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Approximate Calculation of Transport Coefficients of Earth and Mars Atmospheric Dissociating Gases

Vladimir V. Riabov*
Worcester Polytechnic Institute, Worcester, Massachusetts 01609-2280

High-temperature transport properties (viscosity, thermal conductivity, binary and multicomponent mass diffusion, and thermal diffusion) of dissociating gases of the Earth and Martian atmospheres have been calculated within the framework of the Chapman–Enskog method. The exponential repulsion potentials of interactions between atoms (N, O, and C) and molecules (N_2, O_2, NO, C_2, CN, CO, and CO_2) were studied. The collision cross sections were calculated from numerous experimental molecular-beam scattering data. The bifurcation approximation to the binary diffusion coefficients and the Wilke–Saxena approximate techniques were effectively used to simplify numerical algorithms of heat transfer calculations.

Nomenclature

a_{ip} = Sonine expansion coefficients, Eqs. (2) and (3)
b = approximation parameter, $1.2A^* \approx 1.452$, Eq. (18)
b_{ip} = Sonine expansion coefficients, Eq. (4)
c_{ip}^{ji} = Sonine expansion coefficients, Eq. (1)
c_{pi} = heat capacity of species i at constant pressure
c_t = approximation coefficient, −0.5, Eq. (22)
c_{vi} = heat capacity of species i at constant volume
D = approximation parameter, Eq. (17)
D_i = energy diffusion coefficients, Eq. (11)
D_{ik} = mass diffusion coefficients, Eq. (1)
D_i^T = thermal diffusion coefficients, Eq. (2)
F_i = bifurcation parameter for species i
f_i = n_i/n, mole fraction of species i
$I^{(l,s)}$ = tabulated integrals, Eq. (16)
k = Boltzmann constant
M = average molecular weight
m_i = molecular mass of species i
N = total number of species
n = average specific number of molecules
p = pressure
q_{ij}^{mp} = matrix elements of the Chapman–Enskog approximation, Eqs. (5) and (7)
R = distance between the centers of mass of the interacting molecules
$\mathcal{R}$ = universal gas constant
r = interatomic distance
T = translational temperature
$\mathcal{T}_{ij}$ = coefficients of binary diffusion
V = interaction potential function, Eq. (14)
z_i = approximation parameters, Eq. (22)
α_i = ρ_i/ρ, mass-concentration of species i
β = parameter of the interaction potential, Eq. (14)
γ = approximation parameter, Eq. (16)
δ_{ij} = Kronecker delta symbols
η = viscosity coefficient
λ = thermal conductivity coefficient
ξ = number of terms in the Sonine polynomial series
ρ = density
σ_{ij} = collision diameter of two molecules i, j
ψ = correction factor, Eq. (11)
$\Omega_{ij}^{(l,s)*}$ = collision integrals, Eq. (16)
$\varkappa_j$ = approximation parameters, Eq. (18)

Subscripts
i = species
in = internal degrees of freedom
0 = monatomic-gas parameter
1 = first approximation, Eqs. (12) and (13)

Introduction

THE transport properties of gas components at high temperatures are important in heat and mass transfer problems of hypersonic vehicle flights in the Earth and Martian atmospheres. This data could be of significant interest in future NASA missions.[1,2] Methods of calculating transport coefficients of dissociating air at high temperatures were developed (see Refs. 3–16). Calculations of the transfer coefficients both by kinetic theory[17] and by approximate methods[12,18–20] are based on data regarding the elastic interaction potentials among mixture components. Experimental investigation of the coefficients has been restricted to the range of temperature $T \leq 2000$ K.[10,17,21–24] At a higher temperature the transport coefficients have only been measured in several unique experiments (i.e., see Refs. 4, 9, 16, and 25–28). Quantum-mechanical calculations of elastic-interaction processes are only possible for molecules with a simple electron structure[29] as well as for nitrogen and oxygen atoms in their ground states.[13,15] The major sources of information on the interaction of molecules at high temperatures are data of molecular-beam scattering experiments.[6–8,10] Different models of intermolecular potentials (the exponential repulsive potential[3,7,10,19,20] and the inverse power attractive and repulsive potentials[6–8,11,30,31]) have been used in these studies. The experimental information on the atom–molecule and molecule–molecule interactions has been also analyzed by Sokolova,[30] Jordan et al.,[31] and Gromov and Eremyan.[19]

Unfortunately, the experimental data regarding atom–atom interactions are unavailable and different approximation techniques should be developed.[9,10,13,15] When the atom–atom interactions are described by an exponential repulsion, the average molecule–molecule interaction can be approximated by an additive-potential method, proposed by Amdur et al.[32] Using this technique, Yun and Mason[3] found the approximate correlations between the atom–molecule and molecule–molecule potentials for air species. This method was effectively used by Riabov[20] for calculations of transfer coefficients of

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*Visiting Associate Professor, Department of Mechanical Engineering, 100 Institute Road. Member AIAA.

dissociating air with sublimation products of graphite. In the present study, the additive-potential method[32] is developed for calculating interaction potentials and transfer coefficients (viscosity, chemically frozen thermal conductivity, multicomponent mass diffusion, and thermal diffusion) for air and gas components of the Martian atmosphere.

The calculations of the transfer coefficients using accurate expressions of the kinetic theory of gases[17,33] are carried out with a great consumption of computing time. The simplifications of the calculation technique were developed by Wilke,[34] Mason and Saxena,[35] Gupta et al.,[16] Kendall et al.,[18] and Riabov.[11,12,20] Considerably simpler transfer-coefficient expressions could be obtained using bifurcational approximation for the binary-diffusion coefficients.[11,18,20] In the present study, this approximate technique has been developed to calculate transfer coefficients for species of the Martian atmosphere.

