JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 18, No. 1, January–March 2004

Collision Integrals for Ion–Neutral Interactions of Nitrogen and Oxygen

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Diffusion and viscosity collision integrals are computed for all ion–neutral binary interactions that occur in high-temperature partially ionized air, using a Tang–Toennies interaction potential. Resonant charge transfer effects are included as appropriate. Results are compared to more accurate computations where available. The computed collision integrals are estimated to be accurate to within ±25% over a temperature range from room temperature to 12,000 K. The data are presented in tabular form, making them immediately useful for engineering computations such as computational-fluid-dynamics simulations of reentry vehicles.

Nomenclature

B^*	=	ratio of collision integrals
C^*	=	ratio of collision integrals
C_{2n}	=	dispersion coefficients, Å^{2n} eV
E	=	collision energy, eV
Q_i	=	transport cross section, Å^2
r	=	separation distance, Å
r_m	=	location of potential minimum, Å
T	=	temperature, K
V	=	interaction potential energy, eV
V_0	=	short-range Tang–Toennies potential constant, eV
α_n, α_i	=	dipole polarizability of neutral(n), ion(i), Å^3
β	=	short range Tang–Toennies potential constant, Å
ϵ	=	depth of potential well, eV
κ	=	Boltzmann constant, 8.61755×10^{-5} eV/K
$\Omega_{i,j}$	=	collision integral, Å^2

Introduction

DURING reentry of space vehicles into planetary atmospheres, the postshock gases will be under severe nonequilibrium conditions, resulting in partial dissociation of the molecules as well as ionization of some of the atoms and molecules. To calculate the transport properties of the resulting mixture for Earth entries, data are needed as a function of temperature for all possible binary interactions of the nitrogen and oxygen species present, including those between atomic or molecular positive ions and the neutral atoms and molecules. For the flow conditions encountered by typical Earth-entry vehicles, multiply ionized species and negative ions can be neglected, and the relevant species are N_2, O_2, NO, N, O, N_2^+, O_2^+, NO^+, N^+, O^+, and e.

From Chapman–Enskog theory[1,2] first-order expressions for the coefficients of viscosity, thermal conductivity, and ordinary diffusion in a gas mixture can be computed using just three binary interaction parameters: the diffusion collision integral $\Omega_{1,1}$, the viscosity collision integral $\Omega_{2,2}$, and the ratio B^*, given by

$$B^* = \frac{5\Omega_{1,2} - 4\Omega_{1,3}}{\Omega_{1,1}} \tag{1}$$

One additional collision integral ratio $C^* = \Omega_{1,2}/\Omega_{1,1}$ is necessary if second-order expressions are desired.

Accurate experimental and theoretical results for these quantities are available for most of the neutral–neutral interactions in air.[3–7] The ion–ion and ion–electron interactions are dominated by Coulomb forces, which can be adequately described using a shielded Coulomb potential over the range of conditions encountered during reentry.[8] Some data on interactions between electrons and neutral atoms or molecules are available from experimental sources.[9] The results for atomic ions interacting with neutral atoms in air are accurately known[10,11]; however, most of the remaining ion–neutral interactions are not well known because experimental results (particularly at high temperatures) are sparse and accurate theoretical calculations are difficult to perform. Such detailed calculations must account for the degeneracies of the various electronic states of the atom, and for collisions involving molecules the cross sections must be determined by averaging over the possible orientations of the collision. Furthermore, for ion–neutral interactions of like species resonant charge exchange must be taken into account when calculating the momentum-transfer cross section and the resulting diffusion collision integral.

Of necessity, various compilations of transport properties for all binary interactions of the atoms, molecules, and ions in air have been prepared for engineering purposes.[12–17] These compilations generally use high-fidelity data where available and fill in the "missing" interactions with approximations. For example, based on the work of Yos,[16] the collision integrals for many of the ion–neutral interactions were simply taken to be the same as those computed for the $N–O^+$ interaction.[18] These collision integrals were later borrowed by Gupta et al.[15] in their compilation. Other approximations, such as the polarization (Langevin) potential used for many interactions in the reviews of Fertig et al.,[12] Capitelli et al.,[13] and Murphy,[14] provide reasonable accuracy for certain interactions, but do not reflect the underlying physics of the interaction, particularly at high energies. Still other approximations attempt to represent the interaction with separate piecewise models for the long- and short-range forces, often resulting in discontinuities in the potential or its first or second derivative. The intermolecular potential is often described using simple models for which collision integrals have been tabulated in the literature in order to avoid the integration of a more realistic potential function. Furthermore, there has often been minimal justification for the values of the parameters used in these models.

