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Computation of air chemical equilibrium composition until 30000K - Part I

Abstract: An algorithm was developed to obtain the air chemical equilibrium composition. The air was considered to be composed of 79% N_2 and 21% O_2 , and the models are 5 chemical species, N_2, O_2, NO, N, O , and 7 chemical species, $N_2, O_2, NO, N, O, NO^+, e^-$, respectively. The air chemical equilibrium composition is obtained through the equilibrium constants method and it was used the Absolute Newton method for convergence. The algorithm can be coupled as a subroutine into a Computational Fluid Dynamics code, given the flow field over an atmosphere reentry vehicle where, due to high velocities, dissociative chemical reactions and air ionization can occur. This work presents results of air chemical equilibrium composition for pressures of 1, 5, 10, 50 and 100 atm in a temperature range from 300 to 30000K.

Keywords: Air composition, Nitrogen chemistry, High temperature, Chemical equilibrium problem, Absolute Newton method

LIST OF SYMBOLS

A_k :	coefficients of thermodynamic data fits ()
f :	function
G_i^0 :	free energy of species i [J/kg mole]
H_i^0 :	specific enthalpy of species i [J/kg mole K]
J_f :	Jacobian matrix of function f
k :	equilibrium constant
M_i :	molecular weight [kg/mole]
m :	number of ionized species
$n_i^{r \text{ or } p}$:	mole number for species i
N :	number of equations
p^0 :	standard state pressure,
p :	products
R_u :	universal gas constant,
r :	reactants
S_i^0 :	entropy of species i [J/kg mole K]
T :	temperature [K]
X_i :	mole fraction of species i
Y_i :	mass fraction of species i
v_i :	stoichiometric coefficient of species i [kg moles]
ρ :	mass density of mixture [kg/m ³]

INTRODUCTION

The utilization of Computational Fluid Dynamics (CFD) techniques to compute the flow field around atmospheric reentry vehicles needs a robust and able algorithm to obtain the air chemical composition in a wide range of pressure and temperature. There are two strategies to deal with the air chemical composition in this kind of flow. The first one considers the air not in chemical equilibrium, and the other considers chemical equilibrium. Each approach has its particularities and difficulties on how to obtain the air chemical composition. In this first part of the work, only the equilibrium method is used, and the non-equilibrium computations shall be presented in the second part.

Due to its iterative codification nature, a CFD code needs to perform many times these chemical computations. This code could be inserted into the main program as a subroutine or library and be called many times during the convergence process. So, this implies the code should be very efficient in processing time terms. This efficiency is reflected in the CFD computational code, and its ability to obtain more quickly the flow field solution in study.

There are many techniques to compute the chemical equilibrium composition. The mostly know and used is the Gibbs free energy minimization (Gordon and McBride, 1994), but due to its inherent generality, it is used to solve problems that involve a high number

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of chemical species as, for example, hydrocarbon combustion. A more simple method, and also widely used, is the equilibrium constants method (Prabhu and Erickson 1988; Sabetta, Favini and Onofri, 1993). This method combines an algebraic combination of the equilibrium constants, mass balance and the electron charge conservation. Besides its simplicity, this method is robust and efficient enough to compute the flow field around reentry vehicles, whose medium is considered to be in chemical equilibrium.

The method presented herein does not divide the study dominium in four regions to obtain the air chemical equilibrium composition in high temperatures, where each region is limited by a series of predominant species as in Prabhu and Erickson (1988) or Smith, Erickson and Eastwood (1967). What is wanted is to obtain the equilibrium chemical composition prefixing the existent chemical species, independently of region. This work presents results of an algorithm that applies the equilibrium constants method to obtain the chemical equilibrium composition for the air, considered to be composed of 79% N_2 and 21% O_2 , and the models are five chemical species, , and seven chemical species, , and it is assumed to be a perfect gas.

THE GOVERNING EQUATIONS

The describing expressions of the chemical equilibrium composition for a given pressure and temperature condition are built in a set of N equations, where N depends on the number of chemical elements present in the considered model.

For the seven chemical species model, considering, the equations are (Eq. 1 to 3):

chemical reaction equation

$$n_{N_2}^r N_2 + n_{O_2}^r O_2 \rightleftharpoons n_{N_2}^p N_2 + n_{O_2}^p O_2 + n_{NO}^p NO + n_N^p N + n_O^p O + n_{NO^+}^p NO^+ + n_{e^-}^p e^- \quad (1)$$

atom conservation equations

$$N \Rightarrow 2n_{N_2}^r = 2n_{N_2}^p + n_{NO}^p + n_N^p + n_{NO^+}^p \quad (2)$$

$$O \Rightarrow 2n_{O_2}^r = 2n_{O_2}^p + n_{NO}^p + n_O^p + n_{NO^+}^p \quad (3)$$

Considering the concentration of the chemical species i , one has (Eq. 4 and 5):

$$N \Rightarrow 2 \frac{Y_{N_2}^0}{M_{N_2}} = 2 \frac{Y_{N_2}}{M_{N_2}} + \frac{Y_{NO}}{M_{NO}} + \frac{Y_N}{M_N} + \frac{Y_{NO^+}}{M_{NO^+}} \quad (4)$$

$$O \Rightarrow 2 \frac{Y_{O_2}^0}{M_{O_2}} = 2 \frac{Y_{O_2}}{M_{O_2}} + \frac{Y_{NO}}{M_{NO}} + \frac{Y_O}{M_O} + \frac{Y_{NO^+}}{M_{NO^+}} \quad (5)$$

Where the fraction of initial mass of the reagent species, N_2 and O_2 , are defined as (Eq. 6 and 7):

$$Y_{N_2}^0 = \frac{X_{N_2} M_{N_2}}{X_{N_2} M_{N_2} + X_{O_2} M_{O_2}} \quad (6)$$

$$Y_{O_2}^0 = \frac{X_{O_2} M_{O_2}}{X_{N_2} M_{N_2} + X_{O_2} M_{O_2}} \quad (7)$$

Where:

$$X_{N_2} = 0,79 \text{ and } X_{O_2} = 0,21$$

so,

$$X_{N_2} + X_{O_2} = 1$$

For an ionized gas, the computation of the equilibrium requires a complementary equation (Eq. 8) on the charge conservation of electrons (William, 2000):

$$\frac{Y_{e^-}}{M_{e^-}} = \sum_{i=1}^m \frac{Y_i}{M_i} \Rightarrow \frac{Y_{e^-}}{M_{e^-}} = \frac{Y_{NO^+}}{M_{NO^+}} \quad (8)$$

Where m is the number of ionized species.

