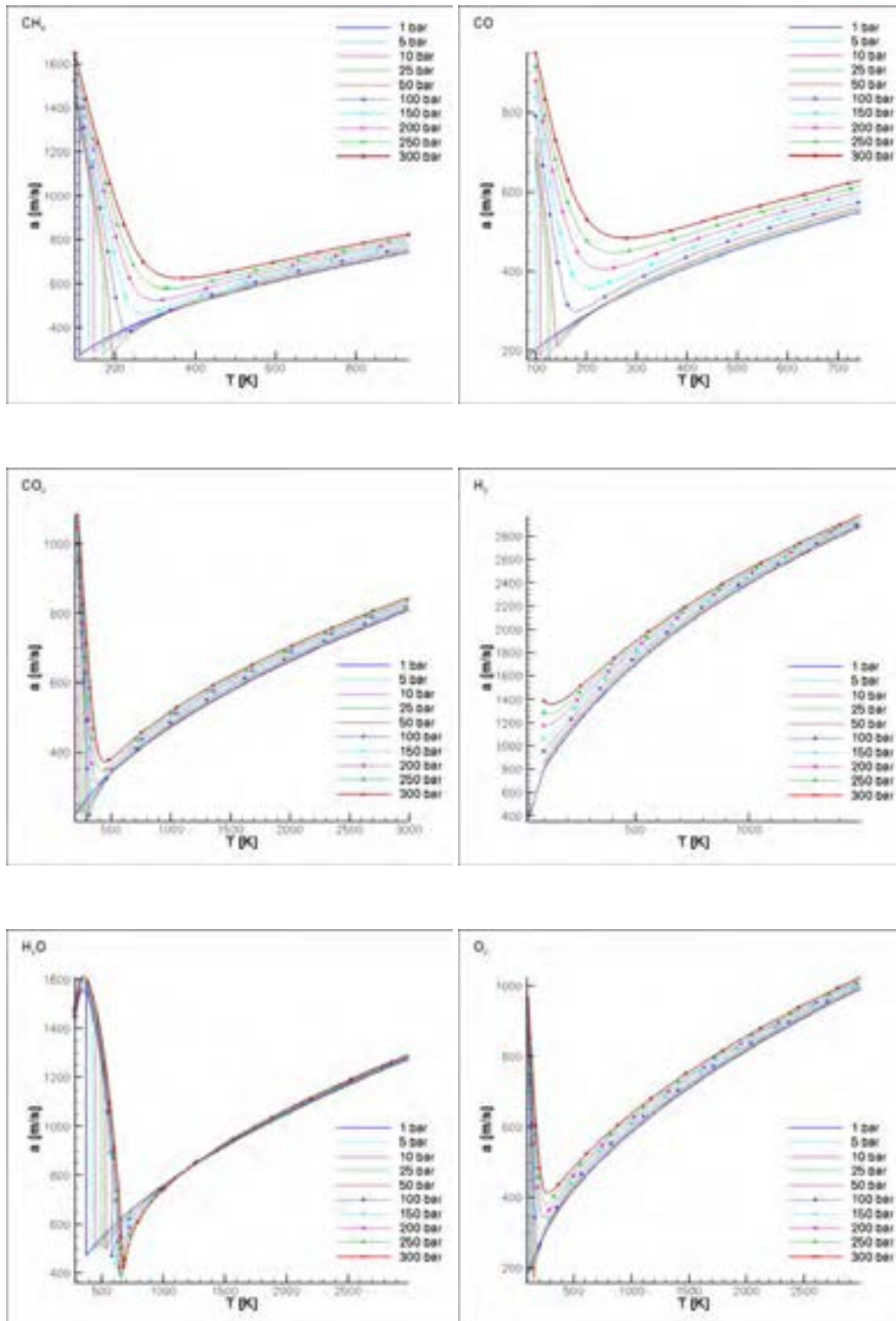


Figura 1.2: Sound speed for some species.

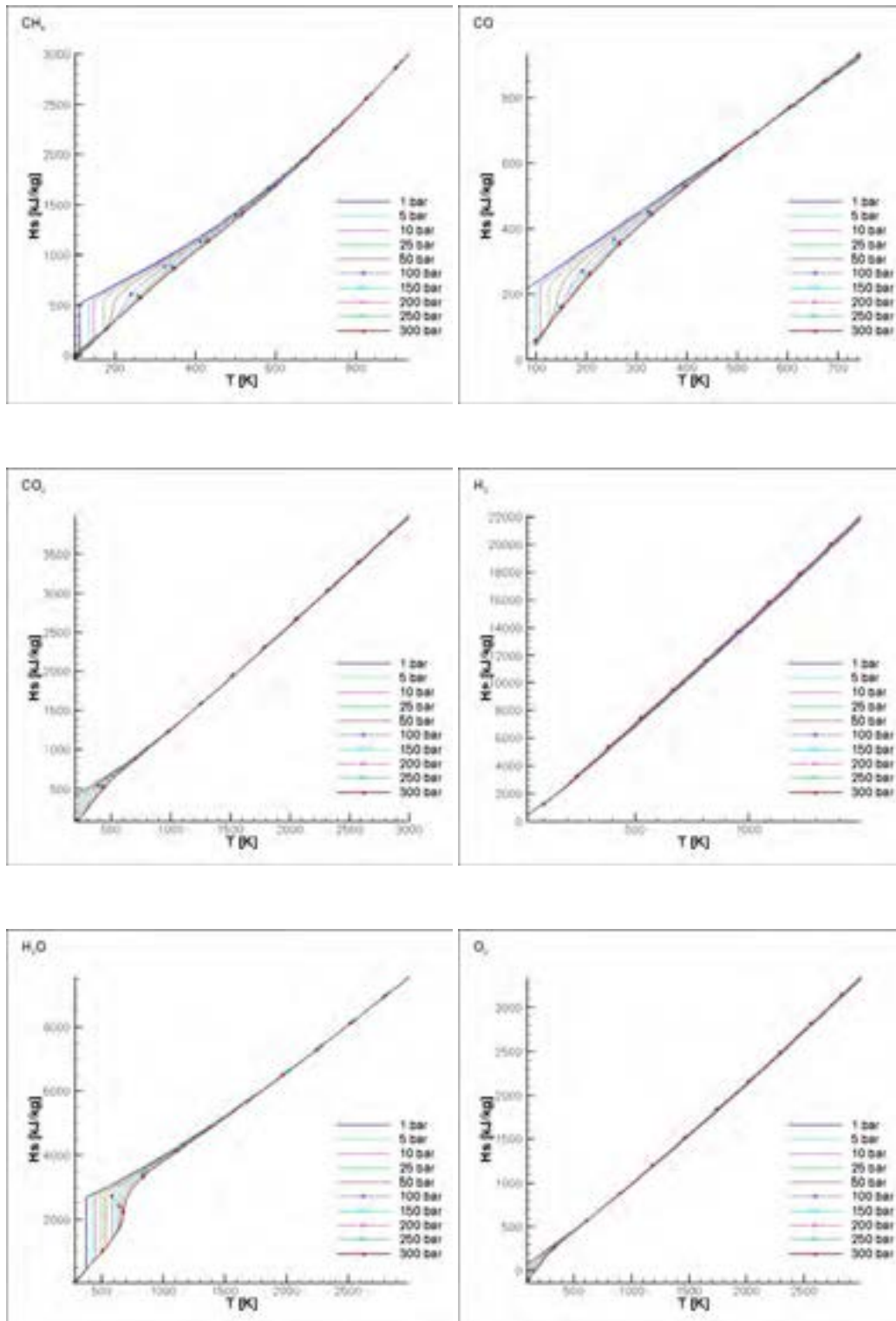


Figura 1.3: Sensible enthalpy for some species.

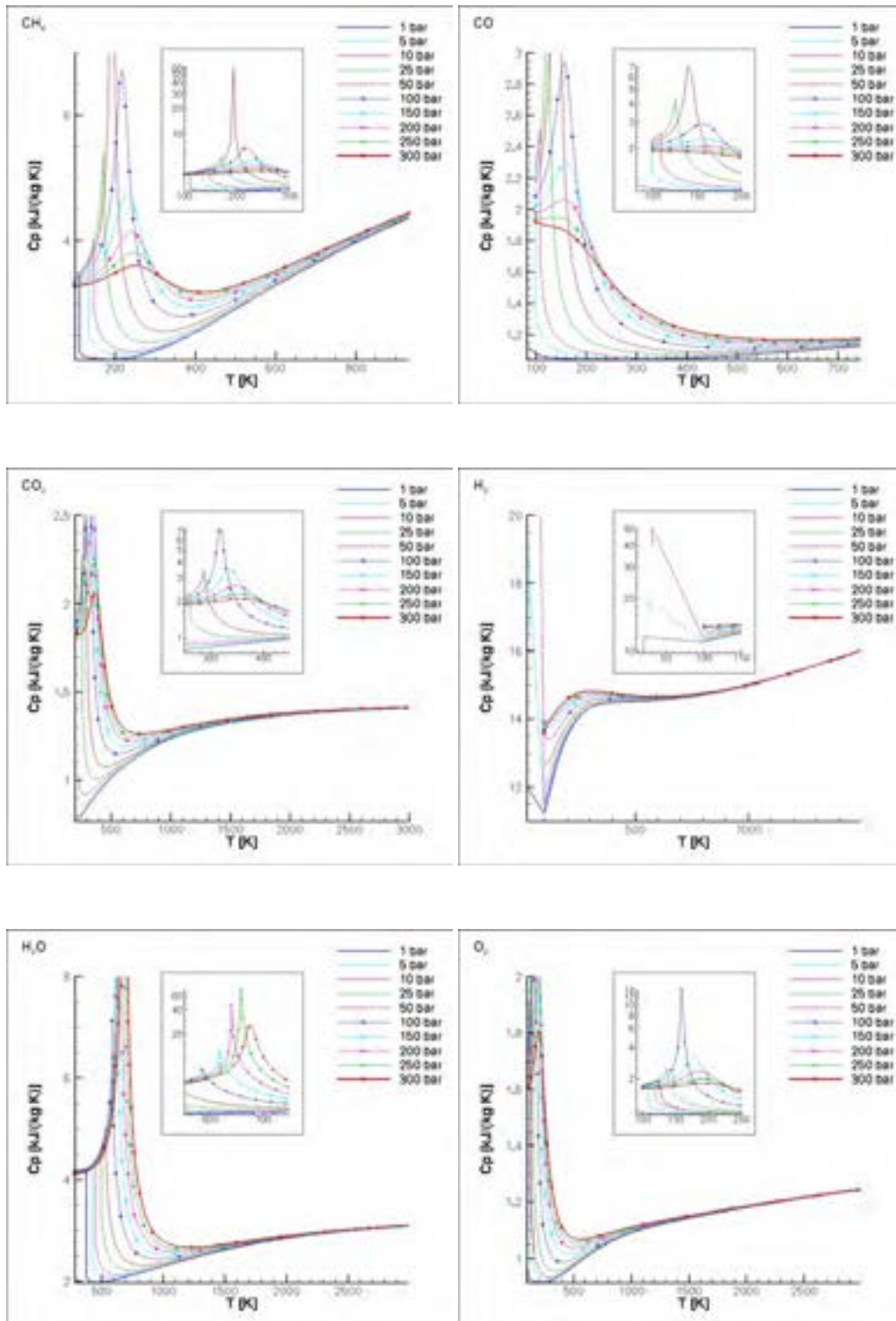


Figura 1.4: Specific heat at constant pressure for some species.