It would be desirable to develop a methodology by which ion–neutral interactions can be approximated by a uniform, continuous, physically plausible potential model with a small number of parameters that are either readily available in the literature or

Received 19 May 2003; revision received 22 August 2003; accepted for publication 22 August 2003.

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computable from such parameters. Although such a model could not capture all of the detailed physics of the interaction (including the statistical weighting of multiple potential energy surfaces[11] or the three-dimensional nature of atom–molecule and molecule–molecule interactions[7]), it might nevertheless be sufficiently accurate as an interim method for the computation of ion–neutral collision integrals until more accurate results become available.

In this paper, we present the results obtained by using an effective potential based on a one-dimensional Tang–Toennies model[19] to represent the ion–neutral interactions over the entire range of separation distances. This form for the potential was originally developed for neutral atom–atom van der Waals interactions but was subsequently generalized and found to work well for other interactions that are primarily repulsive with a shallow well.[6,20–22] Extension of this potential model to ion–neutral interactions should be reasonable because the model includes the relevant long-range polarization and dispersion terms as well as the short-range repulsion forces.

The collision integrals are computed by numerical computational methods,[10,11] and the predictions for the diffusion and viscosity collision integrals $\Omega_{1,1}$ and $\Omega_{2,2}$ are compared to accurate theoretical calculations for N—O^+ and N^+—O. The predicted viscosity collision integrals $\Omega_{2,2}$ are also compared to accurate calculations for N—N^+ and O—O^+. The $\Omega_{1,1}$ and $\Omega_{2,2}$ results for 25 ion–neutral interactions are presented over a range of temperatures between 300 and 12,000 K in a tabular format that should facilitate their incorporation into existing engineering codes.

Method

The Tang–Toennies form for the effective potential is physically plausible. It is a continuous function dominated by an exponential repulsion term at short separation distances between the interacting species and by the damped dispersion and polarization terms at long range:

$$V = V_0 e^{-r/\beta} - \sum_{n=2}^{\infty} \left[1 - e^{-r/\beta} \sum_{k=0}^{2n} \frac{(r/\beta)^k}{k!} \right] \frac{C_{2n}}{r^{2n}} \tag{2}$$

The dispersion parameters C_6, C_8, and C_{10} of each binary interaction can be determined from the combining relations of Koutselos and Mason[23] using known C_6 and dipole, quadrupole, and octopole polarizabilities of the individual species involved. In a recent paper Selle and Riedel[24] have compiled from carefully selected sources the values for the dispersion coefficient C_6 and the dipole polarizability α for all neutral and ionic components of air as well as the quadrupole polarizability α_q of the neutral species. These data are used for all species in this paper. Quadrupole polarizabilities of the ions as well as octopole polarizabilities of all species are estimated from the data of Koutselos and Mason.[23] Polarization forces are then used to determine C_4 and make corrections to the values of C_6, C_8, and C_{10} as described in Ref. 24. The C_{2n} coefficients for $2n > 10$ are estimated from the recursion relations[7,25]

$$C_{2n+4} = C_{2n-2}(C_{2n+2}/C_{2n})^3 \tag{3}$$

We found only minor changes in the results arising from terms of the series after C_{12}, and therefore truncated our calculations after C_{16}.

The short-range repulsion constants V_0 and β of the Tang–Toennies potential are calculated from the location r_m and depth ϵ of the potential well minimum by requiring that $V(r_m) = -\epsilon$ and $V'(r_m) = 0$. The well parameters are found from the relations[26,27]

$$r_m = \frac{K_1\left(\alpha_n^{1/3} + \alpha_i^{1/3}\right)}{[\alpha_n \alpha_i (1 + 1/\rho)]^{.095}} \tag{4}$$

$$\epsilon = \frac{K_2 \alpha_n (1 + \rho)}{r_m^4} \tag{5}$$

where the parameter ρ is given by

$$\rho = \frac{K_3 \alpha_i / \sqrt{\alpha_n}}{1 + (2\alpha_i/\alpha_n)^{2/3}} \tag{6}$$

