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## TRANSPORT PROPERTIES OF PARTIALLY IONIZED GASES

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**Résumé.** — Nous discutons des principaux problèmes apparaissant lors du calcul des coefficients de transport de gaz partiellement ionisés. La convergence de la méthode de Chapman-Enskog, l'influence des interactions électron-atome, ion-atome, ion-ion, ainsi que l'influence des états excités sur les propriétés de transport ont plus particulièrement retenu notre attention. Même si, dans ce travail, nous avons tenu compte de certains effets de déséquilibre, l'ensemble des résultats correspond aux plasmas en LTE.

Nous discutons, ensuite, la précision des tableaux disponibles dans la littérature et, pour finir, nous présentons une application des résultats obtenus à un problème concernant la chimie des plasmas.

**Abstract.** — The main problems arising in the calculation of transport coefficients of partially ionized gases are discussed. Particular attention is given to the convergence of the Chapman-Enskog method, to the influence of electron-atom, ion-atom and ion-ion interactions and of the electronically excited states in affecting the transport properties of a plasma. The bulk of results refer to LTE plasmas, even though some non equilibrium effects are taken into account.

The accuracy of available tabulations is then discussed and an application of present results to a problem of plasmachemistry interest is finally presented.

1. **Introduction.** — Thermal plasmas are often used as chemical reactors for the treatment of different materials, the plasma being thought of as a source of heat for the endothermic processes [1]. The optimization of a plasma reactor requires the knowledge of plasma properties such as the thermal conductivity, the viscosity ( $\eta$ ) and the electrical conductivity ( $\sigma$ ). The computation of these quantities is straightforward for a low temperature gas ( $T < 2\,000$  K,  $p = 1$  atm.), where neither dissociation nor ionization occurs. As the temperature increases, the electronic levels of the atoms (or of the molecules) begin to be populated and dissociation as well as ionization reactions have to be taken into account.

The thermal conductivity of a L.T.E. plasma can now be calculated as a sum of three contributions (translational, internal and reactive). The problems, arising in the evaluation of each of these terms as well as in the computation of  $\eta$  and  $\sigma$ , will be discussed in this paper. Emphasis will be given to L.T.E. plasmas, even though some non equilibrium effects will be taken into account. The accuracy of available tabulations will be discussed at the light of the results presented in this paper. Finally an application of the present results to problems of plasma chemistry interest will be presented.

2. **Transport coefficients.** — 2.1 TOTAL THERMAL CONDUCTIVITY. — The calculation of the total ther-

mal conductivity of a  $v$ -components gas is based on the expression of the heat flux vector  $\mathbf{q}$  [2]

$$\mathbf{q} = -\lambda' \nabla T + \sum_{i=1}^v n_i h_i \mathbf{v}_i - nkT \times \sum_{i=1}^v D_i^T \mathbf{d}_i / m_i n_i - \lambda_{\text{int}} \nabla T. \quad (1)$$

Here  $\mathbf{v}_i$  and  $\mathbf{d}_i$  are the diffusion velocity and the diffusion force of the  $i$ th species, respectively, while  $\lambda'$  and  $\lambda_{\text{int}}$  are the translational and internal thermal conductivities. The quantities  $n_i$ ,  $h_i$ ,  $T$ ,  $D_i^T$  and  $m_i$  are, in the order, the number density, specific enthalpy, temperature, multi-component thermal diffusion and mass of the  $i$ th species.

Eq. (1) can be rearranged [2, 3, 4] as follows

$$\mathbf{q} = -(\lambda + \lambda_{\text{int}} + \lambda_{\text{R}}) \nabla T \quad (2)$$

$$\lambda = \lambda' + (\rho k/n) \sum_{i,j=1}^v E_{ij} D_i^T D_j^T / n_i m_j m_i. \quad (3)$$

Here  $\rho$  is the mass density and  $E_{ij}$  is defined as an element of the inverse of the matrix whose general element is  $D_{ij} m_j$  ( $D_{ij}$  is the multicomponent diffusion coefficient).  $\lambda$ , defined by eq. (3), represents the true translational thermal conductivity corresponding to a mixture which has come to a steady state composition in the temperature gradient.

According to the Chapman-Enskog method [3, 4],  $\lambda$  (not to be confused with  $\lambda'$ ) can be calculated as

$$\lambda_4 = - (75/8) k(2 \pi kT)^{1/2} / |q| \times \begin{vmatrix} q_{ij}^{11} & q_{ij}^{12} & q_{ij}^{13} & n_i \\ q_{ij}^{21} & q_{ij}^{22} & q_{ij}^{23} & 0 \\ q_{ij}^{31} & q_{ij}^{32} & q_{ij}^{33} & 0 \\ 0 & n_i/m_j^{1/2} & 0 & 0 \end{vmatrix} \quad (4)$$

Here  $\lambda_4$  represents the fourth approximation to  $\lambda$  in the Chapman-Enskog method. To obtain the third approximation  $\lambda_3$ , all  $q^{mp}$  blocks (each block is a matrix of  $v$  order) with  $m$  or  $p > 3$  are deleted in eq. (4), while in this formalism the first C-E approximation vanishes.

The problem of convergence of eq. (4) has been studied in detail in ref. [4] for argon plasmas. It turns out that  $\lambda_3$  is two times bigger than  $\lambda_2$  when the ionization degree of the plasma is greater than 50 %, while  $\lambda_4$  and  $\lambda_3$  are practically the same. Similar results have been obtained in this paper for an atmospheric nitrogen plasma (see Fig. 1).

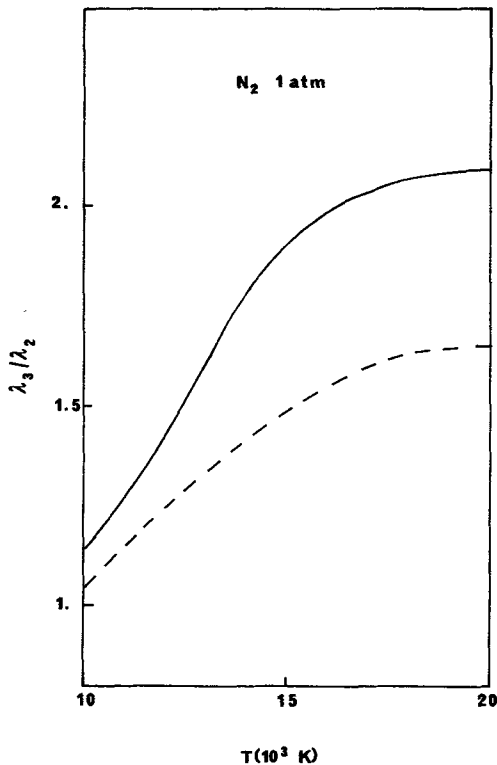


FIG. 1. — Values of  $\lambda_3/\lambda_2$  as a function of temperature for a nitrogen plasma (— results obtained without  $O(1)$  terms in the charged-charged collision integrals; - - - - - the same with  $O(1)$  terms).

The primary cause of the slow convergence of the C-E theory lies in the fact that the mass of the electrons is very much different from that of the heavy components, a secondary cause being represented by the different behaviour of the cross-sections for the various interactions.