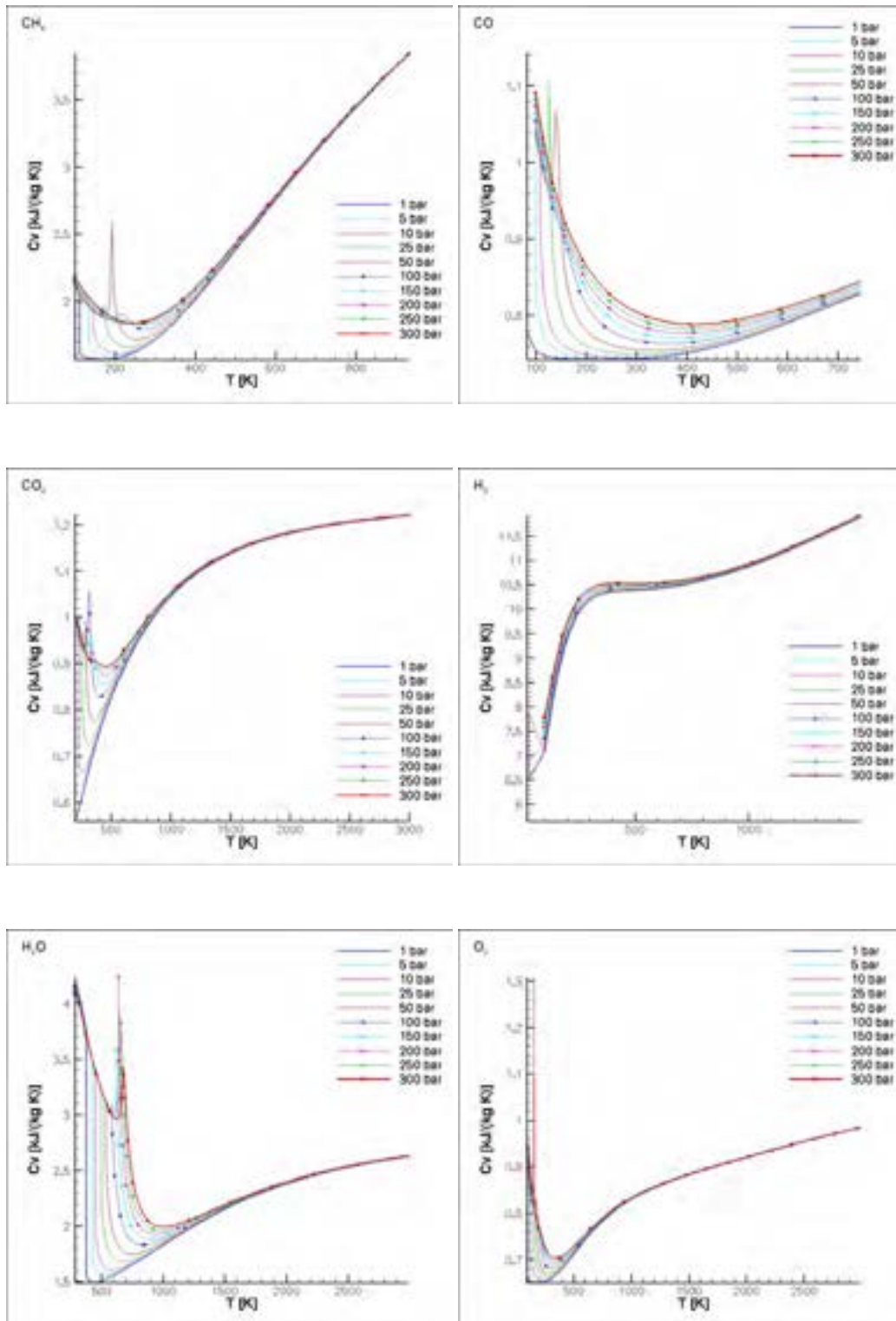


Figure 1.5: Specific heat at constant volume for some species.

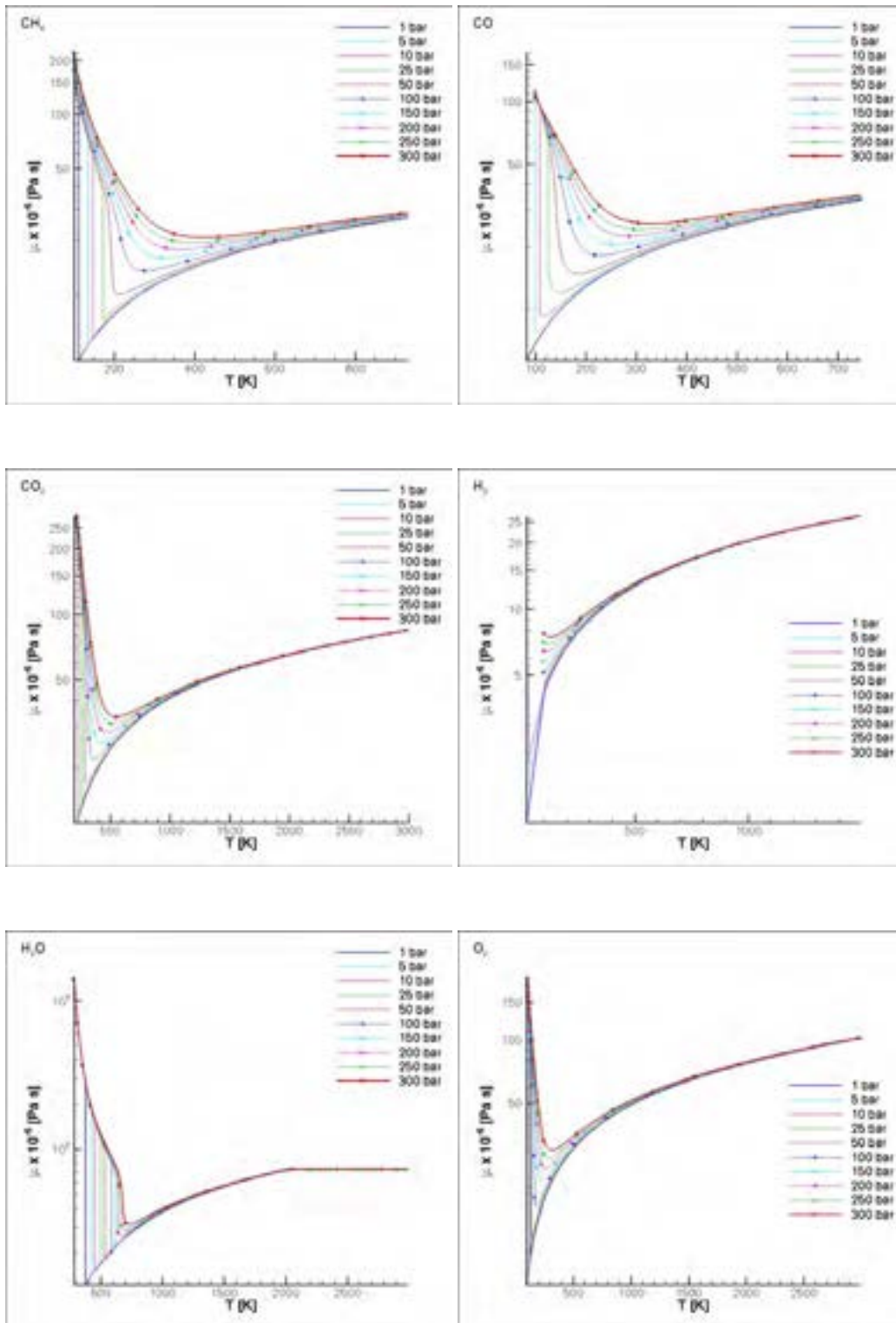


Figura 1.6: Dynamic viscosity for some species.

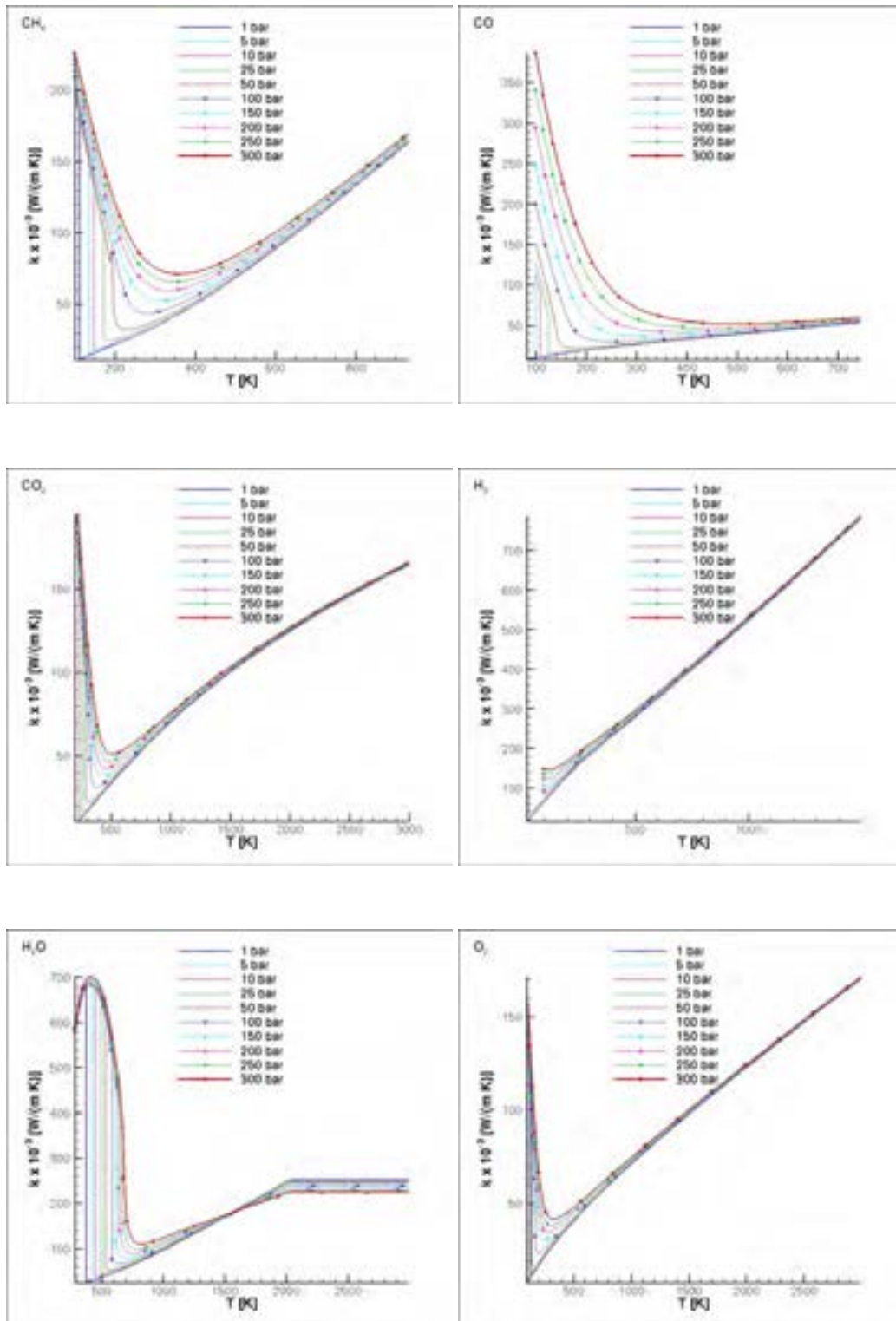


Figura 1.7: Thermal conductivity for some species.