For the completeness of the equation set solution, complementary equations are necessary. These equations are defined from independent chemical reactions that involve the considered chemical species. The chemical expressions are (Eq. 9 to 12):

$$N_2 \rightarrow 2N \quad (9)$$



Now, it is necessary to express the equilibrium constants for each chemical reaction equation. These expressions are (Eq. 13 to 16):

$$k_9 = \rho \frac{(Y_N)^2 M_{N_2}}{Y_{N_2} (M_N)^2} \Rightarrow \left(\frac{k_{10} (M_N)^2}{\rho M_{N_2}} \right) Y_{N_2} - (Y_N)^2 = 0 \quad (13)$$

$$k_{10} = \rho \frac{(Y_O)^2 M_{O_2}}{Y_{O_2} (M_O)^2} \Rightarrow \left(\frac{k_{11} (M_O)^2}{\rho M_{O_2}} \right) Y_{O_2} - (Y_O)^2 = 0 \quad (14)$$

$$k_{11} = \frac{M_{N_2} M_{O_2}}{(M_{NO})^2} \frac{(Y_{NO})^2}{Y_{N_2} Y_{O_2}} \Rightarrow \left(k_{12} \frac{(M_{NO})^2}{M_{N_2} M_{O_2}} \right) Y_{N_2} Y_{O_2} - (Y_{NO})^2 = 0 \quad (15)$$

$$k_{12} = \frac{1}{\rho} \frac{M_{NO^+} M_{e^-}}{M_{NO}} \frac{Y_{NO}}{Y_{NO^+} Y_{e^-}} \Rightarrow \left(k_{13} \rho \frac{M_{NO}}{M_{NO^+} M_{e^-}} \right) Y_{NO^+} Y_{e^-} - Y_{NO} = 0 \quad (16)$$

The non-linear equation system is given by the equation set (Eq. 17 to 23):

$$f_1(Y) = 2 \frac{Y_{N_2}}{M_{N_2}} + \frac{Y_{NO}}{M_{NO}} + \frac{Y_N}{M_N} + \frac{Y_{NO^+}}{M_{NO^+}} - 2 \frac{Y_{N_2}^0}{M_{N_2}} = 0 \quad (17)$$

$$f_2(Y) = 2 \frac{Y_{O_2}}{M_{O_2}} + \frac{Y_{NO}}{M_{NO}} + \frac{Y_O}{M_O} + \frac{Y_{NO^+}}{M_{NO^+}} - 2 \frac{Y_{O_2}^0}{M_{O_2}} = 0 \quad (18)$$

$$f_3(Y) = \frac{Y_{NO^+}}{M_{NO^+}} - \frac{Y_{e^-}}{M_{e^-}} = 0 \quad (19)$$

$$f_4(Y) = \left(\frac{k_9 (M_N)^2}{\rho M_{N_2}} \right) Y_{N_2} - (Y_N)^2 = 0 \quad (20)$$

$$f_5(Y) = \left(\frac{k_{10} (M_O)^2}{\rho M_{O_2}} \right) Y_{O_2} - (Y_O)^2 = 0 \quad (21)$$

$$f_6(Y) = \left(k_{11} \frac{(M_{NO})^2}{M_{N_2} M_{O_2}} \right) Y_{N_2} Y_{O_2} - (Y_{NO})^2 = 0 \quad (22)$$

$$f_7(Y) = \left(k_{12} \rho \frac{M_{NO}}{M_{NO^+} M_{e^-}} \right) Y_{NO^+} Y_{e^-} - Y_{NO} = 0 \quad (23)$$

Where the equilibrium constants, k_z , the considered chemical species molecular weights, M_i , and the mixture density, ρ , are known.

To obtain the equations for a five chemical species model N_2, O_2, NO, N, O , one just eliminates the chemical species NO^+ and e^- from the model described above.

THERMODYNAMIC DATA

To obtain the equilibrium composition, it is necessary to compute the thermodynamic properties enthalpy (H_i), entropy (S_i) and the Gibbs free energy (G_i^0) for each chemical species included in the model. The polynomial expressions that are used for these computations are based on the works from Gupta et al. (1990) and Gordon and McBride (1994):

entropy

$$\frac{S_i^0}{R_u} = A_1 \ln(T) + A_2 T + \frac{A_3}{2} T^2 + \frac{A_4}{3} T^3 + \frac{A_5}{4} T^4 + A_7 \quad (24)$$

specific enthalpy

$$\frac{H_i^0}{R_u T} = A_1 + \frac{A_2}{2} T + \frac{A_3}{3} T^2 + \frac{A_4}{4} T^3 + \frac{A_5}{5} T^4 + \frac{A_6}{T} \quad (25)$$

Gibbs free energy

$$\frac{G_i^0}{R_u T} = \frac{H_i^0}{R_u T} - \frac{S_i^0}{R_u} \quad (26)$$

The polynomial expressions coefficients, a_0 to a_7 , are those given by Gupta et al. (1990). They were computed for 5 temperature ranges, from 300 to 30000 K (300 K $\leq T \leq 1000$ K, 1000 K $\leq T \leq 6000$ K, 6000 K $\leq T \leq 15000$ K, 15000 K $\leq T \leq 25000$ K, 25000 K $\leq T \leq 30000$ K). As these curves do not present continuous behavior in their frontiers, the coefficients A_1 to A_7 were linearly smoothed in the borders to avoid an abrupt variation of thermodynamic properties.

EQUILIBRIUM CONSTANTS

According to Pinto and Lage (2001) and Carvalho and McQuay (2007), the equilibrium constant for a chemical reaction at constant pressure and temperature is a function of the Gibbs free energy:

$$k_{p,j} = \exp\left(-\frac{\Delta G_j^0}{RT}\right) \quad (27)$$

Where

$$\Delta G_j^0 = \sum_i \nu_i^p G_i^0 - \sum_i \nu_i^r G_i^0 \quad (28)$$

and ν_i is the stoichiometric coefficient of chemical species i .

To compute the equilibrium constants for the 4 independent chemical reactions in the equation set, it is necessary to express Eq. 27 as function of molar concentration. So,

$$k_j = k_{p,j} \left(\frac{p^0}{RT}\right)^{\Delta n} \quad (29)$$

Where $\Delta n = \sum_i \nu_i^p - \sum_i \nu_i^r$ for each independent chemical reaction. Then, for the reactions in the model, one has:

Reactions 9 and 10: $\Delta n=1$

Reaction 11: $\Delta n=0$

Reaction 11: $\Delta n=-1$

SOLUTION METHOD

A much known method for solving a non-linear equation set is the Newton method (Pinto and Lage, 2001), whose convergence process is described by the iteration, as follows. One starts with:

$$Y_i - \sigma_i \Rightarrow Y_i \quad (30)$$

with

$$\sigma = J_f^{-1} f(Y) \quad (31)$$

Where J is the Jacobian for the partial derivatives of the function $f(Y)$. In this work $f(Y)$ set of Eq. 17 to 23.

As it is widely known, a non-linear equation system can present a number of solutions, both negative and positive, or a solution that involves negative and positive values. Due to the complexity in obtaining the equilibrium chemical composition for a gas mixture reacting chemically, the Newton method must be modified in such a way that values which do not correspond to physical meaning are avoided. For the model described above, only positive values shall be allowed as results from the Newton method. We adopted the modified method proposed by Meintjes and Morgan (1989), and the iteration process suffered a simple modification:

$$|Y_i - \sigma_i| \Rightarrow Y_i \quad (32)$$

That means, through the iteration process, if one of the possible solutions is negative, it is replaced by its absolute value. The applied method, with this modification, was called the Absolute Newton Method.