Simplified expressions for  $\lambda$  have been obtained considering that the distribution functions of the heavy components are not affected by the electron-heavy particles collisions; as a consequence  $\lambda$  can be splitted into two contributions, one coming from the electrons ( $\lambda_E$ ) and the other from the heavy components ( $\lambda_H$ ) [5]

$$\lambda = \lambda_E + \lambda_H. \quad (5)$$

It should be pointed out that  $\lambda_H$  is unaffected from the properties of the electrons, while  $\lambda_E$  depends on the collisions between electrons and the other species. One of the causes of the slow convergence of the C-E method (i.e. the mass of electrons) disappears in  $\lambda_H$ , so that it is possible to use a different level of approximation for the two terms of eq. (5). This problem has been considered in detail in [5]; the results show that the 3rd approximation to  $\lambda_E$  and the second one for  $\lambda_H$  give the same results as those obtained with the complete 3rd approximation (as given by eq. (4)).

The working equation for  $(\lambda_E)_3$  is [5]

$$(\lambda_E)_3 = \frac{75}{8} n_e^2 \left( \frac{2 \pi kT}{m_e} \right)^{1/2} q^{22} / |q^{11} q^{22} - (q^{12})^2|$$

where  $n_e$  and  $m_e$  are the number density and the mass of electrons respectively,  $k$  is the Boltzmann constant.

Expressions for  $q$  are available in [5]; they are complicated functions of the number densities of all species and of the transport cross-sections between electrons and all other species.

The second approximation to  $\lambda_H$  is of the form :

$$(\lambda_H)_2 = 4 \begin{vmatrix} L_{11} & \dots & L_{1v} & x_1 \\ \vdots & & \vdots & \vdots \\ L_{v1} & \dots & L_{vv} & x_v \\ x_1 & \dots & x_v & 0 \end{vmatrix} \begin{vmatrix} L_{11} & \dots & L_{1v} \\ \vdots & & \vdots \\ L_{v1} & \dots & L_{vv} \end{vmatrix} \quad (7)$$

where  $x_i$  is the molar fraction of the  $i$ th component and the  $L_{ij}$ 's are functions of the collision integrals between heavy components, of the temperature, of the molecular weights and of the composition (see ref. [2]).

Attempts to simplify eq. (7) have been made in ref. [6].

The reactive thermal conductivity  $\lambda_R$ , which represents the contribution due to the chemical reactions occurring in the plasma, can be calculated with a good approximation by means of the general Butler-Brokaw expression [7]

$$\lambda_R = - \frac{1}{RT^2} \times \begin{vmatrix} A_{11} & \dots & A_{1\mu} & \Delta H_1 \\ \vdots & & \vdots & \vdots \\ A_{\mu 1} & \dots & A_{\mu\mu} & \Delta H_\mu \\ \Delta H_1 & \dots & \Delta H_\mu & 0 \end{vmatrix} \begin{vmatrix} A_{11} & \dots & A_{1\mu} \\ \vdots & & \vdots \\ A_{\mu 1} & \dots & A_{\mu\mu} \end{vmatrix} \quad (8a)$$

Elements  $\bar{A}_{1\mu}$  ( $\mu$  is the number of independent chemical reactions) are given by

$$A_{ij} = A_{ji} = \sum_{k=1}^{v-1} \sum_{l=k+1}^v \frac{RT}{pD_{kl}} x_k x_l \times \left( \frac{n_k^{(i)}}{x_k} - \frac{n_l^{(i)}}{x_l} \right) \left( \frac{n_k^{(j)}}{x_k} - \frac{n_l^{(j)}}{x_l} \right) \quad (8b)$$

where  $D_{kl}$  represents binary diffusion coefficient and  $n_k$  are stoichiometric factors, while  $\Delta H_i$  represents the enthalpy difference involved in the  $i$ th chemical reaction.

The same equation can be used for the transport of electronic energy, while the internal contribution due to the vibrational energies is satisfactorily given by the Eucken approximation [2]

$$\lambda_{\text{int}} = \sum_{i=1}^v (\lambda_{\text{int}})_i \left( 1 + \sum_{j=1}^v \frac{D_{ii}}{D_{ij}} \frac{x_j}{x_i} \right) \quad (9a)$$

$$(\lambda_{\text{int}})_i = \frac{pD_{ii}}{RT} \left( c_{pi} - \frac{5}{2} R \right) \quad (9b)$$

where  $c_{pi}$  is the specific heat at constant pressure.

**2.2 VISCOSITY.** — The equations for the viscosity are very similar to those reported for  $\lambda$ , even though in this case the C-E first approximation does not vanish. As in the case of  $\lambda$ ,  $\eta$  can be expressed as the sum of two contributions [5]

$$\eta = \eta_H + \eta_E \simeq \eta_H. \quad (10)$$

Due to the mass of electrons  $\eta_E \ll \eta_H$ , so that the calculation of  $\eta$  can be performed with the first approximation of the C-E method, as can be appre-

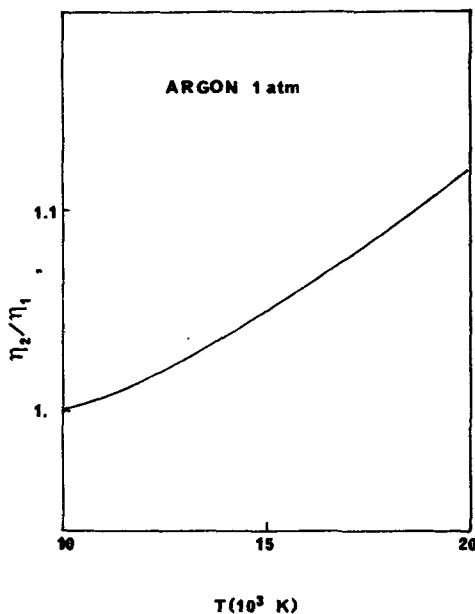


FIG. 2. — Values of  $\eta_2/\eta_1$  as a function of temperature for an argon plasma (see ref. [4]).

ciated from figure 2 [3]. Higher approximations of the C-E method for  $\eta$  are available in [8].

**2.3 ELECTRICAL CONDUCTIVITY.** — The electrical conductivity  $\sigma$  is defined by the equation

$$\mathbf{J}_E = -\sigma \mathbf{E} \quad (11)$$

where  $\mathbf{E}$  is the electrical field and  $\mathbf{J}_E$  is the charge flux density. Due to the mass of electrons, the electrical conductivity is mostly due to the electrons so that the C-E method poorly converges for  $\sigma$ . Once again the third approximation must be used for  $\sigma$  (see ref. [5]).

**3. Collision integrals (transport cross-section).** — Accurate calculations of transport coefficients can be obtained once the collision integrals (transport cross-section) of the different interactions are known. These quantities can be obtained by performing three integrations [2]. First, one determines the classical deflection angle  $\theta(b, E)$  as a function of impact parameter  $b$  and relative energy  $E$

$$\theta(b, E) = \pi - 2b \int_{r_c}^{\infty} \frac{dr}{r^2 |F(r, b, E)|^{1/2}} \quad (12)$$

where the classical turning point or distance of closest approach  $r_c$  is the outermost root of

$$F(r, b, E) = 1 - b^2/r^2 - V(r)/E \quad (13)$$

where  $V(r)$  is the interaction potential.