Equation (6) represents the ratio of the dispersion and induction forces and was introduced by Cappelletti et al.[26] for ion–neutral interactions as a correction to the neutral–neutral formulas. In Eq. (6), assuming that the polarizabilities are in units of $Å^3$ (m^{-30}), $K_3 = 1Å^{(-1.5)}$; ρ is therefore a dimensionless quantity. The empirical constant $K_1 = 1.767$ was determined from neutral–neutral calibrations.[28] The constant $K_2 = 5.2$ was fixed[26] using Li^+—He and Li^+—Ne as reference systems. Use of these constants in Eqs. (4) and (5) return r_m and ϵ in units of Å and eV, respectively. The computed well parameters ϵ and r_m together with the resulting Tang–Toennies potential parameters for all 25 interactions are reported in Table 1.

Table 1 Potential well characteristics and parameters of the Tang–Toennies potential function for selected ion–neutral interactions

Interaction	ϵ, eV	r_m, Å	V_0, KeV	β, Å	C_4, Å^{4}eV	C_6, Å^{6}eV	C_8, Å^{8}eV	C_{10}, Å^{10}eV
NO^+—N_2	0.1091	3.262	24.86	0.2542	125.28	547.48	2,450.0	6,869
NO^+—O_2	0.1023	3.239	24.09	0.2517	113.83	492.49	2,185.8	6,155
NO^+—NO	0.1075	3.257	42.26	0.2420	122.40	483.63	2,208.4	5,863
NO^+—N	0.0800	3.157	131.32	0.2097	79.20	248.74	1,086.8	2,747
NO^+—O	0.0637	3.094	45.20	0.2194	57.74	201.05	836.4	2,221
N_2^+—N_2	0.0893	3.574	450.09	0.2209	125.28	698.76	4,302.0	17,156
N_2^+—O_2	0.0833	3.554	421.24	0.2196	113.83	629.93	3,851.7	15,279
N_2^+—NO	0.0879	3.569	1,163.31	0.2069	122.40	631.42	3,869.6	14,332
N_2^+—N	0.0629	3.486	7,891.48	0.1769	79.20	344.35	1,974.8	6,357
N_2^+—O	0.0484	3.436	1,121.13	0.1924	57.74	270.43	1,527.6	5,106
O_2^+—N_2	0.1554	2.845	4.89	0.2656	125.28	344.11	928.7	1,173
O_2^+—O_2	0.1472	2.819	4.90	0.2615	113.83	304.64	811.1	1,061
O_2^+—NO	0.1535	2.839	7.37	0.2534	122.40	283.70	853.8	1,033
O_2^+—N	0.1189	2.724	17.21	0.2186	79.20	123.41	400.9	527
O_2^+—O	0.0980	2.648	10.29	0.2191	57.74	100.62	280.1	430
N^+—N_2	0.1260	3.074	14.14	0.2540	125.28	409.76	1,439.1	3,188
N^+—O_2	0.1186	3.050	14.32	0.2503	113.83	364.89	1,270.4	2,864
N^+—NO	0.1241	3.068	23.87	0.2412	122.40	348.09	1,302.6	2,754
N^+—N	0.0942	2.961	77.77	0.2063	79.20	164.24	623.3	1,339
N^+—O	0.0762	2.891	37.63	0.2101	57.74	132.13	459.1	1,080
O^+—N_2	0.1418	2.940	6.96	0.2625	125.28	370.57	1,115.0	1,832
O^+—O_2	0.1339	2.914	7.00	0.2586	113.83	329.02	979.0	1,652
O^+—NO	0.1396	2.934	10.84	0.2502	122.40	309.69	1,017.6	1,601
O^+—N	0.1075	2.821	28.27	0.2152	79.20	139.78	481.3	801
O^+—O	0.0879	2.748	15.75	0.2170	57.74	113.53	345.4	651

Table 2 Diffusion collision integrals $\Omega_{1,1}$ (Å^2) as a function of temperature (K) for selected ion–neutral interactions

