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# ABSTRACT

The development of a new generation of ablative thermal protection systems based on carbon-phenolic composite materials demands the accurate determination of transport properties of pyrolysis gases mixed in various atmospheres. The present work provides recommended collision data for the calculation of the transport properties for Mars and Earth re-entries. A review of available potential data is given for species in the atmospheres of Earth and Mars. Additional data are provided for species formed during the degradation of the theoretical ablative composite for open testing material. Dipole polarizabilities are calculated from *ab initio* methods and used for the calculation of transport properties of reduced pyrolysis mixtures over a temperature range representative of the boundary layer for atmospheric entry flows.

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# I. INTRODUCTION

Over the last 60 years, numerous manned and unmanned space exploration missions were carried out successfully. When spacecraft interact with a planetary atmosphere at very high reentry speeds, a strong bow shock is formed in front of the vehicle and a massive amount of free-stream kinetic energy is transformed into thermal energy. The development of Thermal Protection Systems (TPSs) to protect spacecraft remains a major concern. A new class of ablative protective materials based on low density carbon/resin composites was engineered for recent and future space missions.<sup>1-3</sup> This lightweight material is produced using a carbon preform which is injected with phenolic resin. Examples of such ablators are PICA (Phenolic Impregnated Carbon Ablator), developed by the NASA Ames Research Center in the 1990s,<sup>4,5</sup> and the European ASTERM material developed by ASTRIUM in the 2000s.<sup>6</sup> More recently, PICA-X<sup>3</sup> was developed by NASA and applied on SpaceX's Dragon capsule.<sup>7</sup> During atmospheric re-entry, part of the heat produced is injected into the surface layer of the ablative heat shield. This causes the thermal protective material to be destroyed by two distinct ablation phenomena.<sup>8-</sup>

The first phenomenon is pyrolysis, which produces gaseous products and results in the carbonization of the phenolic resin inside the material. The gases are transported into the flow by diffusion and convection, where they mix with shock heated air and change the chemical composition of the flow. The second phenomenon is the ablation of the carbon preform and carbonized resin. This ablation is due to chemical reactions (oxidation, nitridation, and sublimation) and mechanical erosion during the descent. When the ablative material of the heat shield starts to recess, particles are introduced into the flow between the bow shock and the vehicle where they interact with each other and affect the thermodynamic and transport properties of the flow surrounding the vehicle. The detailed modeling of ablation phenomena is necessary for understanding and predicting the surface heating during re-entry. An accurate estimate of the heat flux impinging on the surface enables an optimal design of the thickness of TPS material needed to protect the capsule. Overestimation of the ablator thickness results in extra vehicle weight and increases the cost of the launch considerably.

To predict accurately the heat produced during the descent, transport properties of pyrolysis mixtures interacting with various

TABLE I	. Composition	of various	atmospheres	(in volume	%). <sup>12</sup>
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	$N_2$	O <sub>2</sub>	$CO_2$	$CH_4$	$H_2$	Ar
Earth	78.1	20.9				0.9
Mars	1.9		95.9			2.0
Titan	98.4			1.4	0.2	
Venus	3.5		96.5			

atmosphere components should be computed with great care. The principal species composing the Earth, Mars, Titan, and Venus atmospheres are represented in Table I. Considering all species appearing in a mixture of the elements C, H, O, and N, which are representative for the latter atmospheres plus the pyrolysis gases, one ends up with a database of 1257 species as determined by Scoggins et al.<sup>13</sup> These species have been selected based on their kinetic viability in the time scales of interest for re-entry test cases, and the availability of accurate thermochemical data for each of them. In the same work, they proposed a reduced species set for two mixtures representative of Mars and Earth entry. The Mars atmospheric boundary layer can be described by a mixture of 10% CO2 and a 90% pyrolysis gases by volume. For Earth, a mixture of 10% air was considered with 90% pyrolysis gases. After reduction and allowing a tolerance of 10% on the maximum thermodynamic relative error, one ends up with reduced mixtures of 32 species for Earth and 23 species for Mars as shown in Table II.

Computing the transport properties of these reduced sets requires atomic and molecular data for the species collision pairs.<sup>22,23</sup> Intermolecular potential data such as the well depth and reference length are used to calculate the collision integrals that appear in the expressions for the species transport properties. Considerable research has been carried out over the years to provide the collision integrals for species collision pairs in various atmospheres. Capitelli et al.<sup>24</sup> provide collision integrals for high temperature air species between 50 and 100 000 K. The database was revised in 2005 by Wright et al.<sup>25</sup> by combining the best available transport data for high temperature 13-species air and ion-neutral data for airargon mixtures.<sup>26</sup> This revision was followed by a publication in 2007<sup>27</sup> that reviewed the transport properties of 17-species weakly ionized CO<sub>2</sub>-N<sub>2</sub> mixtures for Mars and Venus atmospheres. Integrals for the Mars and Titan atmosphere were documented by André et al.<sup>19</sup> Additionally, Bruno et al.<sup>28</sup> computed helium-hydrogen collisional integrals for Jupiter. More recently, Colonna et al.<sup>29</sup> derived transport properties for silicon species in combination with argon, oxygen, and carbon for their use in modern technology. Although the literature provides transport data for various atmospheres, accurate collision data for contaminated pyrolysis mixtures are still not available.