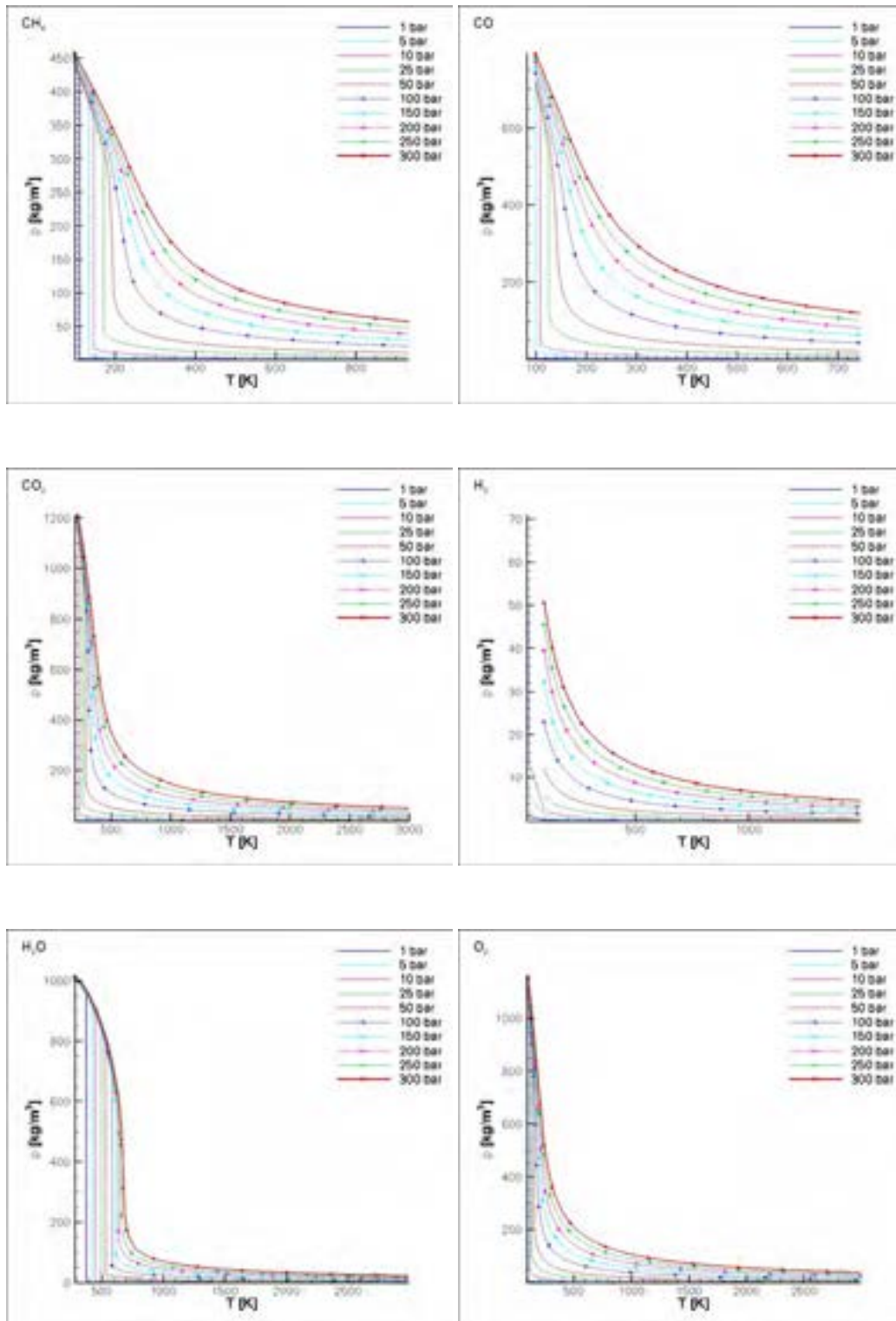


Figura 1.8: Density for some species.

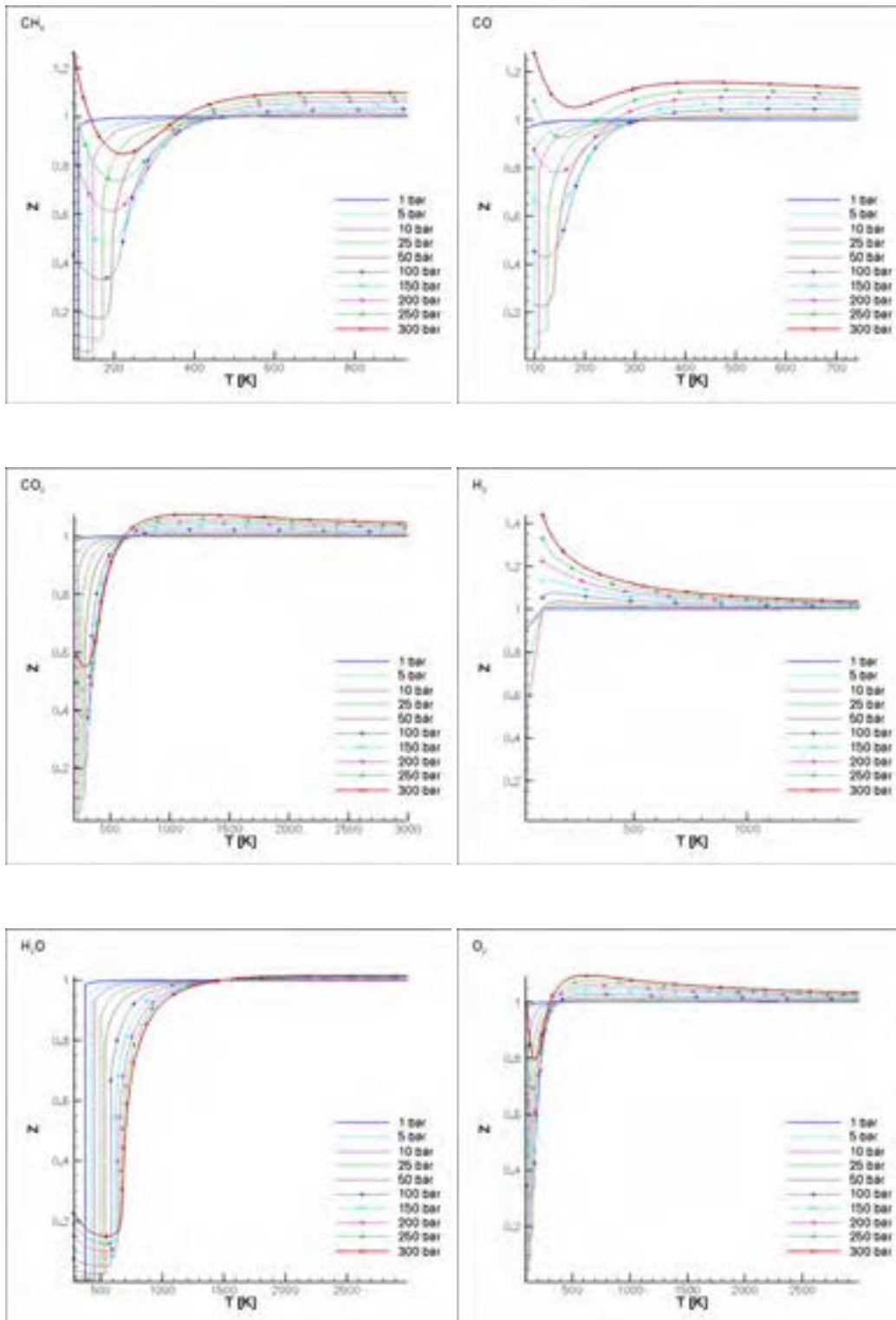


Figura 1.9: Compressibility factor for some species.

2 The Suggested Strategy

2.1 The “Exact” Real Gas Model: GERG-2008

The GERG-2008 equation of state [4] is considered the reference equation of state for the thermodynamic properties of natural gases, similar gases, and other mixtures. This equation is an expanded version of the GERG-2004 equation [5]. GERG-2008 is explicit in the Helmholtz free energy as a function of density, temperature, and composition. The equation is based on 21 natural gas components: methane, nitrogen, carbon dioxide, ethane, propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, hydrogen, oxygen, carbon monoxide, water, hydrogen sulfide, helium, and argon. Over the entire composition range, GERG-2008 covers the gas phase, liquid phase, supercritical region, and vapour-liquid equilibrium states for mixtures of these components.

The basis for the development of this fully consistent mixture model and its evaluation is the continuously updated database composed of more than 125000 experimental data for multiple thermodynamic properties in different fluid regions. About 76% of the collected data accounts for binary mixtures, and the remaining 24% accounts for multi-component mixtures, including various types of natural gases, hydrocarbon mixtures, and other mixtures.

As a multi-fluid correlation, the GERG-2008 mixture model uses accurate equations of state in the form of fundamental equations for each mixture component along with several functions developed for the binary mixtures of the components to take into account the residual mixture behavior. This allows for an accurate description of the properties of multi-component mixtures over a wide range of compositions. The different binary correlation equations were developed using a linear structure optimization method and nonlinear multi-property fitting techniques in an iterative procedure. For most of the 210 binary systems that result from the 21 components studied in [4], adjusted reducing functions for density and temperature were used. For a number of well-measured binary mixtures of important natural gas components, binary-specific or generalized departure functions were additionally developed. For binary mixtures for which only limited or poor data are available, which neither allow for the development of a departure function nor the fitting of the parameters of the reducing functions, different combining rules for the pure component critical parameters are used. This combined strategy proved to be clearly superior to the early model for mixtures of natural gas components.