Temperature, K	300	500	1,000	2,000	3,000	4,000	5,000	6,000	8,000	10,000	12,000
NO^+—N_2	33.9	24.2	14.6	9.68	8.13	7.35	6.87	6.54	6.10	5.79	5.59
NO^+—O_2	32.2	22.5	13.7	9.25	7.82	7.11	6.66	6.36	5.93	5.64	5.44
NO^+—NO[a]	49.2	41.6	35.0	31.1	29.4	28.2	27.3	26.6	25.7	25.1	24.7
NO^+—N	25.0	17.5	11.3	8.21	7.20	6.68	6.34	6.10	5.76	5.52	5.36
NO^+—O	21.4	14.8	9.64	7.20	6.38	5.94	5.65	5.43	5.13	4.91	4.76
N_2^+—N_2[b]	49.1	43.7	37.0	32.2	30.1	28.9	28.1	27.5	26.6	26.0	25.6
N_2^+—O_2	31.6	23.3	15.2	10.9	9.53	8.85	8.41	8.11	7.69	7.39	7.17
N_2^+—NO	32.2	23.1	15.2	11.2	9.85	9.18	8.74	8.44	8.02	7.73	7.51
N_2^+—N	24.9	18.1	12.6	9.94	9.03	8.54	8.21	7.98	7.65	7.41	7.23
N_2^+—O	21.3	15.6	11.0	8.87	8.10	7.68	7.38	7.17	6.86	6.63	6.46
O_2^+—N_2	32.9	23.2	13.9	8.55	6.78	5.92	5.40	5.05	4.60	4.30	4.10
O_2^+—O_2[a]	48.5	40.9	34.2	30.6	28.7	27.5	26.1	25.3	24.2	23.6	23.2
O_2^+—NO	30.7	22.2	13.6	8.47	6.77	5.94	5.44	5.10	4.66	4.37	4.17
O_2^+—N	23.2	16.7	10.4	6.87	5.72	5.14	4.79	4.54	4.21	3.99	3.84
O_2^+—O	19.5	13.9	8.63	5.88	4.98	4.52	4.23	4.02	3.74	3.54	3.40
N^+—NO	31.3	22.4	13.8	9.02	7.48	6.71	6.24	5.92	5.50	5.21	5.01
N^+—N_2	30.6	22.1	13.7	8.99	7.43	6.65	6.17	5.85	5.41	5.11	4.91
N^+—O_2	30.5	21.7	13.2	8.63	7.17	6.44	5.98	5.68	5.26	4.98	4.79
N^+—N[c]	43.3	38.2	34.3	31.4	30.0	29.0	28.3	27.7	26.9	26.2	25.6
N^+—O[d]	21.6	15.1	10.9	8.33	7.07	6.21	5.56	5.06	4.33	3.82	3.44
O^+—NO	31.4	22.4	13.6	8.64	7.01	6.21	5.73	5.40	4.97	4.68	4.48
O^+—N_2	31.7	22.8	13.8	8.68	7.01	6.18	5.68	5.34	4.90	4.60	4.40
O^+—O_2	33.7	23.4	13.7	8.45	6.80	6.00	5.51	5.19	4.76	4.47	4.28
O^+—N[d]	23.3	16.3	11.8	9.23	8.09	7.36	6.80	6.34	5.60	5.02	4.56
O^+—O[c]	33.6	29.6	27.0	24.9	23.8	23.1	22.6	22.2	21.6	21.1	20.8

[a]From Ref. 33 combined with Tang–Tonnies results in Eq. (8). [b]Ref. 34. [c]Ref. 10. [d]Ref. 11.

Once the interaction potential has been defined, the details of calculating the transport collision integrals have been described in our prior publications,[4,10,29] and only a brief outline follows here. The scattering phase shifts resulting from collisions of the particles can be calculated from the interaction potentials either semiclassically[10,30] or quantum mechanically.[31] For the reduced masses and temperature range considered in this work, quantum mechanical effects are very small, and the semiclassical approach is sufficient. The transport cross sections $Q_i(E)$ for a range of collision energies E are obtained from weighted summations of the computed phase shifts and, in accordance with Chapman–Enskog theory,[1,2] the collision integrals as a function of temperature are then determined by numerical integration of an average of the cross sections over a Boltzmann distribution,

$$\Omega_{n,s}(T) = \frac{2(n+1)}{\pi(s+1)![2n+1-(-1)^n](\kappa T)^{s+2}} \times \int_0^\infty e^{-E/\kappa T} E^{s+1} Q_n(E)\,\mathrm{d}E \tag{7}$$

The scaling factor that accounts for the normalization to scattering of hard spheres has been set to unity in Eq. (7).

