

Transport properties of high temperature air in local thermodynamic equilibrium

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Abstract. In the paper new calculated transport coefficients of air in the temperature range 50–100 000 K are presented. The results have been obtained by means of the perturbative Chapman-Enskog method, assuming that the plasma is in local thermodynamic equilibrium (LTE). The calculations include viscosity, thermal conductivity, electric conductivity and multicomponent diffusion coefficients. For the calculation, a recent compilation of collision integrals obtained by Capitelli *et al.* [1] has been utilized. Analytical expression for all transport coefficients and thermodynamic parameters of the air plasma are also reported.

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1 Introduction

The transport properties of the air at high temperature are important for many applications, as the reentry problem and the technological applications of thermal plasmas.

Accurate evaluations of transport coefficients can be obtained when the transport cross-sections of the different interactions are known. However, there are still uncertainties in the value of the intermolecular potentials. For this reason, values of calculated transport properties are continuously updated when new sets of collision integrals are available. In the paper, calculations of transport coefficients of air at atmospheric pressure are presented, based on the recent compilation of collision integrals obtained by Capitelli *et al.* [1].

Moreover, the plasma composition and the thermodynamic properties relevant for the transport equations have been obtained from the internal partition functions tabulated recently by Giordano *et al.* [2].

In the calculation, the following species were considered: N_2 , N_2^+ , N , N^+ , N^{2+} , N^{3+} , N^{4+} , O_2 , O_2^+ , O_2^- , O , O^- , O^+ , O^{2+} , O^{3+} , O^{4+} , NO , NO^+ and e^- . Comparisons with experimental values of Asinovsky *et al.* [13] and Schreiber *et al.* [14], with theoretical values obtained by Murphy [9] and with the tables of Yos [10] are presented.

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2 Method of calculation

Diffusion, viscosity, electric and thermal conductivity are related to some physical properties of the gas. Diffusion represents the transfer of mass from a region to another due to a gradient in the concentration (ordinary diffusion) or a temperature gradient (thermal diffusion); viscosity is the transport of momentum because of a gradient in the velocity; thermal conductivity is the transport of thermal energy resulting from the presence of thermal gradients, chemical reactions or internal degrees of freedom in the plasma; electric conductivity is the transport of mass of electrons and ions due to gradients in concentration, pressure and temperature.

In the present work, the assumption is made that in an electron-neutral or electron-ion two-body collision, only the momentum of the electron is appreciably altered; electron speed, momentum and speed of heavier particle do not change appreciably. Consequently, electron-heavy encounters are expected to have little effects on the distribution function of heavier species. Therefore, heavy and electron transport coefficients are considered independent.

A non-reacting mixture, composed by molecules without internal degrees of freedom is initially considered. The transport coefficients appear in the expressions of the fluxes of mass, momentum and energy, derived from the hydrodynamic equations of change, related directly to the Boltzmann equation. The diffusion velocity \bar{V}_i of the

i th species is given by [3]

$$\bar{\mathbf{v}}_i = \left(\frac{n^2}{n_i \rho} \right) \sum_j m_j D_{ij} \mathbf{d}_j - \frac{1}{n_i m_i} D_i^T \frac{\partial \ln T}{\partial \mathbf{r}} \quad (1)$$

where the term

$$\mathbf{d}_i = \frac{\partial}{\partial \mathbf{r}} \left(\frac{n_i}{n} \right) + \left(\frac{n_i}{n} - \frac{n_i m_i}{\rho} \right) \frac{\partial \ln p}{\partial \mathbf{r}} - \frac{n_i m_i}{p \rho} \left(\frac{\rho}{m_i} \mathbf{X}_i - \sum_j n_j \mathbf{X}_j \right) \quad (2)$$

contains diffusion forces, due to concentration n_i/n and pressure gradients, and the external force \mathbf{X}_i on the i th species. Here n , p and ρ are the total number density, pressure and mass density of the gas. Moreover, D_{ij} is the multicomponent diffusion coefficients and D_i^T the multicomponent thermal diffusion coefficients of the i th species. Similarly, the expression of the viscosity is derived by calculating the pressure tensor \mathbf{p} in terms of the perturbation of the distribution function [3]. The coefficient of viscosity η is defined by the following expression

$$\mathbf{p} = p\mathbf{I} - 2\eta\mathbf{S} \quad (3)$$

where \mathbf{S} is the rate of shear tensor [3] defined as

$$S_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial v_{0\beta}}{\partial x_\alpha} + \frac{\partial v_{0\alpha}}{\partial x_\beta} \right) - \frac{1}{3} \delta_{\alpha\beta} \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{v}_0, \quad (4)$$

where \mathbf{v}_0 is the mass average velocity, given by

$$\mathbf{v}_0 = \frac{1}{\rho} \sum_i n_i m_i \bar{\mathbf{v}}_i. \quad (5)$$

The energy flux vector \mathbf{q} can be written as (5)

$$\mathbf{q} = -\lambda \frac{\partial T}{\partial \mathbf{r}} + \frac{5}{2} kT \sum_i n_i \bar{\mathbf{v}}_i + \frac{kT}{n} \sum_{i,j} \frac{n_i D_i^T}{m_i \mathcal{D}_{ij}(1)} (\bar{\mathbf{v}}_i - \bar{\mathbf{v}}_j). \quad (6)$$

