

Coupled relaxations in a plasma with strong thermodynamic nonequilibrium

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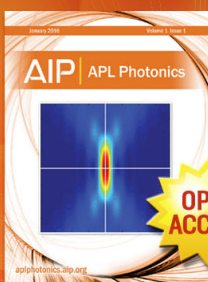
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Coupled relaxations in a plasma with strong thermodynamic nonequilibrium

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The problem of coupled thermal and chemical relaxation in a nitrogen-argon plasma mixture is studied for the case of thermodynamic nonequilibrium. Firstly, the equations which describe the time evolution of macroscopic quantities such as temperature and concentration are studied; then, the computation of some plasma evolutions is performed. As a result, the coupled thermal effect on the reaction and the chemical effect on thermal relaxation are shown.

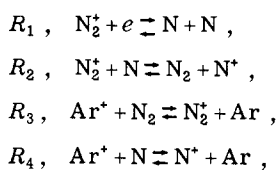
I. INTRODUCTION

Many reactions frequently occurring in plasmas, such as charge exchange and dissociative recombination, occur in very short characteristic times, approaching the relaxation time between the electronic temperature and the translational or vibrational temperature. The energies of these reactions range from a fraction of an electron-volt to ten electron-volts, implying that thermal and chemical relaxation are strongly coupled when the plasma thermal energy is less than one electron-volt.

While the problem of coupled relaxation has been studied extensively in the case of ternary dissociation of a bimolecular gas with vibrational relaxation, very little work has dealt with the case of ionic binary reactions.

However, it is clear that this problem must be surmounted for any study of the kinetics of these reactions in the presence of strong thermodynamical nonequilibrium (as for example in the dissociative recombination of the N_2^+ ion^{1,2}).

This paper considers a plasma in which the following reactions occur:



Nonequilibrium is assumed between the electron translational temperature, the nitrogen vibrational temperature, and the translational temperature of heavy species. Relaxation is then calculated using arbitrary initial conditions.

II. HYDRODYNAMIC EQUATIONS

The plasma is assumed to be a mixture of chemical species q in the quantum state i . The local plasma state is completely described by the knowledge of the one-particle velocity and the position distribution functions f_{qi} . The time evolutions of these functions are described by a Boltzmann equation system

$$df_{qi}/dt = J_{qi}[(f_{q'i'})].$$

Hydrodynamic equations can be obtained from the

Boltzmann equations by a well-known method.^{3,4} Hydrodynamic equations are intended to mean those which describe the time evolution of macroscopic quantities such as temperature, concentration, etc. Hence, the hydrodynamic equations depend on the type of quasi-equilibrium found in the plasma.

In the present case, the following hypotheses are made:

- (i) the plasma comprises the species N_2 , N , Ar , N_2^+ , N^+ , Ar^+ , e ;
- (ii) electronic states can be ignored;
- (iii) the electron translational velocity distribution has a Maxwell form at temperature T_e ;
- (iv) a Maxwell-Boltzmann equilibrium exists for translational and rotational energies of heavy species at temperature T . Vibrational energy satisfies a Boltzmann distribution at temperature T_v .

It is also assumed that there is no macroscopic velocity. In fact, if pressure variations induced by chemical reactions are sufficiently low, this model also describes uniform flow. The most dubious hypothesis is that concerning the vibrational energy and electronic states. As pointed out by Refs. 5-7, a multistate description would be far more realistic, but the model obtained would require the use of unknown process rates.

III. HYDRODYNAMIC EQUATIONS FOR CHEMICAL SPECIES

These equations can be written:

$$\begin{aligned} \frac{Dn_{N_2}}{Dt} &= K_{N_2}, \quad \frac{Dn_{N_2^+}}{Dt} = K_{N_2^+}, \quad \frac{Dn_e}{Dt} = K_e, \\ \frac{Dn_N}{Dt} &= K_N, \quad \frac{Dn_{N^+}}{Dt} = K_{N^+}, \\ \frac{Dn_{Ar}}{Dt} &= K_{Ar}, \quad \frac{Dn_{Ar^+}}{Dt} = K_{Ar^+}, \end{aligned}$$

When the chemical reactions occurring in the plasma are only the four given in the introduction, it is easy to prove that the quantities, $n_{Ar} + n_{Ar^+}$, $n_e - n_{Ar^+} - n_{N^+} - n_{N_2^+}$, $n_N + n_{N^+} + 2n_{N_2} + 2n_{N_2^+}$, and $n_{N_2^+} + n_{N_2} - n_e$ remain constant throughout the time evolution.