The GERG-2008 wide-range equation of state is able to represent the most accurate experimental binary and multi-component data for gas-phase and gas-like supercritical densities, sound speeds, and enthalpy differences mostly to within their low experimental uncertainties. The normal range of validity of GERG-2008 includes temperatures from (90 to 450) K and pressures up to 35 MPa where the most accurate experimental data of the thermal and caloric properties are represented to within their accuracy. The extended validity range reaches from (60 to 700) K and up to 70 MPa.

The superiority of the GERG-2008 equation of state with respect to other equations of state (for example, AGA8-DC92 [6] and PengRobinson [7] equation) was extensively demonstrated [4]. The GERG-2008 wide-range equation of state represents a property database with applications for natural gases and other mixtures over the entire fluid region. Hence, it became an ISO Standard (ISO 20765-2/3) for natural gases (gas phase, liquid phase, vapour/liquid equilibrium).

It is observed that simplified cubic models, like the PengRobinson equation [7], generally achieve an accurate description of only the $pTxy$ relation of (binary) mixtures. Compared to the AGA8-DC92 equation of state [6], the new equation of state achieves important and fundamental improvements in the description of gas-phase and gas-like supercritical densities of natural gas mixtures containing, for example, high fractions of nitrogen, carbon dioxide (important to simulate oxy-combustion processes in supercritical CO₂ cycles), or ethane, or

substantial amounts of ethane, propane, and heavier hydrocarbons. The GERG-2008 equation of state allows for the accurate description of natural gas/hydrogen mixtures, low-calorific natural gases, and other mixtures of uncommon composition. Moreover, the new equation is much more accurate for rich natural gases and in the description of all caloric properties and also satisfies the demands on the accuracy in the description of liquid-phase properties and vapour-liquid equilibrium states.

The structure of the new mixture model was kept as simple as possible to allow for the development of computing-time saving algorithms and an easy expansion to additional components.

The GERG-2008 equation of state is implemented in the widely used REFPROP software developed by NIST [1]. This software was adopted to tabulate single species properties at different temperatures and pressures. It was also used to tabulate the same properties for certain mixtures used to validate the mixing rules developed in this work.

2.2 The Strategies for Numerical Simulation of Real Gases

Inter-molecular forces in real fluids are so important to change the characteristics of the mixture (i.e., its volume, sensible internal energy and enthalpy, specific heats, sound speed, . . .); their effects (apart from pressure and temperature) strongly depend on the components of the mixture and their concentration. This explains why fluid-dynamic numerical simulation of real fluids have different logical paths than ideal gases.

2.2.1 The Standard Strategy: Choice of a Real Gas Equation of State

Whilst to simulate ideal gases the thermo-dynamic and transport properties of a mixture are obtained by using mixing rules and single species data, the path to simulate real fluids is conceptually in the opposite direction. The logical path consists in assuming a simplified equation of state for imperfect fluids (the Peng-Robinson [7] equation is the most commonly adopted), and then analytically derive expressions for thermo-dynamic quantities of the mixture, e.g., sensible internal energy or enthalpy and specific heat [8, 9, 10, 11]. Their single species counterpart is found by taking functional derivatives relative to the concentrations with both pressure and temperature fixed.

It is observed that the articles on numerical simulation of supercritical gases usually have the same structure, and in particular they present the model for the equation of state adopted, compare the associated thermo-dynamic and transport properties of some single species with those obtained through other simplified models and the model currently considered “exact” (included in the NIST database [1]), and then show the numerical simulation results. It is stressed that no comparison (validation) for mixtures is provided.

2.2.2 A New Non-Standard Strategy: Mixing Rules Based on Tabulation of the “Exact” Real Gas Model

Adopting the standard strategy implies implementing in a numerical code a specific module that is strongly related to the particular equation of state chosen. Hence, when a new and more accurate model is developed, a new module has to be implemented. To avoid this, the strategy suggested in this work consists in adopting the same logical path used for ideal gases, i.e., in deriving mixture properties from single species properties, and in assuming

$$p = Z\rho R_g T \quad (2.1)$$

as equation of state, where the whole non-linearities of the imperfect mixture are in the compressibility factor, Z . This can be achieved through accurate tabulation of single species thermo-dynamic and transport properties and development of mixing rules characterized by the lowest error as possible ($\lesssim 5\%$). Of course, assuming such a strategy, the error with respect to “exact” single species quantity will be automatically zero. Hence, the validation has to be done by considering only mixtures. In this work, the reference and “exact” data comes from the GERG-2008 equation of state [4], both for single species tabulation and mixture validation. The software REFPROP [3] of NIST [1] was used to generate the tables for single species and the reference data of the mixtures adopted to validate the suggested mixing rules. If mixing rules characterized by a reasonable error

($\lesssim 5\%$) are found, the implemented code will not depend on the specific simplified equation of state. When a more accurate “exact” model will be developed, it will be only necessary to generate the new single species tables.

2.3 The Suggested Mixing Rule Strategy

Many quantities (density, ρ , compressibility factor, Z , sensible internal energy, e_s , sensible enthalpy, h_s , specific heats at constant pressure and volume, C_p and C_v , their ratio, γ , sound speed, a , dynamic viscosity, μ , thermal conductivity, k , entropy, S) are firstly tabulated for each chemical species by using the software REFPROP [3] of NIST [1]. Such quantities are tabulated with steps $\Delta T = 5$ K and $\Delta p = 5$ bar in the ranges $T \in [100 : MAX_T^i]$ K and $p \in [1 : 400]$ bar (1, 5, 10, ..., 400 bar).

- The individual species maximum temperature range MAX_T^i changes with the species i and depends on the accuracy range of the selected real gas model and its convergence. For methane, the GERG-2008 model provides accurate data up to 625 K, and beyond this limit solution converges up to 935 K. For oxygen, the GERG-2008 model provides accurate data up to 1000 K, and beyond this limit solution converges up to 1500 K.
- The selected real gas model is the GERG-2008 model for each chemical species when the reference mixture quantities are calculated by means of REFPROP.
- The enthalpy is set to zero at the NBP (Normal Boiling Point) for each species to manage positive values of h_s and e_s in the widest range as possible.

It is observed that the mixture validation phase of the mixing rules suggested below will show that some of the tabulated quantities will not be required.

Tables obtained in the previous step cannot be used in a fluid dynamic code since temperature above the MAX_T^i will be found although the chemical species will have small concentrations due to chemical reactions. Hence, an extrapolation procedure is required.

Single species data previously obtained through REFPROP [3] of NIST [1] are extrapolated performing these steps.

1. Departure functions of the tabulated quantities (here, generically named A) are derived, i.e.,

$$\Delta A^P(T, p) = A(T, p) - A^o(T), \quad (2.2)$$

$A(T, p)$ being the actual quantity and $A^o(T)$ the reference quantity at the same temperature and 1 bar.

2. Since the obtained departure functions show small wiggles beyond the GERG-2008 accuracy range (that depends on the considered species), these data are filtered.
3. The filtered departure functions are extrapolated from MAX_T^i up to 5000 K ($\Delta A^P(T, p) = 0$ at 5000 K) at each tabulated pressure.
4. The extrapolated quantities are then rebuild as $A(T, p) = \Delta A^P(T, p) + A^o(T)$.

At the end of this procedure, each chemical species has a table with steps $\Delta T = 5$ K and $\Delta p = 5$ bar in the ranges $T \in [100 : 5000]$ K and $p \in [1 : 400]$ bar (1, 5, 10, ..., 400 bar). Such tables have 981×81 temperature and pressure nodes ($(5000 - 100)/5 + 1 = 981$; $400/5 + 1 = 81$), each having different quantities.

Once tabulated individual species properties at different pressures and temperatures, a set of mixing rules was defined. These mixing rules mainly consist in weighted averages of individual species properties through molar, volumetric or mass fractions. They were determined by synergically using thermodynamics theory and empirism and resulted in the lowest percent error, with respect to the “exact” GERG-2008 real gas model, in the validation analysis of the binary mixtures considered in this work.

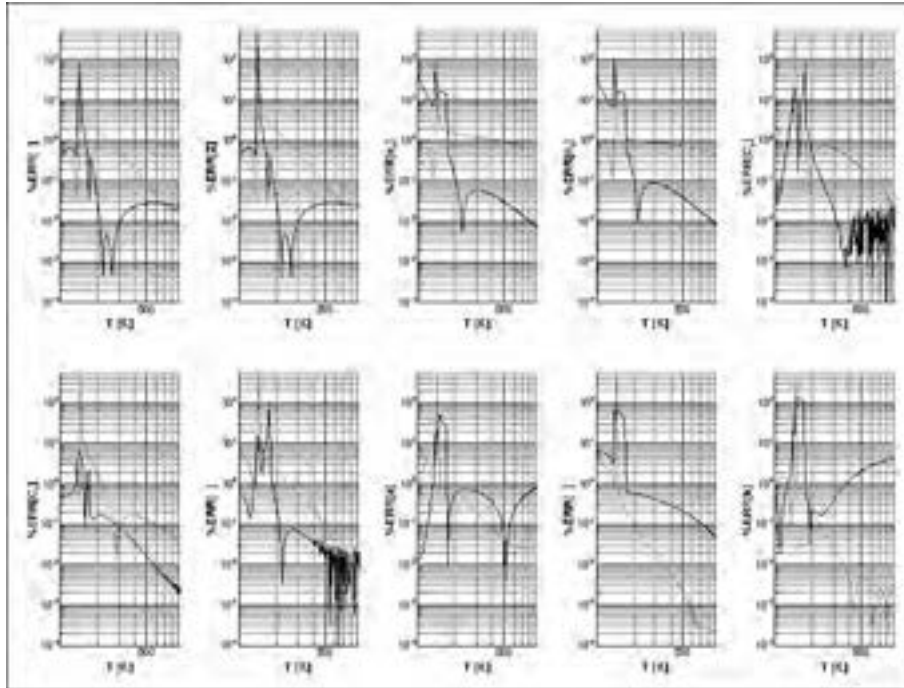


Figura 2.1: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH₄/O₂ (0.25/0.75 in mole fractions) at 25 bar.

The developed mixing rule strategy based on the tabulation of the GERG-2008 real gas model data, is here validated by considering mixtures at different compositions and pressures. Comparison with the commonly adopted Peng-Robinson cubic equation is also provided. In particular, the validation and comparison are performed calculating the percent error of the new mixing rule strategy and of the Peng-Robinson model with respect to the GERG-2008 data.

The validation is performed for CH₄/O₂ binary mixtures with molar compositions 0.25/0.75, 0.50/0.50, 0.75/0.25, and pressures 25 bar, 50 bar, 100 bar, 200 bar, 300 bar. Figures 2.1-2.3 for sub-critical conditions, and Figs. 2.4-2.15 for super-critical conditions, report such validation analysis. They also report the comparison with the Peng-Robinson model, showing the good accuracy of the new suggested mixing rule strategy. It is observed that when the Peng-Robinson model did not converge, hence not providing any result for a specific quantity, the associated percent error value was forced to 1000. In this way points where Peng-Robinson model failed to converge are easily identified.

