PHYSICAL REVIEW A VOLUME 44, NUMBER 6 15 SEPTEMBER 1991

Viscosity of high-temperature iodine

Steve H. Kang and Joseph A. Kunc
Department of Aerospace Engineering and Department of Physics, University of Southern California,
Los Angeles, California 90089-1191

(Received 6 March 1991)

The viscosity coefficient of iodine in the temperature range $500 \leq T \leq 3000$ K is calculated. Because of the low dissociation energy of the I_2 molecules, the dissociation degree of the gas increases quickly with temperature, and $I+I_2$ and $I+I$ collisions must be taken into account in calculations of viscosity at temperatures greater than 1000°. Several possible channels for atom-atom interaction are considered, and the resulting collision integrals are averaged over all the important channels. It is also shown that the rigid-sphere model is inaccurate in predictions of the viscosity. The approach of the present work is general and can be used for other diatomic gases with arbitrary dissociation degree.

INTRODUCTION

Because a significant dissociation of iodine can be achieved at low temperature, it is a particularly attractive candidate for theoretical and experimental studies of chemical nonequilibrium in continuous flows. However, viscosity and other transport coefficients of iodine have neither been measured nor calculated. Therefore, in this paper, we calculate the viscosity of high-temperature ($500 \leq T \leq 3000$ K) iodine in equilibrium by considering the fact that the gas dissociation degree, and subsequently the frequency of atom-atom and atom-molecule collisions, increases rapidly with temperature.

Viscosity of gas with particles of mass m at temperature T can be calculated as [1,2]

$$\eta = \frac{5}{16}\frac{(\pi m k T)^{1/2}}{\pi\sigma^2\Omega^{(2,2)*}} , \tag{1}$$

where k is Boltzmann's constant and σ is the particle collision diameter. The so-called collision integral $\Omega^{(2,2)*}$ is a dimensionless quantity that depends on the temperature and on the force law (for the interparticle potential) through the collision scattering angle χ. The scattering angle is averaged over all possible initial impact velocities g and all possible impact parameters b to produce the collision integral which has the following form when inelastic collisions are neglected:

$$\Omega^{(2,2)*} = \sigma^{-2}\int_0^\infty \gamma^7 \exp(-\gamma^2)\,d\gamma \int_0^\infty (1-\cos^2\chi)\,b\,db , \tag{2}$$

where $\gamma^2 = mg^2/4kT$. If inelastic collisions are taken into account, the expression for the viscosity is the same as Eq. (1), but the collision integral for viscosity is more complicated [3]:

$$\Omega^{(2,2)*} = (2\pi)^{-1}(\sigma Q_{\text{int}})^{-2}\sum_{i,j,k,l}\exp(-\varepsilon_i-\varepsilon_j) \times \int_0^\infty \gamma^3\exp(-\gamma^2)\,d\gamma \int_0^\pi \int_0^{2\pi} \sin\chi\left[\gamma^4(1-\cos^2\chi)+\tfrac{1}{3}(\Delta\varepsilon)^2-\tfrac{1}{2}(\Delta\varepsilon)^2\sin^2\chi\right] \times I_{ij}^{kl}(g,\chi,\phi)\,d\chi\,d\phi , \tag{3}$$

where the internal partition function for the target particle is

$$Q_{\text{int}} = \sum_i \exp(-\varepsilon_i) , \tag{4}$$

and where the internal quantum states of the colliding particles are denoted by the subscripts i, j, k, l, and $\varepsilon_i \equiv E_i/kT$, with E_i being the energy of the ith quantum state. A binary collision of two particles initially in states i and j results in scattering of particles through the polar angle χ and the azimuthal angle ϕ, with the particles ending up in states k and l, respectively. The differential cross section for the scattering is $I_{ij}^{kl}(g,\chi,\phi)$, and $\Delta\varepsilon = \varepsilon_k+\varepsilon_l-\varepsilon_i-\varepsilon_j = \gamma^2-\gamma'^2$, where the prime refers to the relative kinetic energy of the particles after the collision.

Since momentum is conserved in elastic as well as inelastic collisions, both types of interactions can contribute to transport of momentum and hence viscosity of the gas. However, taking the following discussion into account, one can say that the contribution of inelastic processes can be neglected in iodine gas at temperatures below 3000 K.

The three lowest electronic states of the I_2 molecule are the ground state $X\,{}^1\Sigma_g^+$, the $B\,{}^3\Pi_u$ state, and the $D\,{}^1\Sigma_u^+$ state, with energies of the excited states equal to 1.95 and 5.09 eV, respectively. The three lowest electronic states of the I atom are $5p^5\,{}^2P^\circ_{3/2}$, $5p^5\,{}^2P^\circ_{1/2}$ and $6s\,{}^4P_{5/2}$, with the excitation energies of the excited states equal to 0.94 and 6.77 eV, respectively.

The ionization potential of the I_2 molecule is 9.31 eV, which is high enough to maintain a low ionization degree of the gas under the conditions considered here. The atomic ionization can also be neglected under these conditions because of the relatively high atomic ionization potential (10.45 eV). In addition, the relative number of excited atomic and molecular ions in the gas is very small. A crude measure of the ionic excitation efficiency is the value of half of the ground-state ionization potential, which is relatively high in ions considered here; this is equal to 10 eV $[I_2^+(X\,^2\Pi_g)]$ and 9.55 eV $[I^+(5p^4\,^3P_2)]$.

In iodine, the typical amount of energy $\Delta E_{\mathrm{in}}/k$ transferred during inelastic collisions to molecular rotation and vibration is very small: less than 100 K in case of the translation-rotation exchange and less than 300 K in case of the translation-vibration exchange. Thus, at higher temperatures, the average ratio $\Delta\varepsilon/\gamma^2 = 2\Delta E_{\mathrm{in}}/E_{\mathrm{tr}}$ (E_{tr} is the impact energy) is always distinctively less than 1. Therefore, the terms with $\Delta\varepsilon$ can be neglected in Eq. (3) and one can approximate the differential cross section for inelastic scattering I_{ij}^{kl} by the cross section for elastic scattering I_{el}. In addition, the summation over internal states can be carried out independently from the translational states. Taking this into account and assuming that the intermolecular potential is a central-force potential, one obtains

$$\Omega^{(2,2)*}=\sigma^{-2}\int_0^\infty \gamma^7\exp(-\gamma^2)d\gamma \times\int_0^\pi(1-\cos^2\chi)I_{\mathrm{el}}\sin\chi\, d\chi\ , \qquad (5)$$

where $I_{\mathrm{el}}\sin\chi d\chi = b db$. The approximation (5) can be verified by investigation of the ratio of the gas viscosity when inelastic collisions are included to the viscosity when the inelastic collisions are neglected. This ratio can be given as [3]

$$\frac{\eta}{\eta_{\mathrm{el}}}\approx\left[1+\frac{4}{15}\left[\frac{\eta_{\mathrm{el}}}{p\tau}\right]\left[\frac{c_{\mathrm{int}}}{k}\right](1-\tfrac{3}{2}\langle\sin^2\chi\rangle)\right]^{-1}\ , \qquad (6)$$

where $\langle\sin^2\chi\rangle$ is the average value of $\sin^2\chi$, c_{int} is the internal heat capacity per molecule, p is the gas pressure, and τ is the relaxation time for the energy transfer between translation and internal states. When the scattering is isotropic ($\langle\sin^2\chi\rangle=\frac{2}{3}$), the correction term in Eq. (6) vanishes. In other words, inelastic collisions have a small effect on the gas viscosity if the anisotropy of the scattering is not significant.