Chapman–Enskog Method and Transfer Coefficients

The Chapman–Enskog iteration technique[13,25] has been used to solve the Boltzmann equation for the case of a quasineutral mixture of nonexcited monatomic gases. At the hydrodynamic stage the solution of the Boltzmann equation is presented as an asymptotic series according to the small parameter Kn, which is the Knudsen number. The expressions for the diffusion and heat fluxes, and the viscous stress tensor through the gradients of species concentrations, temperature, pressure, and the components of strain tensor are given in Refs. 17, 33, 36, and 37.

The calculation of the transfer coefficients is based on the solution of integral equations using the Sonine polynomial series, i.e., $c_{i0}^{ji}(\xi)$, $a_{i0}(\xi)$, $a_{i1}(\xi)$, $b_{i0}(\xi)$.[7,33,36] The expressions of the coefficients through the Sonine terms are

$$D_{ij} = (\rho n_i/2nm_j)(2kT/m_i)^{1/2} c_{i0}^{ji}(\xi) \tag{1}$$

$$D_i^T = (n_i m_i/2)(2kT/m_i)^{1/2} a_{i0}(\xi) \tag{2}$$

$$\lambda' = -\frac{5}{4} k \sum_{j=1}^{N} n_j \left(\frac{2kT}{m_j}\right)^{1/2} a_{j1}(\xi) \tag{3}$$

$$\eta = \frac{1}{2} kT \sum_{j=1}^{N} n_j b_{j0}(\xi) \tag{4}$$

The approximate magnitudes of the transfer coefficients are functions of a number of valuable nonzero terms in the polynomial series ξ, which could be calculated from the following system of the linear algebraic equations:

$$\sum_{j=1}^{N} \sum_{p=0}^{M} q_{ij}^{mp} a_{jp} = -\frac{15\sqrt{\pi}}{2} n_i \delta_{m1} \tag{5}$$

$$\sum_{j=1}^{N} \sum_{p=0}^{M} \tilde{q}_{ij}^{mp} b_{jp} = 5n_i \left(\frac{2\pi m_i}{kT}\right)^{1/2} \delta_{m0} \tag{6}$$

$$\sum_{j=1}^{N} \sum_{p=0}^{M} q_{ij}^{mp} c_{jp}^{hk} = 3\sqrt{\pi}(\delta_{ik} - \delta_{ih})\delta_{m0} \tag{7}$$

where indexes are $i, h, k = 1, \ldots, N$; $m = 0, 1, \ldots, M$, $M = \xi - 1$.

The coefficients q_{ij}^{mp} and q_{ij}^{mp} in Eqs. (5–7) could be calculated using bracket integrals.[33,36] The expressions for the coefficients and integrals are given in Refs. 17, 33, 36, and 38–41. The form of the thermal conductivity coefficient in the case of monatomic gas mixture is[17,36,39]

$$\lambda_0 = \lambda' + \lambda'', \qquad \lambda'' = \frac{\rho k}{n} \sum_{i+1}^{N} \sum_{j=1}^{N} \frac{E_{ij} D_i^T D_j^T}{n_i m_i m_j} \tag{8}$$

where E_{ij} is the matrix of elements $D_{ji} m_i$.

Calculation methods for the thermal conductivity have been analyzed (see Refs. 35 and 42–49). In calculating the thermal conductivity of polyatomic gases, the contribution of the internal degrees of freedom of the molecules should be taken into account by introducing the Eucken correction[50] in Eq. (8). In the case of $\xi = 1$, the Eucken correction term has been obtained by Galkin et al.[44–46] The same technique could be applied in the general case at $\xi > 1$.[11,37] The expression of the thermal conductivity of polyatomic gas mixture is

$$\lambda = \lambda_0 + \sum_{i=1}^{N} n_i c_{vi} D_i \tag{9}$$

In Eq. (9) the diffusion coefficients D_i are calculated using binary diffusion coefficients $\mathcal{T}_{ij}$, collision integrals $\Omega_{ij}^{(1,1)*}$, and correction terms $\psi_i^{(M)}$ as follows:

$$\mathcal{T}_{ij} = \frac{3}{16n} \sqrt{\frac{2\pi kT(m_i + m_j)}{m_i m_i}} \frac{1}{\pi \sigma_{ij}^2 \Omega_{ij}^{(1,1)*}} \tag{10}$$

$$D_i = \left(\sum_{j=1}^{N} \frac{f_j}{\mathcal{T}_{ij}}\right)^{-1} \frac{1}{[1 - \psi_i^{(M)}]} \tag{11}$$

The correction terms[11,37] $\psi_i^{(M)}$ are functions of ξ and bracket integrals.[36] Nonelastic collisions have been evaluated using the Mason–Monchick approximate method.[47–49] The Brokaw effect,[51] which is significant in the analysis of the reactive thermal conductivity for a flow in chemical equilibrium, has not been calculated.

