Collision Integrals for the Transport Properties of Dissociating Air at High Temperatures

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Collision Integrals for the Transport Properties of Dissociating Air at High Temperatures

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Collision integrals (transport cross sections) for atomic and molecular interactions of importance in high-temperature air are calculated based on accurate force laws which have recently become available. The tabulations include the collision integrals for diffusion, viscosity, and thermal conductivity, and the collision integral ratios A^*, B^*, and C^* needed for mixture calculations, and cover the range from 1000° to 15 000°K for the major interactions N–N, O–O, N–O, N–N_2, O–O_2, O–N_2, N_2–N_2, O_2–O_2, and N_2–O_2. Average potential energy functions, but no collision integrals, are given for the minor interactions O–NO, O_2–NO, N_2–NO, and NO–NO. The calculations all refer to atoms and molecules in their ground states only. Calculational errors are estimated to be about 5% over the temperature range, but may occasionally rise as high as 10%. The relative magnitudes of the average collision integrals are discussed briefly for their bearing on the qualitative behavior of the corresponding gas mixtures, and on the assessment of the errors involved in some approximations commonly used in calculations of transport properties of air.

I. INTRODUCTION

KNOWLEDGE of the transport properties of air at high temperatures is of obvious importance in many applications. Since experimental data in this range are very difficult to obtain, recent efforts have been largely theoretical, and a number of calculations have been reported in the past few years.[1] Unfortunately, the different calculations do not agree at all well among themselves, the spread between the lowest and highest viscosities, for instance, being more than a factor of 2 at 8000°K.[1,2] The cause of this is the crude models of the intermolecular forces which have been used.[1] For several years work has been carried out in this laboratory on the various intermolecular forces among the species present in dissociating air at high temperatures. The availability of these results[3-6] makes possible the use of more refined interaction models, so that the uncertainty in the transport properties can be reduced from a factor of 2 to something on the order of 10 or 20%.

The purpose of the present paper is to tabulate collision integrals (transport cross sections) for dissociating air based on the more accurate intermolecular force results. We give direct tabulations of the collision integrals $\bar{\Omega}^{(1,1)}$ (diffusion) and $\bar{\Omega}^{(2,2)}$ (viscosity and thermal conductivity), and the collision integral ratios A^*, B^*, and C^* (mixtures) for the major interactions N–N, O–O, N–O, N–N_2, O–O_2, O–N_2, N_2–N_2, O_2–O_2, and N_2–O_2. We also present results for the minor interactions O–NO, O_2–NO, N_2–NO, and NO–NO, but no direct tabulations, since the collision integrals for these interactions can be obtained with sufficient accuracy as averages of the tabulated collision integrals.

The tabulations cover the range from 1000° to 15 000°K. Below 1000°K the transport properties of air are already known with reasonable accuracy, and above 15 000°K we do not have sufficiently accurate intermolecular force information.

The tabulations refer to atoms and molecules in their ground states only. Above about 8000°K there will be appreciable ionization and electronic excitation, and the tabulations are no longer *sufficient* for a complete calculation of transport properties. They are still *necessary*, however, as long as collisions between ground-state atoms and molecules have any influence on the transport properties.

II. CALCULATION PROCEDURE

The details of our calculation procedure are outlined in a previous paper on the transport properties of dissociating hydrogen.[7] When two atoms can interact along any one of a number of potential-energy curves, it is necessary to calculate the collision integrals for each curve separately and

[1] For a brief review and commentary on recent calculations see W. L. Bade, E. A. Mason, and K. S. Yun [J. Am. Rocket Soc. 31, 1151 (1961)].
[2] P. E. Liley, *Thermodynamic and Transport Properties of Gases, Liquids, and Solids* (American Society of Mechanical Engineers, New York, 1959), p. 40.
[3] J. T. Vanderslice, E. A. Mason, and E R. Lippincott, J. Chem. Phys. 30, 129 (1959).
[4] J. T. Vanderslice, E. A. Mason, and W. G. Maisch, J. Chem. Phys. 31, 738 (1959).
[5] J. T. Vanderslice, E. A. Mason, and W. G. Maisch, J. Chem. Phys. 32, 515 (1960).
[6] J. T. Vanderslice, E. A. Mason, W. G. Maisch, and E. R. Lippincott, J. Chem. Phys. 33, 614 (1960).
[7] J. T. Vanderslice, S. Weissman, E. A. Mason, and R. J. Fallon, Phys. Fluids 5, 155 (1962).

then average with a suitable statistical weight factor for each curve.[8] For nonspherical, nonpolar molecules the procedure of first averaging the potential over all orientations and then calculating the collision integrals for the resulting single effective-potential curve is usually assumed to be adequate. The calculation of collision integrals for a given potential usually involves some compromise in choosing an algebraic function which fits the potential fairly well in the important range of intermolecular separation distances, and for which calculations of collision integrals are already available (since these require extensive numerical integration). It may be necessary to fit a given potential piecemeal in order to cover an extended temperature range.[9] For the purpose of estimating what range of molecular separations is most important in determining a given transport property in a given temperature range, the method of Hirschfelder and Eliason[10] is useful.

