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Thermodynamic and Transport Properties for Inductive Plasma Modeling

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A review is given of models for the thermodynamic and transport properties of inductive plasmas under conditions of local thermodynamic equilibrium. The thermodynamic properties of individual species are computed using a statistical mechanics formulation based upon the rigid rotator and harmonic oscillator model. Complex cut-off criteria for the electronic levels and anharmonicity corrections are not needed for practical equilibrium calculations. An efficient iterative technique is proposed for the calculation of the equilibrium mixture thermodynamics properties. Through a Schur-complement approach the number of unknowns in the nonlinear system, which determines the equilibrium chemical composition, may be reduced to the number of basic elements. The method is demonstrated for equilibrium air computations. The plasma transport properties are computed with the method of Chapman and Enskog. Accurate formulas for the heavy particle and electron transport properties are discussed. Through a straightforward argument the result of Butler and Brokaw for the reactive thermal conductivity is shown to be valid for ionized equilibrium mixtures. Computed results for the thermodynamic and transport properties of air are compared with numerical and experimental results of other researchers.

Nomenclature

c = global concentration, mol/m^3
D_{ij} = binary diffusion coefficient, m^2/s
h = enthalpy per unit mole, J/mol
$\boldsymbol{J}$ = Jacobian matrix
K = equilibrium constant (unit varies)
M = molar mass, kg/mol
m = mass, kg
N = number of particles
N_A = Avogadro number, part./mol
n_c = number of elements in the mixture
n_r = number of chemical reactions
n_{sp} = number of chemical species
p = pressure, Pa
R = universal gas constant, J/(mol K)
T = temperature, K
$\boldsymbol{W}$ = diffusive mole flux, mol/(m^2 s)
X^c = constant in mass-conservation equations
x = mole fraction
$\bar{x}$ = natural logarithm of the mole fraction
Y^c = constant in mass-conservation equations
y = mass fraction
$\bar{y}$ = natural logarithm of the mass fraction
Z = mole ratio (number of moles/initial number of moles)
$\boldsymbol{z}$ = right-hand side vector in Newton equation
z_i = number of electron charges of the species
Δh^r = heat of reaction per unit mole, J/mol
$\Delta \boldsymbol{x}$ = unknowns in Newton equation
μ^o = chemical potential for unit pressure, J/(mol K)
ν = stoichiometric coefficient
ξ = reduced formation coefficients
ρ = density, kg/m^3
φ = formation coefficient

Subscripts and Superscripts

c = related to element-conservation equations
e = electron species
h = heavy species (i.e., nonelectron)
i = mixture species i
o = initial
p = related to pressure
r = related to chemical reaction equations
x = related to mole fractions
y = related to mass fractions

Introduction

IN an inductive plasma torch a gas at ambient temperatures is heated in an electrodeless manner to a plasma state, with peak temperatures of about 10,000 K. The highly pure plasma thus obtained is well suited for a wide variety of industrial and scientific applications.[1] In the aerospace industry air inductive plasmas are used to test thermal protection systems for re-entry space vehicles.

Facilities capable of reproducing the severe heat conditions of atmospheric reentry, with run times of half an hour or more, were originally developed by Russian researchers.[2] The European Space Agency (ESA) has recognized the advantages of inductive heating in terms of chemical plasma purity. It therefore decided to sponsor, together with the Belgian Federal Office for Scientific, Technical, and Cultural Affairs, the construction of a 1.2 MW inductively-heated plasmatron wind tunnel at the von Kármán Institute (VKI).[3] The facility was inaugurated on 8 December 1997, and is now operational.[4]

Numerical models play an important role in the design and study of a high-enthalpy facility.[5] At pressures typically used in inductive plasmatrons (from 0.01 to 1 atm), equilibrium models provide

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reasonable estimates for design purposes,[6] as air inductive plasmas are then known to be reasonably close to thermochemical equilibrium. Such models are also required to analyze the results of spectroscopic or probe measurements in the plasma.[7] Adequate models of thermodynamic and transport properties are an essential part of any plasma flow model. For example, basic heat-flux rate determination directly depends on total enthalpy, density, viscosity, and thermal conductivity.

The purpose of this paper is to offer a review of the approach taken by the research group at the VKI toward efficient and accurate modeling of thermodynamic and transport properties of arbitrary chemically reacting mixtures in thermochemical equilibrium. This work is mainly oriented toward inductive plasmas, in a pressure range below and around atmospheric pressure, for temperatures up to 15,000 K (Ref. 1). The presented models have been coded in a Fortran library called pegase (perfect gas equation).[8]

Single-Species Thermodynamics

Plasmas can be considered as chemically reacting mixtures of individual species (atoms, molecules, ions, and electrons). The internal energy partly comes from the translation and partly from internal degrees of freedom (electronic, rotational, and vibrational). If the molecules are assumed to rotate as rigid bodies and oscillate harmonically about their centers of mass, the internal energy modes are independent. The contribution of individual modes to the thermodynamic properties can then simply be summed together.

The calculation of the thermodynamic properties of individual species is presented in standard textbooks.[9,10] Here, comments are made on the relative importance of corrections to this basic theory and the practical implementation of it.

Electronic Contribution Cutoff Criteria

Various authors have discussed the need to terminate the summation over the electronic quantum number when computing the electronic contributions, as the mathematical expressions diverge. Cutoff criteria may be divided into two categories:

1) First is the stand-alone category, based on practical considerations (retain only observed excitation levels, consider only valence states[11]) or physical considerations (retain only the levels lying below the ionization potential[12]).

2) Second is the interaction-based category, requiring a knowledge of the environment, be it mechanical (the radius of an electronic orbit cannot be bigger than the mean distance between atoms) or electromagnetic[13] (the presence of charged particles reduces the attraction between the nucleus and the farthest orbits, lowering the ionization potential, which is called the Debye effect); they require the knowledge of the mixture composition.