Transfer coefficients could be obtained using the technique described previously by the Gauss method of the solution of the linear algebraic equation system (5–7). The number of arithmetic calculations should be approximately equal to $(\xi \times N)^3$. As a result, a significant amount of calculations per one set of the gasdynamic parameters should be made. To reduce computational time different approximate methods of computing the transfer coefficients have been developed. Wilke[34] developed a simple method to estimate the viscosity coefficient of a gas mixture:

$$\begin{gathered} \eta_1 = \sum_{i=1}^{N} \eta_i \left(1 + \sum_{k=1,k\neq i}^{N} G_{ik} \frac{f_k}{f_i}\right)^{-1} \\ \eta_{ik} = \frac{5}{16} \frac{(2\pi m_{ik} kT)^{1/2}}{\pi \sigma_{ij}^2 \Omega_{ij}^{(2,2)*}}, \qquad G_{ik}^{\eta} = \frac{2m_k}{m_i + m_k} \frac{\eta_i}{\eta_{ik}} \end{gathered} \tag{12}$$

A similar expression for the thermal conductivity coefficient was proposed by Mason and Saxena[35]:

$$\begin{gathered} \lambda_1 = \sum_{i=1}^{N} \lambda_i' \left(1 + \sum_{k=1,k\neq i}^{N} G_{ik}^{\lambda} \frac{f_k}{f_i}\right)^{-1}, \qquad G_{ik}^{\lambda} = L_{ik} \frac{\lambda_i}{\lambda_{ik}} \\ \lambda_i' = \lambda_{0i} \left(0.115 + 0.354 \frac{c_{pi} m_i}{k}\right), \qquad \lambda_{0i} = \frac{15}{4} \eta_i \frac{k}{m_i} \qquad (13) \\ L_{ik} = \frac{[1.25(6m_i - 5m_k) + 3m_k B_{ik}^*](m_i - m_k) + 8m_i m_k A_{ik}^*}{2A_{ik}^*(m_i + m_k)^2} \end{gathered}$$

Parameters G_{ik}^{λ} and G_{ik}^{η} were analyzed by Ferziger and Kaper[33] in detail. The computational results using Eqs. (12) and (13) correlate well with experimental data[23,34] for viscosity of binary and triple mixtures under room temperatures and for thermal conductivity under the conditions $T \leq 1000$ K. The applicability of the approximate formulas (12) and (13) for equilibrium dissociating air was considered by Gupta et al.[16] and Riabov.[11,12] Other approximations for the thermal conductivity coefficient were analyzed by Ferziger and Kaper,[33] Mason and Monchick,[47] and Lebed and Riabov.[48] These techniques require a small amount ($\sim N^2$) of calculations.

Interaction Potentials

Numerous experimental data on the molecule–molecule and atom–molecule interactions were obtained (see Refs. 6, 7, 10, 14, 31, and 32). The first investigations[8,30,32] were based on the assumption of an inverse power dependence of the interaction potential $V = K/R^s$ on the distance between the centers of mass of the molecules R. The analysis of the experimental conditions provided by Leonas[7] and Cubley and Mason[10] shows that the parameter s is not constant. They recommended the use of repulsive potential in the form:

$$V = V_0 \exp(-\beta R) \tag{14}$$

Table 1 Potential parameters for interactions of air species

Interaction	Coefficient V_0, eV	Coefficient β, Å^{-1}	Source
O–O	1410	4.14	Cubley and Mason[10]
O–N	348.2	3.41	Cubley and Mason[10]
$O-O_2$	4530	4.039	Riabov[20a]
$O-N_2$	860.4	3.331	Riabov[20a]
O–NO	2142	3.717	Riabov[20a,b]
N–N	86.0	2.68	Cubley and Mason[10]
$N-O_2$	905.7	3.32	Riabov[20b]
$N-N_2$	184.9	2.614	Riabov[20b]
N–NO	428.6	2.983	Riabov[20b]
O_2-O_2	1.485×10^4	3.964	Riabov[20a]
O_2-N_2	2316	3.267	Riabov[20b]
O_2-NO	6373	3.644	Riabov[20a,b]
N_2-N_2	415.7	2.573	Riabov[20a]
N_2-NO	52.38	1.761	Riabov[20]
NO–NO	2678	3.303	Riabov[20a,b]

[a] Data correlate at high accuracy with data of Cubley and Mason.[10]
[b] Data correlate at high accuracy with data of Leonas.[7]

Table 2 Potential parameters for interactions of Martian atmospheric species

Interaction	Coefficient V_0, eV	Coefficient β, Å^{-1}	Source
C–C	348	3.37	Gromov and Eremyan[19]
C–O	700.5	3.755	Riabov[20]
C–N	173	3.025	Riabov[20]
$C-O_2$	1997	3.659	Riabov[20]
$C-N_2$	398.5	2.956	Riabov[20]
C–NO	947.6	3.33	Riabov[20]
C–CN	587.4	3.109	Riabov[20]
C–CO	1368	3.496	Riabov[20]
$C-CO_2$	4843	3.5	Riabov[20]
N–CN	271.5	2.771	Riabov[20]
N–CO	615.7	3.149	Riabov[20a]
$N-CO_2$	1855	3.156	Riabov[20]
O–CN	1302	3.488	Riabov[20]
O–CO	3095	3.882	Riabov[20a]
$O-CO_2$	1.31×10^4	3.879	Riabov[20]
O_2-CN	3600	3.416	Riabov[20]
O_2-CO	9683	3.808	Riabov[20]
O_2-CO_2	4.268×10^4	3.822	Riabov[20a]
N_2-CN	621.7	2.724	Riabov[20]
N_2-CO	22.17	1.432	Riabov[20]
N_2-CO_2	4738	3.118	Riabov[20a]
NO–CN	1568	3.084	Riabov[20]
NO–CO	4075	3.473	Riabov[20a]
$NO-CO_2$	1.613×10^4	3.51	Riabov[20]
CN–CN	950.6	2.879	Riabov[20]
CN–CO	2371	3.253	Riabov[20]
$CN-CO_2$	7868	3.268	Riabov[20]
CO–CO	6280	3.646	Riabov[20a]
$CO-CO_2$	2.494×10^4	3.654	Riabov[20a]
CO_2-CO_2	1.049×10^5	3.666	Riabov[20a]

[a] Data correlate at high accuracy with data of Leonas.[7]

This approximation has been successfully used to describe the interaction of inert gases[7] and of identical atoms.[9,10] The additive-potential method, proposed by Amdur et al.[32] for approximate calculations of $V(R)$, gives acceptable accuracy in calculating the parameters of the atom–molecule and molecule–molecule interactions.[3,10] According to this method, the interaction potential of the molecules AB and CD is written as[3,7]

$$V(R) = V(r_{AC}) + V(r_{BC}) + V(r_{AD}) + V(r_{BD}) \tag{15}$$

The potential in Eq. (15), averaged over equiprobable orientations, determines the effective spherically symmetric potential corresponding to the point force center. This approximating procedure was described in detail by Yun and Mason[3] and Cubley and Mason.[10] The combinatorial rule,[3] $V_{ij} = (V_{ii}V_{jj})^{1/2}$, is usually employed to make up the currently unknown data on the interaction potential.

