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High Temperature Transport Properties of Dilute Nitrogen Atoms[1]

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Calculations of the transport coefficients viscosity and thermal conductivity and the diffusion collision cross section of nitrogen atoms have been carried out as a function of temperature. The dilute gas transport properties of nitrogen atoms depend only on the interactions between two nitrogen atoms along various electronic potential energy curves. The results presented here include contributions from 16 potential energy curves, four of which dissociate to two ground-state nitrogen atoms with the others also dissociating to two nitrogen atoms, at least one of which is in an excited electronic state. Thirteen of the potential energy curves are represented by the Hulburt–Hirschfeleder potential which is the best general purpose atom–atom potential. This potential depends only on the experimental spectroscopic constants and not on any adjustable parameters. Where spectroscopic constants are unavailable, fits of the Hulburt–Hirschfelder potential to *ab initio* quantum mechanical results are used for two states and a fit of the Morse potential is used for the other state. The results presented here should be especially useful under conditions where nitrogen atoms are at high temperatures, such as during Space Shuttle re-entry.

KEY WORDS: nitrogen; thermal conductivity; transport properties; viscosity.

1. INTRODUCTION

The theromophysical properties of nitrogen (N) atoms are important in air at high temperatures, in the chemistry and physics of the upper

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atmosphere [1], and in a variety of applications [2–4]. Experimental thermophysical property data are sparse [5–9] for N atoms because of the high temperatures required. Thus, theory is usually relied on to calculate thermophysical properties of N atoms. In this paper, the viscosity, thermal conductivity, and diffusion of N atoms are obtained using the kinetic theory of gases. The transport properties are the viscosity [10], η;

$$\eta(\mu\mathrm{Pa}\cdot \mathrm{s}) = 2.669\frac{\sqrt{MT}}{\sigma^2\Omega^{(2,2)*}} \tag{1}$$

the diffusion coefficient [10], D;

$$D(m^2\cdot s^{-1}) = 2.594\times 10^{-7}\frac{\sqrt{T^3/M}}{p\sigma^2\Omega^{(1,1)*}}, \tag{2}$$

the translational contribution to the thermal conductivity [10], λ_{tr};

$$\lambda_{\mathrm{tr}}(W\cdot m^{-1}\cdot K^{-1}) = 8.322\times 10^{-2}\frac{\sqrt{T/M}}{\sigma^2\Omega^{(2,2)*}} \tag{3}$$

and the internal contribution to the thermal conductivity [11,12], λ_{int};

$$\lambda_{\mathrm{int}}(W\cdot m^{-1}\cdot K^{-1}) = 1.203\mathrm{x}10^4\frac{pD}{T}(C_p - 20.786) \tag{4}$$

where T is the temperature in K, M is the molecular weight in $\mathrm{g}\cdot\mathrm{mol}^{-1}$, p is the pressure in bar, C_p is the molar heat capacity at constant pressure in $\mathrm{J}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}$, and $\sigma^2\Omega^{(1,1)*}$ and $\sigma^2\Omega^{(2,2)*}$ are the diffusion and viscosity collision integrals in $10^{-20}\,\mathrm{m}^2$, respectively, determined by the interaction between two N atoms as they "follow" a particular electronic potential energy curve. Equation (4) is valid subject to the assumption that the transport of internal energy is due only to a diffusion mechanism [11, 12].

2. INTERACTION POTENTIALS

When two ground-state (^{4}S) N atoms interact, they can follow [13] any of four electronic potential–energy curves corresponding to an N_2 molecule; the electronic states are the ground $X^1\Sigma_g^+$ state and the excited $A^3\Sigma_u^+$, $^5\Sigma_g^+$, and $^7\Sigma_u^+$ states. Spectroscopic information [14] and quantum mechanical calculations [15, 16] indicate that these four states are all bound although the latter two states have very small well depths (dissociation energies).