The purpose of the present paper is to provide recommended collision data for the calculation of equilibrium transport properties of ablation species for Mars and Earth re-entries. The present paper is structured as follows. First, the transport closure is given based on atomic and molecular data in Sec. II. The transport properties are derived starting from the intermolecular potential parameters used to compute the collision integrals for each interaction pair. Depending on the type of interaction, i.e., neutral-neutral and ionneutral, different methods are used to calculate the collision integrals. At the end of the section, recommended integrals are presented for all interaction types. In Sec. III, these integrals are used for calculating the equilibrium transport properties of reduced pyrolysis mixtures and the results are thereafter compared with collision integrals computed using the NASA Chemical Equilibrium and Applications (CEA) database.

# II. TRANSPORT CLOSURE BASED ON ATOMIC AND MOLECULAR DATA

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#### A. Collision integrals for transport properties

According to the theory of dilute gases by Chapman and Enskog,<sup>30</sup> the transport properties of a multicomponent mixture are obtained via the solution of linear transport systems containing collision integrals for all pairs. The  $\Omega$ -integrals entering in the linear transport system are defined as

$$\Omega_{ij}^{(l,s)}(T) = \sqrt{\frac{k_B T}{2\pi\mu_{ij}}} \int_0^\infty \exp(-\gamma^2) \gamma^{2s+3} Q^l(g) \mathrm{d}\gamma, \qquad (1)$$

where quantity  $\gamma$  is related to the relative velocity, g, via  $\gamma = g\sqrt{\mu_{ij}/2\pi k_B T}$ , where  $\mu_{ij} = m_i m_j/(m_i + m_j)$  is the reduced mass of the colliding pair. The symbol  $Q^l(g)$  denotes the *l*-order transport cross section

$$Q^{l}(g) = 2\pi \int_{0}^{\infty} (1 - \cos^{l}\chi)bdb, \qquad (2)$$

where *b* is the impact parameter and  $\chi = \chi(b, g)$  is the scattering angle which follows from the dynamics of a (classical) binary collision

$$\chi(b,g) = \pi - 2b \int_{0}^{\infty} \frac{dr/r^2}{r^2 - \sqrt{1 - V_{ij}^{eff}(r,b,g)/E^{kin}(g)}},$$
 (3)

with the relative kinetic energy being  $E^{kin}(g) = \mu_{ij}g^2/2$ . The effective potential,  $V_{ij}^{eff}$ , is given by the sum of the interaction potential and a centrifugal contribution

$$V_{ij}^{eff}(r,b,g) = V_{ij}(r) + E^{kin}(g) \left(\frac{b}{r}\right)^2.$$

$$\tag{4}$$

Figure 1 illustrates the dynamics of a binary collision. The deflection angle, and thus the collision itself, depends on several parameters: *b*, the impact parameter, which is the distance of closest approach in the absence of the interaction, *g*, the relative velocity, and  $V_{ij}(r)$ , the interaction potential. Depending on the temperature and distance *r* between the particles, a different description of the interaction potential will be used. Collision integrals can be expressed in their reduced dimensionless form denoted by the superscript \*,

$$\Omega_{ij}^{(l,s)*} = \frac{\Omega_{ij}^{(l,s)}}{\Omega_{ijRS}^{(l,s)}},$$
(5)

where  $\Omega_{iiRS}^{(l,s)}$  is the collision integral for a rigid sphere,

**TABLE II.** Summary of the species belonging to the reduced Mars and Earth mechanisms<sup>13</sup> with their corresponding pure species interaction Lennard-Jones potential parameters, calculated polarizabilities<sup>a</sup> (Bohr cubed), experimental polarizabilities,<sup>b</sup> and numbers of effective electrons [Eq. (18)]. The annotation (d) stands for doublet multiplicity. The references refer to the origin of the Lennard-Jones parameters.

	Atmo	sphere				$\alpha_i, a_0^3$	$\alpha_i, a_0^3$	
Species	Earth	Mars	$\sigma_{ii}$ , Å	$\varepsilon_{ii}$ (eV)	References	Calculated	Expt.	N <sub>eff</sub>
$C(^{3}P)$	•	•	2.940	6.153	14	12.5724	11.88	4.00
CH	•	•	2.750	6.891	14	15.1742		3.80
CH <sub>4</sub>	•	•	3.746	12.184	14	17.0234	16.52	8.00
HNC	•		3.828	20.024	14	18.4569		8.40
HCN	•		3.630	49.031	14	17.1141		8.40
$CN(^{2}\Sigma^{+})$	•		3.856	6.4671	15	21.3997		7.00
CO	•	•	3.690	7.902	15	13.1949	13.18	7.60
CO <sub>2</sub>	•	•	4.444	17.384	16	17.1755	16.92	12.00
$C_2(^1\Sigma_q^+)$	•	•	3.913	6.791	15	48.9535		12.00
$C_2(^3\Pi_u)$	•	•	3.913	6.791	15	31.8498		6.00
$C_2H(^1\Sigma^+)$	•	•	3.243	46.366	15	25.5128		8.11
$C_2 H_2(^{1}\Sigma^{+})$	•	•	4.635	18.021	16	17.1123	23.53	10.00
$C_2H_4(^1\Sigma_{\alpha}^+)$		•	3.270	46.122	14	28.0173	28.26	12.00
CNCN	•		3.856	6.460	15	35.4167	33.84	16.22
CN-NC	•		3.856	6.460	15	37.6151		16.22
NC-CN( $^{2}\Sigma_{\alpha}^{+}$ )	•		3.856	6.460	15	33.4657		16.22
$C_3(^1\Sigma_a^+)$	•	•	3.245	46.135	15	33.7618		9.33
$C_3(^3A)$	•	•	3.245	46.135	15	29.9792		9.33
$C_3H(d)$	•		4.1	18.008	14	34.6612		10.23
$C_3 HN^c$	•		4.715	18.245	14	40.933		16.22
$HCCCCH(^{2}A'')$	•	•	5.180	30.773	14	40.2702		18.00
$C_4H_2(^2A')^c$	•	•	5.180	30.773	14	59.6642	45.96	18.00
C <sub>6</sub> H <sub>2</sub>	•	•	5.180	30.773	14	88.4516		24.15
$C_8H_2$	•		5.680	42.683	14	139.99		32.12
$C_9H_8^{c}$	•	•	5.960	50.722	17	111.268		42.09
A10 <sup>c</sup>	•	•	8.517	35.036	16	438.96		140.03
$H(^{2}S)$	•	•	2.708	3.188	15	5.128 88	4.5	1.00
OH	•	•	2.750	6.866	14	7.5093		5.57
H <sub>2</sub>	•	•	2.827	5.145	15	5.5461	5.31	2.00
$H_2O$	•	•	2.726	30.679	14	9.8059	10.13	6.00
$N(^{4}S)$	•		3.298	6.153	15	7.6335	7.42	5.00
NO	•		3.599	7.840	15	11.5586	11.46	8.27
$N_2(^1\Sigma_g^+)$	•		3.681	7.884	18	11.907 5	11.54	8.40
$O(^{3}P)^{\circ}$	•	•	2.660	6.030	19	5.1978	5.41	6.00
O(S)	•	•	2.660	6.030	19	5.321 44	5.41	6.00
$O_2(^3\Sigma_g^+)$	•	•	3.433	9.738	18	10.5156	10.54	9.33
$O_2(^1\Delta_{\varphi})$	•	•	3.433	9.738	18	10.2788		9.33
$C^+(^2P)$	•	•				6.606 924		