It is concluded that the new mixing rule strategy performs generally better than Peng-Robinson model, but it does not for e_e and h_s in the liquid/liquid region (very low temperatures), and for μ and k . Prediction of e_e and h_s via the new mixing rule strategy can be hardly improved since the unknown mixing enthalpy is higher for liquids than for gases. Prediction of μ and k are instead expected to be improved by integrating the present methodology with the commonly used Wilke’s [12, p. 258] [13] [14, p. 14] and Mathur’s [14, p. 15] [15] laws for mixtures.

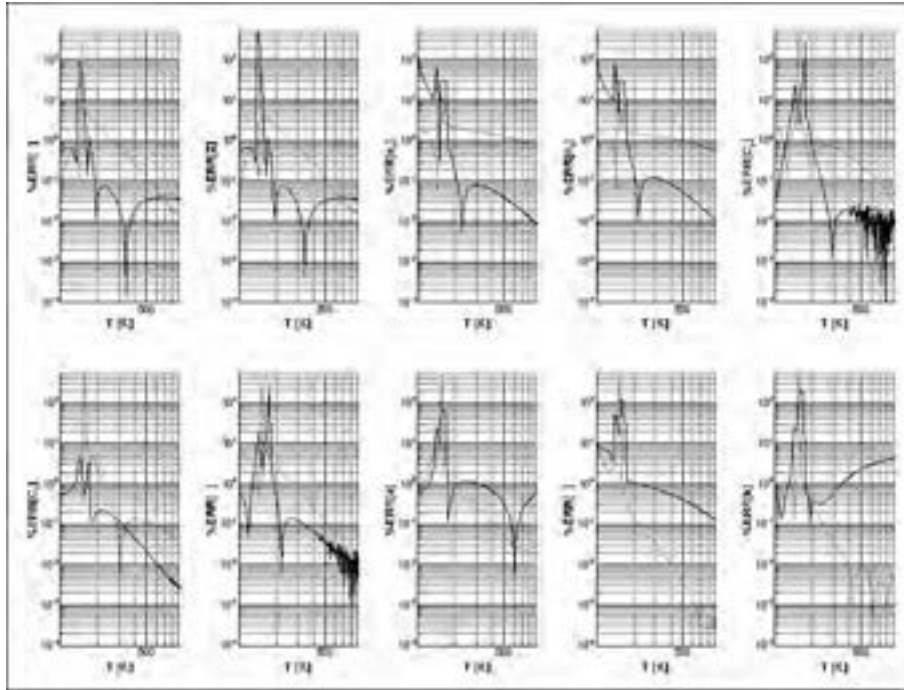


Figura 2.2: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH₄/O₂ (0.50/0.50 in mole fractions) at 25 bar.

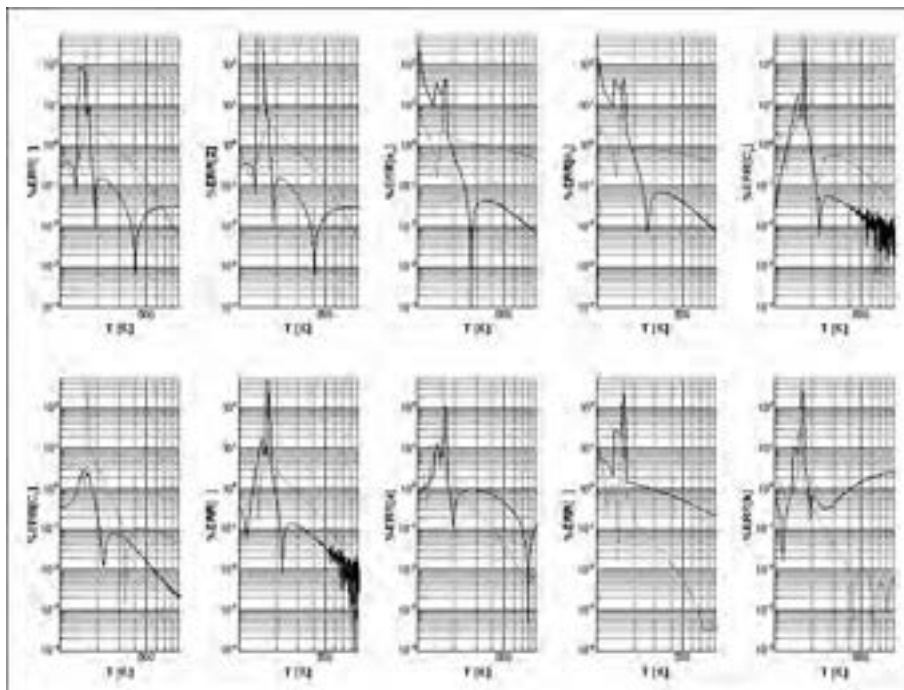


Figura 2.3: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH₄/O₂ (0.75/0.25 in mole fractions) at 25 bar.

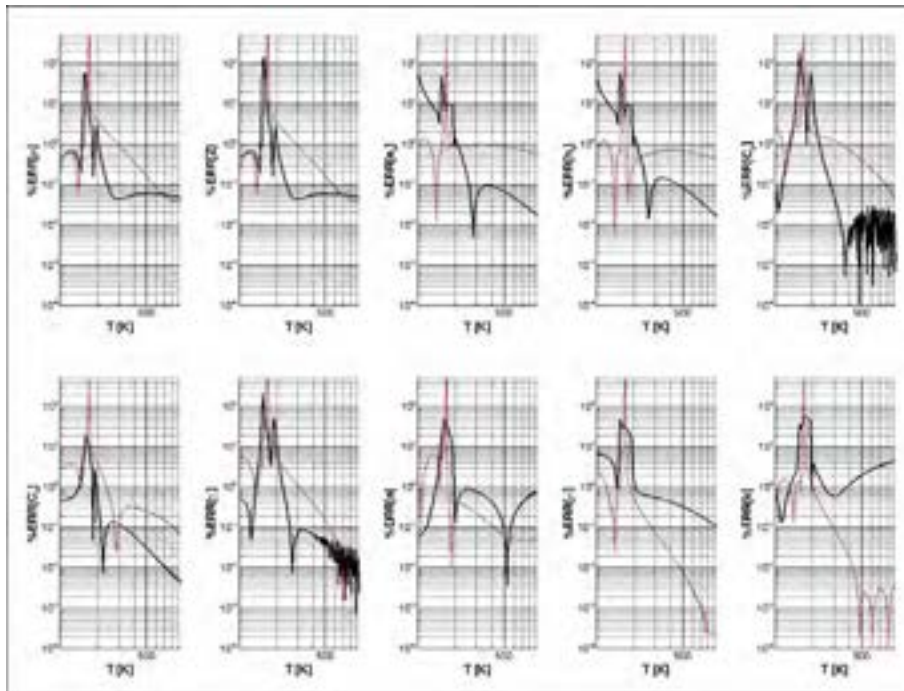


Figura 2.4: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH_4/O_2 (0.25/0.75 in mole fractions) at 50 bar.

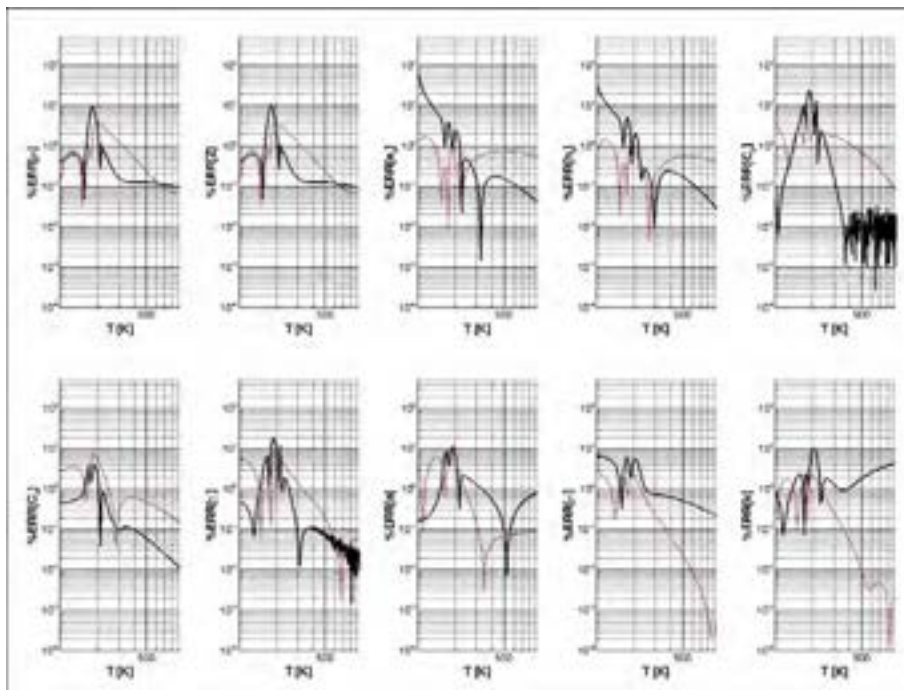


Figura 2.5: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH_4/O_2 (0.25/0.75 in mole fractions) at 100 bar.

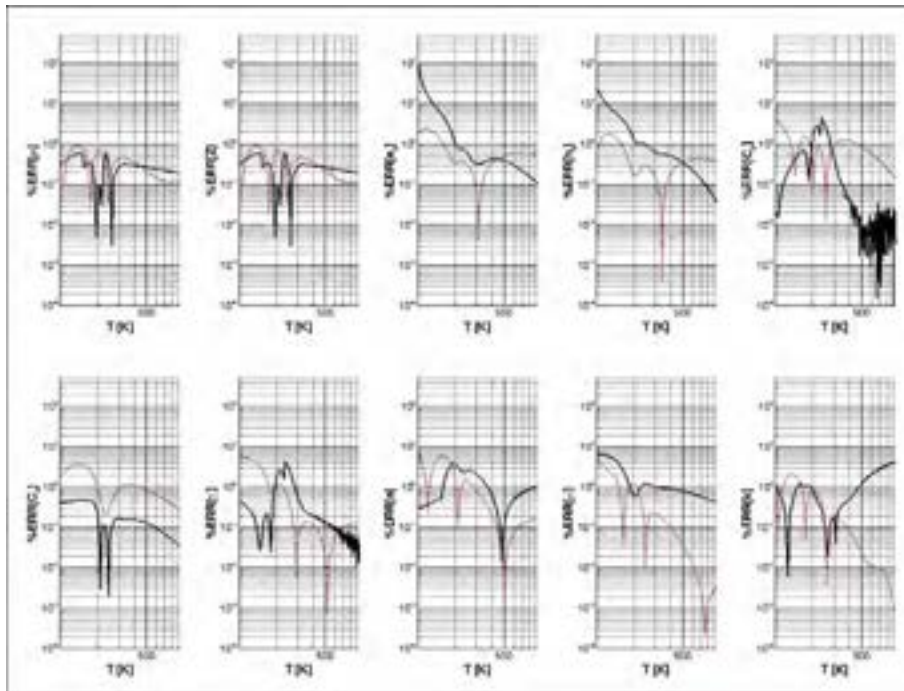


Figura 2.6: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH₄/O₂ (0.25/0.75 in mole fractions) at 200 bar.