Most elaborate cutoff criteria bring considerable complications in the computations. The impact of the two-variable dependence transforms the species into real gases, just as using the Van der Waals or virial expansion equations of state would. In addition, corrections requiring a knowledge of the mixture composition drastically increase the time needed to compute the equilibrium composition: because the equilibrium constants are computed from the partition functions of the species, they become composition dependent.

The effect of the number of electronic levels has been assessed by computations of the single-species enthalpy, while varying the maximum number of electronic levels within a reasonable range of observed levels (taken from Gurvich et al.[14]). Figure 1 shows the results for the N^+ ion. The curves for six to nine levels are superimposed. The number of significant levels to include in the case of atoms, up to 15,000 K, is summarized in Table 1.

This truncation is compared to the results of various reference tables (JANAF,[15] NASA,[16] ESA,[17] and Gurvich et al.[18]). Of these, JANAF and NASA tables are limited to 6000 K, and ESA tables provide the properties as a function of different ionization potential lowering cutoff criteria. Gurvich et al.[18] offer a comprehensive set of data up to 20,000 K, i.e., at a temperature high enough to see the effect of the number of electronic levels considered. Figure 2 shows a comparison for O, where it is seen that all references agree quite well except, at higher temperatures, ESA. The reason for this deviation is the inclusion of all theoretical energy levels with an ionization potential lowering value of $\Delta E = 10^4$ cm $^{-1}$, whereas Gurvich et al.[18] only use observed levels.

Table 1 Number of electronic levels to be considered in the 13-species air model

Atoms	Number of levels	Molecules	Number of levels
Ar	9	N_2	9
Ar^+	2	$N_2{}^+$	15
N	5	NO	5
N^+	6	NO^+	8
O	5	O_2	5
O^+	5	$O_2{}^+$	7

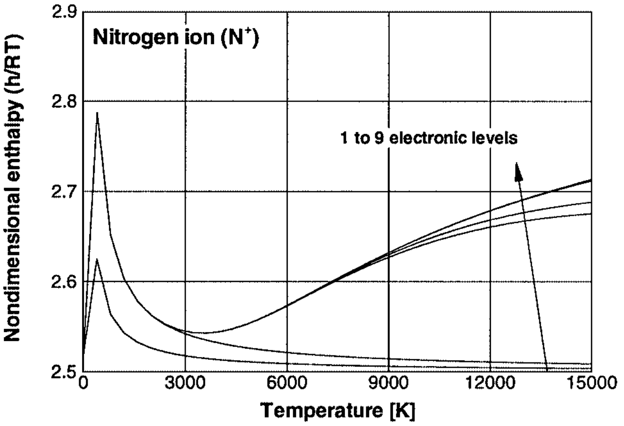


Fig. 1 Enthalpy of N^+ ion as a function of the number of electronic levels.

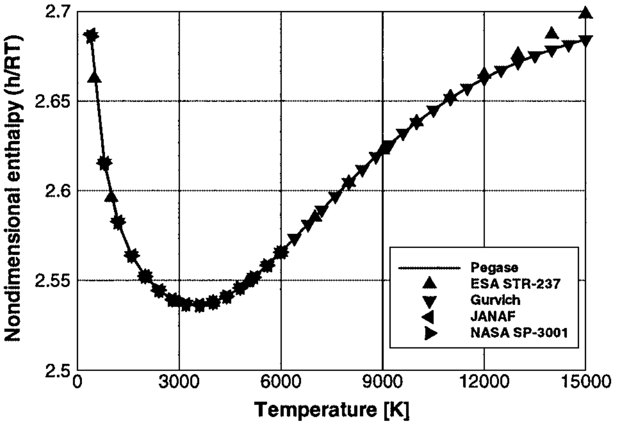


Fig. 2 Enthalpy of O atom compared to various authors.

Anharmonicity Corrections

Anharmonicity corrections come from the fact that the molecules stretch while rotating, changing the natural frequencies.[19] Likewise, the vibrations alter the moment of inertia. Thus, rotation and vibration are coupled and should be treated together. Mayer and Mayer[20] provide a first-order correction to the harmonic oscillator result. This term should be considered dependent on the electronic levels[21]; hence all internal modes are fully coupled. However, an infinite number of rotational and vibrational levels are still assumed, leading to an overestimation of the energy. A clear improvement is obtained by direct summation[21] over a finite number of rotational and vibrational states. The best accuracy is obtained by the numerical solution of Schrödinger's equation.[22]

The harmonic oscillator and first-order (loosely and fully coupled) anharmonicity models were implemented with the newest sets of spectroscopic data available.[11] They are compared in Fig. 3 with reference data for the O_2 molecule (with a variable number of electronic

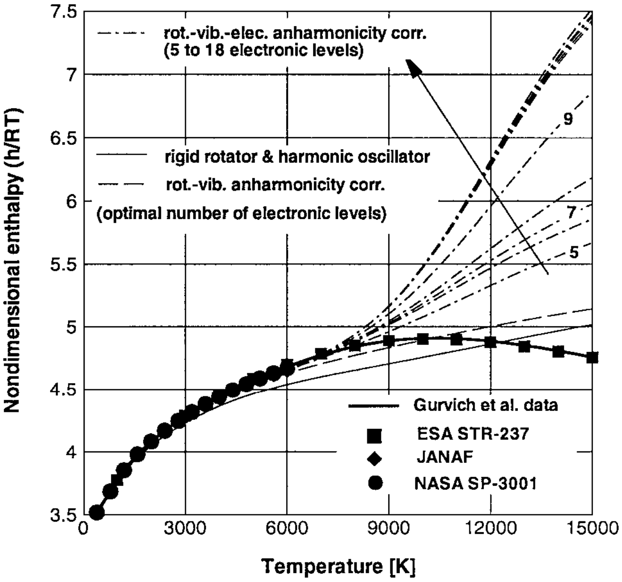


Fig. 3 Effects of anharmonicity on the enthalpy of O_2 molecule.