<sup>a</sup>Calculation method: Gaussian 16 B3LYP/aug-cc-pvtz.<sup>20</sup>

<sup>b</sup>Experimental values from the NIST database.<sup>21</sup>

<sup>c</sup>C<sub>4</sub>H<sub>2</sub>: butadiyne, A10: ovalene, C<sub>9</sub>H<sub>8</sub>: indene, C<sub>3</sub>HN: cyanoacetylene.

$$\Omega_{ijRS}^{(l,s)} = \sqrt{\frac{k_B T}{2\pi\mu_{ij}}} \frac{(s+1)!}{2} \left(1 - \frac{1}{2} \frac{1 + (-1)^l}{1 + l}\right) \pi \sigma_{ij}^2, \tag{6}$$

where  $\sigma_{ij}$  is the hard-sphere diameter.

According to the Chapman-Enskog theory, transport properties of a gas mixture can be computed by solving the Boltzmann equation using a Sonine polynomial expansion. Due to the rapid convergence of the expansion, only the first term is required to

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**FIG. 1**. Elastic binary collision between 2 particles with *b*, the impact factor and  $\chi$ , the deflection angle.

accurately represent the coefficients of viscosity, thermal conductivity, and ordinary diffusion as explained in the work of Palmer and Wright<sup>31</sup> and Wright *et al.*<sup>25</sup> Only three reduced expressions for the collision integrals are necessary to compute the binary transport coefficients for a dilute gas mixture, using this first order approximation of the Chapman-Enskog method: the diffusion integral  $\Omega_{ij}^{(1,1)*}$ , the viscosity integral  $\Omega_{ij}^{(2,2)*}$ , and the dimensionless ratio  $B^*$ ,

$$B^* = \frac{5\Omega_{ij}^{(1,2)*} - 4\Omega_{ij}^{(1,3)*}}{\Omega_{ii}^{(1,1)*}}.$$
(7)

Note that to calculate second order terms in the transport approximation, the additional ratio  $C^*$  needs to be determined,

$$C^* = \frac{\Omega_{ij}^{(1,2)*}}{\Omega_{ii}^{(1,1)*}}.$$
(8)

Additional collision integral ratios are necessary for the accurate calculation of electron transport properties in partially ionized gases as higher-order terms of the Sonine expansion are required.

#### **B.** Intermolecular potentials

The methods to determine the intermolecular potential describing the forces between individual species are multiple and are either experimental or quantum-based as described by Capitelli *et al.*<sup>32</sup> As a matter of fact, beam experiments can be used to characterize the repulsive part of the potential. When experiments are not available, interaction energies may be calculated using accurate *ab initio* methods.<sup>33–39</sup> However, the most common approach is to use semiempirical rules to describe the entire or just a part of the potential. Depending on the mixture temperature and therefore the relative kinetic energy between the species, different potential models describe the attraction-repulsion forces are due to the crossing and repulsion of the electron clouds. To describe those short range

interaction forces, the exponential repulsive Born-Mayer potential<sup>40</sup> is generally used. The Born-Mayer potential is accurate for temperatures above 2000 K. At lower temperatures, the particles' trajectories are influenced by the potential at larger distances. Long-range interaction forces are modeled using a more appropriate potential, such as the Lennard-Jones or (12, 6) potential to this extent,

$$V_{ij}(r) = \varepsilon_{ij} \left( \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right), \tag{9}$$

with  $\varepsilon_{ij}$  being the reference potential energy and  $\sigma_{ij}$  being the reference potential length.