The algebraic functions which we have used for the potential energy $\varphi(r)$ are the exp–6 potential,[11]

$$\varphi(r) = \epsilon\left(1 - \frac{6}{\alpha}\right)^{-1}\left[\frac{6}{\alpha}e^{\alpha(1-r/r_m)} - \left(\frac{r_m}{r}\right)^6\right], \quad (1)$$

where α, ϵ, and r_m are constants; the 12–6–3 potential,[12,13]

$$\varphi(r) = 4\epsilon_0\left[\left(\frac{\sigma_0}{r}\right)^{12} - \left(\frac{\sigma_0}{r}\right)^6 + \delta\left(\frac{\sigma_0}{r}\right)^3\right], \quad (2)$$

where ϵ_0, σ_0, and δ are constants; the 8–4 potential,[14]

$$\varphi(r) = \epsilon\left[\left(\frac{r_m}{r}\right)^8 - 2\left(\frac{r_m}{r}\right)^4\right], \quad (3)$$

where ϵ and r_m are constants; the exponential repulsive potential,[15]

$$\varphi(r) = \varphi_0 e^{-ar}, \quad (4)$$

where φ_0 and a are positive constants; and the inverse power attractive and repulsive potentials,[16]

$$\varphi(r) = \pm K/r^s, \quad (5)$$

where K and s are positive constants. The only potential among the foregoing for which the existing tabulations were not adequate was the 8–4 potential, for which Hassé and Cook tabulated only functions corresponding to $\bar{\Omega}^{(1,1)}$ and $\bar{\Omega}^{(2,2)}$. The values of $\bar{\Omega}^{(1,2)}$ and $\bar{\Omega}^{(1,3)}$ needed to calculate the mixture functions B^* and C^* were therefore generated as needed by means of numerical differentiation from the recursion formula

$$\bar{\Omega}^{(l,n+1)} = \bar{\Omega}^{(l,n)} + [T/(n+2)](d\bar{\Omega}^{(l,n)}/dT). \quad (6)$$

Table I summarizes the potential forms we have used in calculating the collision integrals.

The various atom-molecule and molecule-molecule interactions are obtained in a first approximation as the sums of the interactions between the constituent atoms, averaged over all molecular orientations.[3,4] Thus the N–N_2, O–O_2, O–N_2, O_2–O_2, and N_2–O_2 interactions listed in Table I have been built up out of the following atom-atom interactions[3–5]:

$$\varphi(\mathrm{N}\cdots\mathrm{N}) = 153.9\,e^{-2.753r}\ \text{ev}, \quad 1.3\ \text{A} < r < 3.2\ \text{A}, \quad (7)$$

$$\varphi(\mathrm{N}\cdots\mathrm{O}) = 161\,e^{-2.654r}\ \text{ev}, \quad 1.8\ \text{A} < r < 2.8\ \text{A}, \quad (8)$$

$$\varphi(\mathrm{O}\cdots\mathrm{O}) = 812\,e^{-3.565r}\ \text{ev}, \quad 1.8\ \text{A} < r < 2.5\ \text{A}, \quad (9)$$

where r is the atom-atom distance. Of these interactions that for O–O_2 is the most uncertain, because at certain favorable orientations and close distances of approach, a strong valence attraction can set in which corresponds to the reaction $\mathrm{O} + \mathrm{O}_2 = \mathrm{O}_3$.

The minor interactions O–NO, O_2–NO, N_2–NO, and NO–NO have also been calculated from Eqs. (7)–(9). The results can be expressed as follows:

$$\text{O–NO:}\ \langle\varphi(R)\rangle = 795\,e^{-2.992R}\ \text{ev}, \quad 1.9\ \text{A} < R < 2.7\ \text{A}; \quad (10)$$

$$\text{O}_2\text{–NO:}\ \langle\varphi(R)\rangle = 2003\,e^{-2.938R}\ \text{ev}, \quad 1.9\ \text{A} < R < 2.7\ \text{A}; \quad (11)$$

$$\text{N}_2\text{–NO:}\ \langle\varphi(R)\rangle = 751\,e^{-2.575R}\ \text{ev}, \quad 1.5\ \text{A} < R < 3.1\ \text{A}; \quad (12)$$

$$\text{NO–NO:}\ \langle\varphi(R)\rangle = 1160\,e^{-2.734R}\ \text{ev}, \quad 1.8\ \text{A} < R < 2.9\ \text{A}; \quad (13)$$

where the pointed brackets indicate an average over orientations, and R is the distance between the

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[10] J. O. Hirschfelder and M. A. Eliason, Ann. N. Y. Acad. Sci. **67**, 451 (1957).
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[16] T. Kihara, M. H. Taylor, and J. O. Hirschfelder, Phys. Fluids **3**, 715 (1960).

TABLE I. Potential-energy functions used for calculation of collision integrals.