RESULTS AND CONCLUSIONS

The developed numerical algorithm was able to obtain the air equilibrium chemical composition for pressures of 1, 5, 10, 50 and 100 atm, for a temperature range varying from 300 to 30000 K. The convergence process needs an initial condition for the mass fractions Y of each chemical species that compose the model. So, the iterative process is described by the following steps:

1. a constant temperature is set.
2. initial values for the chemical species mass fractions are chosen.
3. the iterative process is started with loops until the desired precision is reached. To obtain the results presented herein the adopted precision was.

The implemented method computes the model mass balance of the chemical species for a given temperature. To be strictly correct, the temperature itself needs to be re-evaluated through the energy equation, which should be coupled with non-linear equations set.

The results are presented as plots of the logarithm of mol fraction and mass fraction as function of the temperature for the chemical composition of the models. Under 1 atm, oxygen (O_2) starts dissociate around 2000 K, being fully dissociated just above 4000 K. On the other side, nitrogen (N_2) starts its dissociation process near 4000 K and finishes it around 9000 K, while the nitrogen monoxide (NO) starts forming on 1800 K and is completely dissociated near 6000 K, having its maximum on 3300 K. This behavior is in agreement with results from Anderson (1989) and William (2000). One observes that, in the studied temperature range, from its beginning to the end, the dissociation processes for both five and seven chemical species models are very likely. This occurs due to the ionized species present in the seven species model show significative mass only above 10000 K.

It is important to observe the pressure effect over the dissociation mechanism. If the pressure increases the

dissociation processes became slower even under high temperatures. This is motivated by the fact that at high pressures the molecules that compose the mixture are closer one to the others, making the mechanisms that pull out the outer layer electrons less effective. The result is that the plotted curves move to the high temperature as the pressure increases, and the opposite occurs when the pressure drops, because the molecules are sparser and the dissociation process is facilitated. This kind of phenomena is observed in all presented plots, both for the five chemical species as for the seven chemical species model.

When comparing our results to those of William (2000) for the 7 species, one can notice a slight deviation in the 5, 10, 50 and 100 atm models. In the worst case, the deviation is about 6% in temperature (~ 615 degrees) in the curves of atomic nitrogen (N) formation at 100 atm. These small deviations can be due to many factors, being the most relevant the method used to obtain the polynomial coefficients to that have a very important role in the thermodynamical properties of chemical species present in the models, and these influence the equilibrium constants evaluation.

Figures 1 to 10 present the evolution of each model for 100, 50, 10, 5 and 1 atm. The 4 first models for 7 chemical species are also compared to the same calculations of William (2000). These values were computed in a 3.33 GHz Intel Core i5 computer, and the maximum time needed to compute 1 convergence was 0.04 seconds, for a case where 16 iterations were used.

The presented results can diverge slightly from those found on literature, but these small differences can be due to many factors. One cause is related to the method used to obtain the polynomial coefficients, A_1 to A_7 , that influences the computation of chemical species thermodynamic properties in the model, and these the equilibrium constants.

The developed algorithm is the first step in the direction of a free library for the simulation of the field flow on reentry vehicles studies.

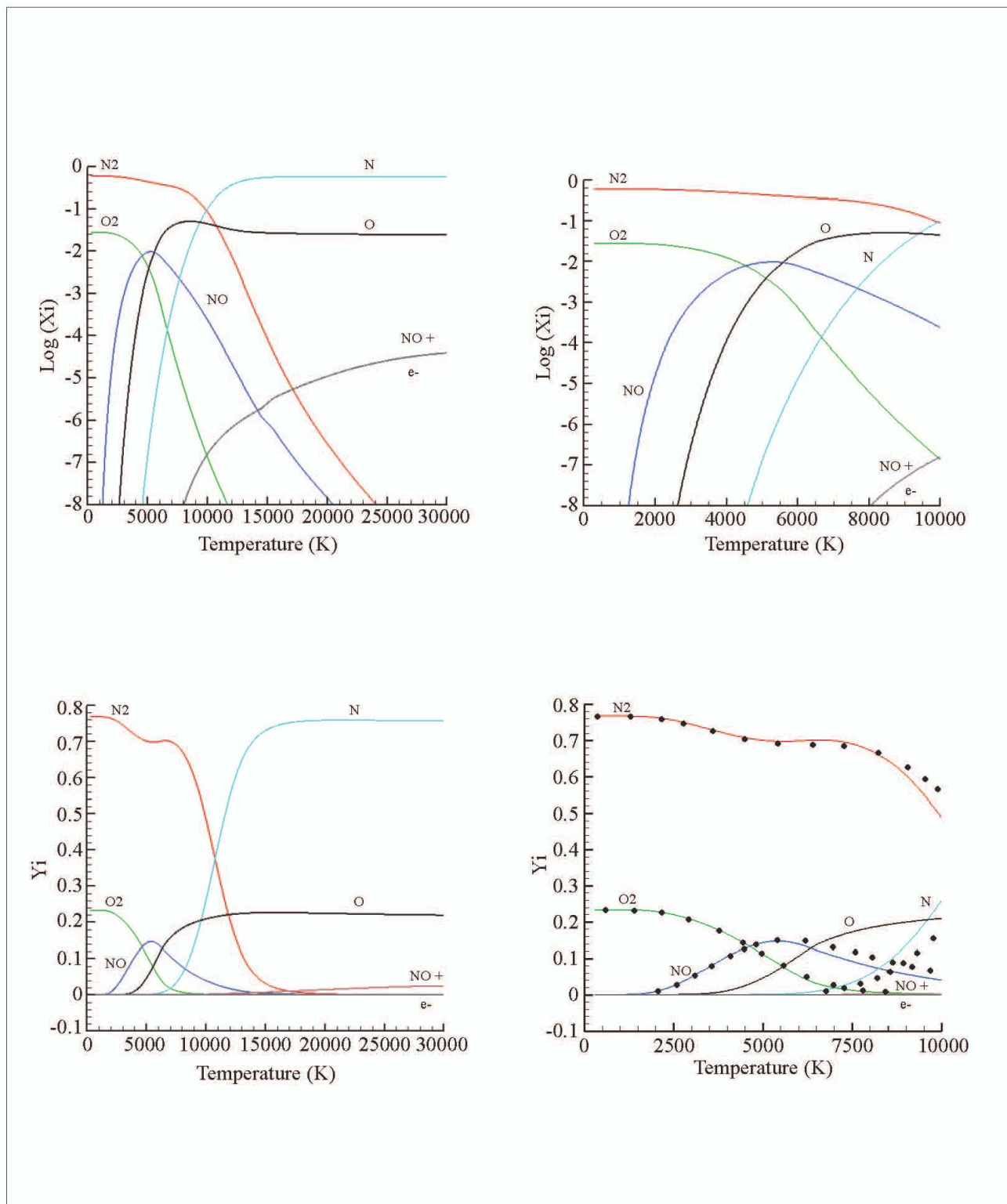


Figure 1. Logarithm of mole fraction and mass fraction to the pressure of the model of seven chemical species. The panels on the right present the details for the range from 0 to 10000 K. The dots on last panel represent the results form William (2000) for the same parameters.