Consequently, three equations can be selected from

among the seven hydrodynamic equations for the chemical species and we take

$$\frac{Dn_e}{Dt} = K_e, \quad \frac{Dn_{N_2}}{Dt} = K_{N_2}, \quad \frac{Dn_{Ar}}{Dt} = K_{Ar},$$

where

$$K_e = -k_{d1} n_{N_2^+} n_e + k_{r1} n_N^2,$$

$$K_{N_2} = k_{d2} n_{N_2^+} n_N - k_{r2} n_{N_2} n_{N^+} - k_{d3} n_{Ar^+} n_{N_2} + k_{r3} n_{Ar} n_{N_2^+},$$

$$K_{Ar} = k_{d3} n_{Ar^+} n_{N_2} - k_{r3} n_{Ar} n_{N_2^+} + k_{d4} n_{Ar^+} n_N - k_{r4} n_{Ar} n_{N^+}.$$

IV. CHOICE OF REACTION RATES

For the kinetics of reaction R_1 as a function of T , T_e , and T_v , O'Malley's model¹ is selected for its simplicity and despite the fact that Bardsley has shown that this model is not entirely realistic.⁸ The value of k_{d1} is taken as: $k_{d1} = 3.3 \times 10^{-12} [1 - \exp(-3120/T_v)] / T_e^{1/2} \text{ m}^3/\text{part. sec.}$

The value of 3.3×10^{-12} is a mean between the results of Hammerling⁹ and Biondi.¹⁰ The reverse reaction rate k_{r1} depends only on the translational temperature T , as in the case of complete thermodynamic equilibrium.

For charge-exchange reactions, we did not derive results concerning the dependence of the reaction kinetics on vibrational temperature T_v , and assume that reaction rates for charge-exchange depend only on the translational temperature T , as in the case of complete local thermodynamic equilibrium.

The rate value for reaction R_2 was taken as $k_{d2} = 1.30 \times 10^{-18} T^{1/2} \text{ m}^3/\text{part. sec.}$

Hardly any rate values are available in the literature for reactions R_3 and R_4 . The only exact one is that of Fehsenfeld¹¹ concerning reaction R_3 at 300 K, which agrees with the limiting values given by Danilov¹² and Dmitriev.¹³ However, no results are available in the temperature range of interest here. The total reaction cross section has been measured by Kaneko *et al.*¹⁴ for a wide range of energy values (0.06 to 10 eV), but their measurement method implies mean energies (for 0.06 eV the energy measured in a thermal energy with Maxwell distribution, but for 10 eV the particles are nearly monoenergetic). Hence, it is difficult to calculate a reaction rate from these results. However, given the absence of other values, this has been done as though the measured cross section was the true total reaction cross section $\sigma(E)$.

It follows that

$$\sigma(E) = 1.11 \times 10^{-19} E + 3.9 \times 10^{-20} \text{ m}^2$$

and

$$k_{d3} = 4.95 \times 10^{-19} T^{1/2} (1 + 4.9 \times 10^{-4} T).$$

The reverse rates values for reactions R_2 and R_3 are easily obtained from the direct rate value and equilibrium constant, since it is assumed that these rates only depend on T .

For reaction R_4 no results are available and the same rate is assumed as for reaction R_2 .

V. HYDRODYNAMIC EQUATION FOR ELECTRON ENERGY

This equation can be written

$$\frac{1}{T_e} \frac{DT_e}{Dt} = \frac{2}{3} \frac{Q_e}{n_e k T_e} - \frac{K_e}{n_e}$$

with

$$K_e = \frac{Dn_e}{Dt},$$

where

$$Q_e = \int J_e \frac{1}{2} m_e v_e^2 dv_e.$$

J_e is the right-hand term of the Boltzmann electron equation, and Q_e is the sum of three terms, the first for elastic collision $(Q_e)_e$ the second for inelastic collision $(Q_e)_i$, and the third for reactive collisions $(Q_e)_r$. Hence, Q_e can also be written

$$Q_e = (Q_e)_e + (Q_e)_i + (Q_e)_r.$$

VI. THE ELASTIC COLLISION TERM $(Q_e)_e$

Since the elastic electron-electron collision gives a zero contribution for this term, only elastic collisions with neutral species and ions need be considered.