Using the collision integrals $\Omega_{ij}^{(l,s)*}$ given in Refs. 10, 17, 33, 36, and 52, the transfer coefficients of multicomponent gas mixture may be calculated by the method described previously. According to Monchick,[52] the expressions for collision integrals calculated for the exponential repulsive potential [see Eq. (14)] take the form:

$$\Omega^{(l,s)*} = \frac{8\gamma^2 I^{(l,s)}(\gamma)}{\beta^2(s+1)!\left[1 - \frac{1}{2}\frac{1+(-1)^l}{1+l}\right]\sigma^2}, \qquad \gamma = \ell n\left(\frac{V_0}{kT}\right) \tag{16}$$

The functions $I^{(l,s)}(\gamma)$ for various l, s, and values $3.5 \le \gamma \le 28.5$ were tabulated by Monchick.[52] In the present study, these functions are approximated by cubic splines.

In this study the additive-potential method has been applied to calculate the dependencies $V(R)$ by the previous method for pairs of species O, N, O_2, N_2, NO, C, CN, CO, CO_2, which are the major components of dissociating gases in the Earth and Martian atmospheres.[1,2] The distance between the centers of mass of the molecules was varied in the range $0.6 \le R \le 5.5$ Å. The results are approximated by an exponential function, using the least-squares method.[20] The basic functions adopted are the atom–atom interaction exponential potentials, the parameters of which are taken from Refs. 10 and 19. Data on the molecular structure are taken from Ref. 53.

The potential parameters V_0 and β obtained in the present study are shown in Table 1 for dissociating air and in Table 2

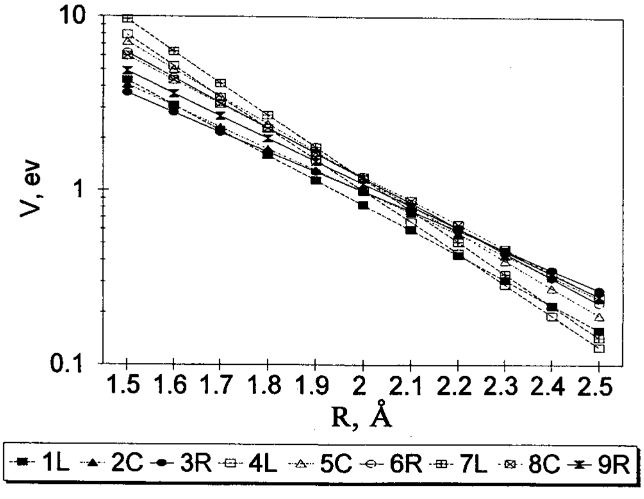

Fig. 1 Interaction potentials of N atoms with molecules: $N-N_2$ (curves 1–3), $N-O_2$ (curves 4–6), N–NO (curves 7–9). Comparison of the present calculations (solid lines 3, 6, and 9) and experimental data of Leonas[7] (dashed lines 1, 4, and 7) and Cubley and Mason[10] data (dot–dashed lines 2, 5, and 8).

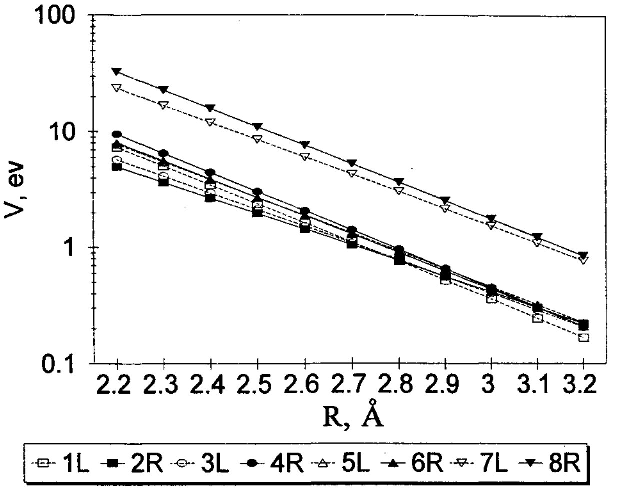

Fig. 2 Interaction potentials of CO_2 molecules with molecules of the Martian atmospheric gases: CO_2–N_2 (curves 1 and 2), CO_2–O_2 (curves 3 and 4), CO_2–CO (curves 5 and 6), and CO_2–CO_2 (curves 7 and 8). Comparison of the present calculations (solid lines 2, 4, 6, and 8) and experimental data of Leonas[7] (dashed lines 1, 3, 5, and 7).

for dissociating Martian atmospheric gases. The calculated interaction potentials are compared with the data of Leonas[7] and Cubley and Mason[10] (see Figs. 1 and 2). The agreement of the results is basically good (see notes in Tables). The additive-potential method used here was extremely important to complete the information on the interaction potentials, especially with the participation of atoms of carbon and oxygen.