In this expression λ represents the thermal conductivity, T the temperature of the plasma and $\mathcal{D}_{ij}(1)$ is the first approximation to the coefficient of diffusion of a binary mixture. Finally, the electron number flux is given by

$$\mathbf{g}_e = n_e \bar{\mathbf{v}}_e = -\frac{n^2}{\rho} m_e D_{ee} \mathbf{d}_e - \frac{D_e^T}{m_e} \frac{\partial \ln T}{\partial \mathbf{r}} \quad (7)$$

where $\bar{\mathbf{v}}_e$ is the diffusion velocity of the electrons as can be seen from equation (1) considering heavy and electrons properties as independent. From equation (2), the term for the electrons can be written as

$$\mathbf{d}_e = \frac{\partial}{\partial \mathbf{r}} \left(\frac{n_e}{n} \right) + \frac{n_e}{n} \frac{\partial \ln p}{\partial \mathbf{r}} + \frac{en_e}{nkT} \mathbf{E}; \quad (8)$$

by combining equations (7, 8) and neglecting terms of order m_e/m_i (in other terms, the contribution of the ions to the electric conductivity is neglected), the electric conductivity is then given by [5]

$$\sigma = e^2 \frac{n_e m_e n}{\rho kT} D_{ee}. \quad (9)$$

By means of the Sonine polynomial expansions of the perturbation distribution functions, the expressions for the transport coefficients are [3, 5, 6, 11, 12]

$$D_{ij}(\xi) = \frac{\rho n_i}{2n m_j} \sqrt{\frac{2kT}{m_i}} c_{i0}^{(j,i)}(\xi), \quad (10)$$

$$D_i^T(\xi) = \frac{m_i n_i}{2} \sqrt{\frac{2kT}{m_i}} a_{i0}(\xi), \quad (11)$$

$$\eta(\xi) = \frac{1}{2} kT \sum_j n_j b_{j0}(\xi), \quad (12)$$

$$\sigma(\xi) = \frac{e^2 n_e^2}{2kT} \sqrt{\frac{2kT}{m_e}} c_{e0}^{(e,e)}(\xi), \quad (13)$$

$$\lambda = \lambda'(\xi) - \frac{k}{2n} \sum_{i,j} \frac{n_i n_j}{\mathcal{D}_{ij}(1)} \left(\frac{D_i^T}{n_i m_i} - \frac{D_j^T}{n_j m_j} \right)^2 \quad (14)$$

where

$$\lambda'(\xi) = -\frac{5}{4} k \sum_j n_j \sqrt{\frac{2kT}{m_j}} a_{j1}(\xi) \quad (15)$$

and

$$\mathcal{D}_{ij}(1) = \frac{3(m_i + m_j)}{16n m_i m_j} \frac{kT}{\Omega_{ij}^{(1,1)}} \quad (16)$$

is the first approximation to the coefficient of diffusion of a binary mixture; $\Omega_{ij}^{(1,1)}$ is the collision integral between molecules of type i and type j [3].

The values of the coefficients $c_{i0}^{(j,i)}(\xi)$, $b_{i0}(\xi)$ and $a_{i0}(\xi)$ are determinate by solving the following linear systems [3]:

$$\sum_j \sum_{m'=0}^{\xi-1} \tilde{Q}_{ij}^{mm'} t_{jm'}^{(h,k)}(\xi) = -R_{im}^{(h,k)}(\xi) \quad (17)$$

in which the matrix $\tilde{Q}_{ij}^{mm'}$ is defined as

$$\left\{ \begin{array}{l} \tilde{Q}_{ij}^{mm'} \quad \text{when } t_{jm'}^{(h,k)} = b_{jm'} \\ \tilde{Q}_{ij}^{mm'} - \frac{n_j \sqrt{m_j}}{n_i \sqrt{m_j}} \tilde{Q}_{ii}^{mm'} \delta_{m0} \delta_{m'0} \\ \quad \text{when } t_{jm'}^{(h,k)} = a_{jm'}, c_{jm'}. \end{array} \right. \quad (18)$$

The dimension of $\tilde{Q}_{ij}^{mm'}$ depends upon the number ξ of terms considered in the expansion and the number

of species considered in the plasma. The expansion coefficients $t_{jm'}^{(h,k)}$ and $R_{im}^{(h,k)}$ are linear combinations of the set of integrals $\Omega^{(l,s)}$ defined by [3]

$$\Omega_{ij}^{(l,s)} = \sqrt{\frac{2\pi kT}{\mu_{ij}}} \int_0^{+\infty} \int_0^{+\infty} e^{-\gamma_{ij}^2} \gamma_{ij}^{2s+3} \times (1 - \cos^l \chi) b db d\gamma_{ij} \quad (19)$$

where μ_{ij} is the reduced mass, χ the deflection angle of the collision in the center of gravity coordinate system, b the impact parameter and γ_{ij} the reduced initial relative speed of the colliding molecules defined by $\gamma_{ij} = \sqrt{\mu_{ij}/2kT} u_{ij}$ in which u_{ij} is the initial relative velocity of two molecules in a binary encounter.

3 Diffusion coefficients

In the present work, $\xi = 1$ for the ordinary diffusion coefficient and $\xi = 2$ for the thermal diffusion coefficient have been assumed. In order to calculate the ordinary diffusion coefficient from equation (10), $c_{j0}^{(j,i)}$ (1) has been evaluated by solving ν linear systems

$$\sum_{j=1}^{\nu} \tilde{Q}_{ij}^{00} c_{j0}^{(h,j)} (1) = -R_{i0}^{(h,i)} \quad h, i = 1, \dots, \nu \quad (20)$$

in which the generic element of the matrix \tilde{Q}^{00} and $R^{(h,i)}$ are

$$\tilde{Q}_{ij}^{00} = \sum_{l=1}^{\nu} \frac{n_l m_l \Omega_{il}^{(1,1)}}{(m_i + m_l) \sqrt{m_j}} \times [n_i m_i (\delta_{ij} - \delta_{jl}) - n_j m_j (1 - \delta_{il})]$$

$$R_{i0}^{(h,i)} = -\frac{3}{16} \sqrt{2kT} (\delta_{ih} - \delta_{ij}). \quad (21)$$

To obtain the coefficient of thermal diffusion with $\xi = 2$, a_{j0} (2) is evaluated by solving the linear system

$$\sum_j \sum_{m'=0}^1 \tilde{Q}_{ij}^{mm'} a_{jm'} (2) = -\delta_{m1} \frac{15}{4} n_i \sqrt{\frac{2kT}{m_i}} \quad (22)$$

in which the coefficients \tilde{Q}_{ij}^{mm} are given by

$$\tilde{Q}_{ij}^{00} = \sum_{k=1}^{\nu} \frac{8n_k m_k \Omega_{ik}^{(1,1)}}{(m_i + m_k) \sqrt{m_j m_i}} \times [n_i m_i (\delta_{ij} - \delta_{jk}) - n_j m_j (1 - \delta_{ik})]$$

$$\tilde{Q}_{ij}^{01} = -\left(\frac{m_i}{m_j}\right)^{\frac{3}{2}} \sum_{k=1}^{\nu} \frac{8n_k n_k m_k^2}{(m_i + m_k)^2} \times (\delta_{ij} - \delta_{jk}) \left[\Omega_{ik}^{(1,2)} - \frac{5}{2} \Omega_{ik}^{(1,1)} \right]$$