If k species exist for neutral species and ions, the term $(Q_e)_e$ can be written

$$(Q_e)_e = \sum_k \int g \sigma_{ek}^k (f'_k f'_e - f_k f_e) \frac{1}{2} m_e v_e^2 \sin \theta d\theta d\varphi d\bar{v}_k d\bar{v}_e.$$

The calculation then gives, for $(Q_e)_e$,

$$(Q_e)_e = 2n_e m_e \sum_k \frac{\nu_{ek} n_k}{m_k} \frac{3}{2} (T - T_e).$$

This result is identical to that of Appleton and Bray,¹⁵ Petschek and Byron,¹⁶ with

$$\nu_{ek} = \frac{4\pi m_e}{2k T_e} \int \frac{f_e}{n_e} \sigma_{ek}^M v_e^5 dv_e,$$

where $v_e = |\bar{v}_e|$ and σ_{ek}^M is then the total momentum cross section.

The knowledge of ν_{ek} (or σ_{ek}^M) is now required. For molecular nitrogen, studies by Gerjuoy and Stein,¹⁷ Anderson and Goldstein,¹⁸ Biondi,¹⁹ Pack and Phelps,²⁰ Frost and Phelps,²¹ and Mentzoni and Row²² have yielded many results, of which the best confirmed value has been selected,

$$\nu_{eN_2} = 1.12 \times 10^{-17} T_e.$$

Here, the influence of vibrational excitation on the collision frequency is not taken into account, although a study by Cottureau and Valentin has shown that this effect is not negligible.²³ For atomic nitrogen, owing to the lack of results, it is assumed that $\nu_{eN} = \nu_{eN_2}$. For argon, many values of σ_{eAr}^M are available, but in line with Ref. 15, the existence of the Ramsauer effect has not been taken into account and a constant value is assumed for σ_{eAr}^M ; hence,

$$\nu_{eAr} = 2.07 \times 10^{-17} T_e^{1/2}.$$

In all the cases the term has a very slight effect on the evolution of electron temperature.

For the ions, the term does not depend on the ionic species. The momentum transfer cross section is Coulombic and gives the well-known term^{15,24}

$$\nu_{ei} = \frac{8}{3} \left(\frac{\pi}{m_e} \right)^{1/2} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{e^4}{(2kT_e)^{3/2}} \ln \frac{64\pi^2 \epsilon_0^3 k^3 T_e^3}{n_e e^6}$$

VII. THE INELASTIC COLLISION TERM $(Q_e)_i$

According to our hypotheses, only two species are able to provide inelastic collisions, N_2 and N_2^+ . Owing to the lack of results for N_2^+ , it is assumed that

$$\frac{(Q_e)_i^{N_2}}{n_{N_2}} = \frac{(Q_e)_i^{N_2^+}}{n_{N_2^+}}$$

The inelastic term can also be written as the sum of two terms, one for the collisions with vibrational transition, the other for collisions with rotational transition

$$(Q_e)_i^{N_2} = (Q_e)_R^{N_2} + (Q_e)_V^{N_2}$$

These terms are usually written

$$(Q_e)_R^{N_2} = (Q_e)_e^{N_2} G_R,$$

$$(Q_e)_V^{N_2} = (Q_e)_e^{N_2} G_V,$$

as can be seen in the work of Gerjuoy and Stein,¹⁷ Frost and Phelps,²¹ Mentzoni and Row,²² Demetriades,²⁵ Lazdinis and Petrie,²⁶ Formato and Gilardini,²⁷ and Ginzburg and Gurevich.^{28,29}

The form given here for $(Q_e)_i$ can always be employed since it defines G_R and G_V . However, its use is appropriate only in cases where G_R and G_V are not dependent on the differences $T - T_e$ and $T_V - T_e$. In actual fact, this condition is satisfied only if the internal energy gap between the levels is much lower than kT_e or if the temperature difference $T_V - T_e$ is much lower than kT_e . It is worth noting that the use of results taken from the literature is sometimes vague, because some research workers give the G value without giving the ν_{ek} value. On the other hand, the G value is often the total value $G = G_R + G_V$.

Consistent with Lazdinis and Petrie, constant values were taken for G_R and G_V : $G_R = 10$, $G_V = 50$, G_V has a high value because transfer between the electron translational energy and the vibrational energy of nitrogen is very efficient, as shown by the work of Schultz^{30,31} and Erhardt and Willmann.³²

In conclusion, it can be stated that the form of the term $(Q_e)_{V_2}^{N_2}$ is debatable.