A further averaging over the impact parameter  $b$  yields the relevant cross-section

$$Q^{(l)}(E) = 2\pi \left\{ 1 - \frac{1 + (-1)^l}{2(1+l)} \right\}^{-1} \times \int_0^{\infty} (1 - \cos^l \theta) b db \quad (14)$$

and the above quantities can in turn be employed for a further energy averaging that produces the collision integrals as a function of temperature

$$\bar{Q}^{(l,s)}(T) = \{ (s+1)! (kT)^{s+2} \}^{-1} \times \int_0^{\infty} Q^{(l)}(E) E^{s+1} e^{-E/kT} dE. \quad (15)$$

The problem of calculating  $\bar{Q}^{(l,s)}$  therefore reduces to the knowledge of  $V(r)$ .

Four interactions are important in thermal plasmas :

- a) Charged-charged ;
- b) Electron-neutral ;
- c) Atom-ion ;
- d) Neutral-neutral.

a) *Charged-charged.* — The screened Coulomb potential can be used for calculating the collision integrals of charged-charged interactions

$$V(r) = \frac{e^2}{r} e^{-r/d} \quad (16)$$

where  $d$  is the Debye length.

They assume the expression [4, 9]

$$\bar{\Omega}^{(l,s)} \propto f(l, s) b_0^2 (\ln A - 0(1) \text{ terms}) \quad (17)$$

where  $A = 2d/b_0$  is the ratio between the Debye length and the average closest impact parameter  $b_0$  (see [5, 9]). To the predominant  $\ln A$  term, these formulas give the same results as those derived by Spitzer and Harm [10], using a different approach. Other formulations have been proposed to calculate the terms after  $\ln A$  (see for example [11]). The results obtained by more sophisticated theories give for atmospheric plasmas results ranging between those obtained with and without the  $0(1)$  terms in eq. (17). The use of eq. (17) with and without  $0(1)$  terms yield therefore lower and upper limits for  $\bar{\Omega}^{(l,s)}$ . Figure 3 shows the effects of the insertion of the  $0(1)$  terms on  $\lambda_E$  for different plasmas. It should be noted that the importance of the  $0(1)$  terms increases for those systems, that, at a given temperature, present an higher ionization degree (i.e. for xenon plasmas) (see also the effects of  $0(1)$  terms in the convergence of C-E approximation in figure 1).

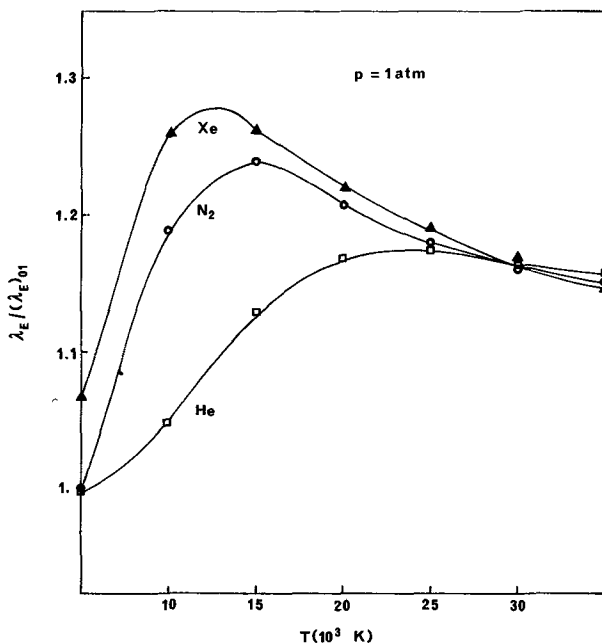


FIG. 3. — Values of  $\lambda_E/\lambda_{E(0(1))}$  as a function of temperature for different plasmas ( $\lambda_{E(0(1))}$  calculated without  $0(1)$  terms).

b) *Electron-neutral.* — Electron-neutral collision integrals are usually obtained by numerical integration of eq. (15) once the momentum transfer cross-

section  $Q^{(l)}$  is known. Tables of these cross-sections are presently available for most gases of plasma chemistry interest [12]. The accuracy of these tabulations depends on the particular system under consideration. It is interesting to know the effect of these cross-sections on  $(\lambda_E)_3$  and  $\sigma$ . Figure 4 reports the values of  $(\lambda_E)_3$  normalized to those obtained by increas-

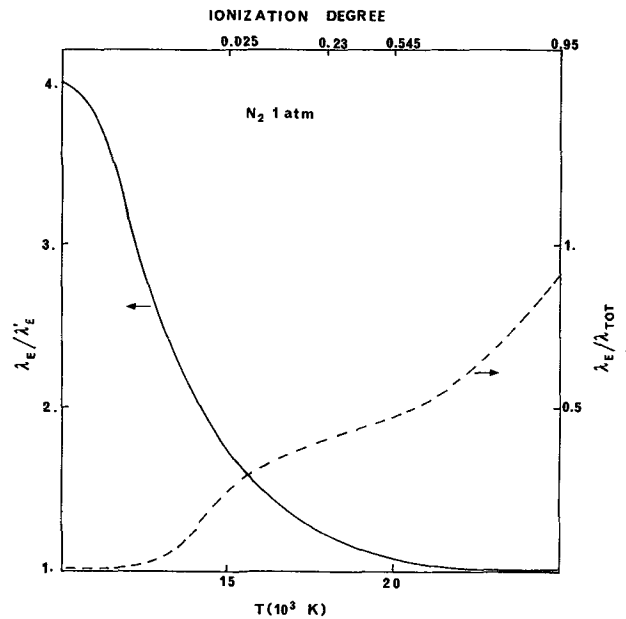


FIG. 4. — Values of  $\lambda_E/\lambda'_E$  and  $\lambda_E/\lambda_{TOT}$  as a function of temperature for a nitrogen plasma ( $\lambda'_E$  has been obtained increasing by a factor 4  $\bar{\Omega}_{e-N_2}^{(l,s)}$ ).

ing by a factor 4 the collision integrals  $\bar{\Omega}_{e-N_2}^{(l,s)}$  and  $\bar{\Omega}_{e-N}^{(l,s)}$ . It should be noted that the electron-neutral cross-sections loose their importance for ionization degrees  $> 2.5\%$ , as a result of the increasing impor-

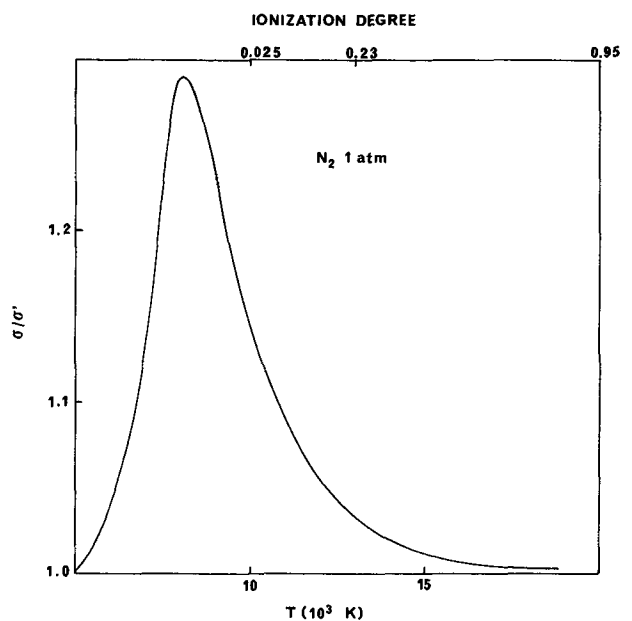


FIG. 5. — Values of  $\sigma/\sigma'$  as a function of temperature for a nitrogen plasma ( $\sigma'$  has been obtained increasing by a factor 2  $\bar{\Omega}_{e-N}^{(l,s)}$ ).

tance of electron-electron collisions. Moreover, one should appreciate that the electron-neutral cross-sections affect  $(\lambda_E)_3$  when this term is a small contribution to the total thermal conductivity (see Fig. 4). Similar arguments apply to the electrical conductivity, as can be appreciated from figure 5.

c) *Atom-ion*. — Atom-ion interactions are often the crucial point in the calculation of the transport properties of partially ionized gases. The corresponding collision integrals strongly affect  $\lambda_H$ ,  $\lambda_R$ ,  $\lambda_{TOT}$  and  $\eta$ .