For interactions between unlike species, combination rules exist to derive the Born-Mayer and Lennard-Jones parameters based on parameters for like species interactions. The Berthelot rule expresses the Lennard-Jones interaction energy for diatomic species,

$$\varepsilon_{ij} = \sqrt{\varepsilon_i + \varepsilon_j},$$
 (10)

and the Lorentz rule gives the combination rule for the potential length,

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j). \tag{11}$$

Similar combination rules were proposed by Kong *et al.*<sup>41</sup> and André *et al.*<sup>19</sup> for the description of polyatomic species. For instance, to determine  $\varepsilon_{ii}$  and  $\sigma_{ii}$ , André *et al.* illustrated the combination rule for CO as follows:

$$\varepsilon_{\rm CO-CO} = \left(\varepsilon_{\rm C-C}\varepsilon_{\rm O-O}\right)^{1/2},\tag{12}$$

$$\sigma_{\rm CO-CO} = \left(\sigma_{\rm C-C}^3 + \sigma_{\rm O-O}^3\right)^{1/3}.$$
 (13)

This rule can be extended to polyatomic CO<sub>2</sub> as follows:

$$\varepsilon_{\rm CO_2-CO_2} = \left(\varepsilon_{\rm C-C} + \varepsilon_{\rm O-O} + \varepsilon_{\rm O-O}\right)^{1/3},\tag{14}$$

$$\sigma_{\rm CO_2-CO_2} = \left(\sigma_{\rm C-C}^3 + \sigma_{\rm O-O}^3 + \sigma_{\rm O-O}^3\right)^{1/3}.$$
 (15)

For modeling pyrolysis mixtures over a re-entry trajectory, a considerable temperature range should be taken into account ranging from low temperatures (300 K) up to 20 000 K. Consequently, a combination of the short- and long-range potentials should be considered. For instance, the Tang and Toennies potential<sup>42</sup> combines the repulsive Born-Mayer potential with a centrifugal term to cover long-range interactions. The phenomenological potential<sup>43</sup> is an alternative to the above methods. This potential was specifically derived for atom-polyatomic and polyatomic-polyatomic interactions. It is an empirical potential based on the binding energy  $\varepsilon_0$  and the equilibrium distance  $r_e$  between both species in the interaction pair,

$$V(r) = \varepsilon_0 \left[ \frac{m}{n(x) - m} \left( \frac{1}{x} \right)^{n(x)} - \frac{n(x)}{n(x) - m} \left( \frac{1}{x} \right)^m \right], \quad (16)$$

with  $x = r/r_e$  and  $n(x) = \beta + 4x^2$ , where the model parameter  $\beta = \{6, ..., 10\}$  denotes the hardness of the interaction electronic distribution densities. The  $\beta$  parameter can be derived empirically as follows:

$$\beta = 6 + \frac{5}{s_1 + s_2},\tag{17}$$

with  $s_1$  and  $s_2$  being the softness of the collision partners (denoted by subscripts 1 and 2). The softness *s* can be determined as the cubic root of the polarizability. The *m* parameters denotes the type of interaction with m = 6 for neutral-neutral and m = 4 for ion-neutral interactions.<sup>44</sup>

The  $N_{eff}$  parameter quantifies the number of electrons that are involved in the collision between particles. Previously, this number was approximated by the number of electrons in the outer shell. However, Koutselos and Mason<sup>45</sup> showed that the overall electronic structure plays a role in the interaction. A correlation formula has been derived by Cambi *et al.*<sup>43</sup> to predict  $N_{eff}$  based on the effective electrons in the bond, the other external electrons, and the core electrons as follows:

$$N_{eff} = \frac{N_t^2 - N_b N_{nb}}{N_t},\tag{18}$$

with  $N_b$  being the number of bound electrons and  $N_{nb}$  being the unbound externally involved ones;  $N_t$  is the sum of both.

The work of Pirani *et al.*<sup>46</sup> showed that an approximation could be found to estimate parameters for Lennard-Jones type potentials of interaction between like molecules based solely on the static dipole polarizability and number of effective electrons, which simplifies their description in the definition of the potential. For neutral-neutral interactions, the parameters are as follows:

$$\varepsilon_0 = 0.72 \frac{C_d}{r_e^6},\tag{19}$$

$$r_e = 1.767 \frac{\alpha_i^{1/3} + \alpha_j^{1/3}}{(\alpha_i \alpha_j)^{0.095}},$$
(20)

$$C_d = 15.7 \frac{\alpha_i \alpha_j}{\left[\sqrt{\alpha_i/N_{eff_i}} + \sqrt{\alpha_j/N_{eff_j}}\right]},$$
(21)

with m = 6 and indices *i* and *j* denoting 2 neutrals.

The phenomenological potential can also be used to describe ion-neutral interactions. In this special case, the equilibrium distance  $r_e$  and binding energy  $\varepsilon_0$  depend on an additional parameter  $\rho$ , which denotes the relative role of the dispersion,

$$r_e = 1.767 \frac{\alpha_i^{1/3} + \alpha_n^{1/3}}{\alpha_i \alpha_n [1 + 1/\rho]^{0.095}},$$
 (22)

$$\varepsilon_0 = 5.2 \frac{z^2 \alpha_n}{r_e^4} [1 + \rho], \qquad (23)$$

$$\rho = \frac{\alpha_i}{z^2 [1 + (2\alpha_i / \alpha_n)^{(2/3)}] \sqrt{\alpha_n}},$$
 (24)

with *z* being the ion charge, m = 4, and indices *i* and *n* denoting an ion and a neutral, respectively.