Calculation of Transport Coefficients

For dissociating gas components in the Earth and Mars atmospheres at temperatures from 2000 to 10,000 K, the collision integrals $\Omega_{ij}^{(l,s)*}$ are calculated, as well as the viscosity η_i and binary-diffusion coefficients, according to Eqs. (16), (10), and (12). The best agreement of the present results on $\Omega_{ij}^{(l,s)*}$ for air is with the data of Leonas,[7] Cubley and Mason,[10] and Gromov and Eremyan.[19] The present data for interactions with participation of carbon correlate well with the results of Leonas,[7] Leonas and Rodionov,[14] Gromov and Eremyan,[19] and Riabov.[20] Here the values of the collision integrals with the parameters in Tables 1 and 2 are intermediate between the results of other studies.[7,19] The difference of the results may reach 25% in the given temperature range (i.e., see Fig. 3). Parameters of the collision-integral ratio[17,33] are approximately constant, i.e., $A^* \approx 1.21$ and $B^* \approx 1.17$.

The viscosity coefficients η_i for air components and species of the Martian atmosphere are shown in Figs. 4 and 5, correspondingly. These data are in good agreement (about 10%) with the data for O_2, N_2, NO, and CO_2 from Refs. 21–24, 52, and the data[15] for O atoms. The calculated viscosity coefficients of equilibrium dissociating oxygen at constant pressures of 0.1 and 1 atm are shown in Fig. 6. These values are in good agreement with experimental data of Hartunian and Marrone.[25]

Further analysis of the transfer coefficients is made for equilibrium dissociating air in the range of temperature from 2000 to 10,000 K, and pressure 1 atm, where the concentration of ions and electrons is negligible. Air-component concentrations were calculated by Predvoditelev et al.[54,55] The results were obtained for exponential repulsion potentials (see Table 1).

The viscosity and chemically frozen thermal conductivity coefficients calculated by the Chapman–Enskog method at $\xi = 1$ [Eqs. (1–11)] are shown in Figs. 7 and 8, correspondingly (filled squares). The results of calculations using the approximate formulas (12) and (13) are presented in Figs. 7 and 8 as empty squares. From comparison of the results, it is found that the approximate formulas provide data with an error of 1% for viscosity and 2% for thermal conductivity. The influence of the higher order of approximation at $\xi = 2$ on the coefficients is insignificant (less than 1%).

The coefficients of multicomponent mass diffusion of molecular nitrogen with other components at pressure $p = 1$ atm (solid lines) and 0.1 atm (dashed lines) are shown in Fig. 9. The influence of pressure is significant at $T \geq 3500$ K, where the level of dissociation is high. The values of multicomponent-diffusion coefficients of atoms is larger by approximately

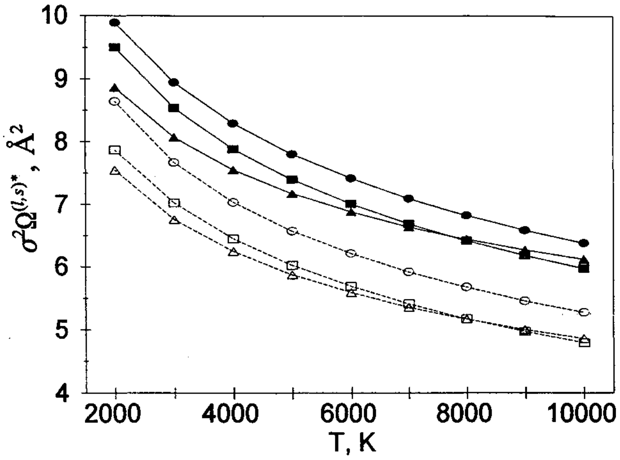

Fig. 3 N_2–N_2 transport collision integrals $\sigma^2\Omega_{ij}^{(2,2)*}$ (solid lines) and $\sigma^2\Omega_{ij}^{(1,1)*}$ (dashed lines). Comparison of the present calculations (■, □) and data of Cubley and Mason[10] (▲, △) and Gupta et al.[16] data (●, ○).

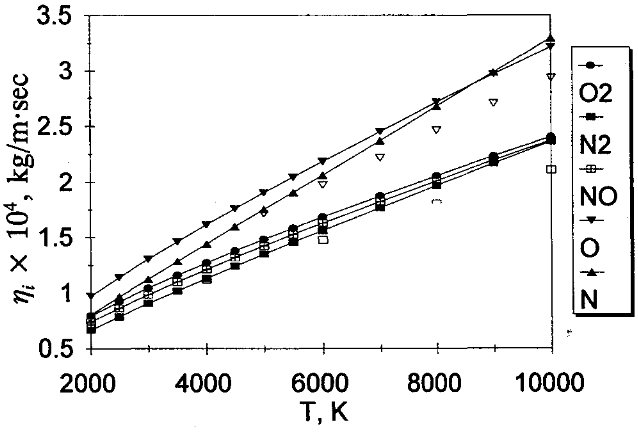

Fig. 4 Viscosity coefficients η_i for air components vs temperature *T*. Comparison of the present calculations and data of Levin et al.[15] (▽, O atoms), and Monchick[52] data (□, N_2).

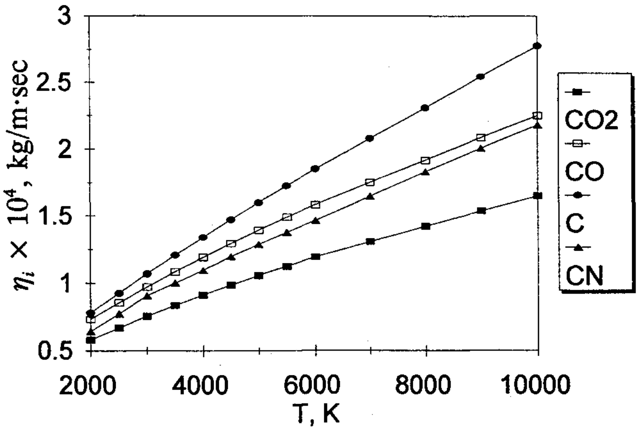

Fig. 5 Viscosity coefficients η_i for components of the Martian atmosphere vs temperature *T*.