Since the degree of ionization in iodine at $T<3000$ K is very small, we neglect in what follows any effects caused by charge exchange during collisions. [It is well known that resonant charge transfer between an ion and a molecule (atom) of the parent gas can significantly affect some transport properties (especially the ion diffusion coefficient and conductivity coefficient, much less gas viscosity).] A similar remark applies to collisions between identical atoms in different states in which resonant transfer of a quantum of internal energy can occur. We neglect the contribution of the resonant processes to the gas viscosity because the atomic excitation in iodine is inefficient under the conditions considered in this work.

VISCOSITY OF DISSOCIATING IODINE

The viscosity of mixture of several components depends on viscosities of the pure components; in the case of a gas being a mixture of N components, the gas viscosity can be expressed as the ratio of two determinants [4–6],

$$\eta_{\mathrm{mix}}=-\frac{\begin{vmatrix} H_{qq'} & x_q \\ x_{q'} & 0 \end{vmatrix}}{|H_{qq'}|}\ , \qquad (7)$$

where

$$\begin{vmatrix} H_{qq'} & x_q \\ x_{q'} & 0 \end{vmatrix} \equiv \begin{vmatrix} H_{11} & \cdots & H_{1N} & x_1 \\ \vdots & & \vdots & \vdots \\ H_{N1} & \cdots & H_{NN} & x_N \\ x_1 & \cdots & x_N & 0 \end{vmatrix}\ , \qquad (8)$$

$$|H_{qq'}| \equiv \begin{vmatrix} H_{11} & \cdots & H_{1N} \\ \vdots & & \vdots \\ H_{N1} & \cdots & H_{NN} \end{vmatrix}\ , \qquad (9)$$

and x_q is the mole fraction (depending on the gas dissociation degree) of the qth component of the mixture. The elements H_{qq} are given by the expressions

$$H_{qq}=\frac{x_q^2}{\eta_q}+\sum_{r=1,\ r\neq q}^{N}\frac{RT}{p\mathcal{D}_{qr}}\left[\frac{2x_q x_r}{M_q+M_r}\right]\left[1+\frac{3}{5}\frac{M_r}{M_q}A_{qr}^*\right] \qquad (10)$$

and

$$H_{qq'}(q'\neq q)=-\frac{RT}{p\mathcal{D}_{qq'}}\left[\frac{2x_q x_{q'}}{M_q+M_{q'}}\right](1-\tfrac{3}{5}A_{qq'}^*)\ , \qquad (11)$$

where M_q is the molecular weight of the qth component, η_q is the viscosity of the pure qth component, $\mathcal{D}_{qq'}$ is the coefficient of mutual diffusion of the components q and q', R is the universal gas constant, and p is the total gas pressure. The units of $\mathcal{D}_{qq'}$ are usually cm^2/sec. Before calculating $\mathcal{D}_{qq'}$ one must define R and p in consistent units. If p is in atmospheres, R must be in cm^3 atm/mol °K (82.056); if R is taken as 8.3143×10^7 erg/mol °K, then p must be in dyn/cm^2. The ratio $A_{qq'}^*$ is defined as the ratio of the average values of the products $\sigma_{qq'}^2\Omega_{qq'}^{(l,s)*}$,

$$A_{qq'}^*=\frac{\langle\sigma_{qq'}^2\Omega_{qq'}^{(2,2)*}\rangle}{\langle\sigma_{qq'}^2\Omega_{qq'}^{(1,1)*}\rangle}\ , \qquad (12)$$

where $\sigma_{qq'}^2$ is the collision diameter for interaction of species q and q'. $\Omega_{qq'}^{(2,2)*}$ is given by an expression similar to Eq. (3) except that it now refers to a collision between two unlike molecules q and q'; $\Omega_{qq'}^{(1,1)*}$ is the collision integral for diffusion (see below). The expression for η_{mix} given by Eq. (7) has the same form regardless of whether molecular collisions are elastic or inelastic [4]. In the first-order approximation, the corrections to $A^*_{qq'}$ accounting for inelastic collisions are negligible and one can use calculated $A^*_{qq'}$ for elastic interactions between the particles.

The viscosity of a binary mixture such as high-temperature dissociating iodine (mixture of I atoms and I_2 molecules) can be obtained from Eq. (7) as

$$\eta_{\text{mix}}=\left[\frac{x_1^2}{H_{11}}+\frac{x_2^2}{H_{22}}-\frac{2x_1x_2H_{12}}{H_{11}H_{22}}\right]\left[1-\frac{H_{12}^2}{H_{11}H_{22}}\right]^{-1}, \tag{13}$$

where the subscripts 1 and 2 denote properties of the I_2 and I components, respectively,

$$H_{12}=-\frac{2x_1x_2RT}{p\mathcal{D}_{12}(M_1+M_2)}(1-\tfrac{3}{5}A^*_{12}), \tag{14}$$

$$H_{11}=\frac{x_1^2}{\eta_1}+\frac{2x_1x_2RT}{p\mathcal{D}_{12}(M_1+M_2)}\left[1+\frac{3M_2A^*_{12}}{5M_1}\right], \tag{15}$$

and

$$H_{22}=\frac{x_2^2}{\eta_2}+\frac{2x_1x_2RT}{p\mathcal{D}_{12}(M_1+M_2)}\left[1+\frac{3M_1A^*_{12}}{5M_2}\right], \tag{16}$$

where

$$D_{12}=2.628\times10^{-3}T^{3/2}(p\langle\sigma_{12}^2\Omega_{12}^{(1,1)*}\rangle)^{-1}\times\left[\frac{M_1+M_2}{2M_1M_2}\right]^{1/2}, \tag{17}$$

where D_{12} is in cm^2/sec, p is in atm, and σ_{12} is in Å.

VISCOSITY CONTRIBUTION OF I_2+I_2 COLLISIONS

We assume in this section that the I_2+I_2 interactions are governed by a single force law specified by the Lennard-Jones (12-6) potential,

$$U_{\text{LJ}}(r)=4\varepsilon\left[\left[\frac{\sigma}{r}\right]^{12}-\left[\frac{\sigma}{r}\right]^{6}\right], \tag{18}$$

where ε is the potential well depth and σ is the intermolecular distance, other than infinity, at which the potential vanishes.