Interaction	Potential energy, ev (r in A)	Range	Ref.
N–N, $X^1\Sigma_g^+$	$-98.09/r^{6.38}$	all temps.	a
$^3\Sigma_u^+$	$-80.35/r^{6.88}$	all temps.	a
$^5\Sigma_g^+$	(exp–6): $\alpha = 12$, $\epsilon = 0.0477$ ev, $r_m = 1.60$ A	all temps.	a
$^7\Sigma_u^+$	$317.8\, e^{-2.753r}$	all temps.	b
O–O, $X^3\Sigma_g^-$	$-194.5/r^{7.83}$	all temps.	c
$^1\Delta_g$	$-123.4/r^{7.89}$	all temps.	c
$^1\Sigma_g^+$	$-141.6/r^{8.64}$	all temps.	c
$^1\Sigma_u^-$	(exp–6): $\alpha = 12$, $\epsilon = 0.6655$ ev, $r_m = 1.597$ A	all temps.	c
$A^3\Sigma_u^+$	$-480.6/r^{11.46}$	low temp.	d
	(exp–6): $\alpha = 12$, $\epsilon = 0.8239$ ev, $r_m = 1.518$ A	high temp.	d
$^3\Delta_u$	$-560.8/r^{9.44}$	low temp.	c
	(exp–6): $\alpha = 12$, $\epsilon = 0.9157$ ev, $r_m = 1.480$ A	high temp.	c
$^3\Pi_u$, $^1\Pi_u$	$339\, e^{-3.570r}$	all temps.	e
$^5\Pi_g$ $^3\Pi_g$, $^1\Pi_g$	$717\, e^{-3.565r}$	all temps.	e
$^5\Sigma_u^-$, $^3\Sigma_u^+$	$1057\, e^{-3.567r}$	all temps.	e
$^1\Sigma_g^+$	$1358\, e^{-3.570r}$	all temps.	e
$^5\Delta_g$, $^5\Sigma_g^+$	$1433\, e^{-3.565r}$	all temps.	e
$^5\Sigma_g^+$	$2114\, e^{-3.567r}$	all temps.	e
$^5\Pi_u$	$2455\, e^{-3.567r}$	all temps.	e
N–O, $X^2\Pi$	$-105.9/r^{7.00}$	all temps.	f
$^4\Pi$	(12–6–3): $\delta = 0.134$, $\epsilon_0 = 3.095$ ev, $\sigma_0 = 1.208$ A	low temp.	f
	$-301.0/r^{10.27}$	high temp.	f
$^2\Sigma$	(8–4): $\epsilon = 0.26$ ev, $r_m = 2.0$ A	all temps.	f
$^4\Sigma$	$430\, e^{-3.570r}$	all temps.	g
$^6\Sigma$	$138\, e^{-2.492r}$	all temps.	g
$^6\Pi$	$351\, e^{-2.866r}$	all temps.	g
$N-N_2$	$387.8\, e^{-2.733R}$	all temps.	b
$O-O_2$	$2162\, e^{-3.479R}$	all temps.	c
$O-N_2$	$357\, e^{2.603R}$	all temps.	g
N_2-N_2	(exp–6): $\alpha = 17$, $\epsilon = 0.00872$ ev, $R_m = 4.011$ A	low temp.	h
	(exp–6): $\alpha = 15$, $\epsilon = 0.01036$ ev, $R_m = 4.046$ A	intermed. temp.	h
	$595/R^{7.27}$	high temp.	h
O_2-O_2	(exp–6): $\alpha = 17$, $\epsilon = 0.0114$ ev, $R_m = 3.726$ A	low temp.	g
	$5580\, e^{-3.355R}$	high temp.	e
N_2-O_2	(exp–6): $\alpha = 17$, $\epsilon = 0.0100$ ev, $R_m = 3.861$ A	low temp.	e
	$762\, e^{-2.524R}$	high temp.	e

[a] Curve-fitting of results reported in reference 3.
[b] Reference 3.
[c] Curve-fitting of results reported in reference 5.
[d] Curve-fitting of results reported in reference 6.
[e] Reference 5.
[f] Curve-fitting of results reported in reference 4.
[g] Reference 4.
[h] Reference 9.

centers of mass of the interacting molecules. The method of averaging has been given previously in connection with the nitrogen interactions,[3] and the extension to heteronuclear molecules needed to obtain Eqs. (10)–(13) is straightforward. For a molecule AB interacting with a molecule CD, there are four terms, one for each of the atom-atom interactions AC, AD, BC, and BD. When the atom-atom interactions are described by an exponential repulsion of the form of Eq. (4), the average molecule-molecule interaction can be written as

$$\langle\varphi(R)\rangle = \varphi_{0AC}e^{-a_{AC}R}(a_{AC}^3 R\, d_A\, d_C)^{-1}$$
$$\cdot[(a_{AC}R + 2)\sinh(a_{AC}\, d_A)\sinh(a_{AC}\, d_C)$$
$$- (a_{AC}\, d_A)\cosh(a_{AC}\, d_A)\sinh(a_{AC}\, d_C)$$
$$- (a_{AC}\, d_C)\cosh(a_{AC}\, d_C)\sinh(a_{AC}\, d_A)]$$
$$+ \text{(3 similar terms for AD, BC, and BD)}, \quad (14)$$

where φ_{0AC} and a_{AC} are the parameters for the AC interaction, d_A is the distance from the center of mass of molecule AB to atom A, and d_C the distance from the center of mass of molecule CD to atom C. The atom-molecule interaction A–CD can be obtained from Eq. (14) by dropping the two terms involving atom B and setting $d_A = 0$.

The range of validity of $\langle\varphi(R)\rangle$ obviously depends on the range of validity of the component atom-atom potentials. This range can be estimated by an averaging procedure[3] whose extension to heteronuclear molecules gives

$$\langle R\rangle = \tfrac{1}{4}r_{AC}[1 + \tfrac{1}{3}(d_A/r_{AC})^2 + \tfrac{1}{3}(d_C/r_{AC})^2]$$
$$+ \text{(3 similar terms for AD, BC, and BD)}. \quad (15)$$

The range of validity of an atom-molecule interaction A–CD can be obtained from Eq. (15) by replacing B by A, and setting d_A and d_B to zero.