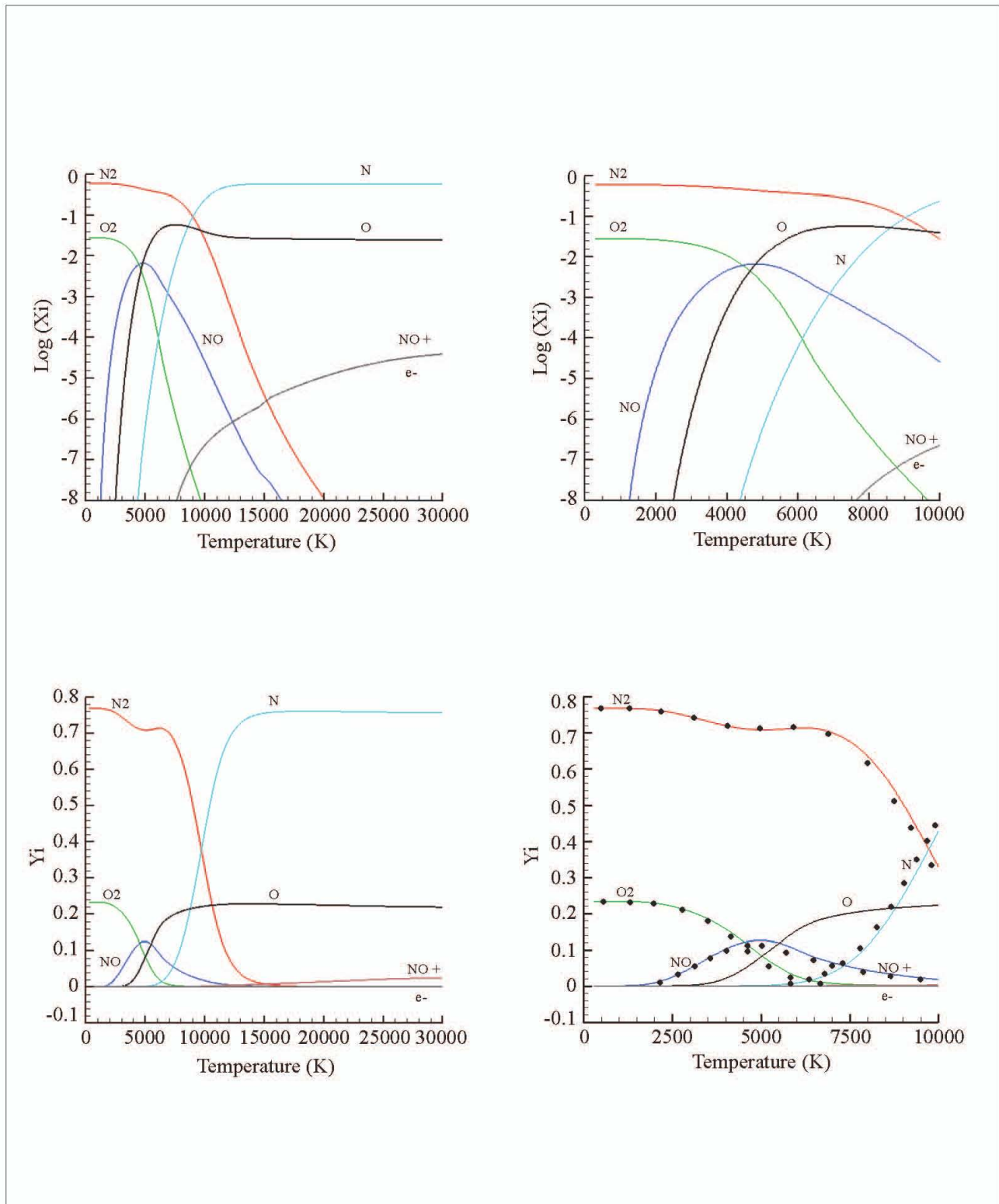


Figure 2. Logarithm of mole fraction and mass fraction to the pressure of the model of seven chemical species. The panels on the right present the details for the range from 0 to 10000 K. The dots on last panel represent the results form William (2000) for the same parameters.

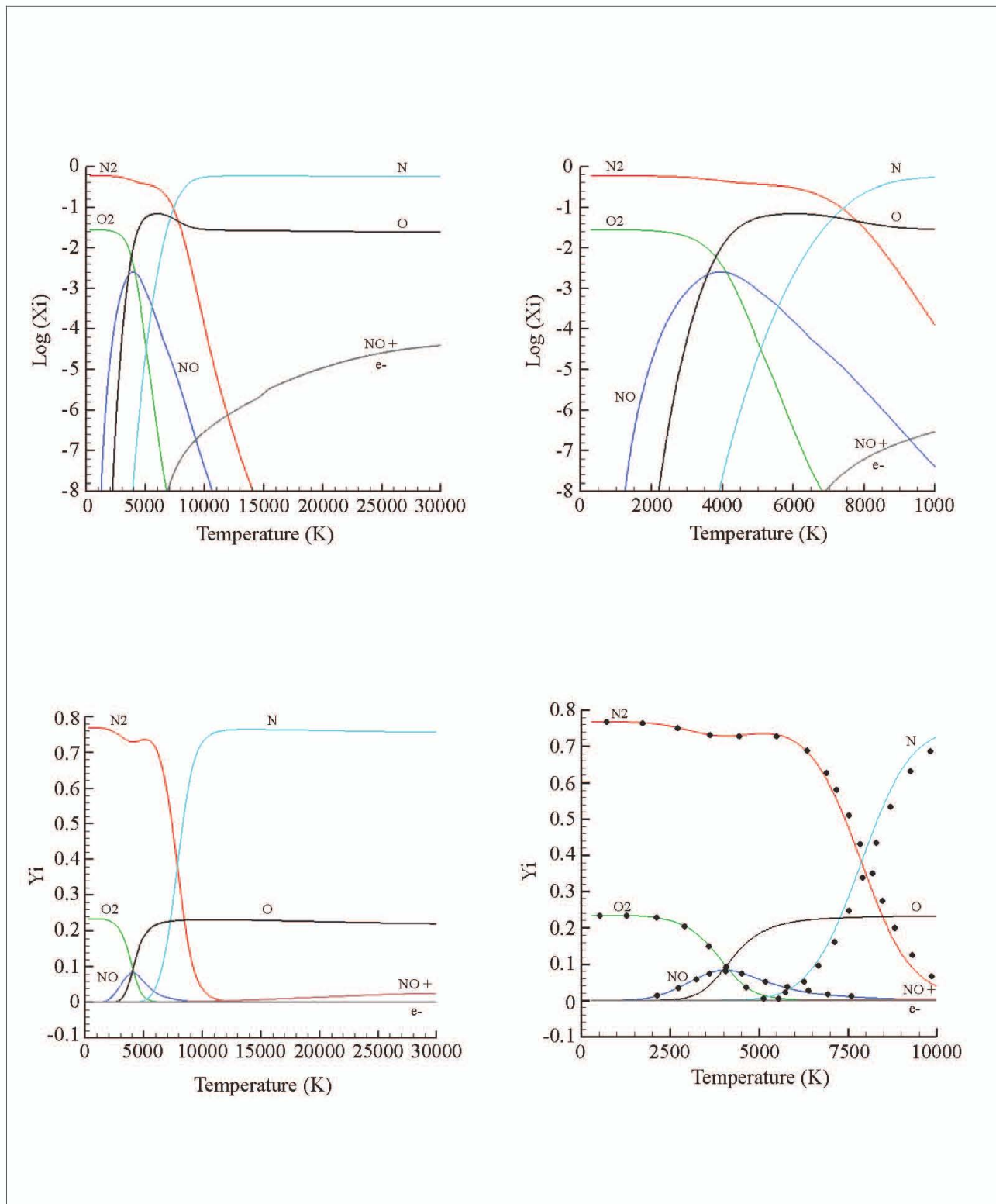


Figure 3. Logarithm of mole fraction and mass fraction to the pressure of the model of seven chemical species. The panels on the right present the details for the range from 0 to 10000 K. The dots on last panel represent the results form William (2000) for the same parameters.