The potential parameters ε and σ for collision systems involving atoms and molecules are denoted by subscripts *mm* (molecule-molecule interaction), *aa* (atom-atom interaction), and *am* (atom-molecule interaction); for example, ε_{am} means the potential well depth for the $I+I_2$ interaction.

The collision diameter for interaction of two identical diatomic molecules can be given as [7]

$$\sigma_{mm}=\tfrac{4}{3}\langle R\rangle+c, \tag{19}$$

where c is a constant and $\langle R\rangle$ is the mean internuclear distance (a function of the rotational and vibrational quantum numbers) in the molecules [8,9],

$$\langle R\rangle=R_0-(2\beta)^{-1}\ln\left[1-\frac{E-A_0}{D}\right], \tag{20}$$

where D (equal to 12 582 cm^{-1}) is the dissociation energy referred to the minimum of the intramolecular potential, and β (equal to 1.799 Å^{-1}) is the constant in the Morse function,

$$V(R)=D(1-e^{-\beta(R-R_e)})^2, \tag{21}$$

which approximates the intramolecular potential of the rotationless molecules.

The position of the minimum of the rotational-vibrational intramolecular potential is

$$R_0=R_e+4l_\alpha^4J(J+1)/R_e^3, \tag{22}$$

where R_e (equal to 2.667 Å) is the molecular bond length, J is the rotational quantum number,

$$l_\alpha^2=\frac{\hbar}{2\beta(2\mu D)^{1/2}}, \tag{23}$$

$$A_0=\frac{\hbar^2J(J+1)}{2\mu R_0^2}, \tag{24}$$

and

$$E=hc[\omega_e(v+\tfrac{1}{2})-\omega_ex_e(v+\tfrac{1}{2})^2+B_eJ(J+1)-D_eJ^2(J+1)^2], \tag{25}$$

where E is the rotational-vibrational energy of molecule excited to the v,Jth vibrational-rotational level and where the other constants have their usual meaning.

Hirschfelder and Eliason suggested [7] that c in Eq. (19) is equal to 1.8 Å. However, a comparison of collision diameters obtained from Eq. (19) with corresponding measured values [10,11] for various collision systems suggests that a more accurate value is $c=1.6$ Å, which is consistent with the conclusions of Pauling [12]. Using $c=1.6$ Å and $\langle R\rangle=R_e$ one obtains from Eq. (19) that $\sigma_{mm}=5.156$ Å when the colliding molecules are in the ground rotational-vibrational-electronic states.

One finds from Eq. (56) that the mean radius [13] of the iodine atom in the ground electronic state is $\langle r_a\rangle=1.324$ Å. This value is close to that obtained from the relationship $\langle r_a\rangle=R_e/2$ suggested by Hirschfelder and Eliason [7] for diatomic homonuclear molecules in the ground electronic state. Consequently, using $c=1.6$ Å and $\langle r_a\rangle=1.324$ Å one obtains from Eq. (19) that $\sigma_{mm}=5.13$ Å.

The intermolecular potential function for interaction of diatomic molecules can be obtained from the Slater-Kirkwood theory [14]. According to the original formulation of the theory, the parameters of the LJ potential for interaction of a particle i and a particle j are [14,15]

$$\varepsilon_{ij}=\frac{b_{ij}}{2(r_i+r_j)^6}, \tag{26}$$

where

$$b_{ij}=\frac{3e\hbar\alpha_i\alpha_j}{2m_e^{1/2}[(\alpha_i/N_i)^{1/2}+(\alpha_j/N_j)^{1/2}]}, \tag{27}$$

and where e is the electronic charge, m_e is the electronic mass, r_i is the van der Waals radius of the ith particle, α_i is the polarizability of the ith particle, and N_i is the number of the valence-shell electrons in the ith particle. A study [16] of intermolecular forces in a number of systems (including the halogen system Cl_2+Cl_2) showed that more accurate potential parameters are obtained when using the so-called "modified" Slater-Kirkwood method. In the latter approach the potential well depth is obtained by multiplying the value obtained from the original formula (26) by a factor β_c that depends on the product $N_i\alpha_i^3$. In the case of the I_2+I_2 interaction $N_i\alpha_i^3=5306$ Å^9 ($N_i=5$ and $\alpha_i=10.2$ Å^3), which gives $\beta_c=2.2$

The van der Waals radius r_i for the I_2 molecule is obtained by assuming that $2r_i/2r_i' \approx \sigma_{mm}/\sigma_{aa}$, where r_i' is the van der Waals radius for the I atom [15,17] and the collision diameter σ_{aa} for two iodine atoms is given by Eq. (55). Consequently, one obtains from Eq. (26) that $\varepsilon_{mm}/k=557$ K.

The values of the collision diameter $\sigma_{mm}=5.156$ Å and the potential well depth $\varepsilon_{mm}/k=557$ K obtained from the "modified" Slater-Kirkwood theory agree well with the corresponding values obtained from viscosity measurements [2], $\sigma_{mm}=4.982$ Å and $\varepsilon_{mm}/k=550$ K. The latter values of the potential parameters are assumed in the present work for interaction of two iodine molecules in the ground electronic states.

Using the potential (18), it is possible to derive an expression [18] for the reduced collision cross sections $S^{(l)}(K)$,

$$S^{(l)}(K)=4\left[2-\frac{1+(-1)^l}{1+l}\right]^{-1}\int_0^\infty(1-\cos^{(l)}\chi)\delta d\delta\ , \tag{28}$$

where K is the impact kinetic energy in units of ε, and δ is the collision impact parameter in units of σ. Subsequently, the collision integrals $\Omega^{(l,s)}$ of Chapman and Cowling [1] are obtained from

$$\Omega^{(l,s)}=\sigma^2\left[\frac{2\pi kT}{\mu}\right]^{1/2}W^{(l,s)}(x)\ , \tag{29}$$

where

$$W^{(l,s)}(x)=\frac{1}{8}\left[2-\frac{1+(-1)^l}{1+l}\right]x^{s+2}$$
$$\times\int_0^\infty\exp(-xK)K^{s+1}S^{(l)}(K)dK\ , \tag{30}$$

with $x=\varepsilon/kT$. The analytic fits to the function $W^{(l,s)}(x)$ are given in the Appendix.