Fit coefficients for modeling neutral-neutral and ion-neutral collision integrals using the phenomenological potential of Pirani are provided by Laricchiuta *et al.*<sup>47</sup>

Charged interactions have been modeled using the Debye-Huckel potential, which is a screened Coulomb potential,<sup>48</sup>

$$V(r) = \frac{1}{4\pi \pm} \frac{z_i z_j q_e^2}{r} \exp\left(-\frac{r}{\lambda_D}\right),$$
(25)

shielded by the Debye length,

$$\lambda_D = \left(\frac{\varepsilon_0 k_B/q_e^2}{n_e/T_e + \sum_{j \in H} z_j^2 n_j/T}\right)^{1/2},\tag{26}$$

where  $T_e$  and T are the free electron and heavy species temperature, respectively,  $\varepsilon_0$  is the vacuum dielectric constant, whereas  $z_{i,j}$  stand for the charges measured in units of the elementary/electron charge (e.g., z = 1 for O<sup>+</sup>).

#### C. Recommended collision integrals

In this review, we have used data considered as references for well-known interactions. Collision data for nitrogen, oxygen, and argon interaction pairs in a 13-species weakly ionized air mixture have been reported by Wright et al.<sup>25</sup> in 2005, which provides data for the pairs between N2, N2, O2, O2, NO, NO+, N, N+, O,  $O^+$ , Ar, Ar<sup>+</sup>, and  $e^-$ . The corresponding ion-neutral interaction for this weakly ionized mixture is provided in Ref. 26. Weakly ionized CO<sub>2</sub>-N<sub>2</sub> mixtures encountered during Mars or Venus entries can be described with 17 chemical species: CO<sub>2</sub>, N<sub>2</sub>, N<sub>2</sub><sup>+</sup>, O<sub>2</sub>, CO, CO<sup>+</sup>, NO, NO<sup>+</sup>, CN, CN<sup>+</sup>, C, C<sup>+</sup>, N, N<sup>+</sup>, O, O<sup>+</sup>, and e<sup>-</sup>. Collision data for these pairs have been published by Wright et al. in 2007.<sup>27</sup> Collision data for high-temperature components of the Jupiter atmosphere have been calculated by Bruno et al.<sup>28</sup> in 2010. The Jovian atmosphere is composed out of helium and hydrogen, and therefore a 10-species mixture has been considered using He, He<sup>+</sup>, He<sup>++</sup>, H, H<sup>+</sup>, H<sup>-</sup>, H<sub>2</sub>, H<sub>2</sub><sup>+</sup>, H<sub>3</sub><sup>+</sup>, and  $e^-$ . More recently, Colonna et al.<sup>29</sup> have reported collision data in silicon-oxygen and silicon-carbon bindings.

Considering the species in Table II, we need to find data for all binary interactions between 32 pure species. Given these species, 528 binary interactions should be calculated. Using the data reported by Wright and Bruno, as previously described, this number is reduced to 465 unknown collision pairs.

As a first approximation for neutral-neutral interactions, the Lennard-Jones potential is often used to model the missing integrals. This has mostly been done for applications where the mixture temperature does not exceed 2000 K. The combustion community, for instance, uses the Lennard-Jones potential formulation in various kinetic mechanisms.<sup>49,50</sup> Consequently, it is therefore relatively easy to retrieve data for the potential parameters in the literature. Table II reports the Lennard-Jones reference potential length  $\sigma$  and binding energy  $\varepsilon$  for the pure species interactions. Starting from the pure species parameters, a combination rule can be used to determine the potential length and binding energy in the pair. The Chemkin transport database<sup>14</sup> by Sandia reports Lennard-Jones parameters for the following pure species in the pyrolysis mixture: C, CH, HCN, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, HCCCCH, C<sub>6</sub>H<sub>2</sub>, C<sub>8</sub>, H<sub>2</sub>, OH, and H<sub>2</sub>O. However, C<sub>3</sub>HN was approximated by C<sub>3</sub>H<sub>2</sub>N and HNC by HNCO in the same Chemkin database. Park et al.<sup>15</sup> reported the Lennard-Jones parameters for the following species: CN, CO, C2, C2H, H, H2, N, and NO. In the publication by Cuardros et al.,16 parameters were published for CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>. Ovalene (A<sub>10</sub> or C<sub>32</sub>H<sub>14</sub>) was approximated by the data of Cuardros for C<sub>10</sub>H<sub>14</sub>. The C<sub>9</sub>H<sub>8</sub> interaction was published by Wang.<sup>17</sup> André et al.<sup>19</sup> provided the O interaction, and Magin

*et al.*<sup>18</sup> provided the  $O_2$  and  $N_2$  interactions. Data for CNCN have been approximated by CN and  $C_3H$  by  $C_3H_2$ .

In the present study, the missing neutral-neutral interactions were calculated using the phenomenological potential of Pirani *et al.*<sup>46</sup> and the fits of Laricchiuta *et al.*<sup>47</sup> To this extent, the dipole polarizabilities are reported in Table II together with their effective electron number  $N_{eff}$ .

Ion-neutral interactions were modeled with the Langevin potential using the empirical laws based on the polarizability and ion charge of the neutral collider by Bruno *et al.*,<sup>28</sup> based on the work of Kihara *et al.*<sup>51</sup> Although electron-neutral interactions may be neglected for the calculation of transport properties,<sup>18</sup> *ab initio* data were provided for them through the data published by Wright *et al.*<sup>25–27</sup> and Bruno *et al.*<sup>28</sup> Missing interactions are approximated by the *e*-C interaction. The charged interactions  $C^+-C^+$  and  $e^--e^-$  follow a Debye-Huckel potential. These integrals were determined using the tabulated collision integrals by Mason *et al.*<sup>52</sup>

All data have been implemented and published through the open source library for plasma flows, MUTATION<sup>++</sup>: Multicomponent Thermodynamic and Transport Properties for Ionized Plasmas written in C++,<sup>53</sup> which is available online at https://github.com/mutationpp/Mutationpp.