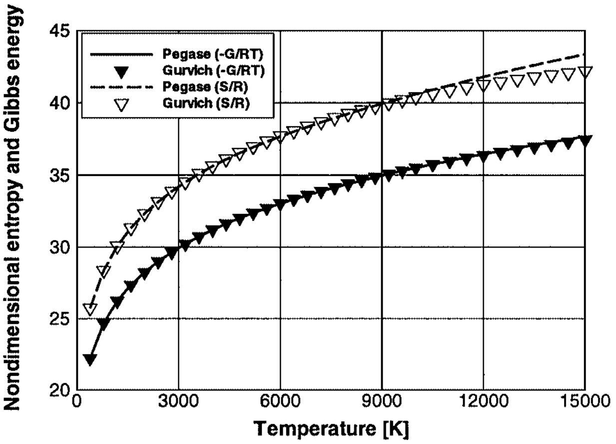


Fig. 4 Gibbs free energy and entropy of O_2 molecule at 1 bar.

levels to estimate the best cutoff). Three clusters of curves can be seen, one for each anharmonicity model. Clearly, the fully coupled model best approaches the reference data. However, above 8000 K the data computed with the direct summation method (Gurvich and ESA) show a different trend. In that range the first-order corrections are totally inadequate. For molecules having low-lying energy levels, the discrepancy appears at such a low temperature (it is not the case with N_2, for which first-order corrections remain accurate up to 15,000 K). Hence, in the case of molecules, it is necessary to include a number of electronic levels based on comparison with reference data to avoid excessive overpredictions at high temperature (see Table 1).

Discrepancies caused by anharmonicity are greatly reduced because molecules dissociate at temperatures where first-order corrections are accurate enough. If the ultimate goal is to obtain accuracy on the mixture properties, then errors from the species come into play weighted by the mass fraction of the species in the mixture, which, in the case of molecules, is practically zero (even for ionized molecules, as shown in later results for air plasma). Furthermore, anharmonicity will cause a change in composition only if it significantly affects the Gibbs free energy, used to compute the equilibrium chemical composition. As shown on Fig. 4 for O_2, there is no difference between the pegase and Gurvich models.

The consideration of anharmonicity increases the computational time and makes the extension to thermal nonequilibrium tedious. Whereas its inclusion gives more physical models, the authors do not consider the gain in accuracy to justify the additional effort and cost involved.

Equilibrium Mixture Composition

A mixture of n_{sp} chemically reacting species is considered, in which all particles are composed out of n_c basic elements. The conservation of these elements in chemical reactions is expressed by n_c mass- and/or charge-conservation equations. The chemical composition of the mixture is completely determined by adding $n_r = n_{sp} - n_c$ reaction equations,[10,23] which only need to be linearly independent. The condition of equilibrium is written as

$$\prod_{i=1}^{n_{sp}} p_i^{\nu_i} = K_p(T) \tag{1}$$

with the equilibrium constant K_p being a function of temperature only.

Practical Implementation

The conservation of mass (or charge) is written, in terms of mass fractions, as

$$\sum_{i=1}^{n_{sp}} \varphi_i^c \frac{y_i}{M_i} = \frac{N_o^c}{m_o N_A} = Y^c \qquad (c = 1 \ldots n_c) \tag{2}$$

The formation coefficients φ_i^c are the number of nuclei of basic component c in the species i. The right-hand side is computed at reference conditions by providing an initial array of mass fractions that sum up to one.

The chemical reaction equations are rewritten in terms of mass fractions if the input conditions are density and temperature. The equilibrium constant can be expressed in terms of the chemical potentials μ_i^o of the species, which correspond to the species Gibbs free energy per unit mole at a pressure of 1 Pa:

$$\prod_{i=1}^{n_{sp}} y_i^{\nu_i^r} = K_y^r \qquad (r = 1 \ldots n_r) \tag{3}$$

with

$$\ln K_y^r = \frac{-1}{RT} \sum_{i=1}^{n_{sp}} \nu_i^r \mu_i^o - \ln(\rho R T) \sum_{i=1}^{n_{sp}} \nu_i^r + \sum_{i=1}^{n_{sp}} \nu_i^r \ln M_i \tag{4}$$

Equations (2) and (3) are expressed in terms of the logarithms of the mass fractions, leading to a linear form for Eq. (3). The final system is expressed as

$$\begin{aligned} &\sum_{i=1}^{n_{sp}} \nu_i^r \bar{y}_i - \ln K_y^r = 0 \qquad (r = 1 \ldots n_r) \\ &\sum_{i=1}^{n_{sp}} \xi_i^c e^{\bar{y}_i} - Y^c = 0 \qquad (c = 1 \ldots n_c) \end{aligned} \tag{5}$$

with

$$\bar{y}_i = \ln y_i \qquad \xi_i^c = \frac{\varphi_i^c}{M_i} \qquad Y^c = \sum_{i=1}^{n_{sp}} \xi_i y_{i,o} \tag{6}$$

An equivalent result is obtained in terms of mole fractions if the input conditions are pressure and temperature:

$$\begin{aligned} &\sum_{i=1}^{n_{sp}} \nu_i^r \bar{x}_i - \ln K_x^r = 0 \qquad (r = 1 \ldots n_r) \\ &\sum_{i=1}^{n_{sp}} \xi_i^c e^{\bar{x}_i} - \frac{1}{Z} X^c = 0 \qquad (c = 1 \ldots n_c) \\ &\sum_{i=1}^{n_{sp}} e^{\bar{x}_i} - 1 = 0 \end{aligned} \tag{7}$$

with

$$\bar{x}_i = \ell n\, x_i \qquad \xi_i^c = \varphi_i^c \qquad X^c = \sum_{i=1}^{n_{\mathrm{sp}}} \xi_i x_{i,o} \tag{8}$$

$$\ell n\, K_x^r = \frac{-1}{RT} \sum_{i=1}^{n_{\mathrm{sp}}} \nu_i^r \mu_i^o - \ell n\, p \sum_{i=1}^{n_{\mathrm{sp}}} \nu_i^r \tag{9}$$

The inverse of the mole ratio Z (number of moles in the mixture divided by the initial number of moles) appears in Eq. (7) as an additional unknown because the number of moles changes as chemical reactions take place.