The potentials given in Eqs. (10)–(13) are approximately equal to the geometric means of some of those listed in Table I. Thus the O–NO potential of Eq. (10) is approximately equal to the mean of the O–N_2 and O–O_2 potentials, the O_2–NO potential to the mean of the O_2–N_2 and O_2–O_2 potentials, the N_2–NO potential to the mean of the N_2–N_2 and N_2–O_2 potentials, and the NO–NO potential to the mean of the N_2–NO and O_2–NO potentials.

III. RESULTS

The collision integrals obtained from the potentials listed in Table I are given in Tables II–X. The calculational errors introduced by inaccurate curve-fitting, due to incomplete data on the potential-energy curves and to the occasional necessity to fit a given curve piecemeal, amount generally to about 5% over most of the temperature range, and may occasionally rise as high as about 10%.[9] In this regard the N–N interaction corresponding to the $^5\Sigma_g^+$ state of N_2 is the worst offender, since the experimental information really consists of only two points on the interaction curve, obtained from predissociation data.[3] An estimate of the maximum error to be expected from this source can be obtained by replacing the exp-6 potential used for this interaction by the cruder rigid-sphere potential. The resulting change in the weighted average collision integrals for N–N interactions is less than 10%.

The foregoing error estimates do not take into account the possibility of systematic errors in the potential curves themselves which formed our starting material. Should any of these potentials be found to be sensibly in error, the error will have been propagated directly into the corresponding collision integrals, although in a weakened fashion. The over-all error will be first reduced by a factor of about 2 or 3 in passing from the potential function to the corresponding collision integral, and then further reduced by an amount depending on the statistical weight factor for that potential.

The collision integrals in Tables II–X are given in units of $A^2(10^{-16}\ cm^2)$; their physical significance is that they would have the value σ^2 if the potentials had corresponded to rigid spheres of diameter σ. In other words, the only difference from a conventional definition of a cross section is the lack of a factor of π. Thus the viscosity and self-diffusion coefficients of a pure gas are given in terms of the tabulated collision integrals by the expressions[17]

$$\eta(\text{g/cm-sec}) = (26.693 \times 10^{-6})(MT)^{\frac{1}{2}}/\langle\bar{\Omega}^{(2,2)}\rangle, \quad (16)$$

TABLE II. Collision integrals for N–N interactions.

T °K	$\langle\bar{\Omega}^{(1,1)}\rangle$, A²	$\langle\bar{\Omega}^{(2,2)}\rangle$, A²	A^*	B^*	C^*
1 000	6.235	7.039	1.129	1.144	0.890
1 500	5.548	6.292	1.134	1.144	0.888
2 000	5.106	5.812	1.138	1.144	0.885
2 500	4.786	5.464	1.142	1.143	0.881
3 000	4.538	5.193	1.144	1.143	0.879
3 500	4.336	4.972	1.147	1.142	0.876
4 000	4.166	4.786	1.149	1.141	0.873
4 500	4.022	4.628	1.151	1.141	0.870
5 000	3.895	4.488	1.152	1.141	0.868
5 500	3.783	4.365	1.154	1.141	0.866
6 000	3.683	4.254	1.155	1.142	0.864
6 500	3.592	4.154	1.156	1.141	0.862
7 000	3.509	4.062	1.158	1.141	0.860
7 500	3.435	3.979	1.159	1.142	0.858
8 000	3.365	3.902	1.160	1.141	0.857
8 500	3.300	3.830	1.161	1.141	0.855
9 000	3.240	3.764	1.162	1.141	0.854
9 500	3.184	3.701	1.162	1.142	0.853
10 000	3.131	3.643	1.163	1.141	0.852
11 000	3.035	3.536	1.165	1.141	0.849
12 000	2.949	3.440	1.166	1.142	0.847
13 000	2.872	3.353	1.168	1.142	0.845
14 000	2.801	3.274	1.169	1.142	0.843
15 000	2.737	3.202	1.170	1.142	0.842

TABLE III. Collision integrals for C–O interactions.

T °K	$\langle\bar{\Omega}^{(1,1)}\rangle$, A²	$\langle\bar{\Omega}^{(2,2)}\rangle$, A²	A^*	B^*	C^*
1 000	6.193	7.182	1.160	1.141	0.925
1 500	5.643	6.564	1.163	1.156	0.922
2 000	5.271	6.139	1.165	1.160	0.916
2 500	4.981	5.821	1.169	1.163	0.913
3 000	4.746	5.567	1.173	1.168	0.911
3 500	4.551	5.355	1.177	1.172	0.908
4 000	4.386	5.174	1.180	1.180	0.907
4 500	4.243	5.016	1.182	1.184	0.905
5 000	4.117	4.876	1.184	1.185	0.903
5 500	4.007	4.752	1.186	1.182	0.900
6 000	3.905	4.640	1.188	1.182	0.899
6 500	3.813	4.537	1.190	1.181	0.898
7 000	3.727	4.438	1.191	1.182	0.897
7 500	3.648	4.352	1.193	1.181	0.897
8 000	3.575	4.271	1.195	1.182	0.897
8 500	3.509	4.194	1.195	1.182	0.896
9 000	3.442	4.118	1.196	1.181	0.895
9 500	3.389	4.058	1.197	1.182	0.895
10 000	3.335	3.996	1.198	1.181	0.895
11 000	3.236	3.883	1.200	1.182	0.894
12 000	3.148	3.782	1.201	1.184	0.894
13 000	3.068	3.692	1.203	1.184	0.893
14 000	2.996	3.609	1.205	1.186	0.893
15 000	2.931	3.534	1.206	1.186	0.893

TABLE IV. Collision integrals for N–O interactions.