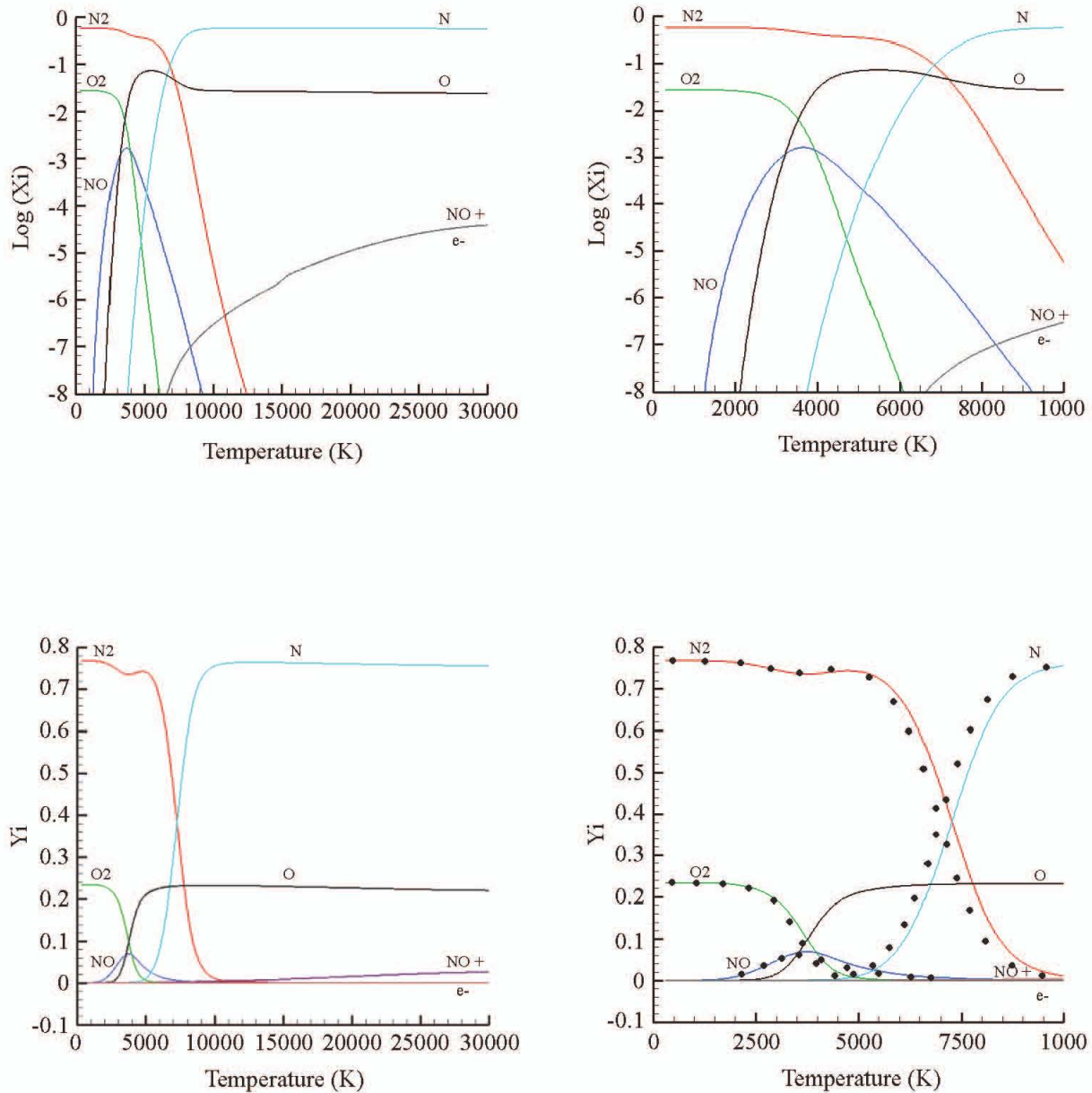


Figure 4. Logarithm of mole fraction and mass fraction to the pressure of the model of seven chemical species. The panels on the right present the details for the range from 0 to 10000 K. The dots on last panel represent the results from William (2000) for the same parameters.