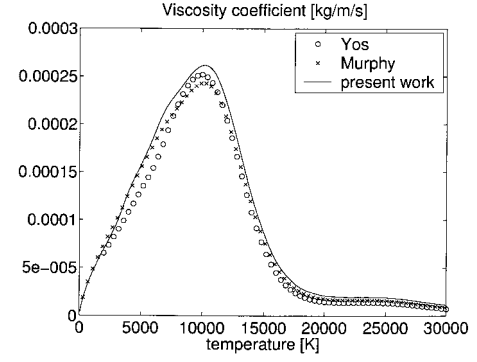


Fig. 1. Viscosity coefficient of air; results obtained in the present work (full line) are compared with those obtained by Murphy (\times) [9] and Yos (\circ) [10].

$$\tilde{Q}_{ij}^{10} = \frac{m_j}{m_i} \tilde{Q}_{ij}^{01} \quad (23)$$

$$\tilde{Q}_{ij}^{11} = \left(\frac{m_i}{m_j}\right)^{\frac{3}{2}} \sum_{k=1}^{\nu} \frac{8n_k n_k m_k}{(m_i + m_k)^3} \times \left[(\delta_{ij} - \delta_{jk}) \left[\frac{5\Omega_{ik}^{(1,1)}}{4} (6m_j^2 + 5m_k^2) - 5m_k^2 \Omega_{ik}^{(1,2)} + m_k^2 \Omega_{ik}^{(1,3)} \right] + 2m_j m_k \Omega_{ik}^{(2,2)} (\delta_{ij} + \delta_{ik}) \right].$$

4 Viscosity

The contribution of the electrons to the viscosity coefficient η is negligible [5]. Consequently, η can be approximated in the following manner

$$\eta \cong \eta_h + \eta_e \cong \eta_h \quad (24)$$

h referring to heavy particles and e to the electrons.

According to the equations (12, 24), to obtain η_h it is necessary to evaluate the coefficients b_{j0} (1) solving the following linear system

$$\sum_{j=1}^{\nu-1} \left(\frac{Q_{ij}^{00}}{R_{i0}} \right) b_{j0} (1) = -1 \quad i = 1, \dots, \nu - 1 \quad (25)$$

with

$$\frac{Q_{ij}^{00}}{R_{i0}} = -\frac{16}{15} \frac{m_i}{m_j} \sum_{k=1}^{\nu-1} \frac{n_k m_k}{(m_i + m_k)^2} \times \left[5m_j (\delta_{ij} - \delta_{jk}) \Omega_{ik}^{(1,1)} + \frac{3}{2} m_k (\delta_{ij} + \delta_{jk}) \Omega_{ik}^{(2,2)} \right]. \quad (26)$$

Figure 1 shows the behavior of the viscosity calculated with equation (12). It increases up to the first ionization reaction; for $T > 10,000$ K it decreases cause the onset of electrons and the increase of the collision integrals for ion-ion interaction.

In the same figure, the theoretical values of Yos [10] and Murphy [9] have also been reported. The agreement is in general satisfactory: the small differences are due to the different sets of collision integrals for heavy particles (including ions) used in the relevant calculations.

5 Total thermal conductivity

The total thermal conductivity of a plasma is calculated as the sum of three contributions:

$$\lambda_{\text{TOT}} = \lambda_{\text{tr}} + \lambda_{\text{int}} + \lambda_{\text{r}} \quad (27)$$

in which λ_{tr} is the translational thermal conductivity calculated with the aid of equations (14, 16), λ_{int} the internal thermal conductivity and λ_{r} the reactive contribution to the total thermal conductivity. Infact, the equations (14, 16) are correct for a non-reacting plasma of simple molecules. It has been assumed that the molecules are spherical and have no internal degrees of freedom. Removing this hypothesis, internal and reactive contributions must be added.

6 Translational thermal conductivity

As for the coefficient of viscosity, the translational thermal conductivity λ_{tr} can be considered as the sum of two contributions, due to the heavy particles and to the electrons

$$\lambda_{\text{tr}} = \lambda_{\text{h}} + \lambda_{\text{e}}. \quad (28)$$

The contribution of the heavy components to the total thermal conductivity is calculated by means of equations (14, 16), using $\xi = 2$ for the heavy contribution and $\xi = 3$ for the electrons one; the separation between the solution of the electron and heavy distribution functions allows two different levels of approximations:

$$\lambda_{\text{tr}} = \lambda_{\text{h}}(2) + \lambda_{\text{e}}(3). \quad (29)$$

To obtain the second order approximation of the heavy translational thermal conductivity, the solutions a_{j1} (2) of the linear system (22) and the coefficients of thermal diffusion obtained solving the same system can be used, as it can be seen in equations (14, 16). The third approximation of the electron contribution to the translational thermal conductivity is calculated using the following expression [5, 12]

$$\lambda_{\text{e}}(3) = \frac{75n_{\text{e}}^2 k}{8} \left(\frac{2\pi kT}{m_{\text{e}}} \right)^{\frac{1}{2}} \frac{1}{q^{11} - (q^{12})^2 / q^{22}} \quad (30)$$

in which

$$q^{11} = 8\sqrt{2}n_{\text{e}}^2 \overline{Q}_{ee}^{(2,2)} + 8 \sum_{j=1}^{\nu-1} n_j n_e \left[\frac{25}{4} \overline{Q}_{ej}^{(1,1)} - 15 \overline{Q}_{ej}^{(1,2)} + 12 \overline{Q}_{ej}^{(1,3)} \right],$$

$$q^{12} = 8\sqrt{2}n_{\text{e}}^2 \left[\frac{7}{4} \overline{Q}_{ee}^{(2,2)} - 2 \overline{Q}_{ee}^{(2,3)} \right] + 8 \sum_{j=1}^{\nu-1} n_j n_e \left[\frac{175}{16} \overline{Q}_{ej}^{(1,1)} - \frac{315}{8} \overline{Q}_{ej}^{(1,2)} + 57 \overline{Q}_{ej}^{(1,3)} - 30 \overline{Q}_{ej}^{(1,4)} \right]$$