In the case of atom-ion interaction, one must distinguish between the resonant case ( $MM^+$ ) and the non resonant one ( $MA^+$ ). In the first case the collision integrals diffusion type ( $l$  odd) can be obtained from the knowledge of the charge transfer cross-sections  $Q_{tr}$

$$M + M^+ = M^+ + M \quad (18)$$

by using [13]

$$Q^{(l)} = 2 Q_{tr} \quad (19)$$

$$Q_{tr} = 1/2(A - B \ln v)^{1/2}. \quad (20)$$

With the approximations (18)-(20), the collision integral diffusion type can be obtained in closed form (see [14]). It appears in the implicit form

$$\bar{Q}^{(l,s)} = \bar{Q}^{(l,s)}(A, B, T \dots) \quad (21)$$

$Q_{tr}$  in turn, can be obtained either by means of experimental techniques or by means of theoretical methods. In this last case, according to a semiclassical approach,  $Q_{tr}$  is given by [13]

$$Q_{tr} = 1/2 \pi b_c^2 \quad (22)$$

where  $b_c$  can be calculated according to the following relation [13]

$$1/\pi = \int_{b_c}^{\infty} (1/hv) \Delta V_{gu}(r) r dr / (r^2 - b_c^2)^{1/2} \quad (23)$$

$\Delta V_{gu}$  represents the difference of gerade-ungerade potential energies arising in the collision. At the distances important for the charge transfer cross-sections,  $\Delta V_{gu}$  can be expressed through an exponential form

$$\Delta V_{gu} = C \exp - (\alpha r) \quad (24)$$

and the integral (23) can be approximated as [13]

$$(C/hv) (\pi b_c / 2 \alpha)^{1/2} \exp - (\alpha b_c) = 1/\pi. \quad (25)$$

In the systems of plasmachemistry interest the collision usually occurs along several potential curves (for ex. for both  $N(^4S)N^+(^3P)$  and  $O(^3P)O^+(^4S)$  cases, one can have  $^{2,4,6}\Sigma_{gu}$ ,  $^{2,4,6}\Pi_{gu}$  potentials). In these

cases the total charge transfer cross-section is obtained by averaging the different contributions [13]

$$\bar{Q}_{tr} = \sum_n g_n Q_{tr}^n / \sum_n g_n. \quad (26)$$

Several methods have been proposed to obtain  $\Delta V_{gu}(r)$ . The first approach, suggested in [15], is based on the extrapolation of spectroscopic potential curves for the states at low spin (i.e.  $^2\Sigma_{gu}$ ,  $^2\Pi_{gu}$ ) and to the finding of appropriate relations between high and low spin potentials. As an example, the following potential relations hold at large internuclear distances for  $NN^+$  and  $OO^+$  collisions [16-18]

$$(\Delta V_{gu})_{sextet} = 3/2(\Delta V_{gu})_{quartet} = 3(\Delta V_{gu})_{doublet}. \quad (27)$$

The most simple approach to calculate all  $\Delta V$  splittings for  $NN^+$  and  $OO^+$  systems is therefore to use extrapolated *experimental* potentials for  $^2\Sigma_{gu}$  and  $^2\Pi_{gu}$  pairs and then to obtain the remaining potentials with the aid of eq. (27).

*Ab initio* quantum mechanical methods have also been used for calculating  $\Delta V_{gu}$  either with simplified methods (Heitler-London [16-18]) or with more sophisticated ones (configuration interactions method [19-21]). A completely different approach uses asymptotic methods [22, 23].

The effect of the different  $\Delta V_{gu}$  calculations on  $\bar{Q}^{(11)}$  of  $NN^+$  and  $OO^+$  systems is represented in figures 6, 7. The collision integrals diffusion type have been obtained by eq. (19)-(25) with the aid of the different potentials, while in the case of experiments [24-25] and of asymptotic methods a direct use of  $Q_{tr}$  has been made.

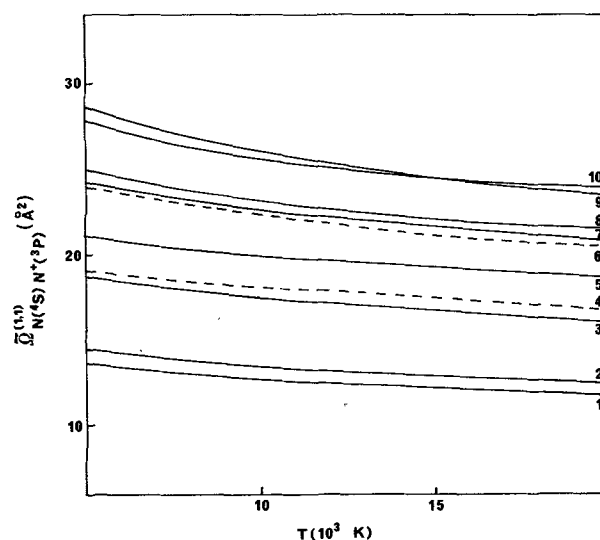


FIG. 6. — Collision integrals diffusion type for  $N(^4S)N^+(^3P)$  (curve 1 : calculated from eq. (18)-(26) +  $\Delta V_{gu}(^2\Sigma, ^2\Pi)$  from [15]; curve 2 : the same with  $\Delta V$  from [45]; curve 3 : the same with  $\Delta V$  of [19]; curve 4 : original values ref. [15]; curve 5 :  $\Delta V$  from [18]; curve 6 : original values of [16]; curve 7 : calculated from the charge transfer cross-sections of [22]; curve 8 :  $\Delta V$  from [20]; curve 9 : calculated from the experimental charge transfer cross sections of [24]; curve 10 :  $\Delta V$  from [16]).

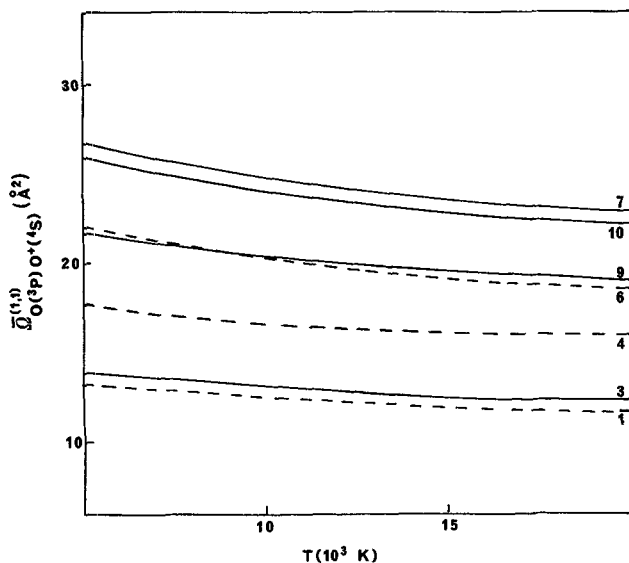


FIG. 7. — Collision integrals diffusion type for  $O(^3P)-O(^4S)$  interaction (curve 3 :  $\Delta V$  from [21]; curve 9 : calculated from the experimental charge transfer cross-sections [25]; the other curves as in figure 6).