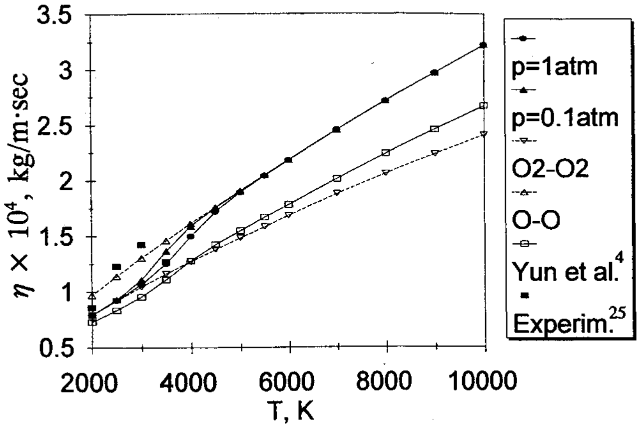

Fig. 6 Viscosity of equilibrium dissociating oxygen at pressures of 0.1 and 1 atm. Comparison of the present calculation results and the experimental data of Hartunian and Marrone[25] (■), and the data of Yun et al.[4] (□).

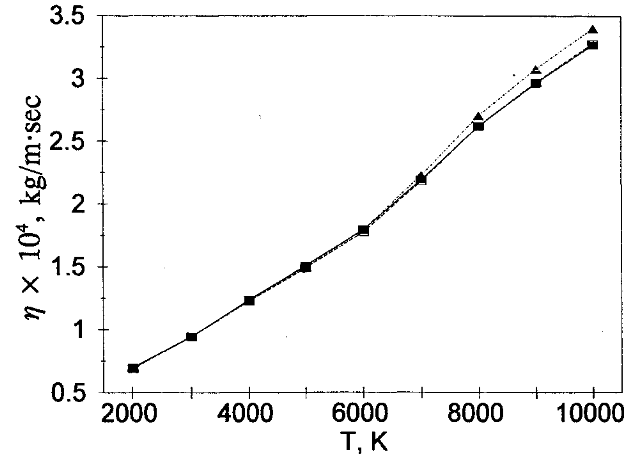

Fig. 7 Viscosity coefficient η for equilibrium air vs temperature T at pressure p = 1 atm. The present results (■) are compared with the Wilke approximation[34] (□) and the bifurcation approximation (▲).

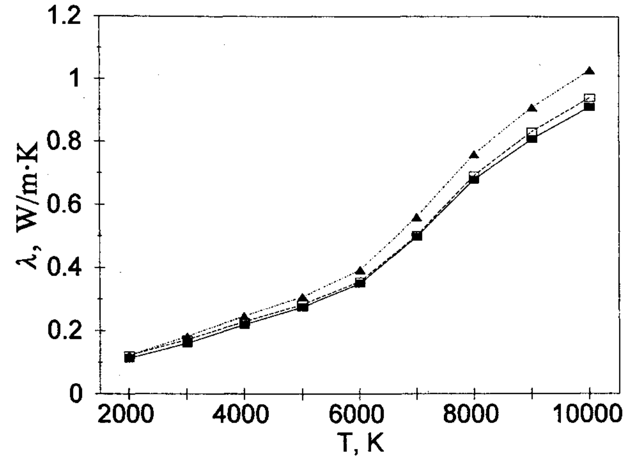

Fig. 8 Coefficient of chemically frozen thermal conductivity λ' for equilibrium air vs temperature T at pressure p = 1 atm. The present results (■) are compared with the Mason–Saxena approximation[35] (□) and the bifurcation approximation (▲).

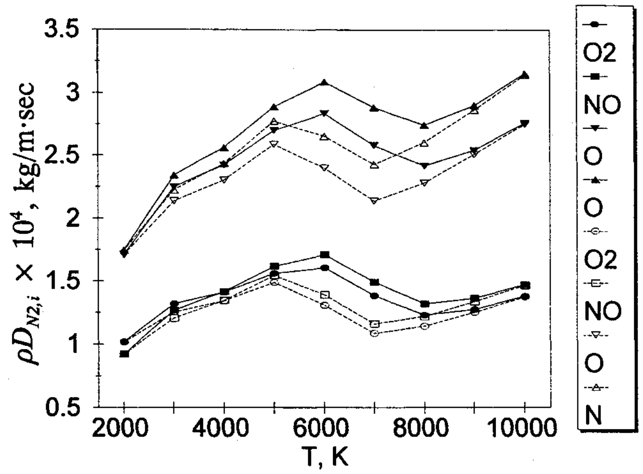

Fig. 9 Multicomponent mass-diffusion coefficients ρD_{ij} for equilibrium air vs temperature T at pressure p = 1 atm (solid lines) and p = 0.1 atm (dashed lines).

the factor of 2 in the total range of temperature and pressure. This phenomenon correlates with the difference in the viscosity of the atomic and molecular species (see Fig. 4).