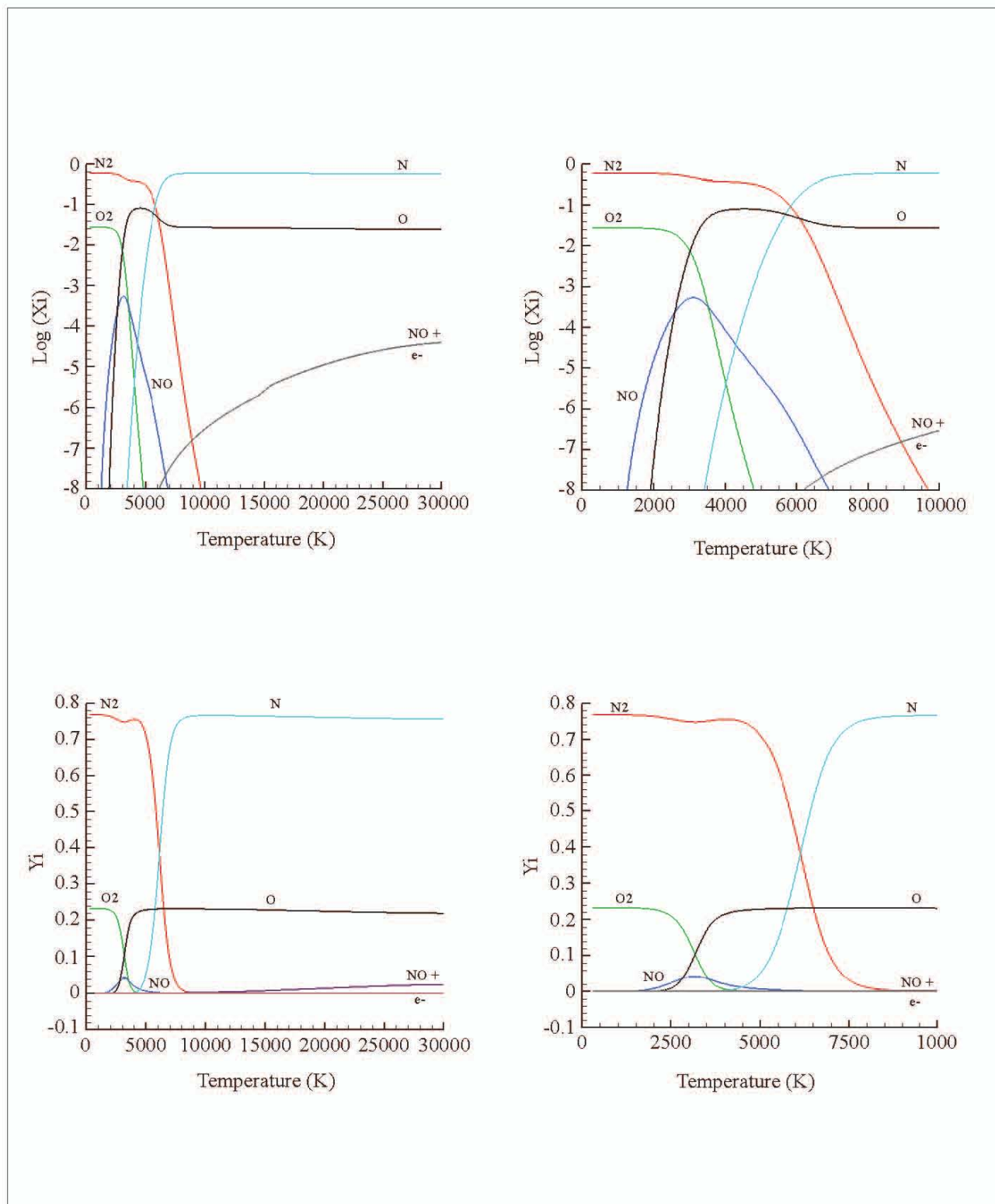


Figure 5. Logarithm of mole fraction and mass fraction to the pressure of the model of seven chemical species. The panels on the right present the details for the range from 0 to 10000 K.

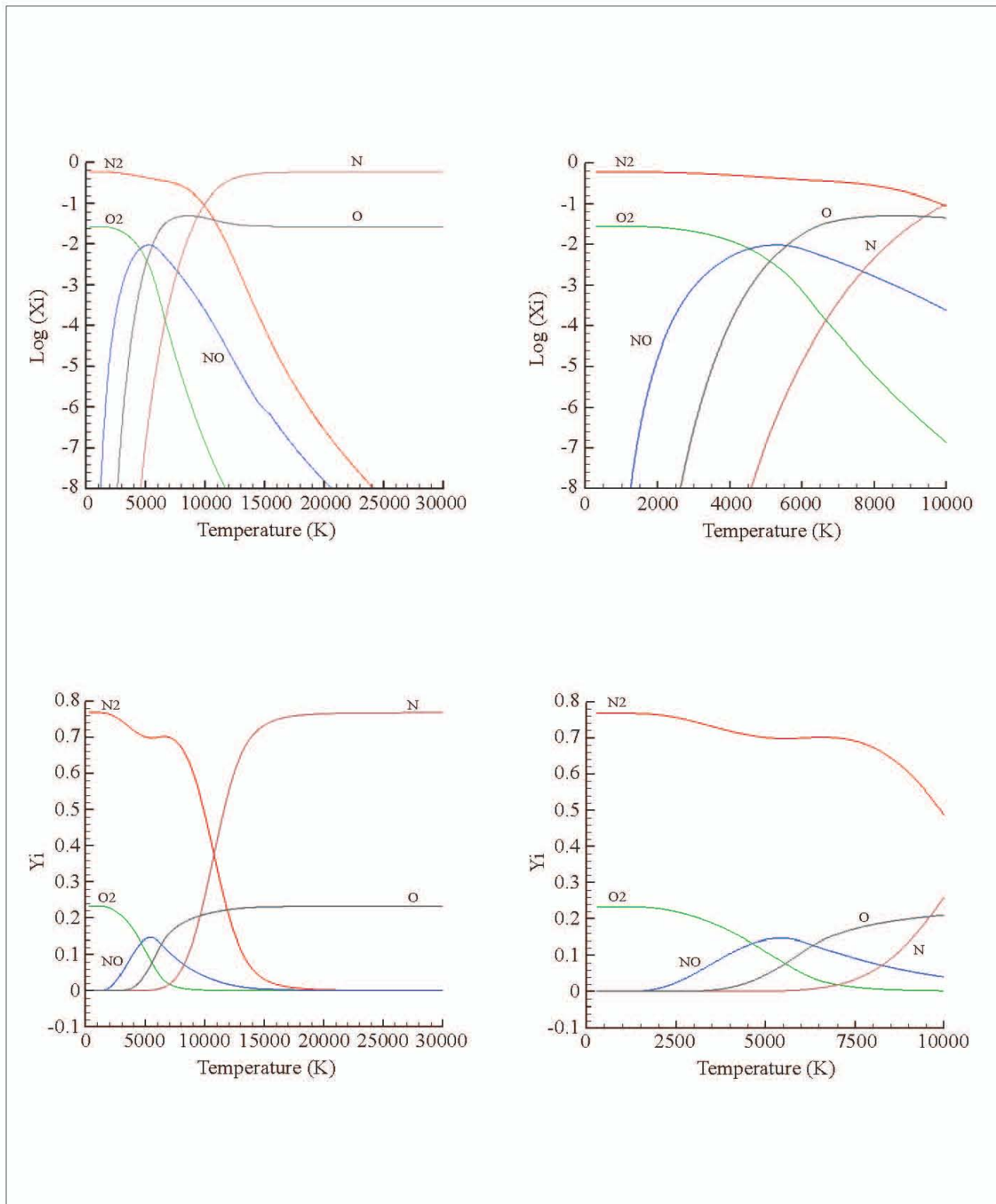


Figure 6. Logarithm of mole fraction and mass fraction to the pressure of the model of five chemical species. The panels on the right present the details for the range from 0 to 10000 K.