#### **III. RESULTS**

In the present work, we have collected and reviewed the available transport data for the Mars and Earth atmosphere in a pyrolysis contaminated mixture. Lennard-Jones parameters are reported in Table II. Combination rules were used whenever data was lacking in the literature. Additionally, the polarizability and number of effective electrons were calculated for their use in the phenomenological potential according to Pirani. Finally, transport properties have been calculated and compared with the CEA database.

As an addition to the data for both atmospheres, Table III summarizes the Pirani parameters (i.e., polarizability and effective number of electrons) for the fictive TACOT material.<sup>9</sup> The latter, Theoretical Ablative Composite for Open Testing (TACOT), is a low-density carbon/phenolic with comparable properties as NASA's PICA. It is made of 10% carbon fibers, 10% of phenolic resin, and a porosity of 80%.

# A. Equilibrium transport properties

The potential data derived in the previous sections were used to compute the reduced collision integrals for all interaction pairs in the 10% air +90% pyrolysis mixture described in Table II. The previously derived collision integrals are now used to calculate equilibrium transport properties in a broad temperature range to accommodate atmospheric re-entry conditions. We will compute the dynamic viscosity and thermal conductivity using the new collision database, which was implemented in the MUTATION<sup>++</sup> plasma library.<sup>53</sup>

The equilibrium mole fractions of the reduced pyrolysis mixture were calculated with the MUTATION<sup>++</sup> equilibrium solver and are provided in Fig. 2 for a pressure of 0.1 atm and a temperature range of 300–5000 K. The major species in the mixture are CH<sub>4</sub>, H, C<sub>2</sub>H<sub>2</sub>, CO, C<sub>3</sub>, C, H<sub>2</sub>, and  $e^-$  [Fig. 2(a)]. Minor species are represented in Fig. 2(b).

Species	$\alpha_i, a_0^3$	N <sub>eff</sub>
$\overline{\mathrm{CH}_2(^1\mathrm{A}_1)}$	16.9769	4.67
$CH_2(^{3}B_1)$	15.2793	4.67
$CH_3(^2A_2'')$	16.4445	6.14
CH <sub>2</sub> OH	21.7884	9.92
CNC	30.3258	9.92
CNN	26.6401	10.5
C <sub>2</sub> (t)	31.8498	6.00
$C_2H(^3\Pi)$	18.3908	8.11
$C_2H_6$	29.0613	14.00
CNCOCN	47.1749	22.29
C <sub>3</sub> (t)	29.9792	9.33
C <sub>3</sub> H <sub>3</sub> (1-propynyl)	39.0220	14.07
C <sub>3</sub> H <sub>3</sub> (2-propynyl)	49.1971	14.07
$C_4(^1A_g)$	37.5316	14.25
$C_4(^{3}\Sigma_{\sigma}^{-})$	52.2894	14.25
$C_5(^{1}\Sigma_{\sigma}^{+})$	70.7677	16.80
$C_6H_5O$	75.3399	30.71
C <sub>6</sub> H <sub>6</sub>	69.3388	30.00
C <sub>6</sub> H <sub>5</sub> OH	75.0955	32.44

<sup>a</sup>Calculation method: Gaussian 16 B3LYP/aug-cc-pvtz.<sup>20</sup>

#### 1. Viscosity

Figure 3(a) represents the dynamic viscosity for the airpyrolysis mixture at 1 atm. As can be observed from the graphs, the viscosity increases with temperature. The shear viscosity of a pure gas is a function of its reduced mass  $m_i$  and its reduced viscosity collision integral  $\Omega_{ii}^{(2,2)*}$  as follows:

$$\eta_i = \frac{5}{16} \frac{\sqrt{\pi k_B T \mu_i}}{\Omega_{ii}^{(2,2)*}}.$$
(27)

The viscosity directly relates to the temperature as  $\eta_i \approx \sqrt{T}$ . When the temperature increases and a considerable amount of charged particles are produced, the collision integral  $\Omega_{ii}^{(2,2)*}$  increases considerably as its compound on charge transfer becomes more important.

Both the Lennard-Jones and Pirani potentials were used to calculate the viscosity in Fig. 3(a). As introduced previously, the Lennard-Jones potential is only accurate up to temperatures of 2000 K. However, from the latter, graphs can be observed that both potentials shown similar results until 5000 K is reached. The viscosity is shown in Fig. 4(a) for various pressures. The pressure only affects the viscosity through changes in the mixture composition.

#### 2. Thermal conductivity

Under local thermodynamic equilibrium (LTE) conditions where composition gradients may be related to temperature gradients via  $X_s = X_s(p, T)$ , the total heat flux generated by an ionized mixture can be determined using total thermal conductivity  $\lambda_{tot}$  and

**TABLE III.** Additional species for the TACOT material. The polarizability<sup>a</sup> (Bohr cubed) and  $N_{eff}$  [Eq. (18)] values for the phenomenological potential have been calculated in the present work. The subscript (t) stands for triplet.

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FIG. 2. The mole fractions are presented for air-pyrolysis gas at 0.1 atm and a temperature range from 300 to 5000 K: (a) shows the major species and (b) shows the minor species in the mixture. The small contributions of CH, HNC, HCN, CNCN,  $C_3$ HN,  $C_9$ H<sub>8</sub>, NO, and  $O_2$  are not shown here.