VIII. THE REACTIVE COLLISION TERM $(Q_e)_r$

This term is derived from the reaction $N_2^+ + e \rightleftharpoons N + N$. The literature fails to reveal any calculations of this factor. However, it can be written

$$(Q_e)_r = \int g \sigma_r^{v=0} (f_N^2 - f_{N_2^+}^{v=0} f_e)^{1/2} m_e v_e^2 \sin \theta d\theta d\varphi d\bar{v}_e d\bar{v}_{N_2^+}.$$

As a result of O'Malley's model only the first level ($v = 0$) makes a contribution.

This term can be also written as the sum of two terms, the first derived from the reverse reaction, the second derived from the direct reaction:

$$(Q_e)_r = (Q_e)_r^d + (Q_e)_r^r,$$

with

$$(Q_e)_r^d = - \int g \sigma_r^{v=0} f_{N_2^+}^{v=0} f_e^{1/2} m_e v_e^2 \sin \theta d\theta d\varphi d\bar{v}_e d\bar{v}_{N_2^+}.$$

Note that in the case of complete thermodynamic equilibrium

$$(Q_e)_r = 0, \text{ hence } (Q_e)_r^r = - (Q_e)_r^d.$$

Taking into account the value given by O'Malley¹

$$\sigma_r^{v=0} = \sigma_0 / E,$$

it is easy to deduce $(Q_e)_r^d = -(k_{d1} n_{N_2^+} n_e) k T_e$.

To obtain $(Q_e)_r^r$, the following argument is employed: Nitrogen atoms exhibit a Maxwellian distribution at temperature T and are unaware in their collisions of the state of the distribution function for the electrons and the N_2^+ ions. Thus, it can be deduced that they give to the electron created the same amount of energy as in the case where the whole plasma is in complete thermodynamic equilibrium at temperature T .

Consequently,

$$(Q_e)_r^r = + k_{r1} n_N^2 k T.$$

The whole term is then written

$$(Q_e)_r = k_{r1} n_N^2 k T - k_{d1} n_{N_2^+} n_e k T_e.$$

The equations giving the time evolution of the electron temperature can be written

$$\begin{aligned} \frac{DT_e}{Dt} = 2m_e(T - T_e) & \left[\frac{n_{N_2} \nu_{eN_2}}{m_{N_2}} (1 + G_R) + \frac{n_{Ar} \nu_{eAr}}{m_{Ar}} + \frac{n_N \nu_{eN}}{m_N} + \left(\frac{n_{Ar^+}}{m_{Ar^+}} + \frac{n_{N^+}}{m_N} + \frac{n_{N_2^+}}{m_{N_2}} \right) \nu_{ei} + \frac{n_{N_2^+} \nu_{eN_2} G_R}{m_{N_2}} \right] \\ & + 2m_e(T_V - T_e) \left(\frac{n_{N_2^+} + n_{N_2}}{m_{N_2}} \right) \nu_{eN_2} G_V + \frac{2}{3} k_{r1} \frac{n_N^2}{n_e} (T - T_e) + \frac{T_e}{3} \left(k_{d1} n_{N_2^+} - k_{r1} \frac{n_N^2}{n_e} \right). \end{aligned}$$

IX. VIBRATIONAL ENERGY EQUATION

The vibrational temperature was assumed to be the same for N_2 and N_2^+ . The vibrational energy equation is thus written

$$\frac{DT_V}{Dt} = \frac{Q_{N_2}^V + Q_{N_2^+}^V - E_{N_2}^V K_{N_2} - E_{N_2^+}^V K_{N_2^+}}{n_{N_2} c_{N_2}^V + n_{N_2^+} c_{N_2^+}^V}$$

where

$$Q_{N_2}^v = \sum_v (K_{N_2}^v) E_{N_2}^v.$$

$E_{N_2}^v$ is the energy level of level v and $K_{N_2}^v$ is the production of molecular nitrogen in level v (same definitions for $E_{N_2^+}^v$ and $K_{N_2^+}^v$); $E_{N_2}^v$ and $E_{N_2^+}^v$ are the mean vibrational energies for species N_2 and N_2^+ , and a harmonic oscillator model is assumed for N_2 and N_2^+ .

The terms $Q_{N_2}^v$ and $Q_{N_2^+}^v$ now remain to be calculated. Elastic collisions obviously make no contribution.

X. TERM RESULTING FROM INELASTIC COLLISIONS WITH NEUTRAL SPECIES AND IONS

Although this term is taken into account, it has almost no influence on the kind of evolution considered here. Hence, a rough model of the Landau-Teller type is taken without accounting for the existence of the different heavy species. The relaxation time³³ was taken as

$$\tau_v = \frac{7.12 \times 10^{-4} \exp[(1.19 \times 10^{-6}/T)^{1/3}]}{p_h}$$

where p_h is the partial pressure of the heavy species.