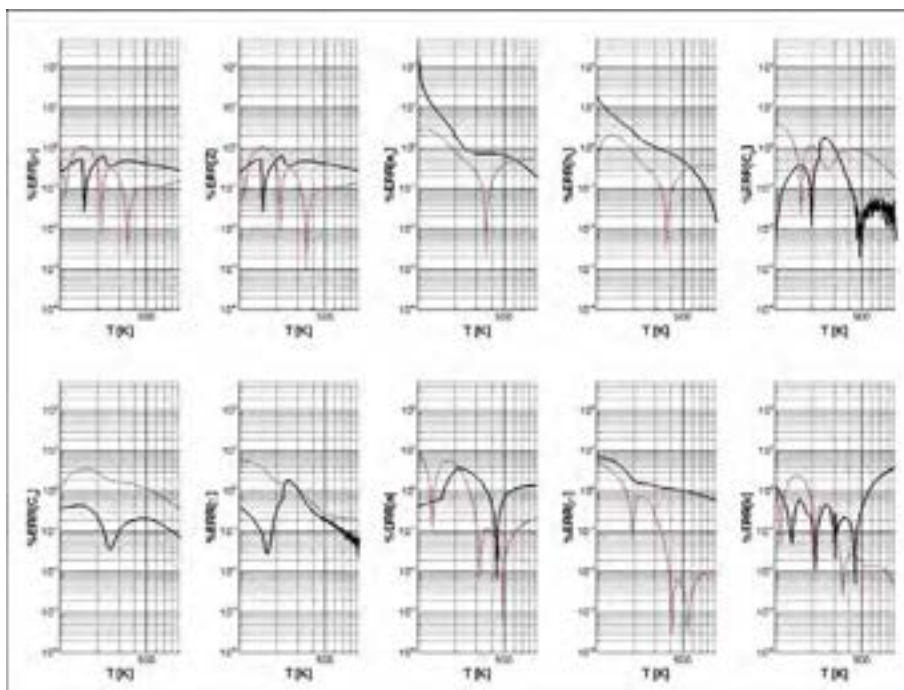


Figura 2.7: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH₄/O₂ (0.25/0.75 in mole fractions) at 300 bar.

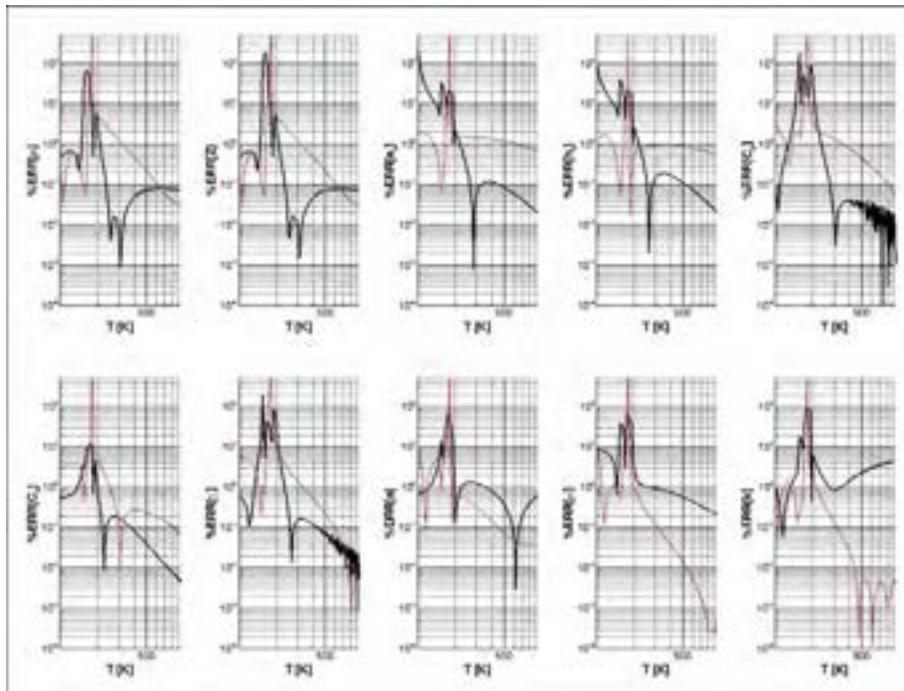


Figura 2.8: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH₄/O₂ (0.5/0.5 in mole fractions) at 50 bar.

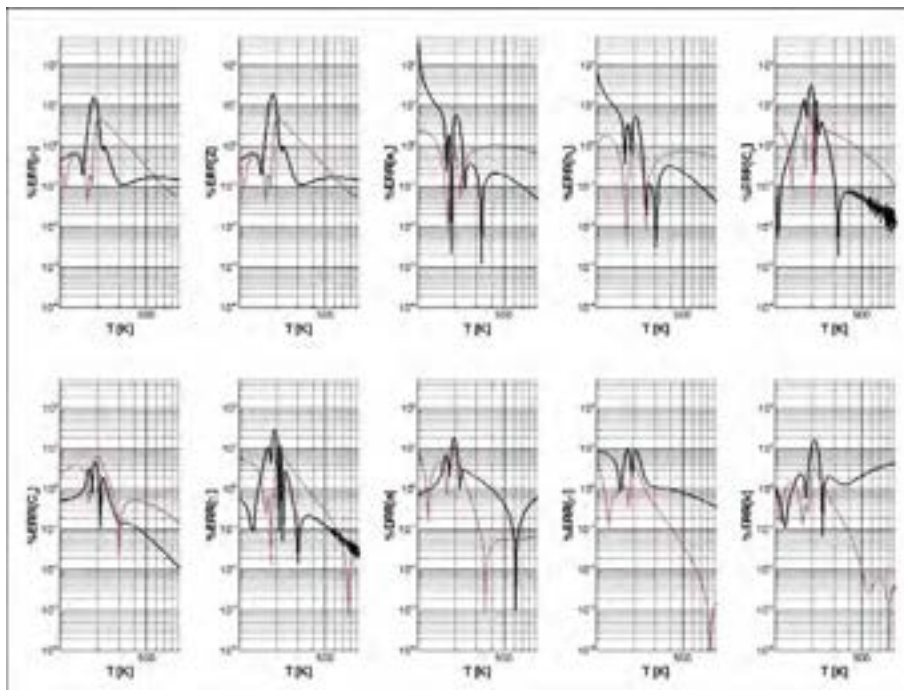


Figura 2.9: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH₄/O₂ (0.5/0.5 in mole fractions) at 100 bar.

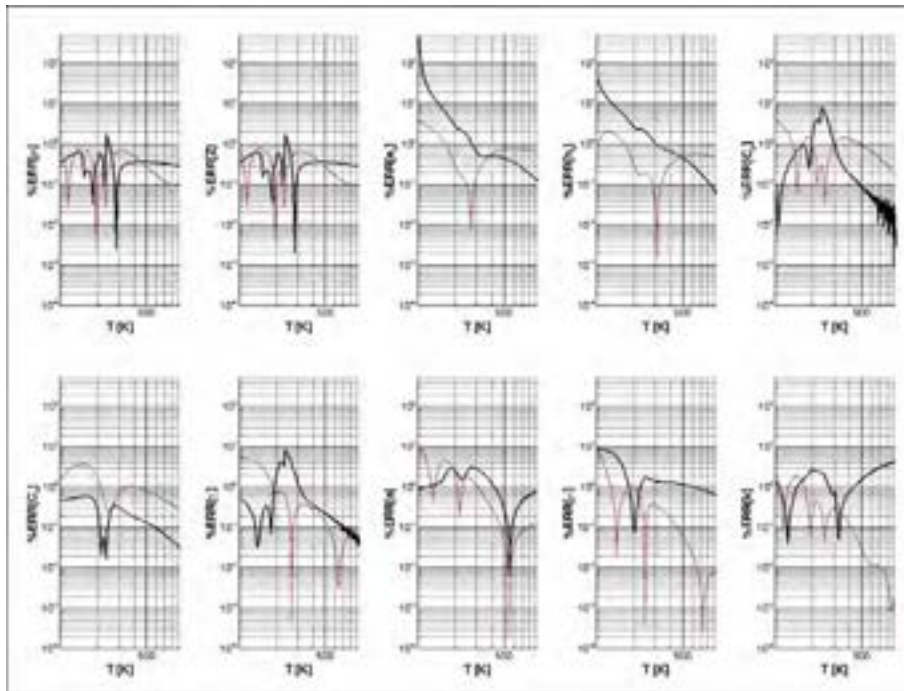


Figura 2.10: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH₄/O₂ (0.5/0.5 in mole fractions) at 200 bar.

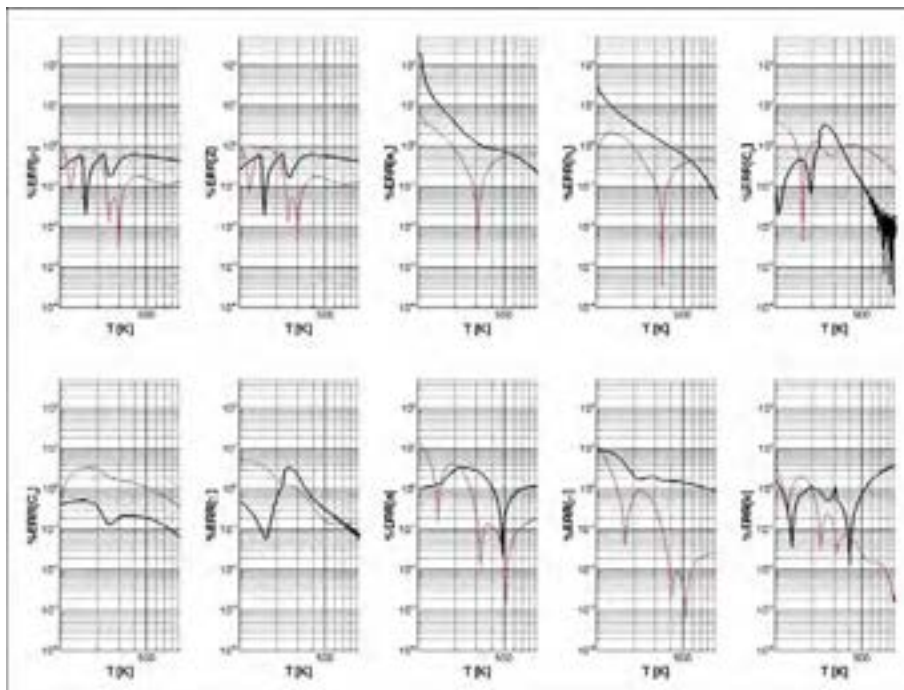


Figura 2.11: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH₄/O₂ (0.5/0.5 in mole fractions) at 300 bar.