FIG. 3. The differences between the Lennard-Jones and Pirani potential are shown for (a) the viscosity and (b) the mixture thermal conductivity for an air-pyrolysis gas at 1 atm. Full lines: Lennard-Jones. Lines with circles: Pirani.

the temperature gradient,

$$\vec{q} = -\lambda_{tot} \vec{\nabla} T. \tag{28}$$

The mixture thermal conductivity consists of 5 distinct contributions,

$$\lambda_{tot} = \lambda_h + \lambda_e + \lambda_{int} + \lambda_r + \lambda_s, \qquad (29)$$

with  $\lambda_h$  being the contribution of the heavy species,  $\lambda_e$  being the one of the free-electrons,  $\lambda_{int}$  being the internal contribution,  $\lambda_r$  being

the reactive one, and  $\lambda_s$  being the Soret thermal conductivity.<sup>54</sup> For high-temperature plasma, the electron energy remains low; the electron contribution can therefore be neglected. The species presented in Table II are not excited internally, and we can therefore also neglect the internal contribution to the total thermal conductivity. The contribution due to thermal diffusion, or Soret effect, is also negligible in this case. In equilibrium calculations, the major contribution to the total conductivity originates from the reactive component  $\lambda_r$  and the heavy particle contribution  $\lambda_h$ . This can simply be



FIG. 4. The transport properties, (a) the viscosity and (b) the thermal conductivity, are shown for an air-pyrolysis gas at 0.01 (line with triangles), 0.1 (line with circles), and 1 (full lines) atm using the Pirani potential. Increasing pressure is indicated by the arrow with index "p."

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FIG. 5. Transport properties are compared between MUTATION<sup>++</sup> and the CEA database showing (a) the viscosity and (b) the thermal conductivity for a simplified pyrolysis mixture at a pressure of 0.1 atm. Ions have been excluded. Line with circles: MUTATION<sup>++</sup>. Full line: CEA.

explained: as temperature rises, chemistry tends to large gradients in mole fractions.

Figure 3(b) shows the total mixture thermal conductivity for the air mixture. Good agreement is obtained between the Pirani and Lennard-Jones potentials. The effect of the pressure is shown in Fig. 4(b). The conductivity shows a higher maximum at high temperatures when the pressure decreases as shown by the line with circles for a pressure of 0.1 atm and the lines with triangles at 0.01 atm.

## 3. Comparison with the CEA database

The transport properties are now compared with the NASA Chemical Equilibrium and Applications (CEA) database. The latter is widely used to compute accurate thermodynamic and transport properties. Its transport database was revised and compiled by Svehla *et al.*<sup>55</sup> and provides data for 65 neutral species, 27 unlike neutral interactions, 14 ion-neutral interactions, and electron gas. The library provides coefficients to calculate the viscosity, thermal conductivity, and binary interactions for a low (300–1000 K) and a high temperature interval (1000–5000 K), respectively.

The pyrolysis mixture under consideration was reduced in order to match the data available in the CEA database. The latter does not account for CNCN,  $C_8H_2$ ,  $C_9H_8$ ,  $A_10$ ,  $C_3H$ ,  $C_3HN$ , and HCCCCH. Figure 5(a) shows the viscosity at 0.1 atm computed with the CEA database (full lines) and the transport data computed in the present work (lines with circles). The phenomenological potential was used to compute the transport at high temperatures. Good agreement is obtained between both libraries. The mixture thermal conductivity shows some discrepancies as can be observed in Fig. 5(b). The position of the peaks in thermal conductivity depends on the mixture composition. As the composition is the same for both calculations, we can find back this agreement in the comparison.

### **IV. CONCLUSIONS**

In the present paper, collision data were reviewed for two ablative mixtures: air-pyrolysis gas mixtures for Earth and CO<sub>2</sub>pyrolysis mixtures for Mars entries. The latest *ab initio* data for well-known interactions were collected and implemented in the MUTATION<sup>++</sup> library. For the first time, potential data are proposed to calculate the transport properties of ablation species in pyrolysis mixtures. Missing interactions with ablation species were calculated by using the phenomenological potential of Pirani. Dipole polarizabilities were recalculated for all species under consideration. This work also reports Lennard-Jones potential parameters for all species in the air- and CO<sub>2</sub>-pyrolysis mixtures under study. Unknown potential parameters were obtained by using combination rules.

Equilibrium transport properties such as the dynamic viscosity and mixture thermal conductivity were analyzed at different pressures and temperatures and compared to the CEA database for a reduced air-pyrolysis mixture. Good agreement was obtained between both libraries.

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## APPENDIX A: FORMULAS FOR THE BORN-MAYER AND TANG-TOENNIES POTENTIAL

# 1. Born-Mayer

To describe those short range interaction forces, the exponential repulsive Born-Mayer potential<sup>40</sup> is generally used,

$$V(r) = A_{ij}e^{-b_{ij}r},\tag{A1}$$

with  $A_{ij}$  being the reference potential and  $b_{ij}$  being the reference length. The Born-Mayer potential is accurate for temperatures above 2000 K.