The collision integrals of rigid spheres with collision diameter σ are

$$(\Omega^{(l,s)})_{\rm RS}=\left[\frac{\pi kT}{2\mu}\right]^{1/2}\sigma^2(s+1)!\frac{[1+2l-(-1)^l]}{[4(1+l)]}\ , \tag{31}$$

and the dimensionless collision integrals $\Omega^{(l,s)*}$ are defined as

$$\Omega^{(l,s)*}=\frac{\Omega^{(l,s)}}{(\Omega^{(l,s)})_{\rm RS}}\ . \tag{32}$$

The viscosity η of a pure component can now be written in the form

$$\eta=\frac{5}{8\sigma^2}\left[\frac{\mu kT}{2\pi}\right]^{1/2}\frac{V(x)}{W^{(2,2)}(x)}\ , \tag{33}$$

where $V(x)$ is a slowly varying function of x,

$$V(x)=\left[1+\frac{b_{12}^2}{b_{11}b_{22}-b_{12}^2}\right. \tag{34}$$

$$\left.+\frac{b_{11}(b_{12}b_{23}-b_{22}b_{13})^2}{(b_{11}b_{22}-b_{12})^2(b_{11}b_{22}b_{33}+2b_{12}b_{13}b_{23}-b_{12}^2b_{33}-b_{23}^2b_{11}-b_{13}^2b_{22})}\right]\ , \tag{35}$$

and

$$b_{11}=4W^{(2,2)}(x)\ , \tag{36}$$

$$b_{12}=7W^{(2,2)}(x)-2W^{(2,3)}(x)\ , \tag{37}$$

$$b_{22}=(\tfrac{301}{12})W^{(2,2)}(x)-7W^{(2,3)}(x)+W^{(2,4)}(x)\ , \tag{38}$$

$$b_{13}=(\tfrac{63}{8})W^{(2,2)}(x)-(\tfrac{9}{2})W^{(2,3)}(x)+(\tfrac{1}{2})W^{(2,4)}(x)\ , \tag{39}$$

$$b_{23}=(\tfrac{1365}{32})W^{(2,2)}(x)-(\tfrac{321}{16})W^{(2,3)}(x)$$
$$+(\tfrac{25}{8})W^{(2,4)}(x)-(\tfrac{1}{4})W^{(2,5)}(x)\ , \tag{40}$$

$$b_{33}=(\tfrac{25137}{256})W^{(2,2)}(x)-(\tfrac{1755}{32})W^{(2,3)}(x)+(\tfrac{381}{32})W^{(2,4)}(x)$$
$$-(\tfrac{9}{8})W^{(2,5)}(x)+(\tfrac{1}{16})W^{(2,6)}(x)+(\tfrac{1}{2})W^{(4,4)}(x)\ . \tag{41}$$

VISCOSITY CONTRIBUTION OF I+I COLLISIONS

Atoms of partially dissociated gases interact according to multiple force laws, each law corresponding to a different alignment of the electronic spins during the atom-atom interaction. In principle, the Chapman-Enskog kinetic-theory problem should be solved when the multiple force interactions are included. It was shown by Mason, Vanderslice, and Yos [19] that the formula (1) retains its original form (and is valid for all degrees of the Chapman-Enskog approximation for mixtures of any complexity) in such a case, but each collision integral must be replaced by a statistical average over the different possible force laws. In other words, for a given pair of colliding atoms, the following replacement is necessary in Eq. (1):

$$\sigma^2\Omega^{(l,s)*} \rightarrow \langle \sigma^2\Omega^{(l,s)*} \rangle = \sum_i p_i \sigma_i^2 \Omega_i^{(l,s)*} , \tag{42}$$

where σ_i and $\Omega_i^{(l,s)*}$ are the collision diameter and the collision integral, respectively, for the ith force law, and p_i is the probability that the colliding atoms will follow the ith potential curve. This probability is obtained as the ratio of the degeneracy of the molecular electronic state corresponding to the ith potential curve to the sum of the degeneracies of all molecular states that can result from interaction (along different potential curves) of these two atoms. The possible potential curves for the interaction of two atoms in particular electronic states can be determined from the Wigner-Witmer rules. The two lowest electronic states in iodine atoms are $5p^5\,{}^2P^\circ_{3/2}$ (the ground state) and $5p^5\,{}^2P^\circ_{1/2}$. According to the Wigner-Witmer rules, an interaction of two ${}^2P$ atoms can lead to the following molecular states: ${}^1\Sigma_g^+$, ${}^1\Sigma_u^-$, ${}^1\Pi_g$, ${}^1\Pi_u$, ${}^1\Delta_g$, ${}^3\Sigma_u^+$, ${}^3\Sigma_g^-$, ${}^3\Pi_g$, ${}^3\Pi_u$, and ${}^3\Delta_u$. (The potential curves for the possible molecular states for ${}^2P_{3/2}+{}^2P_{3/2}$, ${}^2P_{3/2}+{}^2P_{1/2}$, and ${}^2P_{1/2}+{}^2P_{1/2}$ atom-atom interactions were given by Mulliken [20].) The excitation energies of the first ($5p^5\,{}^2P^\circ_{1/2}$) and the second ($5p^4 6s\,{}^4P_{5/2}$) excited atomic states are 0.94 and 6.77 eV, respectively. Thus, in the range of temperatures considered here, one can assume that most of the atoms are in the ground state, and the dominant atom-atom interactions are those between atoms in the ground (${}^2P^\circ_{3/2}$) electronic states. Therefore, we take into account in averaging (42) only the interactions between two ground-state iodine atoms. The corresponding potentials (a total of ten; see Fig. 1 in Ref. [20]) represent the molecular states that dissociate into two ${}^2P^\circ_{3/2}$ iodine atoms.

When the atom-atom potentials have a minimum (three curves out of the ten Mulliken's potentials mentioned above), the collision integrals of I+I interactions are calculated (fitting first the particular I+I potential curve to a Lennard-Jones curve) in the same way as the collision integrals for I_2+I_2 interactions.

In the cases of the atom-atom interactions following a repulsive potential,

$$U_i(r)=\frac{c_i}{r^{t_i}} \tag{43}$$

(r is an interatomic distance, and c_i and t_i are constants), the collision integrals are [7]

$$\Omega^{(l,s)}=\left[\frac{\pi kT}{2\mu}\right]^{1/2}\left[\frac{t_i c_i}{kT}\right]^{2/t_i} A^{(l)}\Gamma[s+2-(2/t_i)] , \tag{44}$$

where μ is the reduced mass of the collision system,

$$A^{(l)}=\int_0^\infty (1-\cos^l\chi)\beta d\beta , \tag{45}$$

and

$$\beta=\left[\frac{\mu g^2}{2t_i c_i}\right]^{1/t_i} . \tag{46}$$

The values of the integrals $A^{(l)}$ are finite for all values of t_i greater than 1 (see Table I), and the relationship between χ and β can be obtained from the equation of binary collision trajectory [21]

$$\chi(\beta)=\pi-2\int_0^{z_m}\left[1-z^2-\frac{1}{t_i}\left[\frac{z}{\beta}\right]^{t_i}\right]^{-1/2} dz , \tag{47}$$

where the upper limit of the integral is the smallest positive root of the expression in the brackets.