$$q^{22} = 8\sqrt{2}n_{\text{e}}^2 \left[\frac{77}{16} \overline{Q}_{ee}^{(2,2)} - 7 \overline{Q}_{ee}^{(2,3)} + 5 \overline{Q}_{ee}^{(2,4)} \right] + 8 \sum_{j=1}^{\nu-1} n_j n_e \left[\frac{1225}{64} \overline{Q}_{ej}^{(1,1)} - \frac{735}{8} \overline{Q}_{ej}^{(1,2)} + \frac{399}{2} \overline{Q}_{ej}^{(1,3)} - 210 \overline{Q}_{ej}^{(1,4)} + 90 \overline{Q}_{ej}^{(1,5)} \right] \quad (31)$$

with

$$\overline{Q}_{ij}^{(l,s)} = \pi \overline{\Omega}_{ij}^{(l,s)} \quad (32)$$

and

$$\overline{\Omega}_{ij}^{(l,s)} = \sigma^2 \frac{\Omega_{ij}^{(l,s)}}{\left[\Omega_{ij}^{(l,s)} \right]_{\text{sr}}}; \quad (33)$$

in equation (32) $\left[\Omega_{ij}^{(l,s)} \right]_{\text{sr}}$ is the collision integral associated with the interaction between species i and j for rigid spherical molecules of diameter σ .

7 Reactive thermal conductivity

Chemical reactions in plasma in chemical equilibrium increase the thermal conductivity. Infact, when the components of a plasma react with one another, additional heat, different from the heat conducted by molecular collisions or by thermal diffusion, is transported as chemical enthalpy of molecules which diffuse cause the existence of concentration gradients. In the present work, the method of Butler and Brokaw [7] has been used to calculate the contribution to the total thermal conductivity. A gas mixture of ν elements which may react with each other chemically is considered. The reactions are written with the independent μ components on the left side and all the other components on the right side:

$$X^i = \sum_{j=\mu+1}^{\nu} n_{ij} X^j \quad i = 1, \dots, \mu. \quad (34)$$

The reactive thermal conductivity has been calculated with the following formula [7]:

$$\lambda_{\text{r}} = \frac{1}{RT^2} \sum_{j=1}^{\nu} A_j \Delta H_j \quad (35)$$

where A_j are the solutions of the following linear system

$$\hat{\mathbf{A}} \cdot \mathbf{A} = \Delta \mathbf{H} \quad (36)$$

in which the matrix \hat{A} is so defined

$$A_{ik} = A_{ki} = \sum_{j=\nu+1}^{\mu} (n_{kj}\Delta_{ij} + n_{ij}\Delta_{kj}) - \Delta_{ik} \\ + \sum_{j=\nu+1}^{\mu-1} \sum_{m=j+1}^{\mu} \frac{\Delta_{mj}(n_{ij}x_m - n_{im}x_j)(n_{kj}x_m - n_{km}x_j)}{x_jx_m} \\ + \sum_{j=\nu+1}^{\mu} \sum_{p=1}^{\nu} n_{ij}n_{kj}\Delta_{pj} \frac{x_p}{x_j}, \quad i \neq k \quad (37)$$

$$A_{kk} = \sum_{j=\nu+1}^{\mu} \Delta_{kj} \frac{(x_j + n_{kj}x_k)^2}{x_jx_k} + \sum_{p=1, p \neq k}^{\nu} \Delta_{pk} \frac{x_p}{x_j} \\ + \sum_{j=\nu+1}^{\mu} \sum_{p=1, p \neq k}^{\nu} n_{kj}^2 \Delta_{pj} \frac{x_p}{x_j} \\ + \sum_{j=\nu+1}^{\mu-1} \sum_{m=j+1}^{\mu} \frac{\Delta_{mj}(n_{kj}x_m - n_{km}x_j)^2}{x_jx_m}$$

where

$$\Delta_{kj} = \Delta_{jk} = \frac{RT}{pD_{ik}(1)}, \quad (38)$$

x_i is the molar fraction of the i th species and $\Delta H_i = \sum_{j=\nu+1}^{\mu} n_{ij}H_j - H_i$ is the heat of the i th reaction. In the calculation the species with x_i very small (*i.e.* $x_i < 10^{-20}$) are excluded.

8 Internal thermal conductivity

The presence of internal degrees of freedom affects the heat flux vector. The exact expression for the coefficient of thermal conductivity depends upon the transition probabilities for the transfer of energy among the degrees of freedom of the molecules. In this work, the assumption of Eucken [3] has been used, applicable when the rate of transfer is sufficiently fast that the distribution of molecules among the various states of freedom is essentially the equilibrium distribution. The simplified expression of Eucken which consider only the vibrational contribution is

$$\lambda_{\text{int}} = \frac{1}{T} \sum_{j=1}^{\nu} \frac{x_j \frac{c_{\text{pint},j}}{R}}{\sum_{i=1}^{\nu} \frac{x_i}{pD_{ij}(1)}} \quad (39)$$

in which $c_{\text{pint},j}$ is the internal molar specific heat at constant pressure of the j th species.

Figure 2 reports the three contributions of the thermal conductivity (translational, internal and reactive) in the temperature range 50–30000 K. The non-monotone behavior is due to the peaks of the reactive thermal conductivity as a consequence of the chemical reactions occurring in the gas.

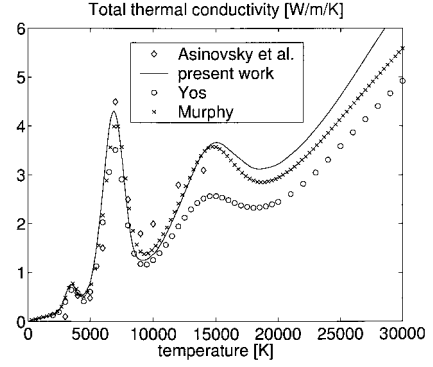


Fig. 2. Total thermal conductivity of air; results obtained in the present work (full line) are compared with those obtained by Murphy (\times) [9], Yos (\circ) [10] and Asinovsky *et al.* (\diamond) [13].