T °K	$\langle\bar{\Omega}^{(1,1)}\rangle$, A²	$\langle\bar{\Omega}^{(2,2)}\rangle$, A²	A^*	B^*	C^*
1 000	7.156	8.418	1.176	1.192	0.877
1 500	6.139	7.227	1.177	1.184	0.881
2 000	5.518	6.494	1.177	1.178	0.884
2 500	5.088	5.984	1.176	1.158	0.886
3 000	4.767	5.606	1.176	1.138	0.887
3 500	4.531	5.310	1.172	1.127	0.887
4 000	4.347	5.075	1.168	1.126	0.886
4 500	4.190	4.899	1.169	1.128	0.885
5 000	4.054	4.745	1.170	1.129	0.885
5 500	3.935	4.610	1.172	1.130	0.884
6 000	3.828	4.490	1.173	1.129	0.884
6 500	3.731	4.381	1.174	1.133	0.883
7 000	3.644	4.282	1.175	1.133	0.882
7 500	3.564	4.191	1.176	1.132	0.882
8 000	3.491	4.108	1.177	1.134	0.881
8 500	3.423	4.031	1.178	1.134	0.881
9 000	3.360	3.959	1.178	1.135	0.880
9 500	3.301	3.892	1.179	1.136	0.879
10 000	3.246	3.829	1.180	1.137	0.879
11 000	3.145	3.714	1.181	1.137	0.878
12 000	3.055	3.611	1.182	1.137	0.876
13 000	2.974	3.518	1.183	1.139	0.875
14 000	2.900	3.433	1.184	1.139	0.874
15 000	2.832	3.356	1.185	1.142	0.874

[17] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), Chap. 8.

TABLE V. Collision integrals for N–N_2 interactions.

T °K	$\langle\bar{\Omega}^{(1,1)}\rangle$, A²	$\langle\bar{\Omega}^{(2,2)}\rangle$, A²	A^*	B^*	C^*
1 000	8.214	9.824	1.196	1.157	0.916
1 500	7.396	8.897	1.203	1.165	0.911
2 000	6.842	8.272	1.209	1.171	0.908
2 500	6.427	7.802	1.214	1.176	0.905
3 000	6.098	7.427	1.218	1.180	0.903
3 500	5.827	7.115	1.221	1.184	0.900
4 000	5.596	6.850	1.224	1.187	0.899
4 500	5.397	6.622	1.227	1.190	0.897
5 000	5.223	6.419	1.229	1.193	0.895
5 500	5.067	6.238	1.231	1.196	0.893
6 000	4.927	6.080	1.234	1.198	0.892
6 500	4.800	5.933	1.236	1.201	0.891
7 000	4.684	5.799	1.238	1.203	0.889
7 500	4.577	5.676	1.240	1.205	0.888
8 000	4.479	5.558	1.241	1.207	0.887
8 500	4.387	5.453	1.243	1.209	0.886
9 000	4.301	5.355	1.245	1.210	0.885
9 500	4.221	5.259	1.246	1.212	0.883
10 000	4.146	5.170	1.247	1.214	0.882
11 000	4.008	5.010	1.250	1.217	0.881
12 000	3.884	4.867	1.253	1.220	0.879
13 000	3.772	4.734	1.255	1.223	0.877
14 000	3.669	4.612	1.257	1.225	0.875
15 000	3.575	4.501	1.259	1.228	0.874

TABLE VI. Collision integrals for O–O_2 interactions.

T °K	$\langle\bar{\Omega}^{(1,1)}\rangle$, A²	$\langle\bar{\Omega}^{(2,2)}\rangle$, A²	A^*	B^*	C^*
1 000	7.509	8.778	1.169	1.131	0.931
1 500	6.890	8.093	1.175	1.137	0.928
2 000	6.467	7.624	1.179	1.141	0.925
2 500	6.148	7.269	1.182	1.144	0.924
3 000	5.894	6.985	1.185	1.147	0.922
3 500	5.683	6.749	1.188	1.149	0.921
4 000	5.503	6.548	1.190	1.152	0.919
4 500	5.347	6.374	1.192	1.154	0.918
5 000	5.210	6.219	1.194	1.156	0.917
5 500	5.087	6.082	1.196	1.157	0.916
6 000	4.976	5.956	1.197	1.159	0.915
6 500	4.875	5.843	1.199	1.160	0.914
7 000	4.783	5.739	1.200	1.162	0.913
7 500	4.697	5.642	1.201	1.163	0.913
8 000	4.618	5.553	1.202	1.164	0.912
8 500	4.545	5.470	1.204	1.166	0.911
9 000	4.476	5.392	1.205	1.167	0.911
9 500	4.411	5.319	1.206	1.168	0.910
10 000	4.350	5.250	1.207	1.169	0.909
11 000	4.238	5.123	1.209	1.171	0.908
12 000	4.137	5.008	1.210	1.173	0.907
13 000	4.045	4.903	1.212	1.175	0.906
14 000	3.961	4.808	1.214	1.176	0.905
15 000	3.884	4.719	1.215	1.178	0.904

TABLE VII. Collision integrals for O–N_2 interactions.