The behaviour of  $NN^+$  and  $OO^+$  systems is indeed very similar, showing a satisfactory agreement between the  $\bar{\Omega}^{(1,1)}$  values obtained by Heitler-London and asymptotic methods and the corresponding experimental ones (i.e. based on  $Q_{tr}$  of ref. [24-25]). The agreement decreases when use is made of experimental potentials or from more sophisticated quantum mechanical methods. This last result is rather surprising since the potentials of ref. [19-21] are in principle more accurate than the Heitler-London potentials.

It should be noted that the different  $\bar{\Omega}^{(1,1)}$  calculations differ by as much as a factor 2, which propagates up to a factor 1.5 in  $\lambda_{TOT}$  and  $\eta$  (see Fig. 8).

The collision integrals viscosity type ( $l = 2, 4, \dots$ ) for  $MM^+$  interactions are not affected by the charge transfer mechanism. They can be therefore calculated from eq. (12)-(15) once the  $V(r)$  potential is known. The same technique can be applied to the calculation of  $\bar{\Omega}^{(l,s)}$  ( $l = 1, 2, 3, \dots$ ) for the non resonant interactions ( $MA^+$ ). Once again the problem reduces to the availability of the different potential curves arising in the collision. The available  $V(r)$  informations are then put in analytical forms, the collision integrals of which are known. The most used atom-ion model potentials are the repulsive exponential potential [26] and the Morse potential [27] for repulsive and bound states respectively

$$V(r) = \Phi_0 \exp - (br) \quad (28)$$

$$V(r) = D \exp - 2C/\sigma(r - r_e) - 2 \exp - C/\sigma(r - r_e). \quad (29)$$

The polarizability model

$$V(r) = - \alpha/2 r^4 \quad (30)$$

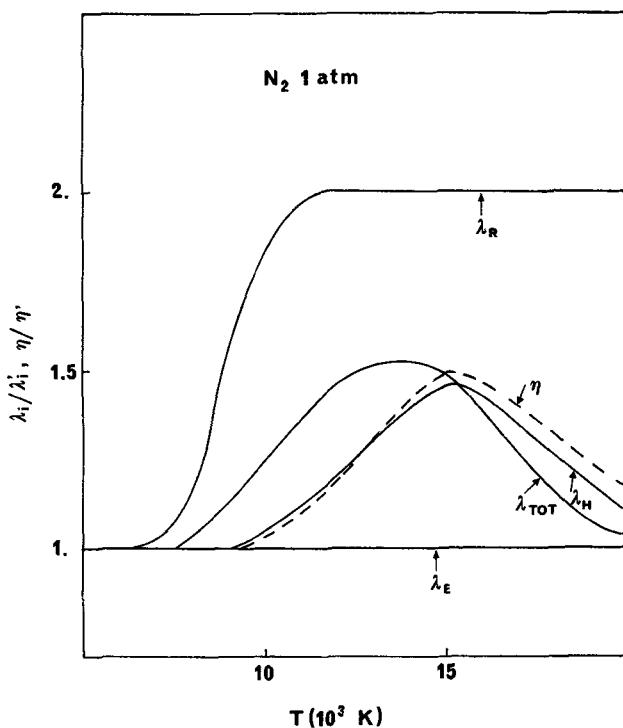


FIG. 8. — Values of  $\lambda_i/\lambda'_i$  and  $\eta/\eta'$  as a function of temperature for a nitrogen plasma (the different contributions  $\lambda'$  as well as the viscosity  $\eta'$  have been calculated increasing by a factor 2  $\bar{\Omega}_{NN^+}^{(1,1)}$ ).

is also often used, specially when potential information are missing. The accuracy of these forms in reproducing the true potential appears, as expected, to be a function of the examined relative energy intervals. This problem can be understood by looking at figure 9, where the collision integrals for the systems  $K^+Ne$ ,  $K^+Xe$  obtained by the above model potentials have been compared with the corresponding ones derived from an accurate fitting of the potentials of ref. [28] at all internuclear distances. In this last case the numerical algorithm developed by Ohara and Smith [29] has been used for computing  $\bar{\Omega}^{(1,1)}$ . It should be used that the exponential repulsive potential works well at high temperature, while the Morse form can be considered a satisfactory approximation to the potential. The use of a polarizability model overestimates the transport cross sections. It is clear that an accurate fitting of the potential gives a more satisfactory temperature dependence of the collision integrals.

In general the knowledge of the potential for  $M^+A$  systems is very scanty. Fortunately the influence of  $M^+A$ ,  $MA^+$  cross-sections on the transport coefficients is in general lower than the corresponding influence of the resonant processes, as can be appreciated from figure 10. Here a variation of a factor 10 of the collision integrals of the  $He-N^+$  and  $He^+-N$  interactions is reflected up to a factor 2.7 on the viscosity and up to a factor 1.3 on the total thermal conductivity, this influence being of course dependent on the temperature range examined. Similar arguments apply to the atom-atom interactions.