In Figure 2, the experimental values of Asinovsky *et al.* [13] and the calculations of Yos [10] and Murphy [9] have also been reported. The differences with the results of Yos are due to both the selection of collision integrals for the different species and to the different kinetic equations used for calculating the different contributions of the total thermal conductivity. In particular, the thermal conductivity of electrons has been calculated by Yos with a phenomenological approach. The differences with Murphy's results are due to the different set of collision integrals especially for electron-electron and ion-atom collision.

9 Electric conductivity

The electric conductivity is calculated by means of equation (9). The third approximation for the ordinary diffusion coefficient D_{ee} [5] has been used, therefore the electric conductivity is given by

$$\sigma = \frac{3e^2 n_e^2 (2\pi/km_e T)^{\frac{1}{2}}}{2 |q|} \begin{vmatrix} q^{11} & q^{12} \\ q^{21} & q^{22} \end{vmatrix} \quad (40)$$

where

$$|q| = \begin{vmatrix} q^{00} & q^{01} & q^{02} \\ q^{10} & q^{11} & q^{12} \\ q^{20} & q^{21} & q^{22} \end{vmatrix} \quad (41)$$

and

$$q^{00} = 8n_e \sum_{j=1}^{\nu-1} n_j \bar{Q}_{ej}^{(1,1)}, \\ q^{01} = 8n_e \sum_{j=1}^{\nu-1} n_j \left[\frac{5}{2} \bar{Q}_{ej}^{(1,1)} - 3 \bar{Q}_{ej}^{(1,2)} \right], \\ q^{02} = 8n_e \sum_{j=1}^{\nu-1} n_j \left[\frac{35}{8} \bar{Q}_{ej}^{(1,1)} - \frac{21}{2} \bar{Q}_{ej}^{(1,2)} + 6 \bar{Q}_{ej}^{(1,3)} \right]. \quad (42)$$

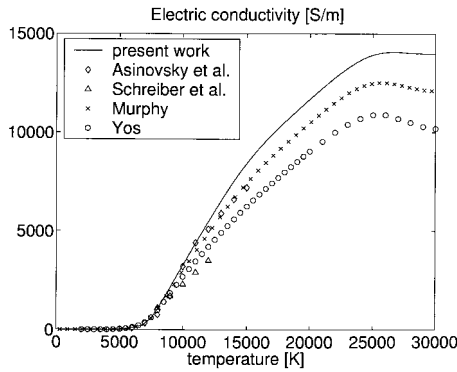


Fig. 3. Electric conductivity of air; results obtained in the present work (full line) are compared with those obtained by Murphy (\times) [9], Yos (\circ) [10], Asinovsky *et al.* (\diamond) [13] and Schreiber *et al.* (Δ) [14].

The values of q^{11} , q^{12} and q^{22} are expressed in equation (31). In Figure 3 is represented the electric conductivity in the temperature range 50–30 000 K. In the same figure, the experimental values of Asinovsky *et al.* [13], Schreiber *et al.* [14] and the calculations of Yos [10] and Murphy [9] have also been reported. The differences have the same origin as those discussed for the total thermal conductivity.

10 Conclusion

In this paper values of the transport properties of air in the temperature range from 50 K to 100 000 K have been presented. For the calculation, use is made of the recent compilation of collision integrals obtained by Capitelli *et al.* [1]. Comparison of the present data with literature values shows a satisfactory agreement specially with the recent calculations of Murphy [9]. Corresponding comparisons with the well known tables of Yos [10] shows some discrepancies even though we note that after 30 years the Yos results [10] differ from the present calculations by not more than 30–35% for the total thermal conductivity and the viscosity. These have been accounted for mainly in terms of differences in the collision integrals used for certain interactions; accordingly, the transport coefficients presented here are expected to be more accurate than previously calculated values, including also the recent calculations of Bottin *et al.* [15] and Fruhauf *et al.* [16].

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Appendix A: Tables of transport and thermodynamic properties

To complete our work, we have reported in Table 1 the numerical values of transport coefficients in the temperature range 50–30 000 K. Note that λ_{int} , not reported

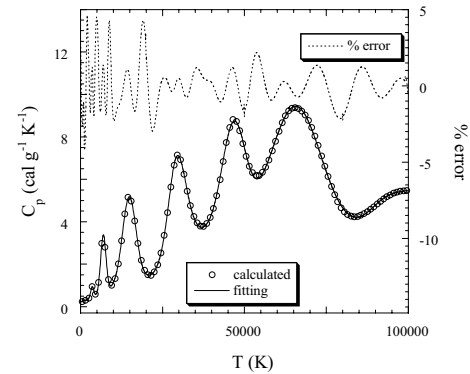


Fig. 4. Calculated and fitted specific heat and relative percent error.

in the table, can be determined by the equation

$$\lambda_{\text{int}} = \lambda_{\text{tot}} - \lambda_{\text{h}} - \lambda_{\text{e}} - \lambda_{\text{r}}.$$

In Table 2, finally, we have reported a sample of the thermodynamic properties of the air mixture in the same conditions, in particular the enthalpy (H), entropy (S), specific heat (c_p) and density (ρ) of the atmospheric (20% O_2 , 80% N_2) mixture.

Appendix B: Fitting of transport and thermodynamic properties

It is very useful to have accurate analytical expressions for transport and thermodynamic properties. In this appendix we report analytical expressions for such quantities in the range 50–100 000 K with an error less than 5% (see Fig. 4 where the calculated data, the fitting curve and the percent error as a function of the temperature have been reported for the specific heat). Higher percent errors (around 10%) can be found in regions where the values are very close to zero.

Fitting the transport coefficients and the thermodynamic functions of the air mixture in a wide temperature range is a complex problem due to the non-monotone behavior of the relevant quantities as a function of temperature. To take into account the appearance and disappearance of the numerous species as well as the dependence of the global quantities on the actual composition, we have chosen two types of function, the Gaussian

$$\gamma(x; c, \Delta) = e^{-[(x-c)/\Delta]^2} \quad (\text{B.1})$$

and the sigmoid

$$\sigma(x; c, \Delta) = \frac{e^{(x-c)/\Delta}}{e^{(x-c)/\Delta} + e^{-(x-c)/\Delta}} \quad (\text{B.2})$$

used as base for the interpolation, with slight changes; we use the symbol “ ζ ” to refer to any term different from the functions in equations (B.1, B.2).