At high temperatures, one or both of the interacting N atoms may be in an excited state and these should be included in the calculations. The excited states of N included in these calculations are the ^{2}D and

Table I. Electronic States of N_2

State[a]	Potential Used	Dissociated N Atoms[b]
$X^1\Sigma_g^+$	HH	$^4S + {}^4S$
$A^3\Sigma_u^+$	HH	$^4S + {}^4S$
$B^3\Pi_g$	HH	$^4S + {}^2D$
$W^3\Delta_u$	HH	$^4S + {}^2D$
$B'^3\Sigma_u^-$	HH	$^4S + {}^2P$
$a'^1\Sigma_u^-$	HH	$^2D + {}^2D$
$a^1\Pi_g$	HH	$^2D + {}^2D$
$w^1\Delta_u$	HH	$^2D + {}^2D$
$^5\Sigma_g^+$	KN	$^4S + {}^4S$
$^7\Sigma_u^+$	FS	$^4S + {}^4S$
$G^3\Delta_g$	HH	$^4S + {}^2D$
$C^3\Pi_u$	HH	$^4S + {}^2D$
$yE^3\Sigma_g^+$	MP	$^4S + {}^2D$
$C'^3\Pi_u$	HH	$^4S + {}^2D$
$b'^1\Sigma_u^+$	HH	$^2D + {}^2P$
$H^3\Phi_u$	HH	$^2D + {}^2D$

[a] The states are listed in order of the bottom of the potential energy well for each state relative to the bottom of the potential energy well for the ground state; usually denoted as T_e by spectroscopists [14].
[b] The dissociation products are mostly from Ref. 26.

^2P states. Sixteen bound electronic states of N_2 that dissociate to one or more ground or excited atomic states are included in the calculations and listed in Table I. Thirteen of the electronic states have been represented by the Hulburt–Hirschfelder (HH) potential (see column 2 of Table I). This potential has been discussed in detail elsewhere [17–20]. It depends only on the experimental vibrational–rotational spectroscopic constants for the given electronic state and not on any adjustable parameters. It is the best available general purpose potential for representing atom–atom interactions with an attractive minimum in the potential [21–25], and it usually gives excellent agreement with experimental Rydberg–Klein–Rees (RKR) potential energy curves for atom–atom and atom–ion interactions [21, 23, 26–28]. It also often reproduces the local maxima sometimes found at larger interatomic separations [29–33].

The theoretical electronic potential–energy curves of Krauss and Neumann [15] for the $^5\Sigma_g^+$ state and of Ferrante and Stwalley [16] for the $^7\Sigma_u^+$ state were carefully fit with the HH potential. This is described in detail in Ref. 20. The resulting fits are referred to as KN and FS, respectively, in Table I. Since some spectroscopic constants are not known for the $E^3\Sigma_g^+$ state, it was fit with a Morse potential (MP in Table I). More details about the potentials and the spectroscopic parameters for the 16 states are given in Ref. [34]. These particular states have been chosen since good quality potential-energy curves are available, leading to good quality transport cross sections.

2.1. Averaged Collision Integrals

When two or more states contribute to the collision integrals, the contributions from each state must be averaged. Using the notation of Ref. [35], the averaged values are given by

$$\sum_k \alpha_{ij,k}\sigma_{ij,k}^2\Omega_{ij,k}^{(\ell,s)*},$$

where k represents the sum over the electronic states and i and j represent the two interacting species (N atoms in this case). The symbol $\alpha_{ij,k}$ represents the probability associated with each electronic state which is the degeneracy of each state divided by the total degeneracy of the electronic states that dissociate to the same atoms [35–37], which is designated as $\omega_{ij,k}$. As an example, for the singlet, triplet, quintet, and septet states that dissociate to ground state N atoms, the degeneracies are 1, 3, 5, and 7, respectively, and the $\omega_{ij,k}$ are 1/16, 3/16, 5/16, and 7/16, respectively.

However, the probability must also account for the fact that atoms in excited electronic states are less likely than ground-state atoms at a particular temperature. Here, we assume the interacting atoms are at local equilibrium which is reasonable since the transport properties are near-equilibrium properties, i.e., the gradients in composition, energy, and momentum are small. The temperature-dependent probability of occupation of the states is given by the Boltzmann factor and

$$\alpha_{ij,k} = \omega_{ij,k}e^{-E_{ij}/kT},$$

where E_{ij} is the energy of separated atoms i and j, relative to the ground state ^{4}S atoms as the zero of energy.