T °K	$\langle\bar{\Omega}^{(1,1)}\rangle$, A²	$\langle\bar{\Omega}^{(2,2)}\rangle$, A²	A^*	B^*	C^*
1 000	8.867	10.61	1.197	1.159	0.915
1 500	7.975	9.610	1.205	1.167	0.911
2 000	7.371	8.926	1.211	1.173	0.907
2 500	6.919	8.406	1.215	1.178	0.904
3 000	6.561	7.998	1.219	1.182	0.902
3 500	6.265	7.659	1.223	1.186	0.899
4 000	6.015	7.374	1.226	1.189	0.897
4 500	5.798	7.126	1.229	1.193	0.895
5 000	5.605	6.899	1.231	1.195	0.894
5 500	5.439	6.712	1.234	1.198	0.892
6 000	5.287	6.535	1.236	1.201	0.891
6 500	5.149	6.374	1.238	1.203	0.889
7 000	5.023	6.228	1.240	1.205	0.888
7 500	4.907	6.094	1.242	1.207	0.886
8 000	4.799	5.971	1.244	1.209	0.885
8 500	4.700	5.851	1.245	1.211	0.884
9 000	4.607	5.744	1.247	1.213	0.883
9 500	4.520	5.641	1.248	1.215	0.882
10 000	4.438	5.548	1.250	1.217	0.881
11 000	4.288	5.369	1.252	1.220	0.879
12 000	4.153	5.213	1.255	1.223	0.877
13 000	4.032	5.068	1.257	1.226	0.875
14 000	3.920	4.940	1.260	1.229	0.873
15 000	3.818	4.818	1.262	1.231	0.872

TABLE VIII. Collision integrals for N_2–N_2 interactions.

T °K	$\langle\bar{\Omega}^{(1,1)}\rangle$, A²	$\langle\bar{\Omega}^{(2,2)}\rangle$, A²	A^*	B^*	C^*
1 000	10.07	11.17	1.110	1.096	0.948
1 500	9.365	10.54	1.126	1.107	0.941
2 000	8.794	10.01	1.139	1.115	0.937
2 500	8.297	9.520	1.147	1.120	0.933
3 000	7.845	9.071	1.156	1.125	0.930
3 500	7.450	8.697	1.167	1.130	0.927
4 000	7.137	8.350	1.170	1.133	0.925
4 500	6.844	8.100	1.184	1.138	0.922
5 000	6.599	7.804	1.183	1.142	0.920
5 500	6.369	7.592	1.192	1.144	0.918
6 000	6.187	7.394	1.195	1.147	0.916
6 500	6.023	7.209	1.197	1.150	0.914
7 000	5.863	7.035	1.200	1.152	0.912
7 500	5.708	6.873	1.204	1.152	0.913
8 000	5.595	6.721	1.201	1.155	0.910
8 500	5.480	6.611	1.206	1.155	0.911
9 000	5.373	6.474	1.205	1.158	0.908
9 500	5.284	6.375	1.206	1.158	0.908
10 000	5.199	6.279	1.208	1.158	0.909
11 000	5.069	6.097	1.203	1.158	0.908
12 000	4.907	5.952	1.213	1.157	0.909
13 000	4.810	5.815	1.209	1.158	0.909
14 000	4.727	5.705	1.207	1.158	0.908
15 000	4.630	5.599	1.209	1.158	0.909

TABLE IX. Collision integrals for O_2–O_2 interactions.

T °K	$\langle\bar{\Omega}^{(1,1)}\rangle$, A²	$\langle\bar{\Omega}^{(2,2)}\rangle$, A²	A^*	B^*	C^*
1 000	8.875	9.896	1.115	1.099	0.939
1 500	8.381	9.470	1.130	1.109	0.935
2 000	8.044	9.226	1.147	1.117	0.933
2 500	7.810	9.020	1.155	1.124	0.931
3 000	7.608	8.840	1.162	1.128	0.930
3 500	7.437	8.672	1.166	1.131	0.928
4 000	7.279	8.516	1.170	1.134	0.927
4 500	7.128	8.368	1.174	1.137	0.927
5 000	7.012	8.246	1.176	1.139	0.926
5 500	6.868	8.090	1.178	1.141	0.925
6 000	6.748	7.963	1.180	1.143	0.924
6 500	6.622	7.827	1.182	1.144	0.923
7 000	6.505	7.702	1.184	1.145	0.923
7 500	6.402	7.586	1.185	1.146	0.922
8 000	6.306	7.479	1.186	1.147	0.922
8 500	6.217	7.379	1.187	1.148	0.921
9 000	6.132	7.285	1.188	1.149	0.921
9 500	6.053	7.197	1.189	1.150	0.920
10 000	5.978	7.114	1.190	1.151	0.920
11 000	5.844	6.960	1.191	1.153	0.919
12 000	5.718	6.822	1.193	1.154	0.918
13 000	5.608	6.696	1.194	1.156	0.917
14 000	5.506	6.580	1.195	1.157	0.916
15 000	5.412	6.473	1.196	1.158	0.916

TABLE X. Collision integrals for N_2–O_2 interactions.