For interactions between an atom or molecule and its ion, resonant charge transfer can significantly increase the size of the momentum-transfer cross section Q_1, which directly affects the diffusion collision integrals $\Omega_{1,s}$. The viscosity cross section Q_2 and the resulting collision integral are unaffected by charge transfer, because of symmetry considerations.[32] At high temperature the resulting momentum-transfer cross section is approximately equal to two times the resonant charge-exchange value.[32] However, at lower temperatures both the charge exchange and isotropic cross sections must be accounted for when computing the momentum transfer cross section.[32] Following the work of Murphy,[14] we combine the charge–exchange and Tang–Toennies contributions to the diffusion collision integral for all interactions between an atom or molecule and its ion using the empirical mixing rule

$$\Omega_{1,s} = \sqrt{\left[\Omega_{1,s}^{ex}\right]^2 + \left[\Omega_{1,s}^{TT}\right]^2} \tag{8}$$

where $\Omega_{1,s}^{ex}$ is the collision integral computed by integrating twice the resonant charge–exchange cross section as discussed above and $\Omega_{1,s}^{TT}$ is the collision integral computed from the Tang–Toennies potential.

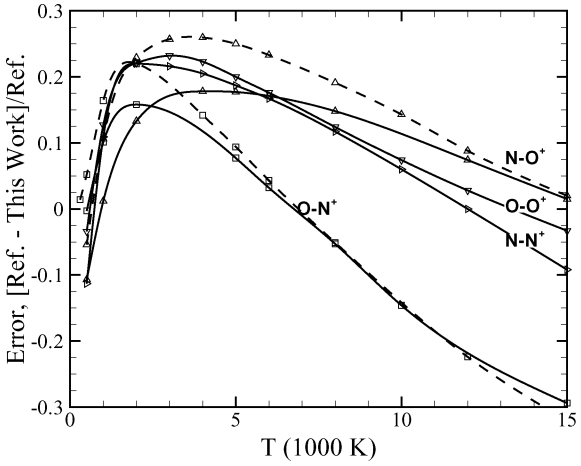

Fig. 1 Relative error of the collision integrals $\Omega_{1,1}$ (– – – curves) and $\Omega_{2,2}$ (—— curves) computed in this work compared with more accurate ab initio determinations: N—O$^+$ and O—N$^+$ from Ref. 11 and N—N$^+$ and O—O$^+$ ($\Omega_{2,2}$ only) from Ref. 10.

Results and Discussion

Tables 2 and 3 show the computed diffusion and viscosity collision integrals for 25 ion-neutral interactions of nitrogen and oxygen. With the exception of the entries with footnotes, all reported values were obtained by integration of the Tang–Toennies potential as already described. In Fig. 1 we compare the results obtained from the present Tang–Toennies formulation with "reference" values previously determined from ab initio computations of the four atom–atomic-ion interactions.[10,11] Only $\Omega_{2,2}$ is shown for the N^+—N and O^+—O interactions, because $\Omega_{1,1}$ would be affected by resonant charge transfer for these cases. These comparisons all show that the predicted viscosity and diffusion collision integrals agree with the benchmark results to within ±25% over the range from room temperature to 12,000 K. Above 12,000 K the population of molecules

Table 3 Viscosity collision integrals $\Omega_{2,2}$ (Å^2) as a function of temperature (K) for selected ion–neutral interactions