TABLE I. The integrals $A^{(1)}$ and $A^{(2)}$ given in Eq. (45) for several values of the exponent t_i of Eq. (43).

t_i	$A^{(1)}$	$A^{(2)}$
2	0.397	0.527
3	0.311	0.353
4	0.298	0.308
6	0.306	0.283
8	0.321	0.279
10	0.333	0.278
12	0.346	0.279
14	0.356	0.280
∞	0.500	0.333

For the repulsive potentials, it has been shown [22,23] that only the region of potential energy near $U_i(r)\simeq kT$ is important in calculating transport coefficients at the temperature T. Furthermore, Hirschfelder and Eliason [7] made a conceivable supposition that the separation between two atoms r is related to the effective collision diameter σ in such a way that the average kinetic energy kT is comparable to the potential energy $U_i(\sigma)$. By using that supposition, the adjusted values of σ and $\sigma^2\Omega^{(l,s)}$ are derived. In order to express the rigid-sphere collision diameter in terms of constants c_i and t_i, the collision integral (44) is equated to the collision integral (31), which gives

$$\sigma^2=\frac{A^{(l)}4(1+l)(t_i c_i/kT)^{2/t_i}\Gamma(s+2-(2/t_i))}{(s+1)![1+2l-(-1)^l]} . \tag{48}$$

If this σ is substituted into Eq. (43), the constant c_i of repulsive potential cancels out, and

$$U_i(\sigma)=\frac{kT}{t_i}\left[\frac{(s+1)![1+2l-(-l)^l]}{4(1+l)A^{(l)}\Gamma(s+2-(2/t_i))}\right]^{t_i/2} , \tag{49}$$

where t_i can be obtained from

$$t_i=\left[-\frac{r}{U_i(r)}\frac{dU_i(r)}{dr}\right]_{r=r_0} \tag{50}$$

[r_0 is the distance between the two atoms when $U_i(r)=kT$]. Because the coefficient of viscosity is defined in terms of $\Omega^{(2,2)*}$, Eq. (49) can be rewritten, since $s=l=2$, as

$$U_i(\sigma)=\theta_{\text{visc}}kT , \tag{51}$$

where

$$\theta_{\text{visc}}=\left[\tfrac{1}{2}A^{(2)}\Gamma\left[4-\frac{2}{t_i}\right]\right]^{-t_i/2}/t_i . \tag{52}$$

Summarizing the above, one can say that the first step to determine the adjusted values of σ from the particular repulsive potential curve is computing the effective value of t_i. After that, the appropriate value of θ_{visc} is calculated, and θ_{visc} is substituted into Eq. (51) to determine $U_i(\sigma)$. The corresponding value of σ, obtained from the potential curve, is the effective (adjusted) value of the collision diameter. Since the collision integral $\Omega^{(l,s)*}$ of the hard sphere is equal to 1, the value of $\sigma^2\Omega^{(l,s)*}$ of the repulsive potentials is equal to σ^2.

Procedures of calculating σ_i and $\Omega_i^{(l,s)*}$ are applied to each potential curve of I+I interactions, and the contribution to the gas viscosity coming from I+I interactions is obtained from

$$\eta = \frac{5}{16} \frac{(\pi m k T)^{1/2}}{\pi\sigma^2 \sum_i p_i \sigma_i^2 \Omega_i^{(l,s)*}} , \tag{53}$$

where the sum is taken over all I+I potential curves taken into consideration.

VISCOSITY CONTRIBUTION OF I+I$_2$ COLLISIONS

The usual mixture rule for evaluation of the collision diameter for unlike particles in terms of the diameters for like particles is

$$\sigma_{am} = (\sigma_{aa} + \sigma_{mm})/2 , \tag{54}$$

where the collision diameter for interaction of two ground-state iodine atoms can be given as [7]

$$\sigma_{aa} = 2\langle r_a \rangle + c , \tag{55}$$

where $c = 1.6$ Å and $\langle r_a \rangle$ is the mean radius of the atoms participating in the collision,

$$\langle r_a \rangle = \int_0^\infty r_a^3 |\psi|^2 dr_a . \tag{56}$$

The wave function ψ is given by a series expansion on the basis-set Slater orbitals [24,25] (with constants C_i, n_i, ζ_i),

$$\psi_{n_i lm}(r_a, \theta, \phi) = \sum_i C_i R_{n_i l}(r_a) Y_{lm}(\theta_a, \phi_a) , \tag{57}$$

where n_i, l, and m are the quantum numbers of the outer-shell electron, $Y_{lm}(\theta_a, \phi_a)$ is a normalized spherical harmonic, and the radial part of the wave function is

$$R_{n_i l}(r_a) = [(2n_i)!]^{-1/2} (2\zeta_i)^{n_i + 1/2} r_a^{n_i - 1} \exp(-\zeta_i r_a) . \tag{58}$$

Assuming that $\langle r_a \rangle = 1.324$ Å and $c = 1.6$ Å, one finds from Eq. (55) that $\sigma_{aa} = 4.248$ Å; this value differs from the value of $\sigma_{\text{Xe-Xe}} = 3.888$ Å, which is sometimes assumed [10,11] for the I+I interaction because xenon is iodine's neighbor in the Periodic Table.

The collision diameter for the atom-molecule interaction, when the atom and the molecule are in the electronic ground states, can now be obtained from the expressions (19), (54), and (55) as

$$\sigma_{am} = c + \langle r_a \rangle + 2\langle R \rangle /3 , \tag{59}$$

so that $\sigma_{am} = 4.702$ Å if the molecule is in the ground rotational-vibrational state.

Using the radical molecule complex (RMC) mechanism [26,27], Blake and Burns calculated [28] the potential parameters for iodine-atom–iodine-molecule interaction. Their result for the potential well depth for the hard-sphere interaction between I and I$_2$ was $\varepsilon_{am}/k = 3069$ K, while for the Sutherland interaction $\varepsilon_{am}/k = 2767$ K (the latter value was recommended for the well depth for the I+I$_2$ interaction). Similar values, 2968 and 2666 K, respectively, were obtained by Thompson [29] from the Monte Carlo quasiclassical trajectory calculations and by Bunker and Davidson [30] from thermodynamic considerations; these values are in agreement with the conclusions of Porter [31]. The geometrical average of the potential well depths obtained by Thompson and by Bunker and Davidson gives $\varepsilon_{am}/k = 2813$ K.

The I+I$_2$ interaction can have some channels (for example, atomic exchange [29]) that may have some importance when viscosity of iodine is considered. Unfortunately, the efficiency of these channels is not accurately known [32–34]. However, the studies of Blake and Burns [28] and of Thompson [29] have suggested that the Lennard-Jones potential with parameters discussed above is an acceptable approximation of the overall forces dominating the I+I$_2$ interaction, even though it ignores such effects as, for example, the quadrupole-quadrupole r^{-5} term in the interaction. Keeping this in mind, we use in this work the Lennard-Jones potential with $\sigma_{am} = 4.702$ Å and $\varepsilon_{am}/k = 2800$ K as an acceptable representation of the overall forces dominating the I+I$_2$ interaction.