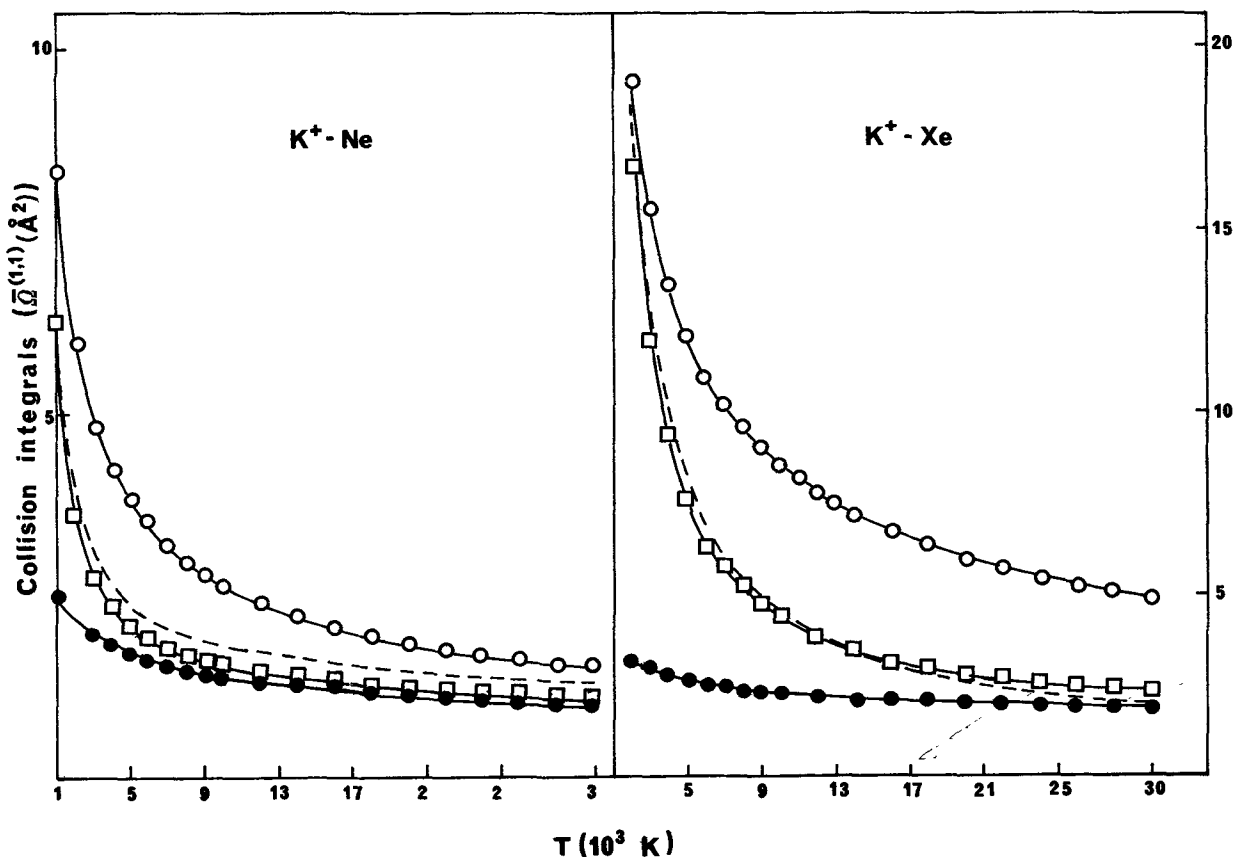


FIG. 9. — Collision integrals of  $K^+$ -Ne and  $K^+$ -Xe interactions as a function of temperature (○—○—○ : polarizability model ; ●—●—● : exponential repulsive model based on potential data of [28]; - - - - : Morse potential based on data of [28]; □—□—□ : accurate fitting of data of ref. [28]).

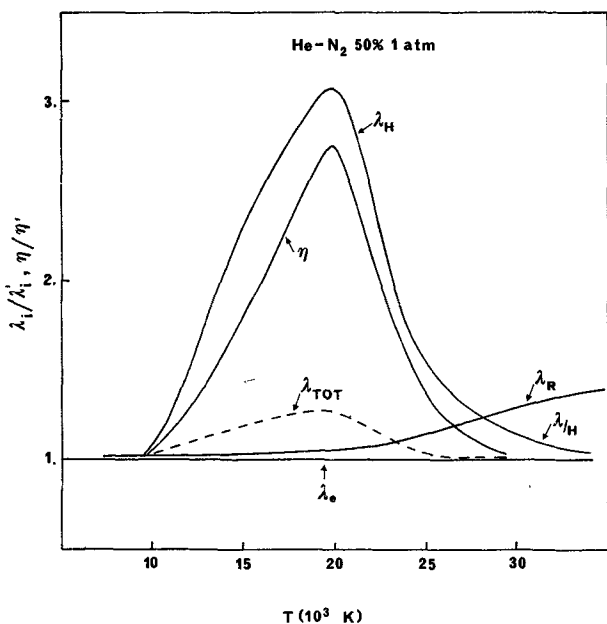


FIG. 10. — Values of  $\lambda_i/\lambda_i^0$  and  $\eta/\eta^0$  as a function of temperature for a 50 % He-N<sub>2</sub> plasma (the different contributions  $\lambda_i^0$  as well as the viscosity  $\eta^0$  have been calculated increasing by a factor 10 all collision integrals of the interactions He-N<sup>+</sup> and He<sup>+</sup>-N).

4. **Excited States.** — The influence of electronically excited states in affecting the transport properties of partially ionized gases has been long neglected because of the ignorance of the transport cross-sections of these species. Recently, however, many research groups have performed *ab initio* quantum mechanical computations of the potential curves of the excited states. From these data it is possible to calculate the transport cross-sections of the excited states and to predict their influence on the transport coefficients.

Let us consider first the so called low lying excited states i.e. the states belonging to the same principal quantum number as the ground state. Many components of plasmas such as oxygen (O(<sup>3</sup>P), O(<sup>1</sup>D), O(<sup>1</sup>S), O<sup>+</sup>(<sup>4</sup>S), O<sup>+</sup>(<sup>2</sup>D), O<sup>+</sup>(<sup>2</sup>P)) and nitrogen (N(<sup>4</sup>S), N(<sup>2</sup>D), N(<sup>2</sup>P), N<sup>+</sup>(<sup>3</sup>P), N<sup>+</sup>(<sup>1</sup>D), N<sup>+</sup>(<sup>1</sup>S)) possess these states, which, on account of their low excitation energies, can be strongly populated in the temperature range 8 000-20 000 K.

Figure 11 shows the collision integrals diffusion type of the interactions NN<sup>+</sup> and OO<sup>+</sup> for the different electronic states. The data for NN<sup>+</sup> have been taken from [30], while those for OO<sup>+</sup> have been calculated



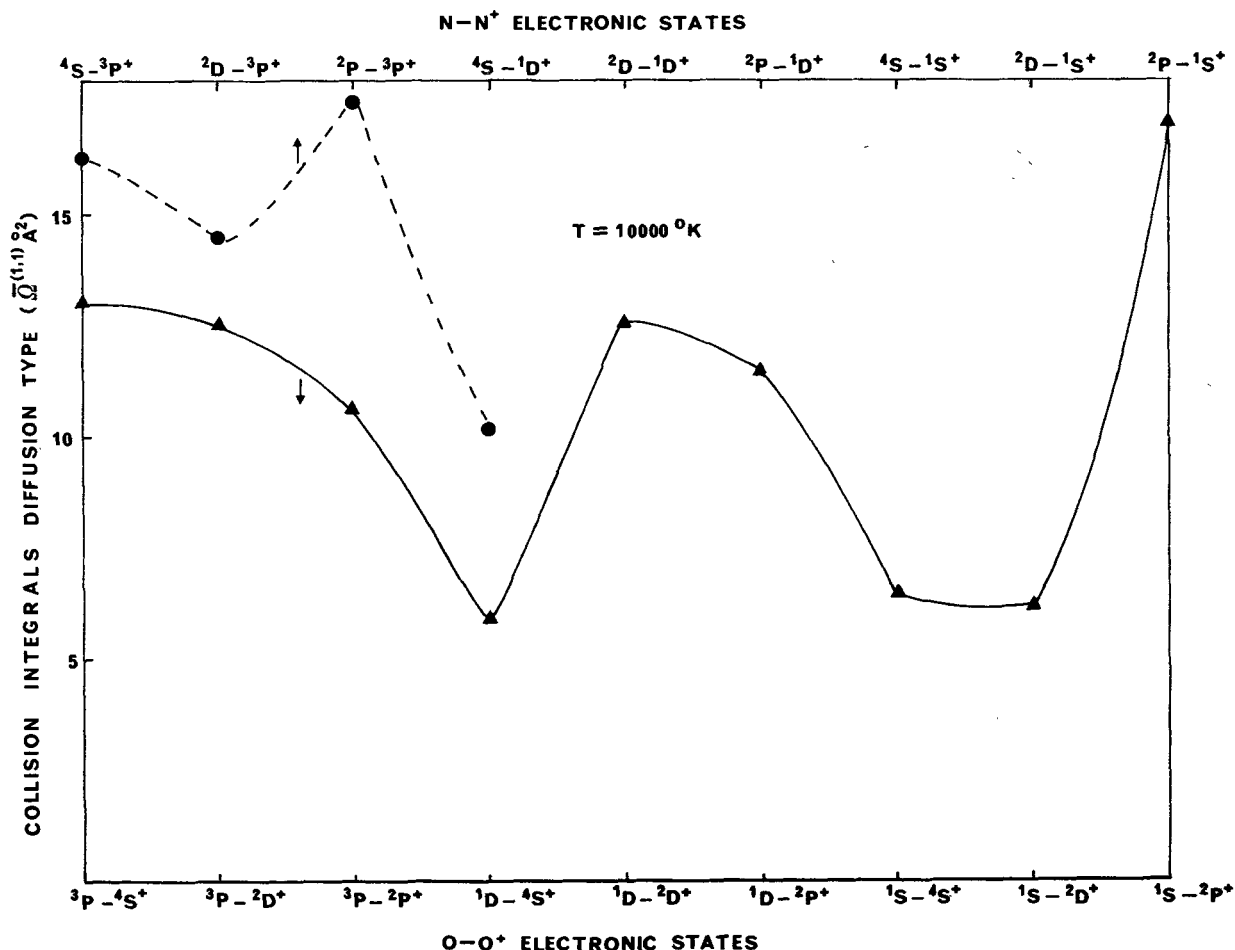
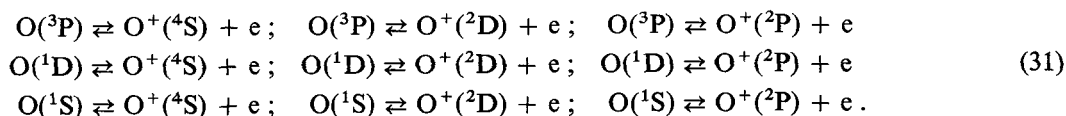