T °K	$\langle\bar{\Omega}^{(1,1)}\rangle$, A²	$\langle\bar{\Omega}^{(2,2)}\rangle$, A²	A^*	B^*	C^*
1 000	9.258	10.48	1.132	1.113	0.933
1 500	8.709	10.05	1.154	1.128	0.924
2 000	8.371	9.802	1.171	1.140	0.919
2 500	8.134	9.598	1.180	1.151	0.915
3 000	7.889	9.412	1.193	1.159	0.911
3 500	7.705	9.246	1.200	1.165	0.909
4 000	7.535	9.080	1.205	1.169	0.908
4 500	7.375	8.916	1.209	1.173	0.906
5 000	7.233	8.766	1.212	1.176	0.905
5 500	7.095	8.620	1.215	1.178	0.904
6 000	6.971	8.484	1.217	1.180	0.902
6 500	6.853	8.354	1.219	1.182	0.901
7 000	6.742	8.232	1.221	1.184	0.900
7 500	6.631	8.110	1.223	1.186	0.899
8 000	6.529	7.991	1.224	1.188	0.898
8 500	6.405	7.853	1.226	1.189	0.897
9 000	6.295	7.724	1.227	1.191	0.896
9 500	6.186	7.603	1.229	1.192	0.896
10 000	6.088	7.488	1.230	1.194	0.895
11 000	5.907	7.278	1.232	1.196	0.893
12 000	5.745	7.089	1.234	1.199	0.892
13 000	5.597	6.918	1.236	1.201	0.890
14 000	5.460	6.760	1.238	1.203	0.889
15 000	5.335	6.615	1.240	1.205	0.888

TABLE XI. Fractions of average collision integrals contributed by individual states (same order as in Table I.)

State		Statistical weight	Temperature, 10^3 °K $\langle\bar{\Omega}^{(1,1)}\rangle$ 1	5	10	15	$\langle\bar{\Omega}^{(2,2)}\rangle$ 1	5	10	15
N-N,	$^1\Sigma_g^+$	1/16 = 0.062	0.106	0.103	0.103	0.103	0.095	0.090	0.089	0.089
	$^3\Sigma_u^+$	3/16 = 0.188	0.246	0.246	0.251	0.255	0.225	0.221	0.223	0.225
	$^5\Sigma_g^+$	5/16 = 0.312	0.108	0.109	0.115	0.120	0.106	0.108	0.116	0.121
	$^7\Sigma_u^+$	7/16 = 0.438	0.540	0.542	0.531	0.522	0.574	0.581	0.572	0.564
O-O, X	$^3\Sigma_g^-$	3/81 = 0.037	0.045	0.045	0.046	0.048	0.042	0.041	0.041	0.042
	$^1\Delta_g$	2/81 = 0.025	0.026	0.026	0.027	0.028	0.024	0.024	0.025	0.025
	$^1\Sigma_g^+$	1/81 = 0.012	0.011	0.011	0.012	0.012	0.010	0.010	0.011	0.011
	$^1\Sigma_u^-$	1/81 = 0.012	0.015	0.011	0.009	0.009	0.013	0.010	0.009	0.008
A	$^3\Sigma_u^+$	3/81 = 0.037	0.027	0.030	0.028	0.026	0.025	0.028	0.026	0.024
	$^3\Delta_u$	6/81 = 0.074	0.077	0.067	0.056	0.052	0.073	0.062	0.052	0.048
	$^3\Pi_u$	6/81 = 0.074	0.056	0.053	0.051	0.050	0.058	0.055	0.054	0.053
	$^1\Pi_u$	2/81 = 0.025	0.019	0.018	0.017	0.017	0.019	0.018	0.018	0.018
	$^5\Pi_g$	10/81 = 0.123	0.112	0.111	0.111	0.110	0.114	0.114	0.114	0.114
	$^3\Pi_g$	6/81 = 0.074	0.067	0.066	0.067	0.066	0.069	0.068	0.068	0.068
	$^1\Pi_g$	2/81 = 0.025	0.022	0.022	0.022	0.022	0.023	0.023	0.023	0.023
	$^5\Sigma_u^-$	5/81 = 0.062	0.061	0.062	0.062	0.063	0.062	0.063	0.064	0.064
	$^3\Sigma_u^+$	3/81 = 0.037	0.037	0.039	0.037	0.038	0.037	0.038	0.038	0.038
	$^1\Sigma_g^+$	1/81 = 0.012	0.013	0.013	0.013	0.013	0.013	0.013	0.013	0.013
	$^5\Delta_g$	10/81 = 0.123	0.131	0.134	0.137	0.138	0.132	0.136	0.137	0.140
	$^5\Sigma_g^+$	5/81 = 0.062	0.066	0.067	0.069	0.069	0.067	0.068	0.070	0.070
	$^5\Sigma_g^+$	5/81 = 0.062	0.071	0.074	0.076	0.078	0.071	0.075	0.077	0.078
	$^5\Pi_u$	10/81 = 0.123	0.146	0.153	0.159	0.161	0.147	0.154	0.159	0.162
N-O, X	$^2\Pi$	4/36 = 0.111	0.131	0.146	0.150	0.153	0.116	0.130	0.132	0.134
	$^4\Pi$	8/36 = 0.222	0.192	0.162	0.176	0.187	0.201	0.143	0.155	0.163
	$^2\Sigma$	2/36 = 0.056	0.086	0.046	0.042	0.043	0.080	0.044	0.040	0.041
	$^4\Sigma$	4/36 = 0.111	0.077	0.087	0.086	0.085	0.078	0.091	0.091	0.091
	$^6\Sigma$	6/36 = 0.167	0.174	0.181	0.172	0.164	0.180	0.195	0.186	0.179
	$^6\Pi$	12/36 = 0.333	0.339	0.378	0.374	0.368	0.345	0.398	0.396	0.392

$$D(\mathrm{cm}^2/\mathrm{sec}) = (2.6280 \times 10^{-3})T^{\frac{1}{2}}/pM^{\frac{1}{2}}\langle\bar{\Omega}^{(1,1)}\rangle, \quad (17)$$

where M is the molecular weight in g/mole, T the temperature in °K, and p the pressure in atm. The pointed brackets around the collision integrals signify that these represent averages over several potential-energy curves (atom-atom interactions), or over all orientations (atom-molecule and molecule-molecule interactions).