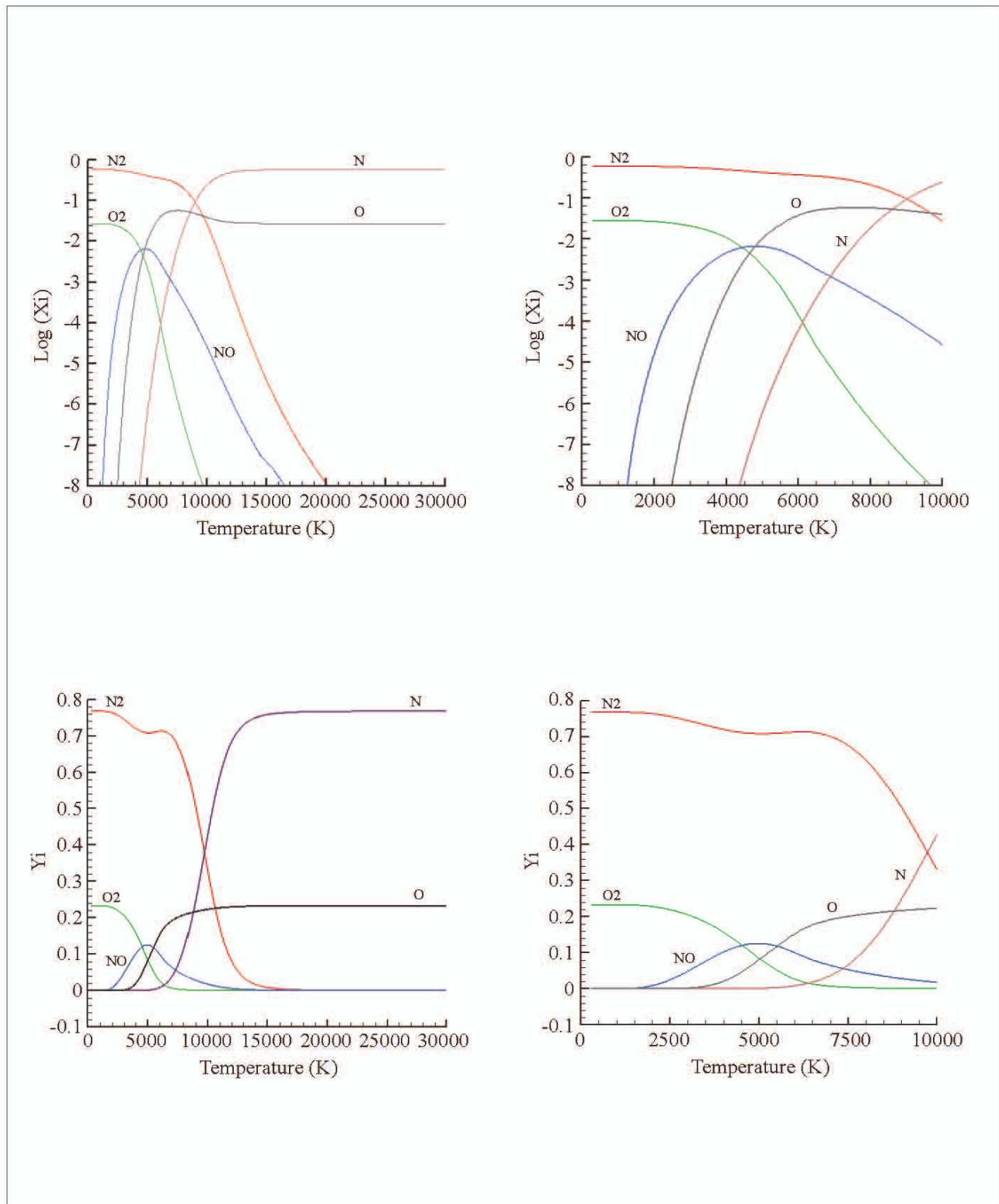


Figure 7. Logarithm of mole fraction and mass fraction to the pressure of the model of five chemical species. The panels on the right present the details for the range from 0 to 10000 K.

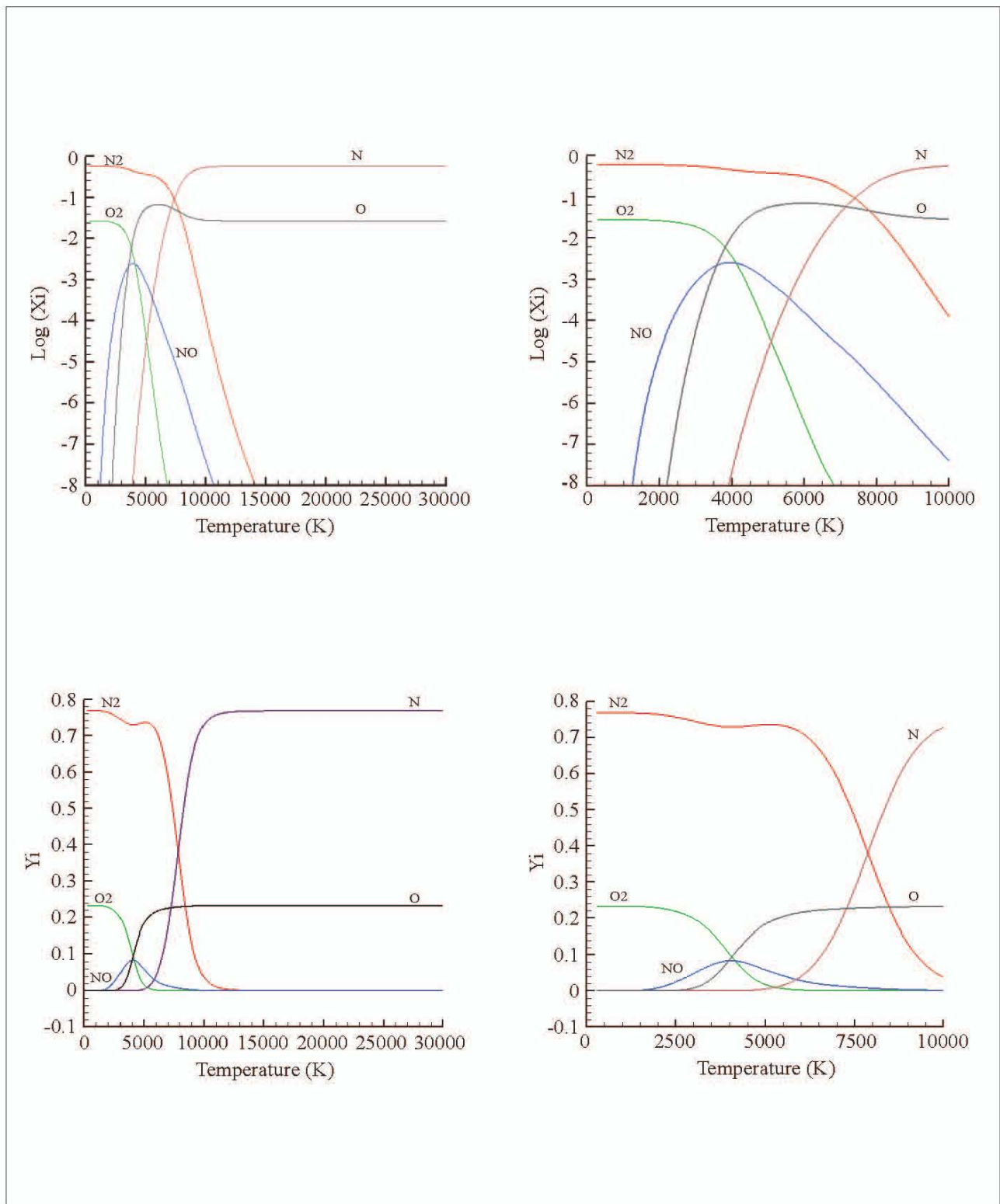


Figure 8. Logarithm of mole fraction and mass fraction to the pressure of the model of five chemical species. The panels on the right present the details for the range from 0 to 10000 K.