Numerical Solution

We shall present here the technique used in the mole fraction approach because it contains an additional equation. The extension to mass fractions is straightforward. The system is solved using the Newton–Raphson technique. In block-matrix form one has

$$\begin{pmatrix} \boldsymbol{J}_{rr} & \boldsymbol{J}_{rc} \\ \boldsymbol{J}_{cr} & \boldsymbol{J}_{cc} \end{pmatrix} \begin{pmatrix} \Delta \bar{\boldsymbol{x}}_r \\ \Delta \bar{\boldsymbol{x}}_c \end{pmatrix} = \begin{pmatrix} -z_r \\ -z_c \end{pmatrix} \tag{10}$$

with the Jacobian and right-hand side submatrices given by

$$\boldsymbol{J}_{rr} = \begin{pmatrix} \nu_1^1 & \cdots & \nu_{nr}^1 \\ \cdots & & \cdots \\ \nu_1^{nr} & \cdots & \nu_{nr}^{nr} \end{pmatrix} \qquad \boldsymbol{J}_{rc} = \begin{pmatrix} \nu_{nr+1}^1 & \cdots & \nu_{n_{\mathrm{sp}}}^1 & 0 \\ \cdots & & \cdots & 0 \\ \nu_{nr+1}^{nr} & \cdots & \nu_{n_{\mathrm{sp}}}^{nr} & 0 \end{pmatrix}$$

$$\boldsymbol{J}_{cr} = \begin{pmatrix} \xi_1^1 e^{\bar{x}_1} & \cdots & \xi_{nr}^1 e^{\bar{x}_{nr}} \\ \cdots & & \cdots \\ \xi_1^{nc} e^{\bar{x}_1} & \cdots & \xi_{nr}^{nc} e^{\bar{x}_{nr}} \\ e^{\bar{x}_1} & \cdots & e^{\bar{x}_{nr}} \end{pmatrix}$$

$$\boldsymbol{J}_{cc} = \begin{pmatrix} \xi_{nr+1}^1 e^{\bar{x}_{nr+1}} & \cdots & \xi_{n_{\mathrm{sp}}}^1 e^{\bar{x}_{n_{\mathrm{sp}}}} & -X^1 \\ \cdots & & \cdots & \cdots \\ \xi_{nr+1}^{nc} e^{\bar{x}_{nr+1}} & \cdots & \xi_{n_{\mathrm{sp}}}^{nc} e^{\bar{x}_{n_{\mathrm{sp}}}} & -X^{nc} \\ e^{\bar{x}_{nr+1}} & \cdots & e^{\bar{x}_{n_{\mathrm{sp}}}} & 0 \end{pmatrix}$$

$$z_r^{(k)} = \sum_{i=1}^{n_{\mathrm{sp}}} \nu_i^k \bar{x}_i - \ell n\, K_x^k \qquad (k = 1 \ldots n_r)$$

$$z_c^{(k)} = \sum_{i=1}^{n_{\mathrm{sp}}} \xi_i^k e^{\bar{x}_i} - \bar{x}_{n_{\mathrm{sp}}+1} X^k \qquad (k = 1 \ldots n_c)$$

$$z_c^{nc+1} = \sum_{i=1}^{n_{\mathrm{sp}}} e^{\bar{x}_i} - 1$$

The linearized system takes a simple form in which the upper n_r rows are constant and equal to the corresponding rows of the stoichiometric matrix. Because the reactions can be arbitrary, the authors have found it always possible to arrange unknowns and reactions such that the upper left $n_r \times n_r$ submatrix $\boldsymbol{J}_{rr}$ be diagonal. The size of the system can then be reduced using the Schur complement of the Jacobian. The system is analytically reduced to

$$\begin{gathered} \left(\boldsymbol{J}_{cc} - \boldsymbol{J}_{cr} \boldsymbol{J}_{rr}^{-1} \boldsymbol{J}_{rc}\right) \Delta \bar{\boldsymbol{x}}_c = \left(\boldsymbol{J}_{cr} \boldsymbol{J}_{rr}^{-1} z_r - z_c\right) \\ \Delta \bar{\boldsymbol{x}}_r = -\boldsymbol{J}_{rr}^{-1} z_r - \boldsymbol{J}_{rr}^{-1} \boldsymbol{J}_{rc} \Delta \bar{\boldsymbol{x}}_c \end{gathered} \tag{11}$$

which allows to compute $\Delta \bar{\boldsymbol{x}}_c$ numerically from a $(n_c + 1) \times (n_c + 1)$ system. Because $\boldsymbol{J}_{rr}^{-1}$ is diagonal, the matrix $(\boldsymbol{J}_{cc} - \boldsymbol{J}_{cr} \boldsymbol{J}_{rr}^{-1} \boldsymbol{J}_{rc})$ is easily computed. $\Delta \bar{\boldsymbol{x}}_r$ is then computed by simple matrix algebra. The gain in computational time is significant because a small number of elements can give birth to a huge number of chemical species ($n_r \gg n_c$). This efficiency is of course important for inclusion in an equilibrium computational fluid dynamics (CFD) code. The method can be viewed as a variant of the work of Gordon et al.[24] and Gordon and McBride[25] at NASA although they use Gibbs' energy minimization (which is equivalent to the present technique, but avoids having to define basic and derived components and is easier to use with condensed phases,[26] which are not considered here). In the NASA method the reduced linear equations are explicitly written by analytical substitution from the original system, whereas in the present approach the original system is inverted using a partly analytical and partly numerical approach.