The absolute values of thermal-diffusion coefficients at ξ = 2 and pressure of 1 atm are shown in Fig. 10. The coefficients are negative for atoms at $T \leq 7000$ K and for molecules of N_2 and NO at $T \leq 2500$ K. The dissociation is the major factor in decreasing the thermal-diffusion coefficients of molecules. These coefficients were taken into account to estimate the magnitude of the parameter λ'' in Eq. (8). This parameter is less than 1% of the total value of λ. This fact is in a good agreement with the results of Muckenfuss and Curtiss.[56]

The transport coefficients of the Martian atmospheric gases have been analyzed under the thermodynamic equilibrium conditions in the range of temperature from 2000 to 6000 K, and pressure 1 atm. In accordance with the study of Mitcheltree and Groffo,[57] we assumed that the Martian undisturbed atmosphere consists of 97% CO_2 and 3% N_2. The equilibrium constants for chemical reactions between nine species were taken from Ref. 57. The thermodynamic functions of species were calculated using data from JANAF tables.[58]

The viscosity and chemically frozen thermal conductivity coefficients calculated by the Chapman–Enskog method at ξ = 2 are shown in Figs. 11 and 12, correspondingly (filled squares). The results of calculations using the approximate formulas (12) and (13) are presented in Figs. 11 and 12 as empty squares. From comparison of the results, it is found that the approximate formulas provide data with an error of 1% for viscosity and 3% for thermal conductivity. The absolute values of the thermal-diffusion coefficients of species having the biggest values of concentration are shown in Fig. 13.

Approximate Method of Calculations of Transfer Coefficients

As mentioned in the Introduction, approximate methods of estimating transfer coefficients should be developed. Considerably simpler expressions than Eqs. (1–9) could be obtained using the bifurcational approximation for the binary-diffusion coefficients.[12,18,59,60] According to this technique, the binary-diffusion coefficients could be approximated by the form

$$\mathcal{T}_{ij} = D/F_iF_j \tag{17}$$

where $D = D(p, T)$ is the parameter of the multicomponent mixture and $F_i = F_i(T)$ is the parameter of the species i. The possibility of using the correlation relation in Eq. (17) was analyzed by Kendall et al.,[18] Bartlett et al.,[59] Rolin et al.,[60] and Riabov[12,20] for various mixtures of complex composition. The results of the present study also indicate high accuracy of the correlation in Eq. (17) for dissociating gases in the atmospheres of Earth and Mars.

The values of F_i for these mixtures are found by the least-squares method for the binary-diffusion coefficients calculated

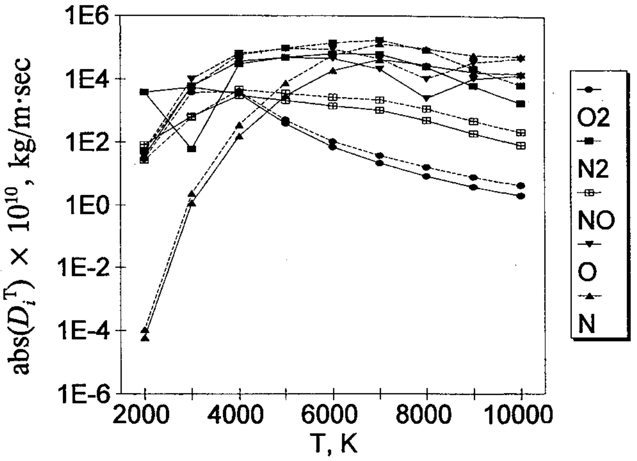

Fig. 10 **Thermal diffusion coefficients D_i^T for equilibrium air vs temperature T at pressure p = 1 atm. The present results (solid lines) are compared with the bifurcation approximation (dashed lines).**

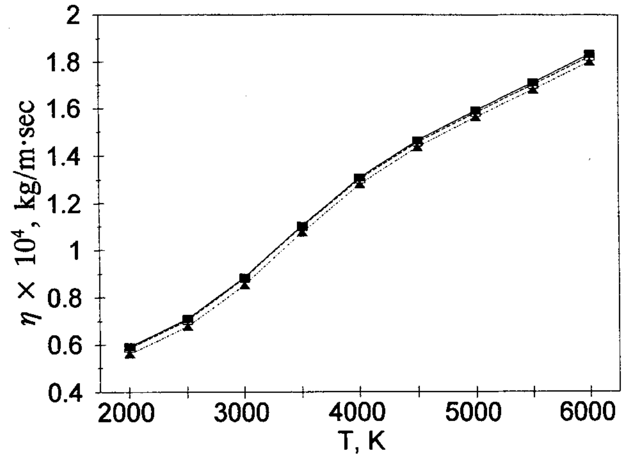

Fig. 11 **Viscosity coefficient η for equilibrium dissociating gases of the Martian atmosphere vs temperature T at pressure p = 1 atm. The present results (■) are compared with the Wilke approximation[34] (□) and the bifurcation approximation (▲).**

from Eq. (10). The values of $D(p, T)$ for molecular oxygen were taken as the normalizing quantities ($F_{O_2} = 1$). The parameters F_i for the system of elements O–N–C with an exponential repulsive potential are shown in Fig. 14. The magnitudes of F_i depend weakly (with the accuracy of 3%) on the temperature in the range $2000 \leq T \leq 10{,}000$ K. The mean relative error is no more than 3% and the maximum error of the complex $\rho\mathcal{T}_{ij}/M$ is 11.5%.[20] This bifurcational model leads to a mean absolute error of the value of the parameter $\rho\mathcal{T}_{ij}/M$, which is more than a factor of 10 less than for the model of equal diffusion coefficients. This confirms the conclusions of Kendall et al.[18] and Riabov.[12,20] The use of the approximations by Eq. (17) is entirely valid for engineering applications because of the small number (~N) of calculations.