XI. TERM RESULTING FROM INELASTIC COLLISION WITH ELECTRONS

It is clear that the amount of translational energy gained or lost by the electrons in these collisions is equal to the amount of vibrational energy lost or gained by nitrogen, respectively.

This gives

$$(Q_{N_2}^v)_e + (Q_{N_2^+}^v)_e = 3n_e k m_e (T_e - T_v) \frac{n_{N_2} + n_{N_2^+}}{m_{N_2}} \nu_{eN_2} G_v.$$

XII. TERM RESULTING FROM REACTIVE COLLISIONS

Let us first examine the term derived from the dissociative recombination R_1

$$(Q_{N_2}^v)_1 = \sum_v (K_{N_2}^v)_1 E_{N_2}^v.$$

From the collision cross section given by O'Malley it follows that

$$K_{N_2}^v = K_{N_2^+}^v, \quad v = 0, \\ K_{N_2^+}^v = 0, \quad v > 0.$$

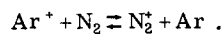
On the other hand,

$$E_{N_2^+}^{v=0} = 0;$$

hence,

$$(Q_{N_2^+}^v)_1 = 0.$$

Let us now consider the term derived from charge exchange, and begin with the reaction R_3



This term can be written

$$(Q_{N_2}^v)_3 + (Q_{N_2^+}^v)_3 = \sum_v (K_{N_2}^v)_3 E_{N_2}^v + \sum_v (K_{N_2^+}^v)_3 E_{N_2^+}^v.$$

The literature does not offer quantitative results concerning the influence of vibrational level on the reaction rate (although a study by Maier and Murad³⁴ showed the

importance of the internal state of nitrogen in this case). An attempt is made with the following hypothesis, which while not realistic, readily gives results: Only transitions between equal levels of N_2 and N_2^+ are possible in the charge exchange process. Under these conditions

$$(K_{N_2^+}^v)_3 = - (K_{N_2}^v)_3,$$

$$(Q^v)_3 = (Q_{N_2}^v)_3 + (Q_{N_2^+}^v)_3 = \sum_v (K_{N_2}^v)_3 (E_{N_2}^v - E_{N_2^+}^v).$$

It remains to calculate $(K_{N_2}^v)_3$. Omitting the index 3 one can write

$$K_{N_2}^v = - \sum_{v''} \int g \sigma_R^{vv''} f_{N_2^+}^{v''} f_{Ar^+} d\Omega d\bar{v}_{Ar^+} d\bar{v}_{N_2} \\ + \sum_{v''} \int g \sigma_R^{vv''} f_{N_2}^{v''} f_{Ar^+}^{v''} d\Omega d\bar{v}_{Ar^+} d\bar{v}_{N_2},$$

or

$$K_{N_2}^v = (K_{N_2}^v)_d + (K_{N_2}^v)_r,$$

and it is assumed

$$\sigma_R^{vv''} = \delta_{vv''} \sigma_R^p \quad \text{with} \quad \delta_{vv''} = 0 \quad \text{if } v \neq v'' \\ \delta_{vv''} = 1 \quad \text{if } v = v''.$$

It remains to be supposed that $K_{N_2}^v$ is independent of v ; that is possible because the direct reaction is always exothermic for any value of v . It is then easy to demonstrate that

$$(K_{N_2}^v)_d = \frac{n_{N_2}}{n_{N_2^+}} (K_{N_2}^v)_d,$$

and

$$(K_{N_2}^v)_r = \frac{\exp(-E_{N_2}^v/kT^*)}{\sum_v \exp(-E_{N_2}^v/kT^*)} (K_{N_2}^v)_r,$$

with

$$T^* = T \frac{T_v}{T_v + (\theta_{N_2^+}/\theta_{N_2})(T - T_v)}.$$

Note here that $(K_{N_2}^v)_r$ derived from the summation of $(K_{N_2}^v)_r$, actually depends on T_v but only slightly. Under these conditions it is not really contradictory to have taken $(K_{N_2}^v)_r$ dependent only on T for the species conservation equation.