Temperature, K	300	500	1,000	2,000	3,000	4,000	5,000	6,000	8,000	10,000	12,000
NO^+—N_2	33.7	25.1	15.8	10.6	8.97	8.16	7.69	7.36	6.90	6.67	6.36
NO^+—O_2	31.8	23.5	14.9	10.2	8.66	7.91	7.47	7.16	6.72	6.50	6.20
NO^+—NO	32.7	24.4	15.6	10.6	8.99	8.20	7.74	7.42	6.97	6.76	6.45
NO^+—N	25.4	18.8	12.3	8.97	7.91	7.37	7.04	6.81	6.46	6.27	6.04
NO^+—O	22.0	15.8	10.4	7.89	7.07	6.62	6.34	6.13	5.82	5.66	5.41
N_2^+—N_2	33.7	25.3	16.8	12.1	10.7	9.93	9.50	9.19	8.74	8.41	8.20
N_2^+—O_2	32.7	24.6	16.1	11.7	10.4	9.67	9.26	8.97	8.54	8.22	8.02
N_2^+—NO	32.7	24.6	16.5	12,1	10.7	10.0	9.59	9.30	8.86	8.54	8.35
N_2^+—N	26.1	19.5	13.6	10.7	9.78	9.26	8.96	8.74	8.40	8.14	7.98
N_2^+—O	22.2	16.5	11.8	9.60	8.85	8.42	8.15	7.95	7.62	7.37	7.21
O_2^+—N_2	31.4	24.1	15.4	9.56	7.59	6.64	6.10	5.74	5.26	4.96	4.73
O_2^+—O_2	31.0	23.6	14.7	9.09	7.27	6.38	5.88	5.55	5.10	4.81	4.59
O_2^+—NO	30.2	23.4	15.1	9.47	7.57	6.65	6.12	5.77	5.31	5.01	4.79
O_2^+—N	23.8	18.2	11.6	7.64	6.37	5.74	5.37	5.13	4.78	4.55	4.38
O_2^+—O	20.8	15.4	9.66	6.54	5.57	5.07	4.78	4.57	4.28	4.08	3.92
N^+—NO	31.2	23.7	15.2	9.97	8.28	7.45	6.98	6.66	6.21	5.92	5.70
N^+—N_2	31.9	23.8	15.3	10.0	8.27	7.42	6.93	6.60	6.14	5.84	5.62
N^+—O_2	30.4	22.9	14.6	9.55	7.96	7.18	6.72	6.41	5.98	5.69	5.47
N^+—N[a]	20.4	16.4	13.3	10.5	9.15	8.33	7.74	7.26	6.48	5.84	5.31
N^+—O[b]	21.8	15.4	11.1	8.61	7.52	6.75	6.13	5.64	4.90	4.37	3.98
O^+—NO	30.5	23.5	15.1	9.61	7.81	6.93	6.43	6.10	5.64	5.35	5.13
O^+—N_2	31.2	23.9	15.3	9.68	7.83	6.92	6.40	6.06	5.59	5.28	5.06
O^+—O_2	31.8	23.6	14.7	9.26	7.52	6.68	6.19	5.87	5.43	5.14	4.92
O^+—N[b]	23.6	16.6	11.8	9.07	7.99	7.37	6.94	6.60	6.02	5.53	5.11
O^+—O[a]	20.5	14.8	11.1	8.72	7.64	6.94	6.39	5.95	5.26	4.75	4.36

[a]Ref. 10. [b]Ref. 11.

is very low, and any remaining ion–neutral interactions are primarily between atoms and atomic ions, where accurate ab initio results are known.

Additional analysis was required for molecular interactions involving resonant charge exchange. The diffusion collision integral for N_2^+—N_2 was evaluated by direct numerical integration of the momentum transfer cross sections tabulated by Phelps.[34] For the interactions NO^+—NO and O_2^+—O_2, charge–exchange cross sections were taken from Moran et al.,[33] and the final diffusion collision integrals were computed by combining the charge-transfer and Tang–Toennies results using the mixing rule, Eq. (8), discussed in the preceding section. As an indication of the accuracy of this approach, Eq. (8) was also used to calculate $\Omega_{1,1}$ for the N_2^+—N_2 interactions and compared with the Phelps[34] data as a reference. The difference was found to be less than 15% over the range from 2000–12,000 K. There were insufficient data on the low-energy charge–exchange cross sections to extend the comparison to lower temperatures.

The number of significant figures presented in Tables 2 and 3 is one greater than justified by the error sources just discussed; however, there is a strong correlation of errors in $Q_i(E)$ for nearby values of the interaction energy E and similarly for the collision integrals $\Omega_{i,j}(T)$ for nearby values of T. Hence, the data as tabulated are useful for applications involving local interpolation or fitting.

The already defined collision integral ratios B^* and C^* were also computed in this work, but the results are not shown in the tables. To the accuracy warranted by the data, B^* was found to be nearly constant, $B^* = 1.1$, for temperatures above approximately 1000 K and varied between 1.3 and 1.2 at lower temperatures for all ion–neutral pairs. This is consistent with predictions based on polarizability, which would lead to a value of $B^* = 1.25$ at the low temperature limit. C^* was found to range from approximately 0.75 at low temperature (less than 1000 K) to a high temperature limit of 0.95 for all ion–neutral pairs.