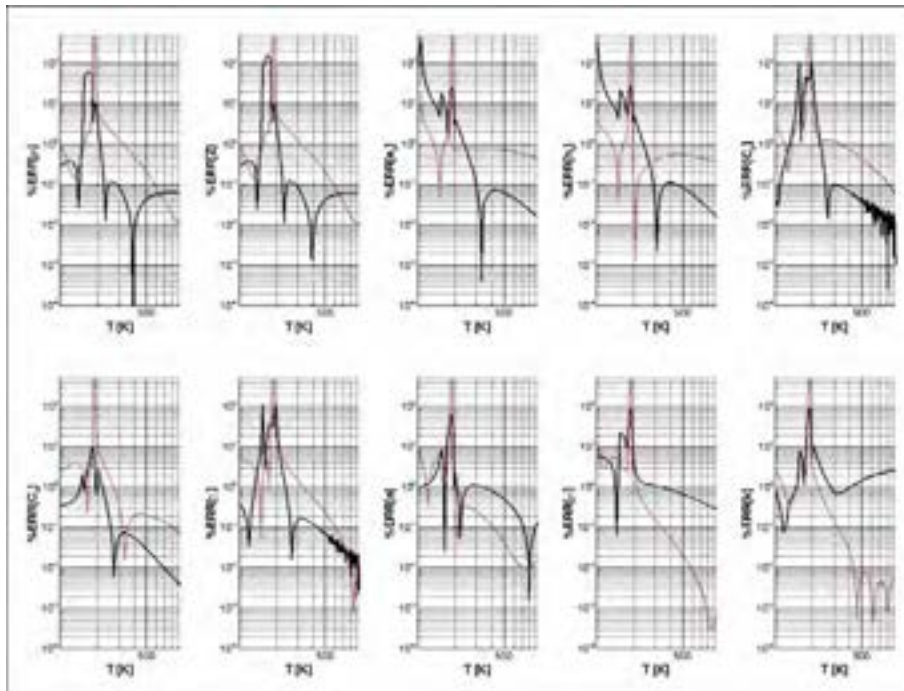


Figura 2.12: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH₄/O₂ (0.75/0.25 in mole fractions) at 50 bar.

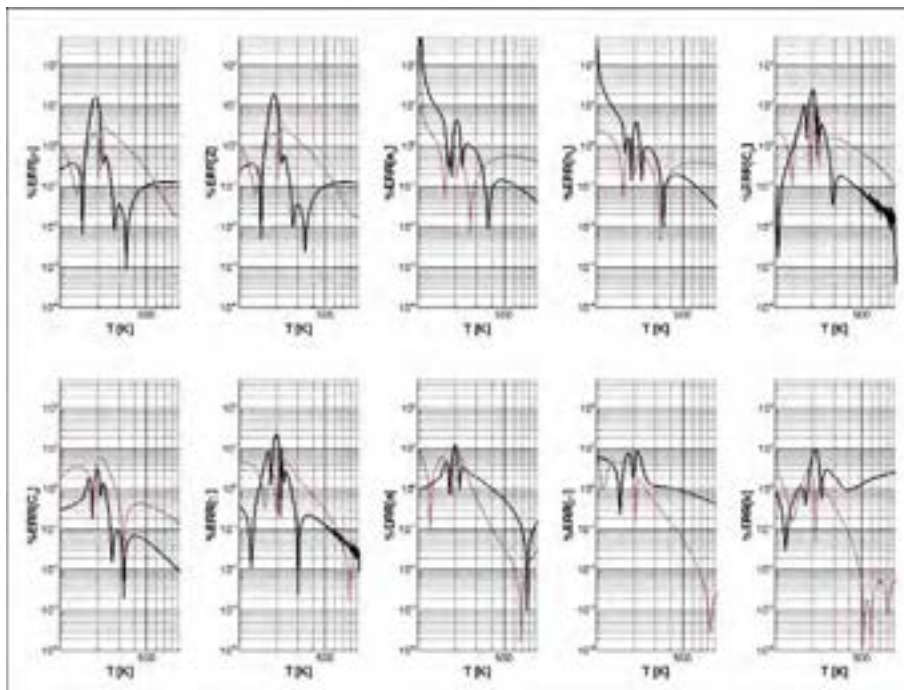


Figura 2.13: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH₄/O₂ (0.75/0.25 in mole fractions) at 100 bar.

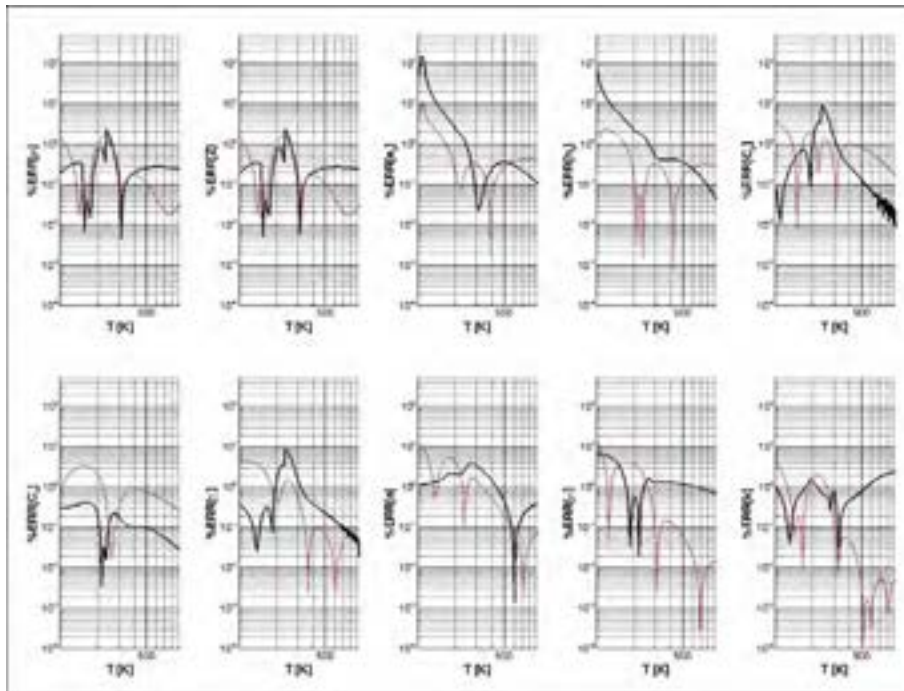


Figura 2.14: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH₄/O₂ (0.75/0.25 in mole fractions) at 200 bar.

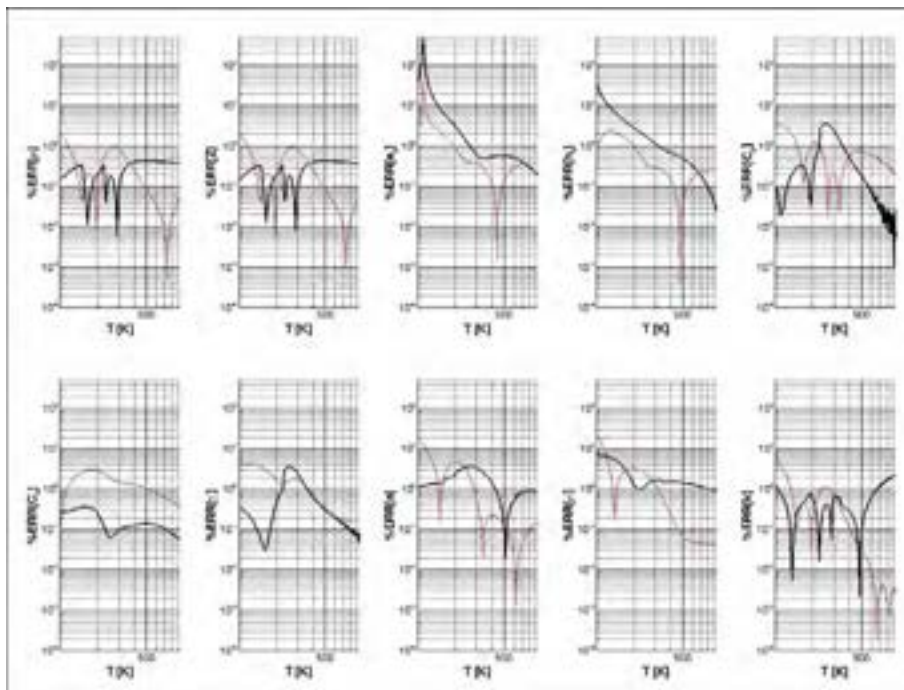


Figura 2.15: Percent errors of the suggested mixing rules and Peng-Robinson cubic equation strategies with respect to the “Exact” GERG-2008 real gas model for different quantities related to the CH₄/O₂ (0.75/0.25 in mole fractions) at 300 bar.

2.4 A First Application: CH₄/O₂ Non-Reactive Mixing

The first high pressure simulation performed in this annual work deals with a confined non-reactive mixing process between a central slot CH₄ jet at 100 m/s and two surrounding slot O₂ jets at 25 m/s, both injected at 300 K and 150 bar. The central jet has a Reynolds number of order 10⁵, while the two surrounding jets have a Reynolds number of order 10⁶. Figures 2.16 and 2.17 show an instantaneous flowfield of some quantities. In particular, Fig. 2.16a show the central CH₄ turbulent core jet mixing with the surrounding O₂. The density gradients associated to this flow are very high, as confirmed by Fig. 2.16b. During the unsteady simulation it was observed that total energy transport equation tends to become unstable: this results in unphysical temperature oscillations around the high gradient regions, especially during the roll-up of vortices associated to the Kelvin-Helmoltz instability experienced by the central slot jet. The associated instantaneous streamwise velocity flowfield is reported in Fig. 2.17a. The turbulent mixing takes place by means of coherent structures released by the central injector and along the the interface between the two chemical species. Such vortices induce pressure fluctuations of order of some bars, as evidenced in Fig. 2.17b.

This high-pressure test was performed on a two-dimensional computational domain having 619524 nodes. The Navier-Stokes equations were solved within the Large Eddy Simulation framework, and in particular by solving a transport equation for the subgrid kinetic energy used to model an eddy viscosity. There are four zones: a central injection zone extending from -4 mm to 0 in the streamwise direction (z) with a width (along y) of 1.2 mm and with 193×132 nodes (zy); two surrounding zones extending from -0.4 mm to 0 in the streamwise direction and from the central slot external wall (wall thickness 0.17 mm) up to 12 mm outward in the transversal direction (y) with 33×217 nodes (zy); a main mixing zone downstream of the injection extending from 0 to 12.2 mm in the streamwise direction and from -12 mm to 12 mm in the transversal direction with 963×602 nodes (zy).