Table 1. Values of transport properties of air at atmospheric pressure in the temperature range 50–30 000 K.

T [K]	D_e^T [kg m ⁻¹ s ⁻¹]	η [kg m ⁻¹ s ⁻¹]	λ_h [W m ⁻¹ K ⁻¹]	λ_e [W m ⁻¹ K ⁻¹]	λ_r [W m ⁻¹ K ⁻¹]	λ_{TOT} [W m ⁻¹ K ⁻¹]	σ [S m ⁻¹]
50	0.0000	0.3479×10^{-05}	0.3765×10^{-02}	0.0000	0.0000	0.5085×10^{-02}	0.0000
100	0.0000	0.7048×10^{-05}	0.7625×10^{-02}	0.0000	0.0000	0.1031×10^{-01}	0.0000
200	0.0000	0.1302×10^{-04}	0.1409×10^{-01}	0.0000	0.0000	0.1906×10^{-01}	0.0000
300	0.0000	0.1801×10^{-04}	0.1948×10^{-01}	0.0000	0.0000	0.2642×10^{-01}	0.0000
400	0.0000	0.2240×10^{-04}	0.2422×10^{-01}	0.0000	0.0000	0.3312×10^{-01}	0.0000
500	0.0000	0.2639×10^{-04}	0.2853×10^{-01}	0.0000	0.0000	0.3961×10^{-01}	0.0000
600	0.0000	0.3008×10^{-04}	0.3252×10^{-01}	0.0000	0.0000	0.4607×10^{-01}	0.0000
700	0.0000	0.3355×10^{-04}	0.3628×10^{-01}	0.0000	0.0000	0.5252×10^{-01}	0.0000
800	0.0000	0.3685×10^{-04}	0.3984×10^{-01}	0.0000	0.6247×10^{-05}	0.5893×10^{-01}	0.0000
900	0.0000	0.4001×10^{-04}	0.4325×10^{-01}	0.2388×10^{-27}	0.2440×10^{-04}	0.6527×10^{-01}	0.2443×10^{-22}
1000	0.0000	0.4304×10^{-04}	0.4653×10^{-01}	0.3168×10^{-24}	0.7156×10^{-04}	0.7152×10^{-01}	0.2882×10^{-19}
1500	-0.2006×10^{-18}	0.5694×10^{-04}	0.6158×10^{-01}	0.9686×10^{-11}	0.4278×10^{-02}	0.1035	0.5593×10^{-06}
2000	-0.4100×10^{-18}	0.6949×10^{-04}	0.7517×10^{-01}	0.2102×10^{-10}	0.1129×10^{-01}	0.1382	0.8832×10^{-06}
2500	-0.6292×10^{-14}	0.8153×10^{-04}	0.8864×10^{-01}	0.3347×10^{-06}	0.7450×10^{-01}	0.2264	0.1120×10^{-01}
3000	-0.1321×10^{-13}	0.9501×10^{-04}	0.1071	0.6977×10^{-06}	0.3428	0.5232	0.1986×10^{-01}
3500	-0.3840×10^{-12}	0.1117×10^{-03}	0.1362	0.1927×10^{-04}	0.5456	0.7599	0.4896
4000	-0.1995×10^{-11}	0.1291×10^{-03}	0.1691	0.9145×10^{-04}	0.3009	0.5507	$0.2162 \times 10^{+01}$
4500	-0.7752×10^{-11}	0.1436×10^{-03}	0.1940	0.3187×10^{-03}	0.2757	0.5548	$0.7197 \times 10^{+01}$
5000	-0.2789×10^{-10}	0.1566×10^{-03}	0.2164	0.1058×10^{-02}	0.4715	0.7810	$0.2273 \times 10^{+02}$
6000	-0.1337×10^{-09}	0.1855×10^{-03}	0.2821	0.5985×10^{-02}	$0.2278 \times 10^{+01}$	$0.2665 \times 10^{+01}$	$0.9857 \times 10^{+02}$
7000	-0.2168×10^{-09}	0.2153×10^{-03}	0.3926	0.2794×10^{-01}	$0.3771 \times 10^{+01}$	$0.4267 \times 10^{+01}$	$0.3277 \times 10^{+03}$
8000	0.1082×10^{-08}	0.2338×10^{-03}	0.4834	0.9915×10^{-01}	$0.1553 \times 10^{+01}$	$0.2179 \times 10^{+01}$	$0.1060 \times 10^{+04}$
9000	0.4561×10^{-08}	0.2509×10^{-03}	0.5355	0.2237	0.4673	$0.1262 \times 10^{+01}$	$0.2146 \times 10^{+04}$
10000	0.9133×10^{-08}	0.2614×10^{-03}	0.5573	0.3873	0.3953	$0.1377 \times 10^{+01}$	$0.3264 \times 10^{+04}$
11000	0.1433×10^{-07}	0.2540×10^{-03}	0.5287	0.5796	0.6235	$0.1775 \times 10^{+01}$	$0.4372 \times 10^{+04}$
12000	0.2012×10^{-07}	0.2219×10^{-03}	0.4385	0.7992	$0.1043 \times 10^{+01}$	$0.2335 \times 10^{+01}$	$0.5478 \times 10^{+04}$
13000	0.2634×10^{-07}	0.1748×10^{-03}	0.3238	$0.1037 \times 10^{+01}$	$0.1513 \times 10^{+01}$	$0.2948 \times 10^{+01}$	$0.6535 \times 10^{+04}$
14000	0.3297×10^{-07}	0.1253×10^{-03}	0.2190	$0.1291 \times 10^{+01}$	$0.1854 \times 10^{+01}$	$0.3462 \times 10^{+01}$	$0.7536 \times 10^{+04}$
15000	0.3976×10^{-07}	0.8617×10^{-04}	0.1454	$0.1547 \times 10^{+01}$	$0.1855 \times 10^{+01}$	$0.3665 \times 10^{+01}$	$0.8418 \times 10^{+04}$
16000	0.4677×10^{-07}	0.5724×10^{-04}	0.9560×10^{-01}	$0.1805 \times 10^{+01}$	$0.1509 \times 10^{+01}$	$0.3531 \times 10^{+01}$	$0.9205 \times 10^{+04}$
17000	0.5388×10^{-07}	0.4003×10^{-04}	0.6795×10^{-01}	$0.2058 \times 10^{+01}$	$0.1076 \times 10^{+01}$	$0.3317 \times 10^{+01}$	$0.9886 \times 10^{+04}$
18000	0.6126×10^{-07}	0.2929×10^{-04}	0.5139×10^{-01}	$0.2318 \times 10^{+01}$	0.6799	$0.3143 \times 10^{+01}$	$0.1052 \times 10^{+05}$
19000	0.6888×10^{-07}	0.2418×10^{-04}	0.4409×10^{-01}	$0.2582 \times 10^{+01}$	0.4387	$0.3142 \times 10^{+01}$	$0.1111 \times 10^{+05}$
20000	0.7689×10^{-07}	0.2110×10^{-04}	0.3990×10^{-01}	$0.2859 \times 10^{+01}$	0.2677	$0.3225 \times 10^{+01}$	$0.1168 \times 10^{+05}$
22000	0.9381×10^{-07}	0.1955×10^{-04}	0.3874×10^{-01}	$0.3446 \times 10^{+01}$	0.1245	$0.3650 \times 10^{+01}$	$0.1277 \times 10^{+05}$
24000	0.1112×10^{-06}	0.1945×10^{-04}	0.3924×10^{-01}	$0.4069 \times 10^{+01}$	0.1124	$0.4264 \times 10^{+01}$	$0.1365 \times 10^{+05}$
26000	0.1273×10^{-06}	0.1804×10^{-04}	0.3628×10^{-01}	$0.4694 \times 10^{+01}$	0.2050	$0.5000 \times 10^{+01}$	$0.1405 \times 10^{+05}$
28000	0.1414×10^{-06}	0.1475×10^{-04}	0.2926×10^{-01}	$0.5300 \times 10^{+01}$	0.3618	$0.5779 \times 10^{+01}$	$0.1402 \times 10^{+05}$
30000	0.1560×10^{-06}	0.1125×10^{-04}	0.2217×10^{-01}	$0.5926 \times 10^{+01}$	0.4521	$0.6494 \times 10^{+01}$	$0.1399 \times 10^{+05}$