Finally, it is interesting to compare the collision integrals computed using the current methodology with those obtained by using a pure Langevin (polarization) potential. The comparison for the case of N—O^+ is shown in Fig. 2, which shows the relative errors of the current (Tang–Toennies) formulation and a pure polarization potential as compared to the ab initio data in Ref. 11. Collision integrals for the polarization potential are computed using the formulas presented in Ref. 13. It can be observed that for this case the simple Langevin potential model gives reasonable results even at the higher temperatures, although the Tang–Toennies results appear to be slightly more accurate, particularly for the viscosity collision integrals. This result is surprising, particularly because the form of the polarization potential differs markedly from an exponential at short separation distances and this region is the dominant contributor to the high-temperature results. The comparison is similar for the O—N^+ interaction (not shown).

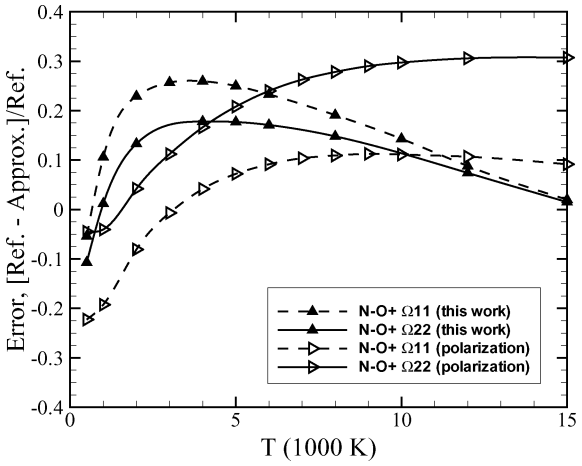

Fig. 2 Relative error of the collision integrals computed in this work and those computed using a polarization potential compared with more accurate ab initio determinations[11] for N—O^+.

The results in Fig. 2 indicate that use of the polarization potential might be a reasonable assumption when no other data are available. However, we believe that the Tang–Toennies potential method presented here is an improvement for several reasons. First, unlike the polarization model the Tang–Toennies model has the correct theoretical form at short range. This would permit flexibility in the computation of the short-range parameters (V_0 and β) that govern the high-temperature collision integrals. For example, experimental or ab initio short-range data could readily be incorporated into the methodology when available, significantly improving the fidelity of the results. Also, because the Tang–Toennies model accounts for

dispersion forces and higher-order polarizability effects the treatment of long-range forces should also be superior to that of the polarization potential. This would be particularly true for highly polarizable ions, such as N_2^+. Finally, the agreement shown in Fig. 2 between the polarizability and ab initio results might not be achievable for other neutral–ion systems. In fact, Capitelli[35] has shown that using the polarizability potential can result in a significant overprediction of collision integrals in many neutral–ion systems.

Conclusions

A Tang–Toennies-based model is presented for the computation of ion–neutral collision integrals in reacting air. The use of a Tang–Toennies effective potential provides a physically reasonable model for ion–neutral interactions and avoids the use of simplistic or piecewise potentials. The calibration comparisons with more accurate data indicates that the results obtained are within ±25% over the critical range from 300–12,000 K. The methodology presented requires only a few physical parameters that are readily available in the literature for many species. Therefore this methodology can be extended to other ion–neutral interactions for which accurate potentials are not available.

Tables are presented for 25 ion–neutral interactions between oxygen and nitrogen species. These tables can be regarded as interim results pending better determinations. In addition to experiments and ab initio theoretical calculations, we suggest that the predictions might be improved by a better determination of the potential well and/or the repulsive wall. The short range parameters V_0 and β of the Tang–Toennies model are sensitive to the well constants, and the representations used in Eqs. (4) and (6) were based on empirical fits that might not be best for all ion–neutral interactions.

Acknowledgments

Support was provided by Contract NAS2-99092 from NASA to the ELORET Corporation. The advice of James Stallcop (NASA Ames Research Center) regarding the effective potential as well as techniques for calculating the long-range dispersion coefficients is acknowledged and appreciated.

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