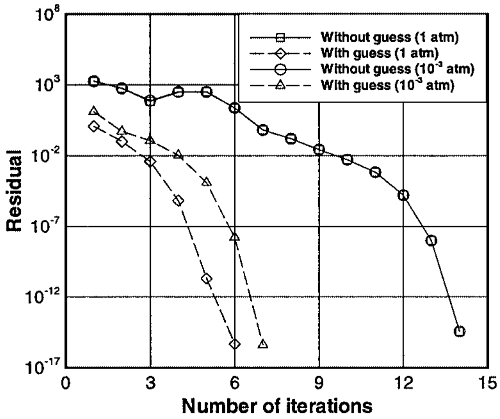


Fig. 5 Convergence properties of the equilibrium composition computation scheme.

The proposed method was found to be very robust even in the case of poor initial estimates for the mole or mass fractions. No underrelaxation needs to be applied (unknowns are simply constrained to remain between $2.6\ 10^{-99}$ and 1.0). When initial fractions of 1.0 are given to each species (a nonphysical choice), 12 orders of magnitude convergence is obtained in fewer than 15 iterations (Fig. 5). When a fair initial estimate is given (e.g., the preceding point in a series of calculations), convergence is obtained within three to seven iterations. This is only slightly better (but of the same order) than the documented convergence performance of Gordon and McBride,[25] both methods being of Newton type.

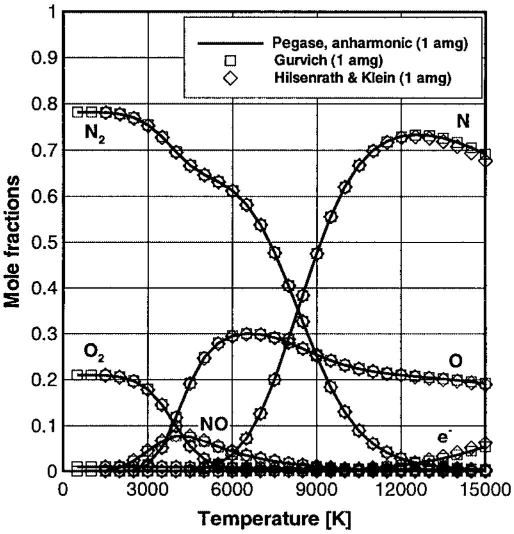
Results

This technique has been used to compute the composition of air plasma (13 species model: O_2, O, O^+, $O_2{}^+$, N_2, N, N^+, $N_2{}^+$, NO, NO^+, Ar, Ar^+, e^-). The results are compared to the tabulated calculations of Hilsenrath and Klein[27] (which include 28 species and virial corrections) and to equilibrium computations performed using pegase with species properties computed from the tables of Gurvich et al.[18] Figure 6 shows the results for normal density (1.29313 kg/m^3), where anharmonicity effects are most likely to be seen. Indeed, the pegase and Gurvich et al.[18] results for $O_2{}^+$ and $N_2{}^+$ show a small difference, although the present computations fit rather well with the reference computations. More discrepancies can be seen with the results of Hilsenrath and Klein[27] (globally, more electrons and ions, less neutrals), which can be caused by several causes. One is the improvement on species data from 1965 to 1989. Another is the inclusion of additional ions. The Debye effect, which favors the formation of ions, can also be a cause. Nevertheless, the effects are very small, and in most of the temperature ranges all data sets superimpose perfectly. Composition has also been computed at lower density; all data sets fit extremely well and will not be presented here.

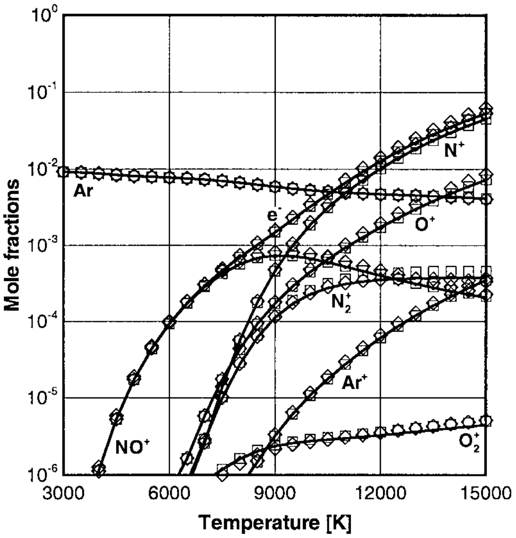
Thermodynamic Properties

Thermodynamic properties are readily obtained by weighting the species properties by the appropriate (mole or mass) fraction, including the formation enthalpy at 0 K for all species but homogeneous molecules and atoms in their natural state, in order to take into account energy released in the gas by chemical reactions between the species.[9,10]

The accuracy of the various models is best checked using enthalpy, which is one of the most important flow parameters, being



a) Neutrals



b) Ions

Fig. 6 Composition of air at 1.29313 kg/m^3.

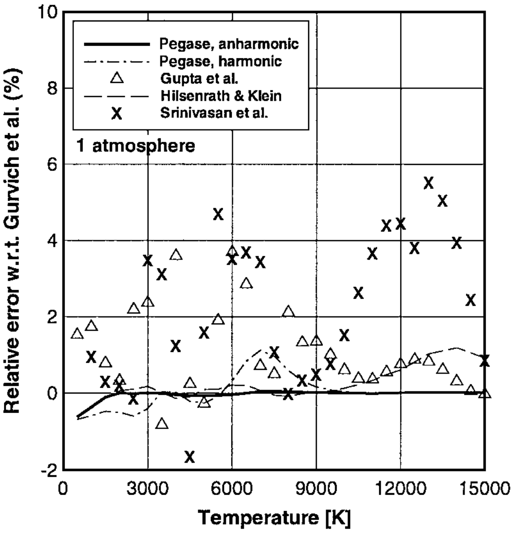


Fig. 7 Relative errors of various models on the enthalpy of air at 1 atm.