For potential–energy curves associated with one or two excited state atoms, the list of states in Table I is incomplete because the required spectroscopic information and/or theoretical calculations for the state are not available. For instance, when ^{4}S and ^{2}D nitrogen atoms collide, they can follow the following six pairs of potential energy curves [30, 36]; $^3\Sigma_{\mathrm{g,u}}$, $^5\Sigma_{\mathrm{g,u}}$, $^3\Pi_{\mathrm{g,u}}$, $^5\Pi_{\mathrm{g,u}}$, $^3\Delta_{\mathrm{g,u}}$, and $^5\Delta_{\mathrm{g,u}}$ where the symbols g and u represent gerade and ungerade, respectively, and denote the symmetry of the wave function upon interchanging the nuclei. Each Σ state has a degeneracy of 3 or 5, and each Π and Δ state has a degeneracy of 6 or 10. The total degeneracy is 80. Thus, the ${}^3\Sigma_g$ state has a probability of 3/80, the ${}^5\Delta_u$ state has a probability of 10/80, etc. Table I shows that only 6 of the 12 states are included in this calculation due to the lack of the required information. The cross section for each state is multiplied by its appropriate probability for these calculations. When information becomes available to permit good quality calculations for the six missing states, their contribution to the collision integrals can be included without redoing these calculations. A similar approach is used for the other potential energy curves associated with N atoms in various states.

The degeneracy averaged viscosity collision integrals, $\sigma^2\Omega^{(2,2)*}$, are given in the second column of Table II as a function of temperature. The results are similar to those obtained previously [20]. For instance, when only the four molecular states dissociating to ground state atoms were considered, the viscosity collision integral at 10,000 K was 3.8943, about 2% less than the present result. This is reasonable. The viscosity collision integral is related to the probability of a collision, and this should increase as atoms in excited states are allowed to collide. However, since the populations of the excited states are small (recall that few atoms are electronically excited even at 10,000 K [38]), the number of collisions increases by only a small amount at 10,000 K. The results show that, at 1000 K, the percent increase is smaller and, at 20,000 K, the percent increase is larger.

Again, there are other interactions that dissociate to the atomic states included in these calculations but they have not been included since information required to calculate good quality collision cross sections is not available. Although inclusion of these states would increase the cross sections, the increase will be small. Thus, the usual conclusion [39] that the consideration of excited states only changes the transport properties by a small amount is demonstrated by these quantitative calculations.

2.2. Excitation Exchange Collision Integrals

Calculation of the diffusion coefficients is more complicated. When the dissociation products are in different states, e.g., dissociation to N atoms in the ^{4}S and ^{2}D states, it is actually the cross section for excitation exchange that determines $\sigma^2\Omega^{(\ell,s)*}$ for odd ℓ [35], e.g., the diffusion collision integral, $\sigma^2\Omega^{(1,1)*}$. The excitation exchange process is for the reaction,

$$N + N^* \rightarrow N^* + N.$$

Table II. Thermophysical Properties of N Atoms

T(K)	$\sigma^2\Omega^{(2,2)*}(10^{-20}\ \mathrm{m}^2)$	$\eta(\mu\mathrm{Pa}\cdot\mathrm{s})$	$\lambda_{\mathrm{tr}}(\mathrm{mW}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1})$
1000	7.2745	43.42	96.68
2000	5.9962	74.49	165.9
3000	5.3798	101.7	226.4
4000	4.9817	126.8	282.3
5000	4.7270	149.4	332.7
6000	4.4956	172.1	383.2
7000	4.3338	192.8	429.3
8000	4.2064	212.4	472.9
9000	4.1021	231.0	514.3
10000	4.0126	248.9	554.2
11000	3.9354	266.2	592.7
12000	3.8679	282.9	629.8
13000	3.8059	299.2	666.2
14000	3.7492	315.2	701.8
15000	3.6975	330.8	736.6
16000	3.6502	346.1	770.7
17000	3.6058	361.2	804.2
18000	3.5645	375.9	837.1
19000	3.5269	390.3	869.2
20000	3.4884	404.9	901.6

The third column of Table I shows that excitation exchange dominates the diffusion process for half the interaction potential energy curves included in our calculations.

This excitation exchange process is discussed in some detail for interacting N atoms in Ref. 36. Crude approximations to the g,u potential energy curves were obtained using the Heitler–London approximation, and excitation exchange cross sections for the ^{4}S + ^{2}D and the ^{4}S + ^{2}P interactions were given, respectively, in Tables I and II of Ref. 36 at 10,000 K.