The results obtained showed the goodness of the approach adopted. The presence of numerical wiggles in the total energy and temperature fields require more robust numerical spatial schemes able to manage contact discontinuities. The required schemes will be implemented in the next year, and the final code and strategy will be validated against a high-pressure experimental test case.

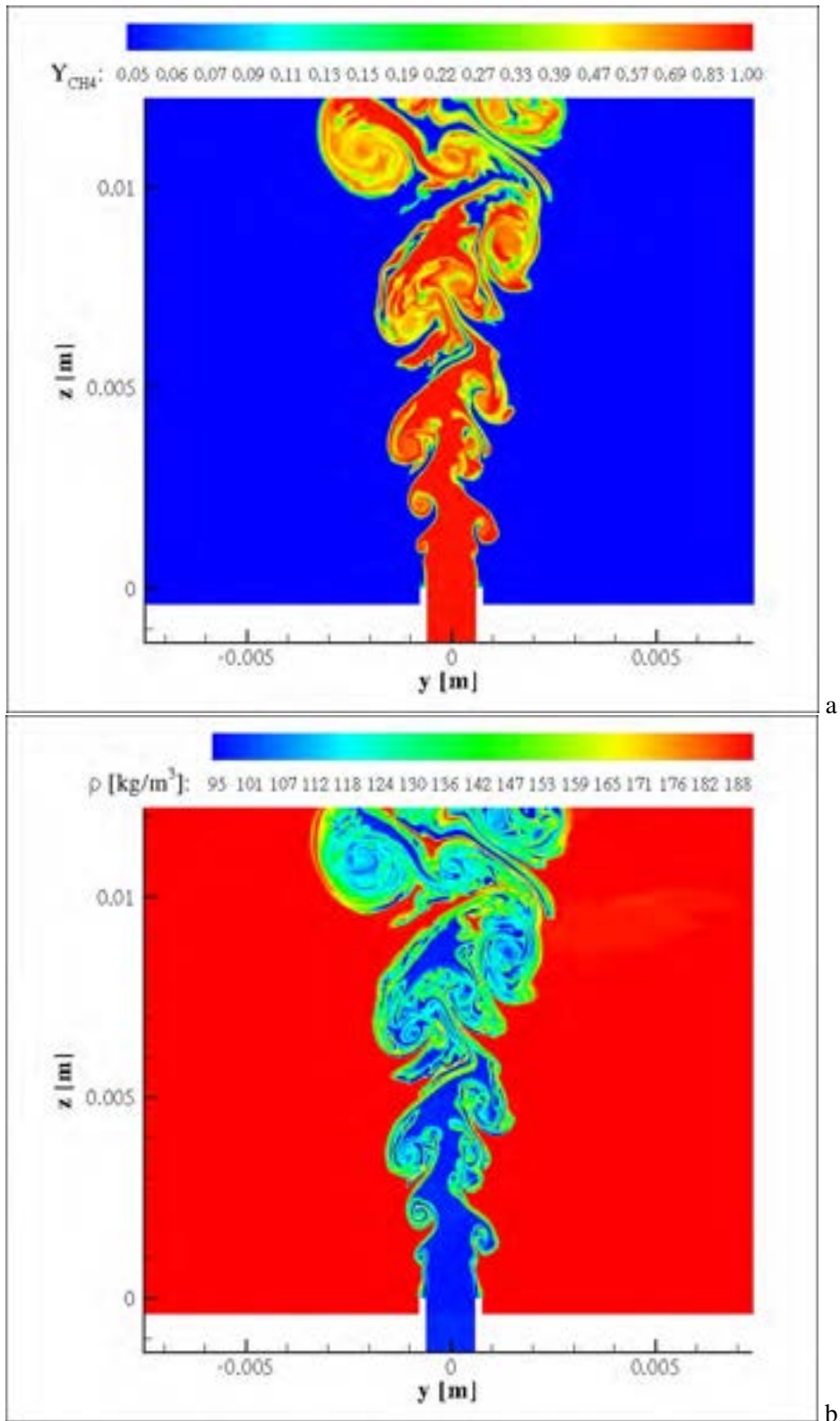


Figura 2.16: Instantaneous CH₄ mass fraction (a) and density distributions (b) predicted in the LES simulation of the confined mixing process between a central slot CH₄ jet and the surrounding slot O₂ jets, both injected at 300 K and 150 bar.

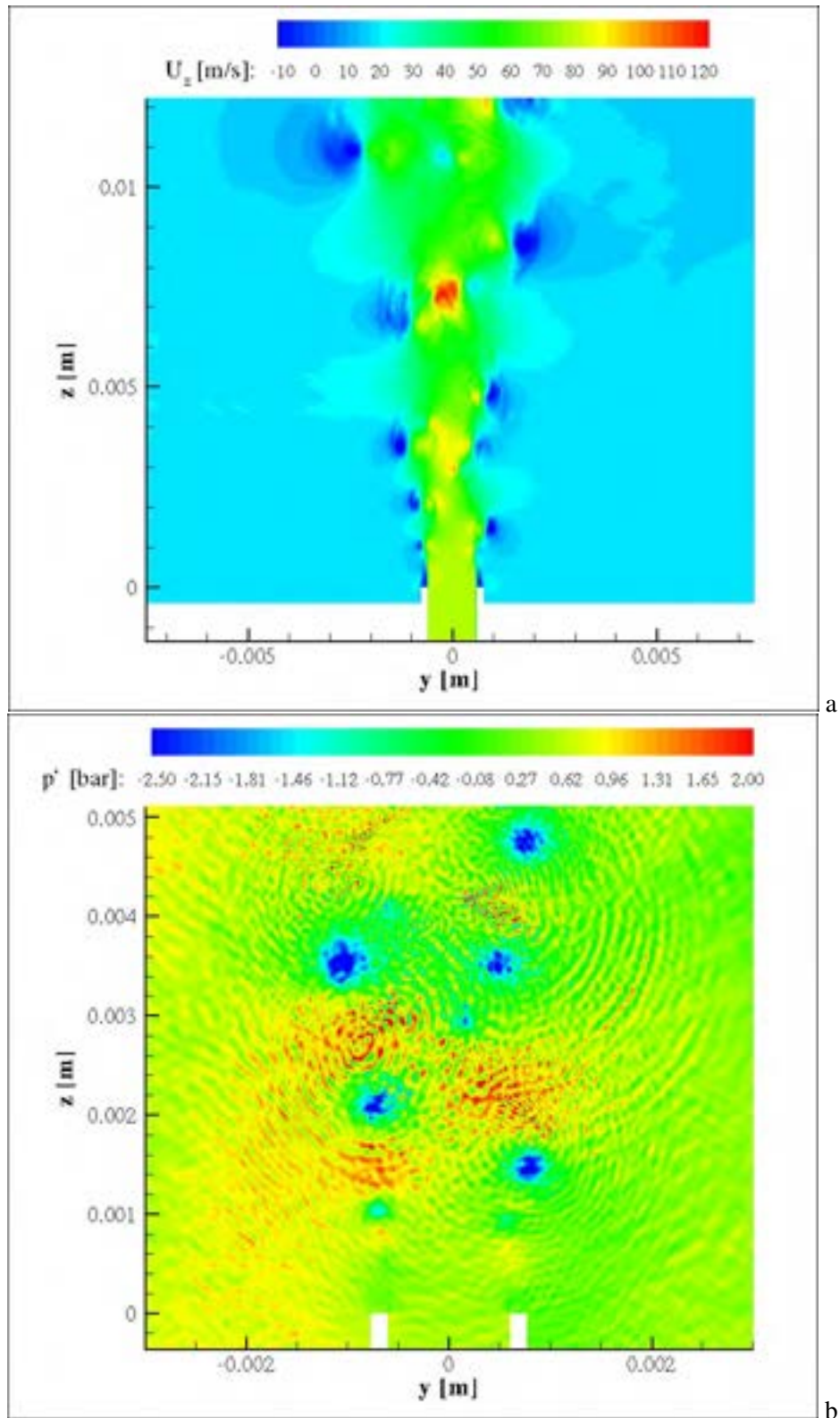


Figura 2.17: Instantaneous streamwise velocity (a) and pressure fluctuation distributions (b) predicted in the LES simulation of the confined mixing process between a central slot CH_4 jet and the surrounding slot O_2 jets, both injected at 300 K and 150 bar.

Bibliografia

- [1] NIST. *Chemical kinetics database*: <http://kinetics.nist.gov/kinetics/index.jsp>.
- [2] Kenneth George Denbigh. *The Principles of Chemical Equilibrium*. Cambridge University Press, Cambridge, fourth edition, 1981.
- [3] NIST. *NIST Reference Fluid Thermodynamic and Transport Properties Database* <http://www.nist.gov/srd/nist23.cfm>.
- [4] Kunz O. and Wagner W. The GER-2008 wide-range equation of state for natural gases and other mixtures: An expansion of GERG-2004. *Journal of Chemical Engineering Data*, 57:3032–3091, 2012.
- [5] Kunz O., Klimeck R., Wagner W., and Jaeschke M.
- [6] Starling K.E. and Savidge J.L. Compressibility factors of natural gas and other related hydrocarbon gases. Technical Report 8, Transmission Measurement Committee, American Gas Association: Washington, DC, 1992. 2nd edition.
- [7] Peng D.Y. and Robinson D.B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.*, 15:59–64, 1976.
- [8] Miller R.S., Harstad K.G., and Bellan J. Direct numerical simulations of supercritical fluid mixing layers applied to heptane-nitrogen. *J. Fluid Mechanics*, 436:p. 1–39, 2001.
- [9] Hickey J.P. and Ihme M. Supercritical mixing and combustion in rocket propulsion. Annual research briefs, Center for Turbulence Research, 2013. p. 21-36.
- [10] Pohl S., Jarczyk M., Pfitzner M., and Rogg B. Real gas CFD simulations of hydrogen/oxygen supercritical combustion. *Progress in Propulsion Physics*, 4:583–614, 2013.
- [11] Masi E., Bellan J., Harstad K.G., and Okong'o N.A. Multi-species turbulent mixing under supercritical-pressure conditions: Modelling, direct numerical simulation and analysis revealing species spinodal decomposition. *J. Fluid Mechanics*, 721:p. 578–626, 2013.
- [12] Bird R.B., Stewart W.E., and Lightfoot E.N. *Transport Phenomena*. John Wiley and Sons, New York, 2nd edition, 2002.
- [13] Wilke C.R. *J. Chem. Phys.*, 18:517–519, 1950.
- [14] Kee R.J., Dixon-Lewis G., Warnatz J., Coltrin M.E., Miller J.A., and Moffat H.K. *The CHEMKIN Collection III, Transport*. Reaction Design, San Diego, 1998. www.reactiondesign.com.
- [15] Mathur S., Tondon P.K., and Saxena S.C. *Molecular Physics*, 12:569, 1967.