The dimensionless ratios A^*, B^*, and C^* are defined as

$$A^* = \langle\bar{\Omega}^{(2,2)}\rangle/\langle\bar{\Omega}^{(1,1)}\rangle,$$
$$B^* = [5\langle\bar{\Omega}^{(1,2)}\rangle - 4\langle\bar{\Omega}^{(1,3)}\rangle]/\langle\bar{\Omega}^{(1,1)}\rangle, \quad (18)$$
$$C^* = \langle\bar{\Omega}^{(1,2)}\rangle/\langle\bar{\Omega}^{(1,1)}\rangle,$$

which are equal to unity for rigid spheres.

Collision integrals for the minor interactions O–NO, O_2–NO, N_2–NO, and NO–NO given by Eqs. (10)–(13) have not been tabulated. They can be calculated directly from Eqs. (10)–(13) with the aid of Monchick's collision integral tabulations[15] for the exponential repulsions, or can be calculated approximately as averages of the present tabulations; i.e., O–NO as the average of O–N_2 and O–O_2, O_2–NO as the average of O_2–N_2 and O_2–O_2, N_2–NO as the average of N_2–N_2 and N_2–O_2, and NO–NO as the average of N_2–NO and O_2–NO. This approximation should be adequate for most applications involving air.

IV. DISCUSSION

It is interesting to see how the individual potential-energy curves corresponding to the different spectroscopic states of N_2, O_2, and NO contribute to the average collision integrals. The fractional contribution of a curve is a combination of its *a priori* statistical weight and the magnitude of its collision integral. Table XI gives some fractions of average collision integrals contributed by the various states, as compared to the statistical weights. Several "anomalies" are apparent. For instance, the $^1\Sigma_g^+$ state of N_2 contributes almost as much as the $^5\Sigma_g^+$ state, although it has only one-fifth the statistical weight.

The relative magnitudes of the average collision integrals are of interest in that they help to determine the qualitative behavior of the corresponding gas mixtures. For instance, below 3000°K the N–O collision integrals are larger than either the N–N or the O–O integrals, rather than intermediate in value as one would have expected if these atoms

had been valence-saturated. This "anomaly" would tend to make the viscosity of a mixture of N and O atoms low, and might possibly even produce a minimum.[18] Of course, this atomic-gas mixture is unlikely at such low temperatures, and above 5000°K the N–O collision integrals do lie between those for N–N and O–O. We further find that the N–N_2 collision integrals lie smoothly between those for N–N and N_2–N_2; those for O–O_2 lie smoothly between those for O–O and O_2–O_2; and those for O–N_2 lie smoothly between those for O–O and N_2–N_2. Such relations are what one expects for ordinary valence-saturated atoms and molecules, but there is no reason to expect them to hold when valence forces between atoms with unpaired electrons are involved. Hydrogen, for instance, does not follow such relations; the collision integrals for H–H are abnormally large compared to those for H–H_2 and H_2–H_2.[7] The significance of this rather unexpected regularity for most of the nitrogen and oxygen collision integrals is that nitrogen-oxygen mixtures of various degrees of dissociation will behave qualitatively like mixtures of ordinary valence-saturated gases. This fact is of some importance because it pertains to the accuracy of several approximate formulas[19–21] which are very convenient for the rapid calculation of transport properties of mixtures, especially multicomponent ones, but which were originally devised largely on the basis of results for valence-saturated gases.

Inspection of the relative magnitudes of the tabulated collision integrals also permits assessment of the errors involved in some approximations which have been used in calculations of the transport properties of air. In the "atom-molecule" binary approximation, N_2, O_2, NO are lumped together as molecules, and N, O as atoms. The correct composition of equilibrium air is used, but only three interactions are considered, atom-atom, atom-molecule, and molecule-molecule, which are usually taken to be the same as the corresponding nitrogen interactions. We see from Tables II–X that deviations from this simple assumption are less than 20% (usually much less); on recalling that there is four times as much nitrogen as oxygen in air, we see that the simple "atom-molecule" binary approximation is unlikely to be in error by as much as 5%.[1] This simple approximation is very useful because it avoids the enormously complicated calculations necessary for mixtures with as many as five components. The accuracy of a more elaborate "ternary" approximation[22] should be even better. In this approximation air at successively higher temperatures is considered to consist in turn of $N_2 + O_2$, $N_2 + O_2 + O$, $N_2 + N + O$, and finally $N + O$. In other words, the oxygen is assumed to be fully dissociated before the nitrogen dissociation begins, so that air never consists of more than three species. In the light of the present results this can be seen to be an excellent approximation, provided that the concentrations of atoms and molecules are accurately calculated for equilibrium air without simplifying assumptions.

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