Table 2. Values of thermodynamic properties of air at atmospheric pressure in the temperature range 50–30 000 K

T [K]	H [cal g ⁻¹]	S [cal g ⁻¹ K ⁻¹]	c_p [cal g ⁻¹ K ⁻¹]	ρ [g m ⁻³]
50	121.77	1.2467	0.24193	7018.1
100	133.87	1.3984	0.24191	3509.0
200	158.06	1.5579	0.24205	1754.5
300	182.28	1.6533	0.24282	1169.6
400	206.62	1.7219	0.24494	877.22
500	231.27	1.7760	0.24874	701.75
600	256.37	1.8212	0.25383	584.77
700	282.03	1.8603	0.25955	501.21
800	308.28	1.8950	0.26541	438.53
900	335.11	1.9263	0.27108	389.77
1000	362.50	1.9550	0.27456	350.76
1500	502.90	2.0702	0.29547	233.83
2000	663.38	2.1705	0.34790	175.79
2500	848.62	2.2740	0.40793	140.58
3000	1099.3	2.4205	0.63995	113.70
3500	1508.1	2.6709	0.94275	91.276
4000	1954.3	2.9104	0.76614	76.625
4500	2281.9	3.0255	0.59639	66.395
5000	2597.4	3.1122	0.71557	58.223
6000	3804.7	3.5402	1.9643	44.181
7000	6692.6	4.5879	3.4157	30.852
8000	9448.3	5.3614	1.8803	23.213
9000	10785	5.5171	1.0318	19.659
10000	11812	5.5557	1.1142	17.230
11000	13148	5.6688	1.6212	15.113
12000	15185	5.9293	2.5217	13.083
13000	18304	6.3853	3.7500	11.101
14000	22651	7.0260	4.8648	9.2751
15000	27767	7.7330	5.1913	7.7689
16000	32708	8.3343	4.5586	6.6522
17000	36741	8.7321	3.4915	5.8680
18000	39735	8.9404	2.5437	5.3119
19000	41937	9.0234	1.9157	4.8967
20000	43663	9.0409	1.5704	4.5673
22000	46658	9.0283	1.5337	4.0505
24000	50274	9.0949	2.2194	3.6281
26000	56186	9.3840	3.8729	3.2280
28000	66273	10.021	6.2045	2.8072
30000	80033	10.905	7.1159	2.4137

The fitting expressions need a large number of parameters (from 10 to 30) to have a good agreement with data points in the range 50–100 000 K (see Eqs. (B.3–B.11) for the expression and Tabs. 3–10 for the function parameters). The fit accuracy is shown in Figure 4 for the specific heat.

The way the interpolation has been performed allows the use of shorter expressions (which means less parameters), limiting the interpolating function to the Gaussians and sigmoids effective in the range of interest, adding an adequate constant for each sigmoid and nothing for each Gaussian out of range. As an example, the parameters necessary to fit the curves at low temperature are listed in Table 11. For different temperature ranges it is possible to choose different parameter subsets.

In the following we present analytical expression for the gas composition (molar fraction), entropy, gas density and mean molar mass, enthalpy, specific heat, thermal and electric conductivity and viscosity.