Now proceeding to the charge exchange reaction R_2 with the same model, one can also write

$$(K_{N_2}^v)_d = \frac{n_{N_2^+}}{n_{N_2}} (K_{N_2}^v)_d$$

$$(K_{N_2}^v)_r = \frac{\exp(-E_{N_2^+}^v/kT^{**})}{\sum_v \exp(-E_{N_2^+}^v/kT^{**})} (K_{N_2}^v)_r,$$

where

$$T^{**} = T \frac{T_v}{T_v + (\theta_{N_2}/\theta_{N_2^+})(T - T_v)}.$$

The total term for charge exchange can be written

$$Q^v = (K_{N_2}^v)_3 E_{N_2}^v (T_v) \left(1 - \frac{\theta_{N_2^+}}{\theta_{N_2}}\right) + (K_{N_2}^v)_3 E_{N_2^+}^v (T^*) \left(1 - \frac{\theta_{N_2^+}}{\theta_{N_2}}\right) \\ + (K_{N_2}^v)_2 E_{N_2}^v (T_v) \left(\frac{\theta_{N_2}}{\theta_{N_2^+}} - 1\right) + (K_{N_2}^v)_2 E_{N_2^+}^v (T^{**}) \left(\frac{\theta_{N_2}}{\theta_{N_2^+}} - 1\right),$$

and the vibrational energy equation is then

$$\begin{aligned} (n_{N_2} c_{N_2}^V + n_{N_2^+} c_{N_2^+}^V) \frac{DT_V}{Dt} &= \frac{1}{\tau_V} n_{N_2} [(E_{N_2}^V)_e - E_{N_2}^V] \\ &+ \frac{1}{\tau_V} n_{N_2^+} [(E_{N_2^+}^V)_e - E_{N_2^+}^V] + 2 \frac{m_e}{m_{N_2}} (T_e - T_V)(m_{N_2} + m_{N_2^+}) \\ &\times \nu_{eN_2} G_V + Q^V - E_{N_2}^V K_{N_2} - E_{N_2^+}^V K_{N_2^+}, \end{aligned}$$

with

$$K_{N_2} = (K_{N_2})_2 + (K_{N_2})_3 \quad \text{and} \quad K_{N_2^+} = (K_{N_2^+})_1 + (K_{N_2^+})_2 + (K_{N_2^+})_3.$$

XIII. EQUATION FOR TRANSLATIONAL AND ROTATIONAL ENERGY OF HEAVY SPECIES

This is derived from the total energy conservation equation which gives,

$$\begin{aligned} \left(\frac{3}{2} n_h + n_{N_2} + n_{N_2^+} \right) k \frac{DT}{Dt} &= -\frac{3}{2} n_e k \frac{DT_e}{Dt} \\ &- (n_{N_2} c_{N_2}^V + n_{N_2^+} c_{N_2^+}^V) \frac{DT_V}{Dt} + K_1 \Delta E_1 + K_2 \Delta E_2 + K_3 \Delta E_3 \\ &+ K_4 \Delta E_4 - E_{N_2}^R K_{N_2} - E_{N_2^+}^R K_{N_2^+} - E_{N_2}^V K_{N_2} - E_{N_2^+}^V K_{N_2^+} \end{aligned}$$

and

$$\begin{aligned} \Delta E_1 &= -5.82 \text{ eV}, \quad \Delta E_2 = -1.04 \text{ eV}, \\ \Delta E_3 &= -0.18 \text{ eV}, \quad \Delta E_4 = -1.22 \text{ eV}. \end{aligned}$$

This provides a complete system of equations, making it possible to calculate some evolutions.

XIV. CALCULATION METHOD

We now have a system of six differential equations of the first order. It is quite clear from the form of the right-hand terms (production terms) that an analytical solution cannot be found.

A numerical computation was made with various initial conditions, using a Taylor method ideal for this case

owing to the analytical form of the production terms. It was verified that convergence was good, by varying the computation step.

XV. IMPORTANCE OF INITIAL CONDITIONS

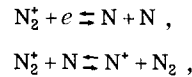
The results obtained depend strongly on the type of the initial ionic species and on the initial electron density. We always considered plasmas with high electron concentration, ranging from a few parts per thousand to a few per cent. The initial pressure was assumed to be 10^{-4} Pa and the initial temperature some thousands of degrees Kelvin. Calculations were done for times ranging from zero to 10^{-3} sec.

Several cases are distinguished:

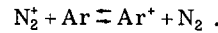
First case: the initial ionic species is N^+ . Whatever the other initial ionic conditions, there is almost no chemical evolution for chemical species in the plasma, even if the electron density is much greater than at thermodynamic equilibrium.

As for temperature, if these are initially equal no evolution occurs. If not, there is a relaxation toward an equilibrium value, but this phenomenon is not dependent on the chemical reactions.