for example directly proportional to the stagnation-point heat-flux rate. Globally, all models were found to be equivalent within engineering standards (5%). Figure 7 shows the enthalpy of 13-species air plasma at atmospheric pressure in terms of the relative error (in percent) compared to the perfect gas mixture enthalpy computed using species properties of Gurvich et al.[18] and the pegase algorithm for composition. Additional comparison is also made with the curve fits of Srinivasan et al.[28] and of Gupta et al.[29] At a glance the curve fits show random scatter within an uncertainty band of 5% (Srinivasan et al.) and 4% (Gupta et al.). First-order anharmonicity corrections with straight cutoff lead to results in fairly good agreement with our chosen reference (0.4% excluding the point at 500 K), whereas results using the harmonic oscillator approach show up to 1.1% deviation. The data of Hilsenrath and Klein[27] agree up to about 9000 K, then starts to deviate up to 1.2%. Because real-gas effects should not be significant (the density being of the order of 10^{-2} kg/m^3), this difference can certainly be attributed to slight changes in the composition (it could be produced by an increase of 7 10^{-3} of the N$^+$ mass fraction and a corresponding decrease of the N mass fraction) caused by the greater number of species treated and the different initial mixture considered. Which of the two sets (Gurvich et al.[18] or Hilsenrath and Klein[27]) should be considered better remains unclear.

Transport Properties

The plasma transport properties are computed by the method of Chapman–Enskog in function of the chemical composition, the temperature and pressure, and the interaction potentials between the various colliding plasma particles.[30] The first-order correction to the equilibrium Maxwell–Boltzmann solution is obtained in terms of a series of Sonine polynomials. Usually, taking the first non-vanishing Sonine contribution in the expression for the transport coefficients provides sufficiently accurate results.

Mixture Rules

Formulas of Hirschfelder

Hirschfelder et al. have derived rigorous expressions for the transport properties of mixtures of gases.[30] They are obtained as ratios of determinants, proportional in size to the number of species involved. For complex mixtures of gases, the computational work involved in both the computation of the determinant entries and the evaluation of the determinants itself is considerable. Therefore approximations to the Hirschfelder formulas, commonly referred to as mixture rules, have been derived by several researchers.

Formulas of Yos

For neutral gas mixtures, where all plasma particles interact through similar short-range neutral-neutral interactions, one finds that the off-diagonal elements in the Hirschfelder formulas are small with respect to the diagonal elements. A straightforward mixture rule may be derived by neglecting all off-diagonal entries.[31] Alas, this approach does not work as well for inductive plasma mixtures in which charged-neutral and long-range charged-charged interactions play an important role. Mixture rules, taking the off-diagonal elements into account in an approximate manner, were derived by Yos[32] and Gupta et al.[33] They were found to be sufficiently accurate for the heavy particle thermal conductivity and viscosity. The contribution of internal degrees of freedom to the energy transport is modeled by means of an Eucken-type approximation.[33]

Formula of Butler and Brokaw

Butler and Brokaw[34] and Brokaw[35] have shown that, under conditions of local chemical equilibrium, the energy transport by diffusion of species reaction enthalpies may be taken into account by means of a reactive thermal conductivity coefficient. The mixture rule approximation proposed by Yos[32] and Gupta et al.[33] was found to be somewhat inaccurate when the degree of ionization is significant. The result of Butler and Brokaw was originally derived for neutral gas mixtures, neglecting thermal and pressure diffusion effects. The contribution of thermal diffusion amounts to no more than about 1% (Ref. 36). The neglect of pressure diffusion is well-justified for typically subsonic inductive plasma flows. However, it is not obvious that a result obtained for neutral gases would also hold for ionized gases. Although some justification was given by Meador and Staton,[37] the authors nevertheless consider it useful to include a more straightforward argument valid for general multicomponent ionized mixtures.

Because of their small mass, electrons tend to diffuse much faster than heavy particles. They thereby cause slight violations of charge neutrality and generate a corresponding electric field. This field dramatically slows down the diffusing electrons and, to a lesser extent, also affects the diffusing ions, such that overall quasineutrality is maintained.[38] In inductive plasmas diffusion is important in a narrow skin layer near the electrically insulated wall surrounding the plasma. Ions and electrons diffuse in the direction normal to the wall in such a manner that the net electric current is zero, a situation referred to as ambipolar diffusion:

$$\sum_{i=1}^{n_{\mathrm{sp}}} z_i \boldsymbol{W}_i = 0 \tag{12}$$

The heavy particle number fluxes under conditions of ambipolar diffusion are given up to order $(m_e/m_h)^{1/2}$ by the following relations[39]:

$$\sum_{j=1}^{n_{\mathrm{sp}}} \left(\frac{1}{cD_{ij}}\right)(x_i \boldsymbol{W}_j - x_j \boldsymbol{W}_i) = \nabla x_i - \left(\frac{z_i x_i}{z_e x_e}\right)\nabla x_e \qquad (i \neq e) \tag{13}$$

The second term on the right-hand side represents the effect of the ambipolar electric field. Following the original argument of Butler and Brokaw,[34] one takes the gradient of the first of Eqs. (7) and applies van't Hoff's relation:

$$\left(\frac{\Delta h^r}{RT^2}\right)\nabla T = \sum_{i=1}^{n_{\mathrm{sp}}} \left(\frac{\nu_i^r}{x_i}\right)\nabla x_i \qquad (r = 1\ldots n_r) \tag{14}$$

Substituting Eqs. (13) into this expression, we find that

$$\left(\frac{\Delta h^r}{RT^2}\right)\nabla T = \sum_{i=1}^{n_{\mathrm{sp}}}\sum_{j=1}^{n_{\mathrm{sp}}} \left(\frac{\nu_i^r}{cx_i D_{ij}}\right)(x_i \boldsymbol{W}_j - x_j \mathrm{W}_i) + \left(\frac{1}{x_e z_e}\right)\sum_{i=1}^{n_{\mathrm{sp}}} \nu_i^r z_i \nabla x_e \tag{15}$$

Here, negligible terms proportional to $D_{ei}^{-1} \sim m_e^{1/2}$ were added for mathematical convenience.