Results for the degeneracy averaged diffusion collision integrals calculated here (without including the Boltzmann factor) at 10,000 K are shown for the five different dissociation products in the second column of Table III, and the results for the excitation cross sections from Ref. 36 are shown in the third column (they did not calculate an excitation cross section for the ^{2}D + ^{2}P dissociation products). The comparison is not quite fair since Nyeland and Mason [36] included (crudely) a contribution from all states and this work includes only half the states. However, almost all of the individual collision integrals calculated here lie between 1 and 10 (most between 3 and 7). If reliable potentials were available for the six states that dissociate to ^{4}S + ^{2}D atoms and that have not been included in these

Table III. Diffusion Collision Integrals for N Atoms, $\sigma^2\Omega^{(1,1)*}$ (10^{-20} m^2), at 10,000 K

Dissociation Products	This Work	Excitation Exchange	"Adjusted"
^{4}S + ^{4}S	3.4586		
^{4}S + ^{2}D	1.3498	8.12	3.2723
^{4}S + ^{2}P	0.4010	14.78	6.4161
^{2}D + ^{2}D	0.5475		
^{2}D + ^{2}P	0.0527		

calculations, the diffusion collision integrals would be similar to those we did calculate. Thus, in the fourth column of Table III, the collision integrals for the states included in this work that undergo excitation exchange have been adjusted as if they included all the states, e.g., the total degeneracy of the eight molecular states of N_2 that dissociate to ^{4}S + ^{2}P atoms is 48. However, only the $B'^3\Sigma_u^-$ state has been included in this calculation with a degeneracy averaged contribution of 3/48. Thus, in the fourth column of Table III, the degeneracy averaged diffusion cross section has been multiplied by 48/3 to force the fractional degeneracies to add to unity. A similar calculation has been done for the ^{4}S + ^{2}D cross sections. A comparison between the third and fourth columns in Table III is more reasonable.

3. TRANSPORT PROPERTIES

The viscosity and the translational contribution to the thermal conductivity are given in the third and fourth columns of Table II, respectively. As expected from the discussion of the collision integrals, the results are very similar to those obtained when only the states dissociating to ground-state atoms were considered [20] since the contribution of excited states is limited. The differences are insignificant at 1000 K and 10% at 20,000 K, as expected, since excited state contributions are larger at high temperatures, e.g., Table IV shows the contribution of each state to the total degeneracy averaged viscosity collision integral at three temperatures. The contribution from molecular states that dissociate to one or two excited states atoms is small even at 10,000 K and becomes significant only at higher temperatures.

4. DISCUSSION AND CONCLUSIONS

Yun and Mason [40] also considered states that dissociate to ground-state atoms, representing the singlet and triplet states with a potential of

Table IV. Contribution to the Degeneracy Averaged Viscosity Collision Integral, $\sigma^2\Omega^{(2,2)*}$ (10^{-20} m^2), of N Atoms as a Function of Temperature

State	1000 K	10,000 K	20,000 K
$X^1\Sigma_g^+$	0.6468	0.3430	0.2819
$A^3\Sigma_u^+$	1.6399	0.8702	0.6273
$B^3\Pi_g$		0.0214	0.0662
$W^3\Delta_u$		0.0279	0.0819
$B'^3\Sigma_u^-$		0.0062	0.0369
$a'^1\Sigma_u^-$		0.0003	0.0036
$a^1\Pi_g$		0.0005	0.0060
$w^1\Delta_u$		0.0005	0.0062
$^5\Sigma_g^+$	1.5992	0.6507	0.5501
$^7\Sigma_u^+$	3.3886	2.0507	1.6960
$G^3\Delta_g$		0.0205	0.0495
$C^3\Pi_u$		0.0075	0.0258
$E^3\Sigma_g^+$		0.0030	0.0106
$C'^3\Pi_u$		0.0094	0.0360
$b'^1\Sigma_u^+$		0.0001	0.0010
$H^3\Phi_u$		0.0009	0.0094

Contributions to the viscosity collision integral less than 10^{-24} m^2 are not included in the table.

the form $-C/r^n$ where r is the separation of the atoms and C and n are adjustable parameters, the quintet state with the exponential-6 potential, and the septet state with the exponential-repulsive potential. Their results, using somewhat less accurate potentials than those used in Ref. 20 and here, were somewhat lower than the results in Ref. 20 (see Table VII) and 3% lower than these results at 1000 K and 13% lower at 15,000 K. Capitelli and Devoto [37] also considered states that dissociate to ground-state atoms. They represented the singlet, triplet, and quintet states with the Morse potential and the septet state with the exponential-repulsive potential. Their results, also involving less accurate potentials that those used in Ref. 20 and here, were similar to the results in Ref. 20 (see Table VII) and are 2% higher than these results at 5000 K and 13% lower at 20,000 K. The small differences at low temperatures are due to the different representation of potentials for the molecular states that dissociate to ground-state atoms. The larger differences at higher temperatures are due to the inclusion of molecular states that dissociate to excited state atoms considered in this work and not in previous work.