Second case: the initial ionic species is N_2^+ . In line with the following reactions:



and



The ionic species N_2^+ disappears and the ions N^+ and Ar^+ are created. Moreover, owing to dissociative recombination, a sharp drop is observed in electron density. Generally, the concentration of Ar^+ reaches a maximum value and then falls. The atomic nitrogen concentration

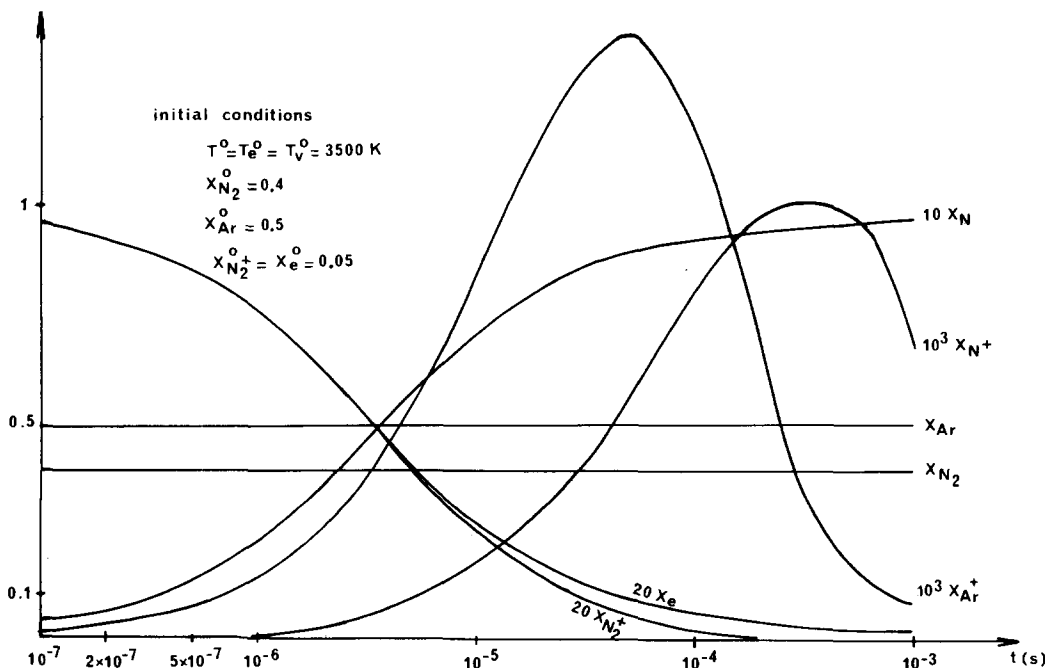


FIG. 1. Concentration of species versus time. The initial ionic species is N_2^+ .

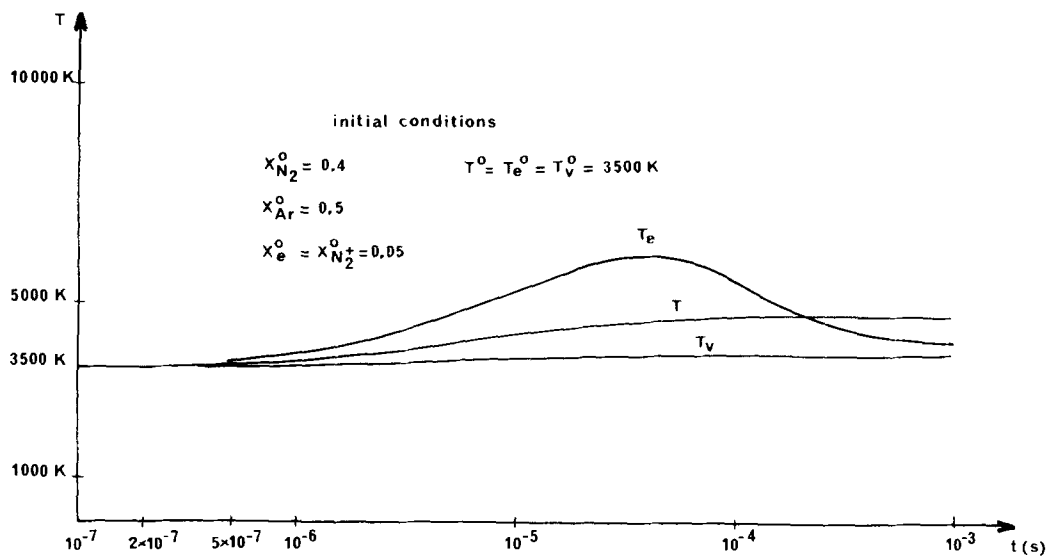


FIG. 2. Temperatures versus time: electron density is initially high and the initial ionic species is N_2^+ .