Following Refs. 12 and 33, the simple algebraic formulas are obtained for η and λ':

$$\eta = \frac{\rho D \varkappa_2}{\varkappa_1 M b}, \qquad \varkappa_1 = M \sum_{j=1}^{N} \frac{\alpha_j F_j}{M_j}, \qquad \varkappa_2 = \sum_{j=1}^{N} \frac{M_j f_j}{F_j} \tag{18}$$

$$\lambda' = \lambda'_0 + \lambda_{\text{in}}, \qquad b = 1.2A^* \tag{19}$$

$$\lambda'_0 = \frac{15}{4} \frac{\rho D \mathcal{R}}{M b} \sum_{j=1}^{N} \frac{f_j}{F_j Q_j}, \qquad Q_j = \sum_{k=1}^{N} L_{jk} f_k F_k \tag{20}$$

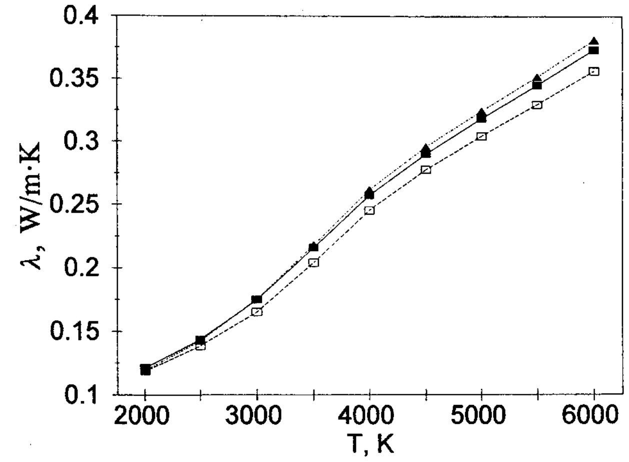

Fig. 12 **Coefficient of chemically frozen thermal conductivity λ' for equilibrium dissociating gases of the Martian atmosphere vs temperature T at pressure p = 1 atm. The present results (■) are compared with the Mason–Saxena approximation[35] (□) and the bifurcation approximation (▲).**

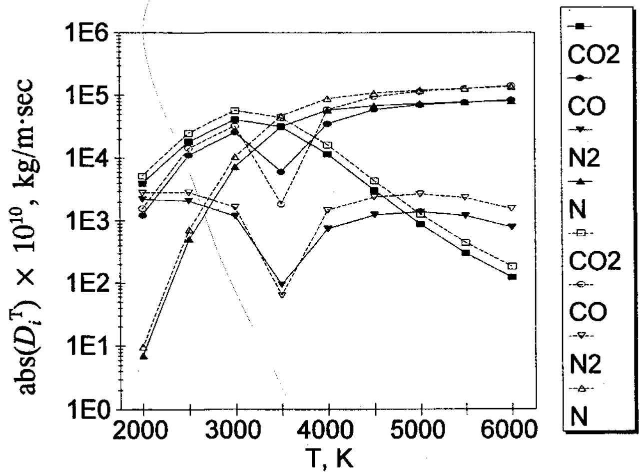

Fig. 13 **Thermal diffusion coefficients D_i^T for equilibrium dissociating gases of the Martian atmosphere vs temperature T at pressure p = 1 atm. The present results (solid lines) are compared with the bifurcation approximation (dashed lines).**

$$\lambda_{\text{in}} = \frac{\rho D \mathcal{R}}{\varkappa_1 M} \sum_{j=1}^{N} \frac{f_j}{F_j} c_{\text{in},j} \tag{21}$$

The thermal-diffusion coefficient is approximated by the expression[12,59]:

$$D_i^T = c_i \frac{\rho D \varkappa_2}{\varkappa_1 M} (z_i - \alpha_i), \qquad z_i = \frac{M_i f_i}{\varkappa_2 F_i} \tag{22}$$

The results of calculating the viscosity, frozen thermal conductivity, and thermal-diffusion coefficients of equilibrium-dissociated air and Martian atmospheric gases under considered conditions using bifurcation approximation are presented in Figs. 7, 8, 11, and 12 (dot–dashed lines), and Figs. 10 and 13 (dashed lines). According to the estimates, the difference in the results of accurate and approximate approaches over the whole temperature range is no more than 3% for the viscosity and 8.5% for the chemically frozen thermal conductivity. The approximation by Eq. (22) is helpful for the qualitative analysis of the thermal-diffusion coefficients. This approximation algorithm was successfully used by Riabov and Provotorov,[61,62] and Riabov and Botin[63] in the structure analysis of the thin viscous shock layers near hypersonic vehicles and near probes in supersonic hydrogen-combustion zones.

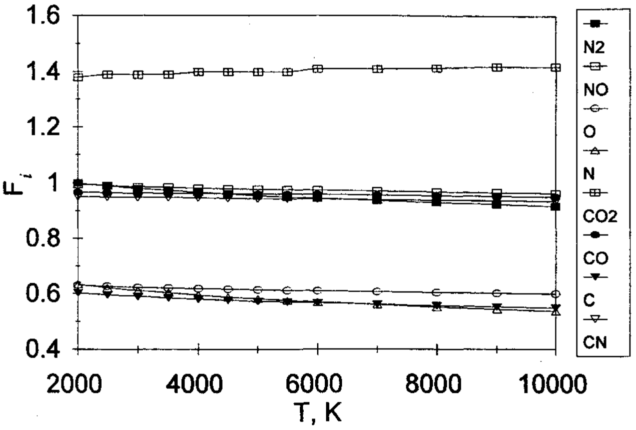

Fig. 14 Parameters F_i vs temperature T.

Concluding Remarks

The obtained results indicate the possibility of applying the approximate bifurcation method and the Wilke–Mason–Saxena technique[33–35] to calculate the transfer coefficients of mixtures of complex composition. The accuracy of these techniques is acceptable for practical applications. This method could be effectively used for solving heat transfer problems in future planetary missions.

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