The combination rules for the Born-Mayer parameters are presented by Bohm and Ahlrichs.<sup>56</sup> They are accurate up to 6% on the repulsive potential,

$$A_{ij} = (A_i^{b_i^{-1}} A_j^{b_j^{-1}})^{b_{ij}/2},$$
 (A2)

$$b_{ij} = 2 \frac{b_i b_j}{b_i + b_j}.$$
 (A3)

TABLE IV. Collision pairs using the data from Wright et al. W05 stands for Wright et al.,<sup>25</sup> W07 for Wright et al.,<sup>27</sup> LAN for the Langevin potential, and DH for Debye-Huckel.

	$C(^{3}P)$	$CN(^{2}\Sigma^{+})$	СО	CO <sub>2</sub>	$N(^4S)$	NO	$N_2(^1\Sigma_g^+)$	$O(^{3}P)$	O(S)	$O_2(^3\Sigma_g^+)$	$O_2(^1\Delta_g)$	$C^+(^2P)$	<i>e</i> <sup></sup>
$\overline{C(^{3}P)}$	W07												
$CN(^{2}\Sigma^{+})$	W07	W07											
CO	W07	W07	W07										
$CO_2$	W07	W07	W07	W07									
$N(^{4}S)$	W07	W07	W07	W07	W05								
NO	W07	W07	W07	W07	W05	W05							
$N_2(^1\Sigma_g^+)$	W07	W07	W07	W07	W05	W05	W05						
$O(^{3}P)^{\circ}$	W07	W07	W07	W07	W05	W05	W05	W05					
O(S)	W07	W07	W07	W07	W05	W05	W05	W05	W05				
$O_2(^3\Sigma_{\varphi}^+)$	W07	W07	W07	W07	W05	W05	W05	W05	W05	W05			
$O_2(^1\Delta_{\varphi})$	W07	W07	W07	W07	W05	W05	W05	W05	W05	W05	W05		
$C^{+}(^{2}P)^{*}$	W07	LAN	W07	LAN	W07	LAN	LAN	W07	W07	W07	W07	DH	
e <sup>-</sup>	W07	W07	W07	W07	W05	W05	W05	W05	W05	W05	W05	DH	DH

# 2. Tang-Toennies

The Tang and Toennies potential<sup>42</sup> combines the repulsive Born-Mayer potential with a centrifugal term to cover the longrange interactions,

$$V(r) = A_{ij}e^{-b_{ij}r} - \sum_{n=3}^{\infty} f_{2n}(r)\frac{C_{2n}}{r^{2n}}.$$
 (A4)

The centrifugal term is the sum of the damping function,  $f_{2n}$ , multiplied by the dispersion coefficient,  $C_{2n}$ , weighted by the intermolecular distance  $r^{2n}$ ,

$$f_{2n} = 1 - e^{-b_{ij}r} \sum_{k=0}^{2n} \frac{(b_{ij}r)^k}{k!}.$$
 (A5)

The Slater-Kirkwood<sup>57</sup> formula for dispersion coefficients using the isotropic dipole polarizability of the interaction pair and the number of effective electrons in the outer shell ( $N_{eff}$ ) gives one of the best approximations compared with experimental data. Three dispersion coefficients (C<sub>6</sub>, C<sub>8</sub>, and C<sub>10</sub>) are sufficient to obtain accurate results.<sup>43</sup>

# APPENDIX B: SPECIES INTERACTION TABLES

Table IV summarizes the interactions taken from the works of Wright *et al.*<sup>25,27</sup> for the collisions between the species:  $C({}^{3}P)$ ,  $CN({}^{2}\Sigma^{+})$ , CO, CO<sub>2</sub>,  $N({}^{4}S)$ , NO,  $N_{2}({}^{1}\Sigma_{g}^{+})$ ,  $O({}^{3}P)$ , O(S),  $O_{2}({}^{3}\Sigma_{g}^{+})$ ,  $O_{2}({}^{1}\Delta_{g})$ ,  $C^{+}({}^{2}P)$ , and  $e^{-}$ .

TABLE V. Collision	pairs	using	the	data	from	Bruno	et a	1.28
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	H( <sup>2</sup> <i>S</i> )	$H_2$	<i>e</i> <sup></sup>	
$H(^2S)$	B10			
$H_2$	B10	B10		
<i>e</i> <sup>-</sup>	B10	B10	DH	

Table V summarizes the interactions taken from Bruno *et al.*<sup>28</sup> for the collisions between  $H(^{2}S)$ ,  $H_{2}$  and  $e^{-}$ .

Table VI summarizes the electron-neutral interaction that use data from other pairs defined in Tables V and IV.

All other interactions use the phenomenological potential of Pirani.

TABLE VI	Electron-neutral	interactions	usina	data	from oth	her nai	irs
IADLE VI.	Liection-neutral	Interactions	using	uala	10111 00	ici pai	11 0

	e—
СН	e-C
$CH_4$	e-C
HNC	e-CN
HCN	e-CN
$C_2(^1\Sigma_g^+)$	e-C
$C_2({}^3\Pi_u)$	e-C
$C_2H(^1\Sigma^+)$	e-C
$C_2H_2(^1\Sigma^+)$	e-C
$C_2H_4$	e-C
CNCN	e-CN
CN-NC	e-CN
$NC-CN(^{1}\Sigma^{+})$	e-CN
$C_3(^1\Sigma_g^+)$	e-C
$C_3({}^3\mathring{A})$	e-C
$C_3H(D)$	e-C
C <sub>3</sub> HN	e-CN
$HCCCCH(^{2}A'')$	e-C
$C_4H_2(^2A')$	e-C
$C_6H_2$	e-C
$C_8H_2$	e-C
$C_9H_8$	e-C
A10	e-C
OH	e-O
H <sub>2</sub> O	e-O

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