DISSOCIATION DEGREE IN LOCAL THERMAL EQUILIBRIUM

The law of mass action for a gas of homogeneous diatomic molecules leads to [35]

$$\frac{y^2}{1-y} = \frac{m}{2\rho V} \frac{Q_a^2}{Q_m} \exp(-\Theta_d/T) , \tag{60}$$

where $\Theta_d = D_0/k$ (D_0 is the dissociation energy), m is the mass of the atoms forming the molecules, ρ and V are the mass density and volume of the gas, respectively, and the dissociation degree $y = N_a/N$, $N = N_a + 2N_m$ (N_a and N_m are numbers of free atoms and free molecules in the gas, respectively) is a constant number of atoms, both free and those bound in the molecules, available in the gas with ongoing dissociation. Here, $Q_a = Q_a^t Q_a^e$ and $Q_m = Q_m^t Q_m^r Q_m^v Q_m^e$ are total partition functions of atomic and molecular components of the gas, respectively, with the superscripts t, r, v, and e referring to translational, rotational, vibrational, and electronic freedom degrees of the species, respectively. The last relationship is valid if all four kinds of energies are independent of one another; such an assumption is well justified in iodine at $T < 3000$ K. Here $Q_m^t = 2^{3/2} Q_a^t$, $Q_a^t = V(2\pi m k T/h^2)^{3/2}$, the rotational partition function $Q_m^r = T/2\Theta_r$ ($\Theta_r = hcB_e/k$), and the vibrational partition function $Q_m^v = [1 - \exp(-\Theta_v/T)]^{-1}$, where $\Theta_v = hc\omega_e/k$; $Q_a^e \approx g_{a,0} + g_{a,1}\exp(-E_{a,1}/kT)$ and $Q_m^e \approx g_{m,0} + g_{m,1}\exp(-E_{m,1}/kT)$, where $E_{a,1}$ and $E_{m,1}$ are the excitation energies of the first excited electronic states in iodine atom and molecule, respectively. Using the above and assuming that the relationship $pV=(N_a+N_m)kT$ is valid, the expression (60) can be written as

$$\frac{y^2}{1-y}=C$$

or

$$y=\frac{C(\sqrt{1+4/C}-1)}{2}\ , \tag{61}$$

where

$$C=n^{-1}\exp(-\Theta_d/T)\times\left[\left[\frac{\pi mk}{h^2}\right]^{3/2}\Theta_r T^{1/2}[1-\exp(-\Theta_v/T)]\frac{(Q_a^e)^2}{Q_m^e}\right]\ , \tag{62}$$

with $n=N/V$, where V is the volume of the gas.

RESULTS AND DISCUSSION

The viscosity coefficient of dissociating iodine in local thermal equilibrium was calculated in a broad range of temperature, and the results are shown in Fig. 1. (The approach of this work can also be used to predict viscosity of the gas in thermal nonequilibrium if the dependence of the dissociation degree on the gas parameters is known.) At low temperature, the dissociation degree is low, and collisions involving atoms have no impact on the viscosity of the gas. As the temperature of the gas increases, the collisions involving atoms become important, and at temperatures greater than about 1000 K, these collisions start to dominate the transport properties of iodine. The decrease of the viscosity of iodine (see Fig. 1) at temperatures about 1000–2000 K is caused by a rapid increase of dissociation and, subsequently, a rapid increase of the $I+I_2$ and $I+I$ collision frequencies at those temperatures. The potential well depths ε for the $I+I_2$ and $I+I$ interactions are much larger than the well depth for the I_2+I_2 collisions which are dominant at lower temperatures. It was shown [36] that the viscosity of gas consisting of particles interacting according to a potential characterized by well depth ε and collision diameter σ can be given as

$$\eta\sim\frac{\sigma^2}{\mu^{1/2}\varepsilon^{1/2}}\ . \tag{63}$$

Therefore, at temperatures 1000–2000 K, the increase of the viscosity resulting from the increase in temperature competes with the decrease of the viscosity, resulting, as indicated by the relationship (63), from the significant increase in the potential well depth of the $I+I_2$ and $I+I$ interactions. As the temperature of the gas continues to increase, the gas becomes highly dissociated, and $I+I$ collisions dominate the kinetic properties of the gas. The gas viscosity then increases monotonically with temperature, as expected for gas containing only one kind of particle.

A numerical analysis shows that the contribution of the rotational-vibrational excitation of molecules to the viscosity of iodine in local thermal equilibrium is very small. (This contribution depends on the collision diameters which in turn depend on the mean internuclear distances of the rotationally and vibrationally excited I_2 molecules.) This is because in most cases the degree of dissociation of iodine in local thermal equilibrium is high when the gas temperature is close to or higher than 1500 K. Therefore, the impact of the rotational-vibrational excitation of molecules on the gas viscosity would be meaningful only at temperatures less than about 1500 K. However, at these temperatures the contribution of the rotational-vibrational excitation of iodine to the gas viscosity is negligible.

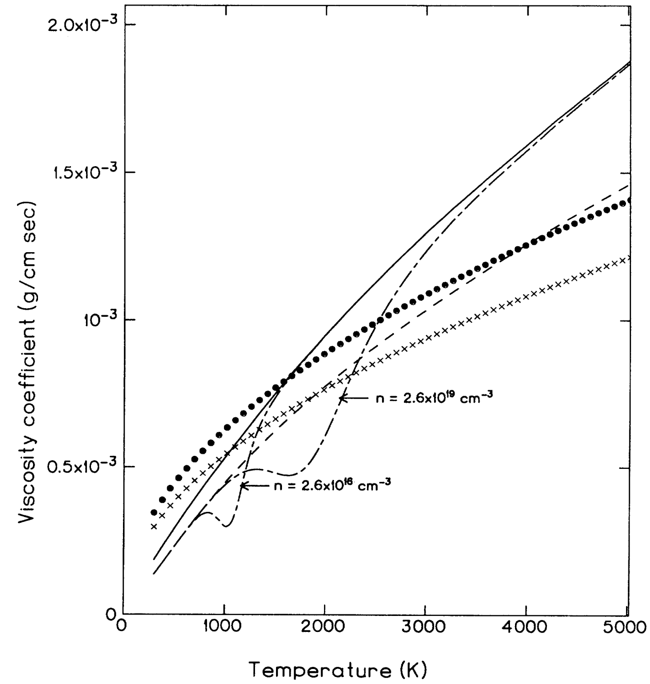

FIG. 1. The viscosity of iodine as function of gas temperature. Solid and dashed line represent viscosities of pure atomic (fully dissociated) and pure diatomic (undissociated) iodine, respectively. The dash-dotted curves represent the viscosities of iodine of particle density n when atom-atom $(I+I)$, atom-molecule $(I+I_2)$, and molecule-molecule (I_2+I_2) collisions are taken into account; the dissociation degree of the gas is taken as that of the gas in the local thermal equilibrium. $(n=n_a+2n_m$, where n_a and n_m are particle densities of free atoms and free molecules, respectively.) The circles and crosses denote the values of viscosity of fully dissociated and undissociated iodine, respectively, as predicted by the rigid-sphere model.