Butler and Brokaw added the constraint that the net diffusive fluxes of elements be zero to the preceding n_r relations (15) in order to fully specify the n_{sp} diffusive number fluxes[34]:

$$\sum_{i=1}^{n_{\mathrm{sp}}} \xi_i^c \boldsymbol{W}_i = 0 \qquad (c = 1\ldots n_c) \tag{16}$$

One notes that in doing so they automatically imposed the ambipolar constraint (12). The second term in the right-hand side of Eq. (15) represents the effect of the ambipolar electric field under conditions of local chemical equilibrium. As no net charge is created in chemical reactions, this term is found to be zero. Hence follows the surprising result that the ambipolar electric field plays a negligible role in the diffusion in ionized mixtures under chemical equilibrium, provided the conservation constraints (16) are imposed. As a useful corollary, the formula of Butler and Brokaw is valid for both nonionized and ionized mixtures.

Formulas of Devoto and Kolesnikov

Devoto[40] has shown that higher-order formulas (i.e., more than a single nonvanishing Sonine polynomial contribution) are needed for the electron transport properties. Rigorous formulas like the Hirschfelder ones could be derived but would be computationally expensive. Fortunately, because $m_e/m_h \ll 1$, one may introduce considerable simplifications without having to compromise on accuracy. Devoto[41] and Kolesnikov and Tirsky[42] have both derived equivalent highly accurate and efficient formulas for the plasma electrical conductivity and electron thermal conductivity. Formulas using two nonvanishing Sonine polynomial terms were found to give excellent results for inductive plasma mixtures.

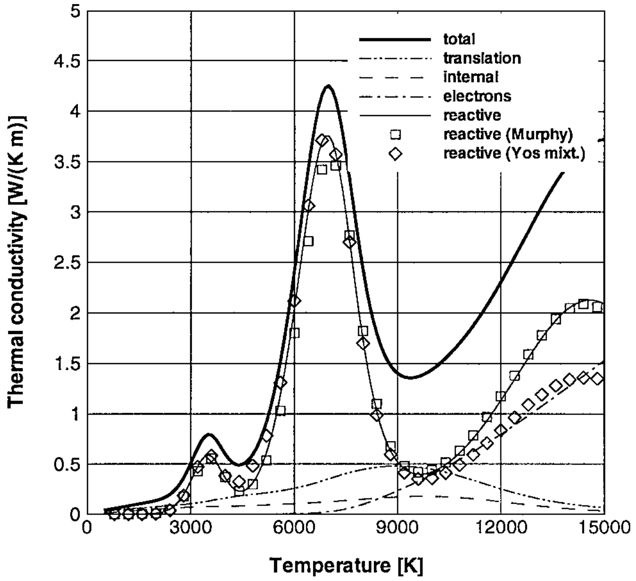


Fig. 8 Components of the thermal conductivity of air at 1 atm.

Results for Air Mixtures

Results are presented for the transport properties of an 11-species air mixture at 1 atm. Collision integrals for interactions involving at least one neutral particle were taken from the recent works of Stallcop et al.[43] and Capitelli et al.[44] Collision integrals for the charged-charged interactions (screened Coulomb potential) were based upon the tabulated results of Devoto[36] and Mason et al.[45] The screening parameter was taken to be the Debye length.

Thermal Conductivity

Figure 8 shows the various components of the thermal conductivity of air at 1 atm. The reaction thermal conductivity yields the dominant contribution for temperatures below 15,000 K. The peak values in the reactive thermal conductivity at temperatures of 3000, 7500, and 15,000 K correspond to, respectively, the dissociation peak of oxygen, of nitrogen, and the ionization peaks of both nitrogen and oxygen. The thermal conductivity of electrons increases strongly with temperatures beyond 10,000 K. One can see that the reactive thermal conductivity computed using Yos's mixture rule gets too low when the temperature increases past 9000 K. On the other hand, the results using the rigorous formulation of Butler and Brokaw agree closely with the calculated results of Murphy.[46]

On Fig. 9 results obtained for the thermal conductivity of air at 1 atm are compared with values of other researchers. The present computation (mixture rules with Butler and Brokaw rigorous approach for the reactive part) is found to be in good agreement with the results of Murphy[46] and Vasil'evsky et al.,[47] calculated from fully rigorous formulations.[48,49] This is clearly not the case above 10,000 K when Yos' mixture rule is used for the reactive thermal conductivity. The derivation of a more accurate mixture rule for the reactive part therefore appears desirable. The results of Gupta et al.[29] are too low for temperatures below 10,000 K because of the somewhat backdated collisional data used for the five-species neutral interactions.[50] Beyond 10,000 K the mixture rule for the reactive thermal conductivity is again an important source of inaccuracy.

Good agreement is found with the experimental results of Asinovsky et al.[51] The experimental values of Devoto et al.[52] overestimate the thermal conductivity at higher temperatures because effects of optically thick radiation were neglected in the processing of their experimental data. Optically thick radiation acts as an additional thermal conductivity, which should be distinguished from the conventional thermal conductivity shown here.

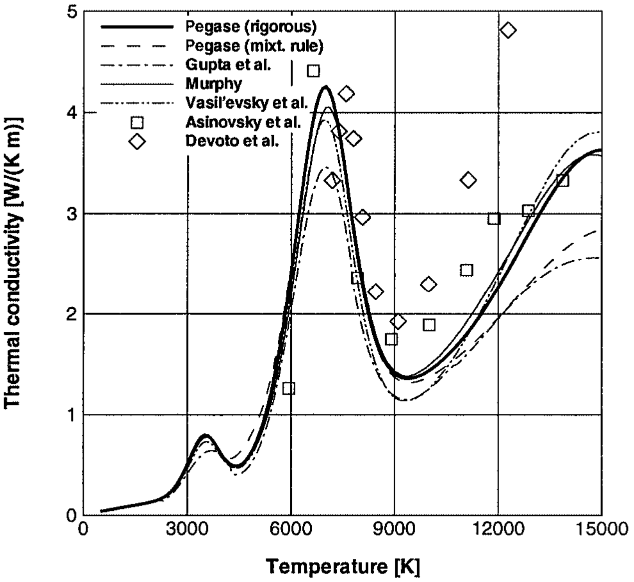


Fig. 9 Thermal conductivity of air at 1 atm.