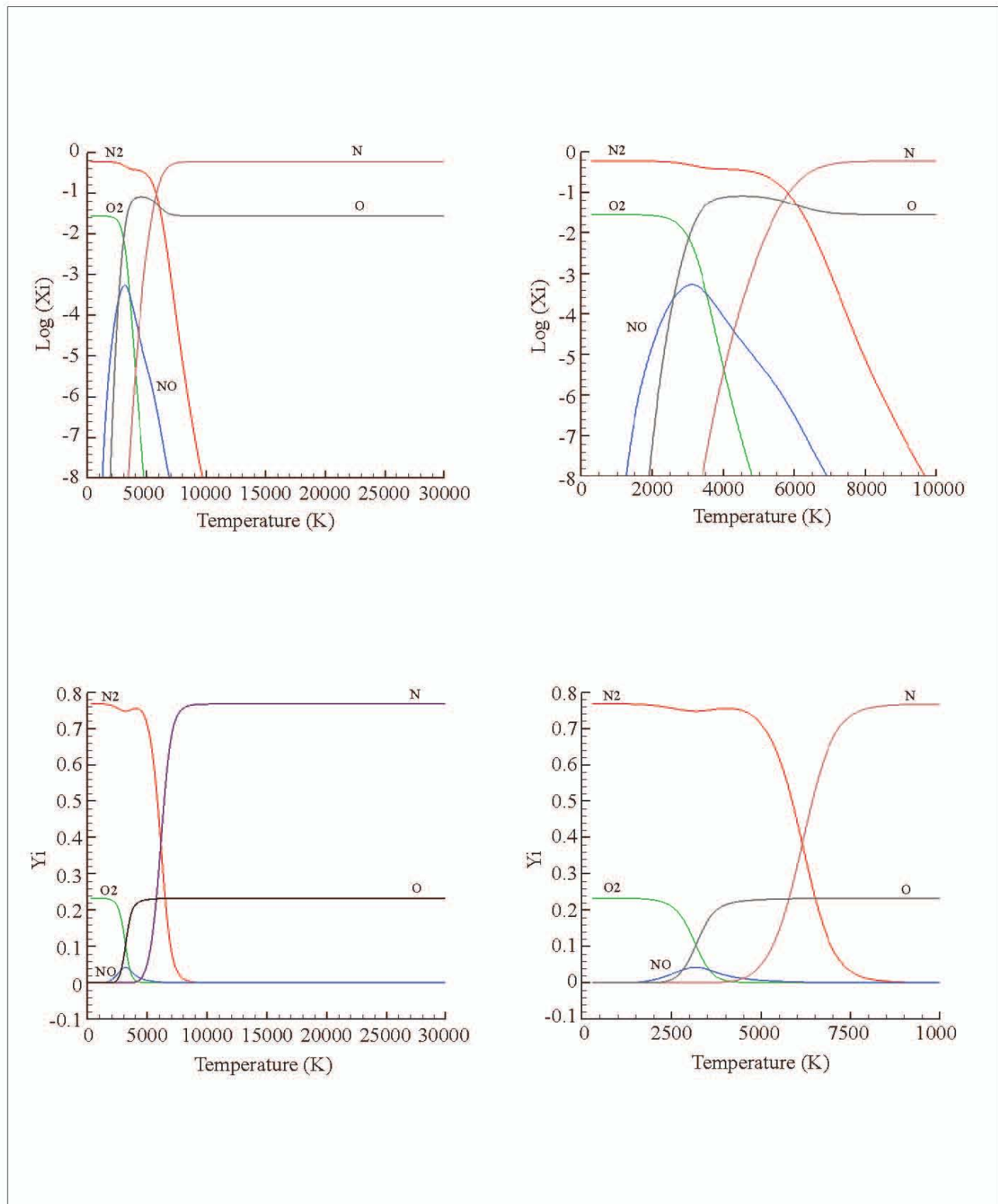


Figure 9. Logarithm of mole fraction and mass fraction to the pressure of the model of five chemical species. The panels on the right present the details for the range from 0 to 10000 K.

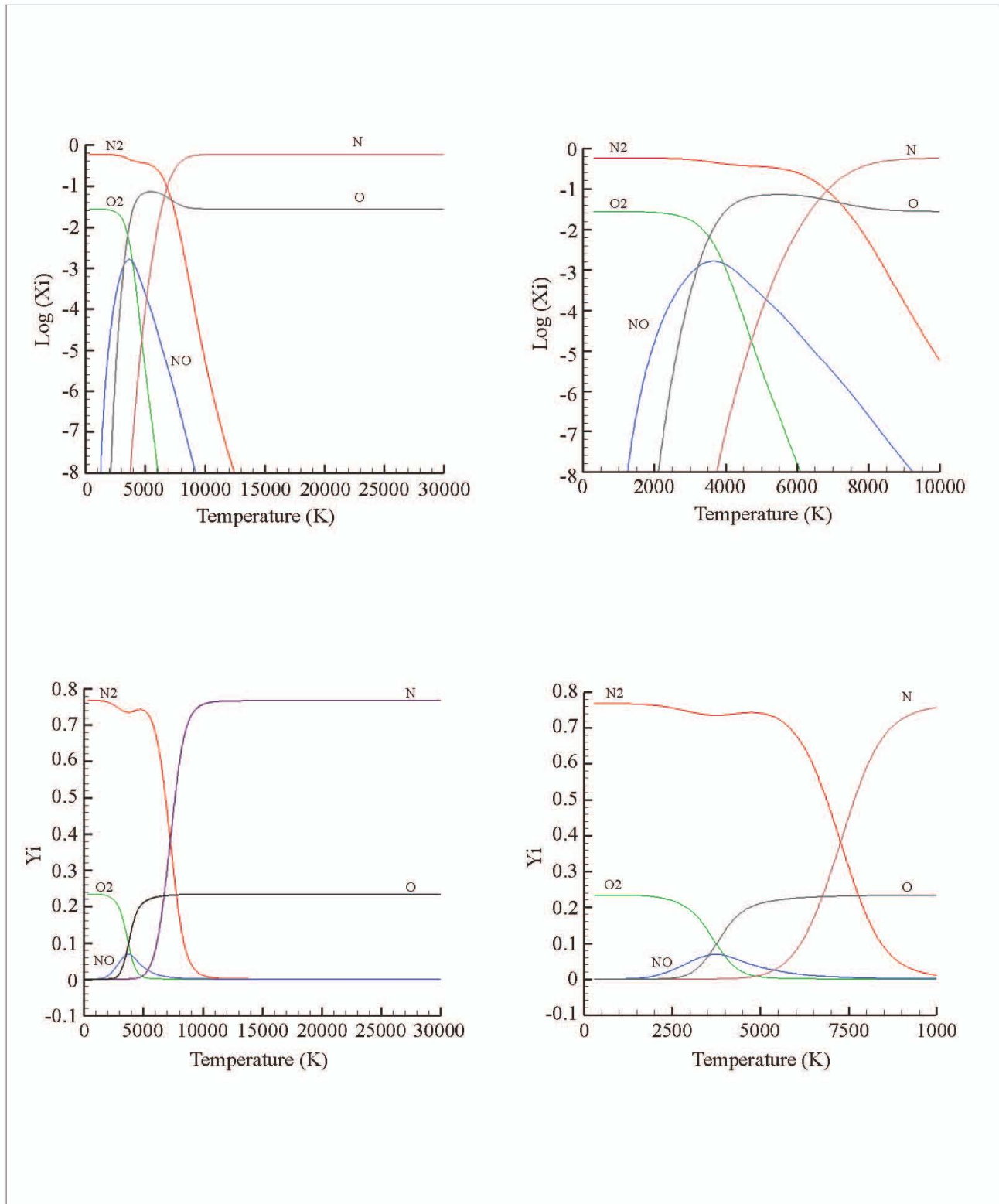


Figure 10. Logarithm of mole fraction and mass fraction to the pressure of the model of five chemical species. The panels on the right present the details for the range from 0 to 10000 K.

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