A quick estimate of the role of the rotational-vibrational excitation of molecules to the viscosity of iodine can be made by use of a simple approximate expression for the mean internuclear distance $\langle R \rangle$ in a "typical" (that is, representing majority of the gas molecules) molecule in iodine of temperature T. Such an expression can be obtained in the following way. In local thermal equilibrium the ratio of the population of the first excited vibrational level ($v=1$) to the population of the vibrational ground state ($v=0$) is equal to 0.36 (at $T=300$ K), 0.74 (at $T=1000$ K), and equal to about 1 (at $T \approx 1500$ K). Thus, the majority of molecules in iodine at $T \lesssim 1500$ K is in the $v=0$ and 1 vibrational states. Therefore, the vibrational quantum number of the typical molecule in such gas is a weak function of temperature T. Consequently, it is reasonable to assume, when calculating the rotational-vibrational energy E in the relationship (20), that the vibrational quantum number of the typical molecule is $v_p=1$. (The choice of $v_p=1$ over $v_p=0$ makes the contribution of the vibrational excitation to the gas viscosity slightly greater than it is in reality.)

The rotational quantum number of the typical I_2 molecule can be taken as the most probable rotational quantum number J_p in the gas in the local thermal equilibrium at temperature T. The value J_p can be obtained from the LTE distribution of the rotational levels after approximation of the distribution by a continuous function of J; such a procedure is justified because the rotational levels in iodine are closely spaced. Then, the most probable rotational quantum number J_p is an integer nearest to

$$J_p' = \left[\frac{kT}{2B_e hc} \right]^{1/2} - \tfrac{1}{2} \approx \left[\frac{kT}{2B_e hc} \right]^{1/2} , \tag{64}$$

where B_e is the rotational spectroscopic constant; one can see from Eq. (64) that the T dependence of the rotational quantum number J_p is stronger than the T dependence of the vibrational quantum number v_p.

Using $v_p=1$ and J_p given by the relationship (64), one obtains from Eqs. (24) and (25) that

$$\frac{E-A_0}{D} = \frac{6\omega_e x_e}{\omega_e} \left\{ 1 + \frac{kT}{3hc\omega_e} \left[1 - \left[\frac{R_e}{R_0} \right]^2 \right] \right\} , \tag{65}$$

where we neglected the higher terms in the expression (25), used the fact that $J_p(J_p+1) \approx J_p^2$, and used the expressions

$$D = \frac{hc\omega_e^2}{4\omega_e x_e} \tag{66}$$

and

$$B_e = \frac{\hbar}{4\pi c \mu R_e^2} . \tag{67}$$

The $\ln(1-x)$ in Eq. (20) can be expanded into a series:

$$\ln(1-x) = -\sum_{n=1}^{\infty} x^n/n \approx -x , \tag{68}$$

because $x=(E-A_0)/D$ is much less than unity at temperatures less than about 1500 K. Consequently, Eq. (22) gives the following expression acceptable at temperatures less than about 1500 K:

$$R_0 \approx R_e + \frac{4\omega_e x_e kT}{hcR_e \beta^2 \omega_e^2} , \tag{69}$$

where we used the fact that $1-(R_e/R_0)^2 \ll 4/\beta R_e$. In the case of iodine one obtains from Eq. (69)

$$\frac{\langle R \rangle}{R_e} \approx 1 + 1.62 \times 10^{-6} T , \tag{70}$$

where T is in degrees Kelvin. This linear dependence becomes a crude estimate when the gas temperature is close or greater than about 1500 K. Then the dependence of $\langle R \rangle / R_e$ on temperature is much stronger, but is still not strong enough to affect the viscosity of iodine significantly [37]. At temperatures higher than 2500 K the relationship (70) is invalid. In such a case the ratio $\langle R \rangle / R_e$ departs substantially from unity [8,9,37], but this fact is practically meaningless because the number of diatomic molecules in iodine is insignificant at the higher temperatures.

We also show in Fig. 1 the viscosities η_0 of pure diatomic (no I atoms are present) and pure atomic (no I_2 molecules are present) iodine calculated from the rigid-sphere model, where

$$\eta_0 = \frac{5}{16} \frac{(\pi m k T)^{1/2}}{\pi \sigma^2} . \tag{71}$$

Summarizing the results of the present work, one can say that in high-temperature ($\gtrsim 1000$ K) iodine (1) dissociation processes should not be ignored in calculations of viscosity, (2) the viscosity of atomic iodine is greater than the viscosity of molecular (diatomic) iodine, and (3) the rigid-sphere model is inappropriate for calculations of the gas viscosity.

One should add that the decrease of viscosity with temperature takes place, to a different degree, in most dissociating gases. However, in most cases it happens at temperatures well above 3000 K.

ACKNOWLEDGMENTS

One of us (J.A.K.) thanks Alex Dalgarno and Evgeni Nikitin for valuable comments. This work was supported by the National Aeronautics and Space Administration, Grant No. NAGW-1061, by the Air Force Office of Scientific Research, Grant No. 88-0119, and URI Grant No. 90-0170.

APPENDIX

The analytic fits to the integrals $W^{(l,s)}(x)$ [Eq. (30)] are

$$W^{(1,1)}(x) = \tfrac{1}{4} x^3 [2.111\,14 x^{-2.845} + 1.433\,29 (x+0.439)^{-2.5} + 566.494) x + 3.675)^{-5.126}$$
$$-0.020\,77 \exp(-0.8093x) - 0.2159 \exp(-0.5867x) + 0.003\,726 \exp(-0.2552x)] ,$$

$$\begin{aligned}W^{(1,2)}(x)={}&\tfrac{1}{4}x^{4}[6.006\,19\,x^{-3.845}+3.583\,23(x+0.439)^{-3.5}+2903.85(x+3.675)^{-6.126}\\&-0.016\,81\exp(-0.8144x)-0.012\,67\exp(-0.6089x)+0.000\,9506\exp(-0.2895x)]\,,\end{aligned}$$

$$\begin{aligned}W^{(1,3)}(x)={}&\tfrac{1}{4}x^{5}[23.0938x^{-4.845}+12.5413(x+0.439)^{-4.5}+17\,789(x+3.675)^{-7.126}\\&-0.013\,69\exp(-0.8196x)+0.000\,2752\exp(-0.3239x)-0.007\,714\exp(-0.6311x)]\,,\end{aligned}$$