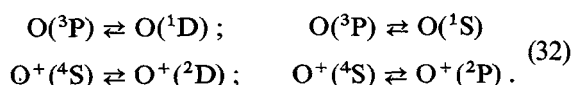
FIG. 11. — Collision integrals diffusion type of  $OO^+$  and  $NN^+$  interactions in different electronic states

in the present work with the aid of eq. (18)-(25) and with the potentials of ref. [21]. It should be noted that the two systems behave similarly, presenting minima in the collision integrals corresponding to  $O(^1D)O^+(^4S)$ ,  $O(^1S)O^+(^4S)$  and  $N(^4S)N^+(^1D)$  interactions. These minima can be explained on the fact that the transfer of more than one electron is less probable than the corresponding one electron case.

Results for oxygen-oxygen and nitrogen-nitrogen atom-atom interactions in different electronic states are available in [13, 31]. The influence of the cross-sections in figure 11 on  $\lambda_R$  and  $\lambda_{int}$  can be studied considering the low lying excited states as new species in the plasma. In this context, under the LTE hypothesis, one can apply eq. (8) inserting in it the following reactions (for oxygen plasmas)



Values of  $\lambda_R$  calculated in this way contain  $\lambda_{int}$ , since this quantity can be calculated from eq. (8) including the reactions



These reactions are however not independent in the present model, since eq. (32) can be expressed through eq. (31).

Figure 12 shows the  $\lambda_R$  values normalized to those obtained by considering all cross-sections equal to the ground state interactions

$$\begin{aligned}
 (\text{i.e. } O(^3P)O^+(^2D) &= O(^1D)O^+(^2D) = \\
 &= O(^3P)O(^1D) = \dots = O(^3P)O^+(^4S)).
 \end{aligned}$$

Differences up to 10 % and 20 % are observed for oxygen and nitrogen plasmas respectively. It should be noted, however, that the cross-section of figure 11 become important in non equilibrium problems.

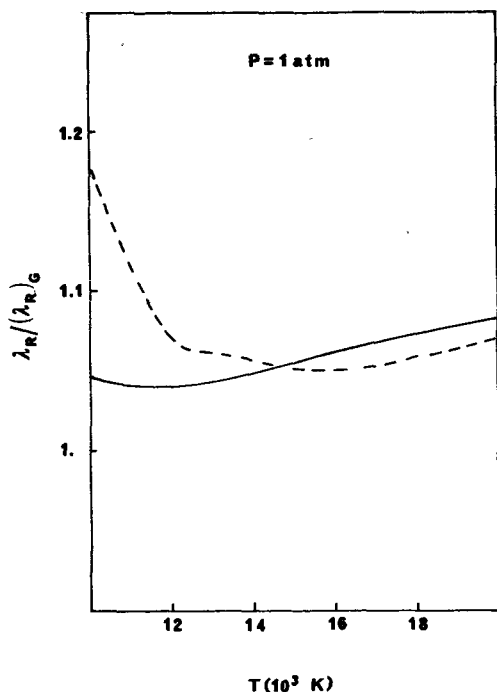


FIG. 12. — Values of  $\lambda_R/\lambda_{RG}$  as a function of temperature ( $\lambda_{RG}$  has been calculated with all cross-sections equal to  $N(^4S)-N(^3P)$  or  $O(^3P)O(^4S)$  see text; — oxygen plasma; - - - - nitrogen plasma).

As for the high lying excited states (i.e. electronically excited states not belonging to the same principal quantum number as the ground state) figure 13 shows the behaviour of the interactions  $H(n)H^+$

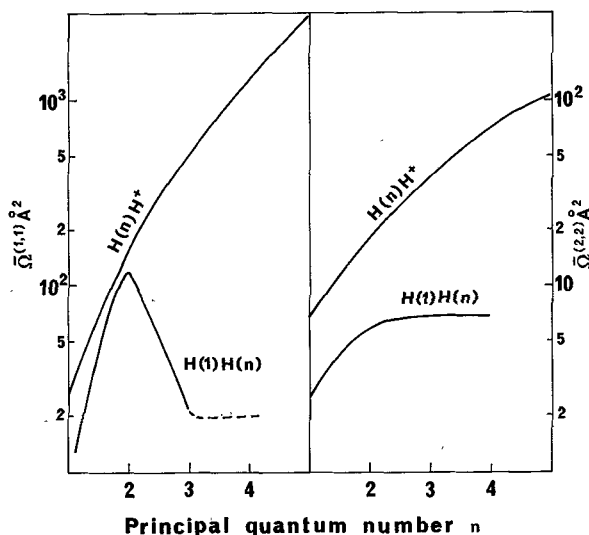


FIG. 13. — Collision integrals diffusion and viscosity type as a function of principal quantum number  $n$  for  $H(n)-H^+$  and  $H(1)-H(n)$  interactions.

and  $H(1)H(n)$ , where  $H(n)$  denotes an hydrogen atom in the  $n$ th principal quantum number. The data have been taken from ref. [32]. It should be noted the strong variation of  $H(n)H^+$  integrals as

a function of the principal quantum number, while the  $H(1)H(n)$  values converge at high  $n$  to the corresponding  $H(1)H^+$  values.

Figure 14 shows the effects of these states on the viscosity (details can be found in ref. [32]). The effects are small (up to 10 %) if use is made of the Griem criterion for calculating the electronic partition function of hydrogen atoms, but they increase (up to 50 %) when the concentration of hydrogen atoms is 5 times that calculated by Griem's criterion. Once again one should stress the importance of these cross-sections on non equilibrium plasmas.