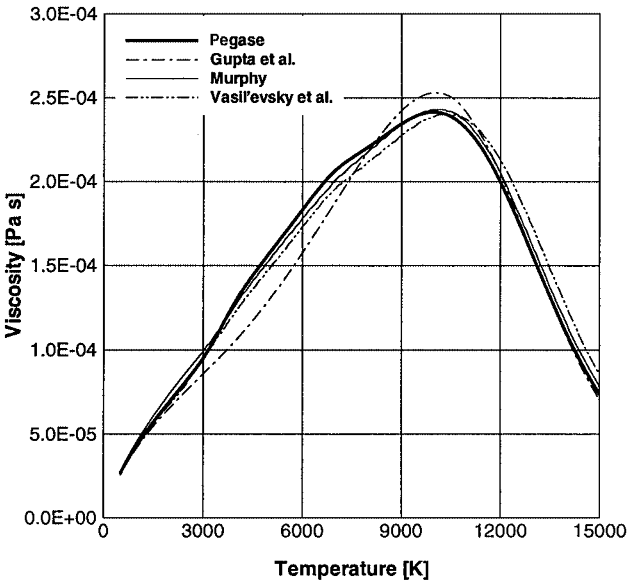


Fig. 10 Viscosity of air at 1 atm.

Viscosity

Figure 10 shows the results obtained for the viscosity of air at 1 atm. The decrease in viscosity values beyond 10,000 K is caused by the appearance of large shielded Coulomb cross sections as ionization occurs. The excellent agreement with the numerical results of Murphy[46] (derived using the rigorous results of Hirschfelder et al.[30]) demonstrates the good accuracy of the present mixture rules. Good agreement is also found with the numerical values of Vasil'evsky et al.[47] The calculated values of Gupta et al.[29] are again too low for temperatures below 10,000 K because of the inaccurate collisional data used.[50] The authors could not as yet find any experimental data for the viscosity of high-temperature air.

Electrical Conductivity

Figure 11 shows the results obtained for the electrical conductivity of air at 1 atm. Excellent agreement is found with the numerical results of Murphy[46] and with the experimental results of Asinovsky et al.[51] and Devoto et al.[52] The values of Vasil'evsky et al.[47] are somewhat lower but still in good agreement.

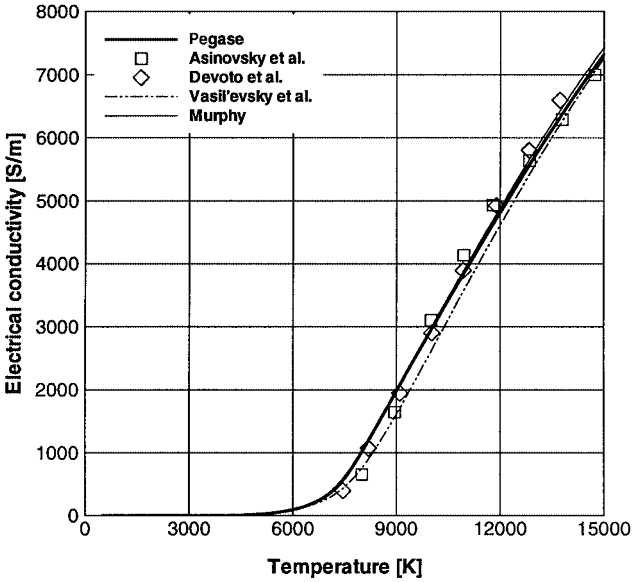


Fig. 11 Electrical conductivity of air at 1 atm.

Conclusion

A review was given of accurate and efficient models of thermodynamic and transport properties for inductive plasma mixtures at pressures lower than or equal to 1 atm and temperatures up to 15,000 K. The thermodynamic properties of individual gaseous species are computed using statistical thermodynamics. We showed that only the first few energy levels were relevant and that sufficient accuracy could be obtained by simply determining the limiting value of the quantum number by comparing the cumulative effects of observed levels.

The rigid rotator-harmonic oscillator model allows simple expressions to be derived for molecules. Anharmonicity corrections were shown to have negligible effect on practical computations of the mixture equilibrium composition. Their effect on the mixture enthalpy amounts to 1.1% for harmonic oscillator approximations and 0.4% with first-order fully coupled anharmonicity corrections, an effect only seen at higher pressures (close to 1 atm and above) and small enough to be neglected. Standard sets of curve fits proposed in the literature show a global accuracy of about 5%.

An efficient and robust method is proposed to compute the equilibrium composition from conservation and chemical reaction equations. The nonlinear system is solved iteratively using a Newton method. The size of the system is analytically reduced to the number of elements in the mixture through a Schur complement approach. In practical applications an average of five iterations was found sufficient to converge 12 orders of magnitude.

The plasma transport properties are computed through the method of Chapman and Enskog. The mixture rules of Yos were found to give accurate results for the heavy particle thermal conductivity and the viscosity. Under conditions of local chemical equilibrium, the energy transport through diffusion of reactive enthalpies may be taken into account in terms of a reactive thermal conductivity. The contributions of thermal and pressure diffusion to the reactive thermal conductivity may be neglected in inductive plasma flows. Through a straightforward argument, Butler and Brokaw's formula was shown to be valid for general multicomponent ionized mixtures.

Higher-order formulas proposed independently by Devoto and Kolesnikov were used to compute the electron transport properties. Formulas based upon two nonvanishing Sonine polynomial terms were found to give highly accurate results for the electrical conductivity and the electron thermal conductivity of inductive plasma mixtures. Computed results for the transport properties of air were found to agree well with the experimental and numerical results of other researchers. However, a better mixture rule would be desirable for the reactive thermal conductivity for strongly ionized mixtures.

The authors' data are available in electronic version on request.

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