$$\begin{aligned}W^{(2,2)}(x)={}&\tfrac{1}{6}x^{4}[6.881\,55x^{-3.855}+2.894\,88(x+0.19)^{-3.211}+7.332\,42(x+0.677\,42)^{-3.303}\\&-660\,079(x+6.7461)^{-7.01}+0.039\,50\exp(-0.9274x)\\&+0.037\,32\exp(-0.8291x)+0.038\,88\exp(-0.6161x)-0.009\,625\exp(-0.2211x)]\,,\end{aligned}$$

$$\begin{aligned}W^{(2,3)}(x)={}&\tfrac{1}{6}x^{5}[26.528x^{-4.855}+9.295\,46(x+0.19)^{-4.211}+24.2190(x+0.677\,42)^{-4.303}\\&-4627\,150(x+6.7461)^{-8.01}+0.036\,63\exp(-0.9349x)\\&+0.030\,94\exp(-0.8314x)+0.023\,95\exp(-0.6232x)-0.002\,128\exp(-0.2489x)]\,,\end{aligned}$$

$$\begin{aligned}W^{(2,4)}(x)={}&\tfrac{1}{6}x^{6}[128.795x^{-5.858}+39.1432(x+0.19)^{-5.211}+104.214(x+0.677\,42)^{-5.303}\\&-37\,063\,500(x+6.7461)^{-9.01}+0.034\,25\exp(-0.9425x)\\&+0.025\,73\exp(-0.8336x)+0.014\,93\exp(-0.6303x)-0.000\,5298\exp(-0.2767x)]\,,\end{aligned}$$

$$\begin{aligned}W^{(2,5)}(x)={}&\tfrac{1}{6}x^{7}[754.095x^{-6.855}+203.975(x+0.19)^{-6.211}+552.647(x+0.677\,42)^{-6.303}\\&-333\,942\,000(x+6.7461)^{-10.01}+0.032\,28\exp(-0.9501x)\\&+0.021\,45\exp(-0.8359x)+0.009\,408\exp(-0.6374x)-0.000\,1466\exp(-0.3045x)]\,,\end{aligned}$$

$$\begin{aligned}W^{(2,6)}(x)={}&\tfrac{1}{6}x^{8}[5169.32x^{-7.855}+1266.89(x+0.19)^{-7.211}+3483.33(x+0.677\,42)^{-7.303}\\&-3342\,750\,000(x+6.7461)^{-11.01}+0.030\,67\exp(-0.9576x)\\&+0.017\,93\exp(-0.8381x)+0.005\,997\exp(-0.6446x)-0.000\,044\,63\exp(-0.3323x)]\,,\end{aligned}$$

$$\begin{aligned}W^{(4,4)}(x)={}&\tfrac{1}{5}x^{6}[132.154x^{-5.86}+29.9505(x+0.1350)^{-5.5}+175.386(x+0.495\,93)^{-5.589\,15}\\&-737\,383\,000\,000(x+7.5377)^{-13.3}-0.091\,63\exp(-1.0424x)\\&-0.002\,420\exp(-0.9133x)-0.001\,657\exp(-0.4796x)\\&-0.003\,243\exp(-0.4646x)-0.016\,29\exp(-0.6493x)-0.008\,924\exp(-0.8070x)]\,.\end{aligned}$$

[1] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University, New York, 1952).

[2] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964).

[3] E. A. Mason, in *Kinetic Processes in Gases and Plasmas*, edited by A. R. Hochstim (Academic, New York, 1969), p. 60.

[4] L. Monchick, K. S. Yun, and E. A. Mason, J. Chem. Phys. **39**, 654 (1963).

[5] S. C. Saxena and R. K. Joshi, Physica **29**, 870 (1963).

[6] T. S. Storvick and E. A. Mason, J. Chem. Phys. **45**, 3752 (1966).

[7] J. O. Hirschfelder and M. A. Eliason, Ann. N.Y. Acad. Sci. **67**, 451 (1957).

[8] J. A. Kunc, J. Phys. B **23**, 2553 (1990).

[9] J. A. Kunc, J. Phys. B (to be published).

[10] C. H. Chen, P. E. Siska, and Y. T. Lee, J. Chem. Phys. **59**, 601 (1973).

[11] J. A. Barker, R. O. Watts, J. K. Lee, and Y. T. Lee, J. Chem. Phys. **61**, 3081 (1974).

[12] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, New York, 1939), p. 178.

[13] A. A. Radzig and B. M. Smirnov, *Reference Data on Atoms, Molecules, and Ions* (Springer, Berlin, 1985).

[14] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

[15] R. A. Scott and H. A. Scheraga, J. Chem. Phys. **45**, 2091 (1966).

[16] W. Brandt, J. Chem. Phys. **24**, 501 (1956).

[17] A. Bondi, J. Phys. Chem. **68**, 441 (1964)

[18] J. O. Hirschfelder, R. B. Bird, and E. L. Spotz, J. Chem. Phys. **16**, 968 (1948).

[19] E. A. Mason, J. T. Vanderslice, and J. M. Yos, Phys. Fluids **2**, 688 (1959).

[20] R. S. Mulliken, J. Chem. Phys. **55**, 288 (1971).

[21] M. A. Eliason, D. E. Stogryn, and J. O. Hirschfelder, Proc. Natl. Acad. Sci. U.S.A. **42**, 546 (1956).

[22] D. D. Konowalow, J. O. Hirschfelder, and B. Linder, J. Chem. Phys. **31**, 1575 (1959).

[23] P. H. Krupienie, E. A. Mason, and J. T. Vanderslice, J. Chem. Phys. **10**, 2399 (1963).

[24] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

[25] A. D. McLean and R. S. McLean, At. Data Nucl. Data Tables **26**, 197 (1981).

[26] J. K. Ip and G. Burns, J. Chem. Phys. **51**, 3414 (1969).

[27] J. A. Blake, R. J. Browne, and G. Burns, J. Chem. Phys. **53**, 3320 (1970).

[28] J. A. Blake and G. Burns, J. Chem. Phys. **54**, 1480 (1971).

[29] D. L. Thompson, J. Chem. Phys. **60**, 4557 (1974).

[30] D. L. Bunker and N. Davidson, J. Am. Chem. Soc. **80**, 5090 (1958).

[31] G. Porter, Discuss. Faraday Soc. **33**, 198 (1962).

[32] R. M. Noyes and J. Zimmerman, J. Chem. Phys. **18**, 656 (1950).

[33] I. D. Clark and R. P. Wayne, in *Comprehensive Chemical Kinetics,* edited by C. H. Bamfond and C. F. Tipper (Elsevier, New York, 1969), p. 4.

[34] M. A. Clyne and H. W. Cruse, J. Chem. Soc. Faraday Trans. **68**, 1377 (1972).

[35] M. J. Lighthill, J. Fluid Mech. **2**, 1 (1957).

[36] J. De Boer and J. van Kranendonk, Physica **14**, 442 (1948).

[37] S. H. Kang and J. A. Kunc, J. Phys. Chem. (to be published).