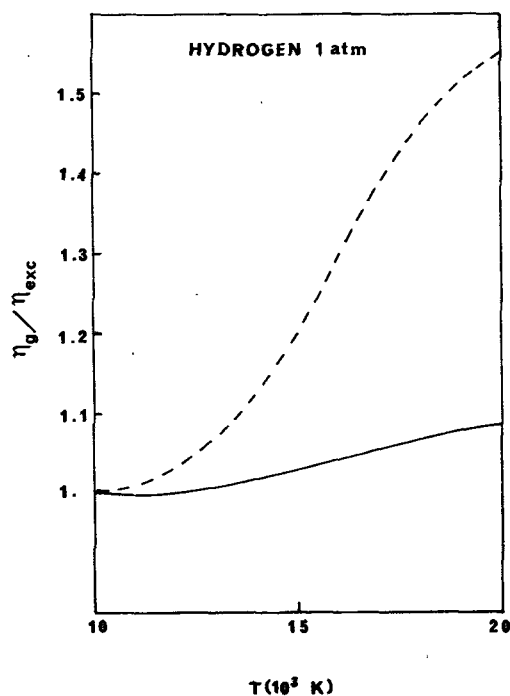


FIG. 14. — Values of  $\eta_g/\eta_{exc}$  as a function of temperature ( $\eta_g$  ground state values, see text; — population density of excited states calculated with Griem's criterion; - - - - population density of excited states increased by a factor 5).

**5. Comparison with the experiments.** — Figure 15 shows a comparison of the total thermal conductivity calculated with the methods described in the present work with several experimental measurements [33-36]. The agreement can be considered satisfactory, even though the errors in the experimental determinations of  $\lambda_{TOT}$  do not yet allow to choose the best set of transport cross-sections for nitrogen. Similar results apply to other gases.

**6. Non equilibrium plasmas.** — So far all considerations have been made on the L.T.E. plasmas.

Very often, however, for atmospheric plasmas it occurs that the electron temperature is greater than the heavy components temperature. The theory of transport coefficients for two temperatures plasmas has been developed in detail [37]. However expressions similar to those reported in the previous pages can

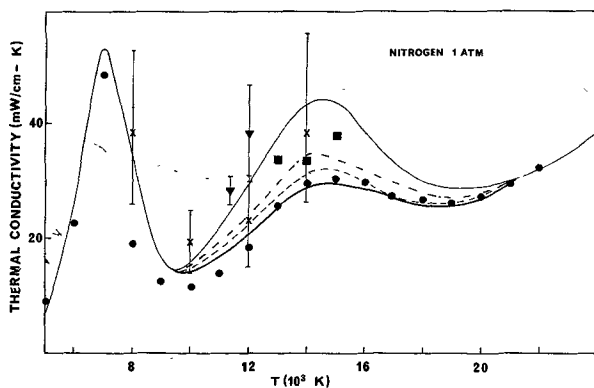


FIG. 15. — Total thermal conductivity compared with experiments (— (thin line) theory [45] — (thick line) theory with  $\Omega_{NN}^{11}$  from [24]; - - - - - theory with  $\Omega_{NN}^{11}$  of [16] - · - · - theory with  $\Omega_{NN}^{11}$  from [18]. Experiments ● [33]; X [34]; ■ [35]; ▼ [36]).

be again used, if the collision integrals for electron-heavy components are calculated at the electron temperature and those for heavy-heavy components at the gas temperature. As for the plasma composition to be inserted in the transport equations, it can be obtained by a two temperatures Saha equation [38, 39]. It is clear that such a procedure can be applied provided the electron distribution function is not too far from a Maxwellian one, so that the C-E method applies. When this is not possible, it is necessary to solve the appropriate Boltzmann equation as in gas lasers discharges.

Finally we want to mention the role of inelastic collisions, which apparently can be neglected for L.T.E. plasmas [40], while their importance increases for molecular gases (see for ex. [41]).

**7. Accuracy of available tabulations.** — Tables of transport coefficients of plasma chemistry interest (rare gases (He, Ar, Xe) [14, 42, 43], diatomic species ( $N_2$ ,  $O_2$ ,  $H_2$ ) [44-46] and of their mixtures (He- $N_2$ , Ar- $N_2$ , Xe- $N_2$ , Ar- $H_2$ ,  $N_2$ - $H_2$ , air) [47, 50, 44]) are presently available.

These calculations have been in general obtained with the higher approximations of the C-E method, after an appropriate choice of the relevant cross-sections. An apparent exception is represented by the well known tabulation of Yos [44] for  $H_2$ ,  $N_2$ ,  $O_2$  and air plasmas. This author in fact uses kinetic formulae of doubtful accuracy utilizing, on the contrary, transport cross-sections of great accuracy. Yos, however, being aware of the inaccuracy of his formulae, modified the transport cross-sections of charged-charged interactions so to reproduce the thermal and electrical conductivity of a completely ionized gas as given by the Spitzer and Harm formulae. As a consequence, Yos' tabulations can be considered satisfactory, even though the agreement of these calculations with more accurate ones is often fortuitous.

The tabulations of ref. [47] include the systems  $H_2$ - $N_2$ , Ar- $N_2$  and Xe- $N_2$  in the temperature range 5 000-35 000 K. The greater uncertainties of these values are essentially due to: a) the electron-nitrogen atom cross-section were put equal to  $4.12 \text{ \AA}^2$ ; b) the  $\Omega_{NN}$  was taken from ref. [15]; c) the ion-atom (non resonant) interactions were calculated according to the polarizability model; d) the internal thermal conductivity of atoms was calculated with insufficient accuracy. At the light of the considerations made in the present work, we believe that  $\lambda_{TOT}$  and  $\eta$  of ref. [47] can be considered accurate within 30-40 %.

Revised tables of Ar- $N_2$  system, including also the electrical conductivity are available in ref. [48].

Tables of Ar- $H_2$  mixtures are also available [49]; in this case the accuracy is better, because the non resonant Ar- $H^+$ , Ar- $H$  interactions have been treated with realistic potentials.

The accuracy of  $N_2$ - $H_2$  mixtures is discussed in [50].

**8. Conclusions.** — As a conclusion we present an application of the present results in the estimation of the heat flux from a plasma to a spherical particle of diameter  $D$  travelling the plasma. This problem is very important in the decomposition of solids in plasmas, since the plasma-particle heat transfer is often thought as the limiting step of the chemical reaction rate.

The following heat balance holds [51]

$$\begin{aligned} \pi D^2 h(T_g - T_p) + h_r(T_g) &= \\ &= q_p \frac{dT_p}{dT} + \Delta H_{T_d} \frac{dn}{dt} + \pi D^2 \epsilon_p \sigma T_p^4 \quad (33) \\ h &= (\lambda/D) (2 + 0.6 R_c^{1/2} P_r^{1/3}). \quad (34) \end{aligned}$$

Here  $\lambda$  is the thermal conductivity of the plasma,  $T_g$  and  $T_p$  are the gas and particle temperature,  $q_p$  is the thermal capacity of the particle,  $\Delta H_{T_d}$  is the enthalpy of decomposition at the temperature of decomposition  $T_d$ ,  $\epsilon_p$  and  $\sigma$  are the particle emissivity and the Stephan-Boltzmann constant,  $h_r(T_g)$  is the contribution of radiation to the heat flux and  $dn/dt$  is the decomposition rate. It appears that  $dn/dt$  is strongly affected by  $\lambda$  and by  $\eta$  which enter in Prandtl and Reynolds numbers. It should also be noted that the thermal conductivity appearing in eq. (34) can be the total one or the frozen

$$(\lambda_f = \lambda_{TOT} - \lambda_R)$$

according to the type of particle-plasma boundary-layer and to the type of catalytic activity of particle [51].

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