Thus, there is reason to believe that there is little error in these results for molecular states that dissociate to ground-state atoms. However, for

Table V. Degeneracy Averaged Diffusion Collision Integrals for N Atoms

T(K)	$\sigma^2\Omega^{(1,1)*}$ (10^{-20} m^2)	T(K)	$\sigma^2\Omega^{(1,1)*}$ (10^{-20} m^2)
1000	6.4956	11000	3.4693
2000	5.4000	12000	3.3973
3000	4.8599	13000	3.3313
4000	4.5060	14000	3.2707
5000	4.2484	15000	3.2164
6000	4.0486	16000	3.1664
7000	3.8874	17000	3.1202
8000	3.7563	18000	3.0775
9000	3.6468	19000	3.0373
10000	3.5520	20000	2.9997

molecular states that dissociate to one or two excited state atoms, accurate potentials are available for less than half the states. At 20,000 K, the contributions of the five sets of dissociation products to the viscosity cross section are 3.1553 (^{4}S + ^{4}S), 0.2700 (^{4}S + ^{2}D), 0.0369 (^{4}S + ^{2}P), 0.0252 (^{2}D + ^{2}D), and 0.0010 (^{2}D + ^{2}P). Thus, the states dissociating to ^{4}S + ^{2}D atoms provide over 80% of the contribution from excited states, leading to results presented here that are roughly 10% higher than previous results [20, 36, 37]. Since only half the states have been considered in this ^{4}S + ^{2}D calculation, it is reasonable to expect that the true viscosity collision integral at 20,000 K is about 10% higher than the result reported here with smaller discrepancies at lower temperatures.

The degeneracy averaged diffusion integral obtained at 10,000 K from the second column in Table III is 3.5520, the result obtained using the charge exchange cross sections in the third column is 4.2049, and the result obtained using the adjusted diffusion cross section in the fourth column is 3.7688. The ^{2}D + ^{2}P dissociation products have been excluded since the population of these dissociation products is very small and an excitation exchange cross section is not available for these states. The differences are significant, a 10% difference between the last two results which is a first approximation to the effect of charge exchange. Of course, if fewer molecular states dissociate to atoms in different states, the charge exchange effect is smaller and *vice versa*.

Thus, the excitation exchange cross sections should be used to calculate diffusion coefficients and, since they have only been calculated at 10,000 K using crude potentials, the diffusion coefficients are not calculated here. The diffusion collision integrals calculated without including excitation exchange are given in Table V but they would be larger if excitation exchange was included. Diffusion coefficients calculated using these collision integrals are an upper limit for the contribution to diffusion from these states.

The contribution of excitation exchange to the transport collision integrals calculated here is relatively small at these temperatures but it is not small for λ_{int}. Since the assumption has been made that the interactions are adiabatic, i.e., they occur along only a single potential energy curve, the only mechanism available for energy exchange is the excitation exchange process. Nyeland and Mason [36] considered the effect of excitation exchange on λ_{int} due to the $^4S + {}^2D$ and $^4S + {}^2P$ interactions between nitrogen atoms and found that λ is increased by a factor of 1.16 relative to λ_{tr} (compared to an incorrect increase by a factor of 1.40 if the erroneously small diffusion cross sections are used in place of the excitation exchange cross sections); the difference is 17%.

Nyeland and Mason showed [36] that, using an impact parameter approximation, it is the difference in energy between the g,u potentials that determines the excitation exchange cross section. Table I shows that excellent potentials are available for the g,u pairs $W^3\Delta_u$; $G^3\Delta_g$ and $B^3\Pi_g$; $C^3\Pi_u$. We are currently doing calculations on these pairs to determine how well the results agree with those of Nyeland and Mason [36] and to determine if the approximations they made that required them to make only a single Heitler–London calculation are reasonable.

Many other interactions are required to determine the transport properties of air. This is discussed in detail in Ref. 41.

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