Molar fractions

$$\chi_i(T) = \sum_{j=1}^4 a_{ij} \sigma(T; c_{ij}, \Delta_{ij}) = \sum_{j=1}^4 a_{ij} \sigma_{ij}(T). \quad (\text{B.3})$$

Specific entropy (cal/K/g)

$$\begin{aligned} S(T) &= \sum_{j=1}^6 a_j \sigma(T; c_j, \Delta_j) + a_7 \gamma(T; c_7, \Delta_7) \\ &\quad + a_8 \exp \left[- \left(\frac{T}{c_8} \right)^{\Delta_8} \right] + d_8 \\ &= \sum_{j=1}^6 a_j \sigma_j(T) + a_7 \gamma_7(T) + a_8 \zeta_8(T; c_8, \Delta_8, d_8). \end{aligned} \quad (\text{B.4})$$

Mean molar mass (g/mol) and gas density (g/m³)

$$\begin{aligned} \bar{M}(T) &= \sum_{j=1}^6 a_j \sigma(T; c_j, \Delta_j) + d \\ &= \sum_{j=1}^6 a_j \sigma_j(T) + \zeta_7(d) \end{aligned} \quad (\text{B.5})$$

$$\rho(T) = \frac{p}{RT} \bar{M}(T). \quad (\text{B.6})$$

Specific enthalpy (cal/g)

$$\begin{aligned} H(T) &= \sum_{j=1}^8 a_j \sigma(T; c_j, \Delta_j) + d \\ &= \sum_{j=1}^8 a_j \sigma_j(T) + \zeta_9(d). \end{aligned} \quad (\text{B.7})$$

Table 5. Coefficients to calculate mean molar mass according to expression (B.5) and gas density according to expression (B.6).

	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6	γ_7
a	1.0355	1.2139	2.3122	7.2030	10.085	4.0978	/
c	61980	43921	28653	13676	6521.3	3384.7	/
Δ	-11923	-7495.6	-5004.1	-3025.8	-1201.1	-561.79	/
d	/	/	/	/	/	/	2.9059

Table 6. Coefficients to calculate specific enthalpy according to expression (B.7). *Specific heat (cal/g/K)*

	a	c	Δ	d
σ_1	8486.7	6946.8	1382.9	/
σ_2	31536	14803	3094.9	/
σ_3	78098	30438	5976.5	/
σ_4	76599	46378	5038.2	/
σ_5	227662	65183	12395	/
σ_6	171430	98269	16314	/
σ_7	-1000.3	1539.5	-1580.2	/
σ_8	-1002.8	3488	-610.06	/
ζ_9	/	/	/	2000

$$c_p(T) = \sum_{j=1}^3 a_j \sigma(T; c_j, \Delta_j) + \sum_{j=4}^9 a_j \gamma(T; c_j, \Delta_j)$$

$$= \sum_{j=1}^3 a_j \sigma_j(T) + \sum_{j=4}^9 a_j \gamma_j(T). \quad (\text{B.8})$$

Thermal conductivity (W/K/m)

$$\lambda_{tot}(T) = \sum_{j=1}^4 a_j \gamma(T; c_j, \Delta_j) + \frac{1}{a_5 + c_5 T^{\Delta_5}}$$

$$= \sum_{j=1}^4 a_j \gamma_j(T) + \zeta_5(T; a_5, c_5, \Delta_5). \quad (\text{B.9})$$

Table 7. Coefficients to calculate specific heat according to expression (B.8).

	a	c	Δ
σ_1	1.4660	7822.6	9413.3
σ_2	2.0586	27693.0	1932.2
σ_3	1.9846	88546.0	5839.2
γ_4	0.51666	3547.4	668.06
γ_5	2.7110	6931.9	1148.7
γ_6	3.9774	14830.0	2877.2
γ_7	3.9040	29169.0	4046.0
γ_8	4.9202	46703.0	5044.4
γ_9	5.9180	65610.0	10886.0

Electric conductivity (S/m)

$$\sigma(T) = \sum_{j=1}^6 a_j \sigma(T; c_j, \Delta_j) + d$$

$$= \sum_{j=1}^6 a_j \sigma_j(T) + \zeta_7(d). \quad (\text{B.10})$$

Viscosity (kg/m/s)

$$\eta(T) = \sum_{j=1}^5 a_j \sigma(T; c_j, \Delta_j) + \frac{d + a_6 \gamma(T; c_6, \Delta_6)}{2 + T^q}$$

$$= \sum_{j=1}^5 a_j \sigma_j(T) + \zeta_6(T; a_6, c_6, \Delta_6, d, q). \quad (\text{B.11})$$

Table 8. Coefficients to calculate thermal conductivity according to expression (B.9).

	γ_1	γ_2	γ_3	γ_4	ζ_5
a	1.6027	3.5183	0.51834	0.046393	-7.3543×10^3
c	14327	6830	3486.3	1295.4	1.7290×10^6
Δ	3174	1252.3	770.33	1065.9	-1.5675

Reducing the temperature range, it is possible to use the same number of fitting parameters without significant loss of accuracy, due to the fact that the sigmoid and gaussian curves are effective only in a limited temperature region.

Table 9. Coefficients to calculate electric conductivity according to expression (B.10).

	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6	σ_7	ζ_8
<i>a</i>	7258.8	6816.7	3402.2	2410.4	12225	-756.31	728.88	/
<i>c</i>	10694	18215	37828	56016	86614	7110.5	7912.4	/
Δ	2977.4	4922.6	4997	4427.9	17218	3306.7	747.54	/
<i>d</i>	/	/	/	/	/	/	/	0.96691

Table 10. Coefficients to calculate viscosity according to expression (B.11).

	σ_1	σ_2	σ_3	σ_4	σ_5	ζ_6
<i>a</i>	2.4206×10^{-4}	1.2681×10^{-4}	-3.4926×10^{-4}	-1.2445×10^{-5}	-4.6583×10^{-6}	1573.6
<i>c</i>	7968.7	2428.4	13037	29022	45190	842.03
Δ	4197.4	2511.6	2983.4	3230	9661.5	2.9207×10^{-4}
<i>d</i>	/	/	/	/	/	-8.2881×10^{-4}
<i>q</i>	/	/	/	/	/	0.94898

Table 11. Reduced set of parameters to calculate the fit in the given range. The exception refers to the parameters which should have different values in the reduced set.

	from (K)	to (K)	parameters	exceptions
<i>S</i>	50	20000	σ_1 - σ_3 , ζ_8	/
<i>M</i>	50	20000	σ_4 - σ_6 , ζ_7	<i>d</i> = 7.4169
<i>H</i>	50	18000	σ_1 - σ_2 , σ_7 - σ_8 , ζ_9	/
<i>c_p</i>	50	20000	σ_1 , γ_4 - γ_6	/
λ_{tot}	2500	100000	γ_1 - γ_3 , ζ_5	/
σ	50	22000	σ_1 - σ_2 , σ_6 - σ_7	/
η	50	23000	σ_1 - σ_3 , ζ_6	/

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