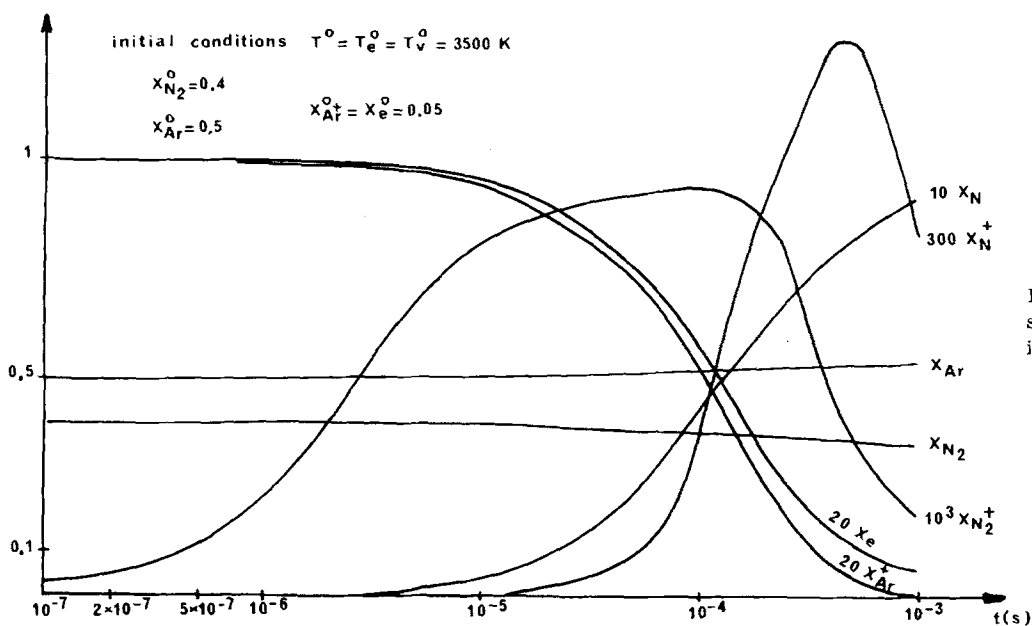


FIG. 3. Concentration of species versus time. The initial ionic species is Ar^+ .

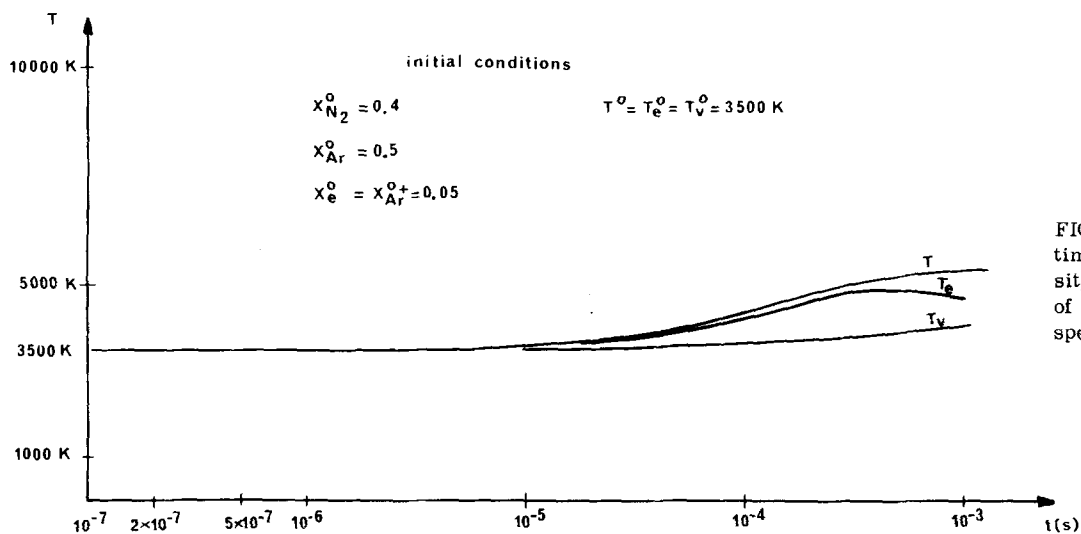


FIG. 4. Temperatures versus time: value of electronic density is the same as in the case of Fig. 2. The initial ionic species is Ar^+ .

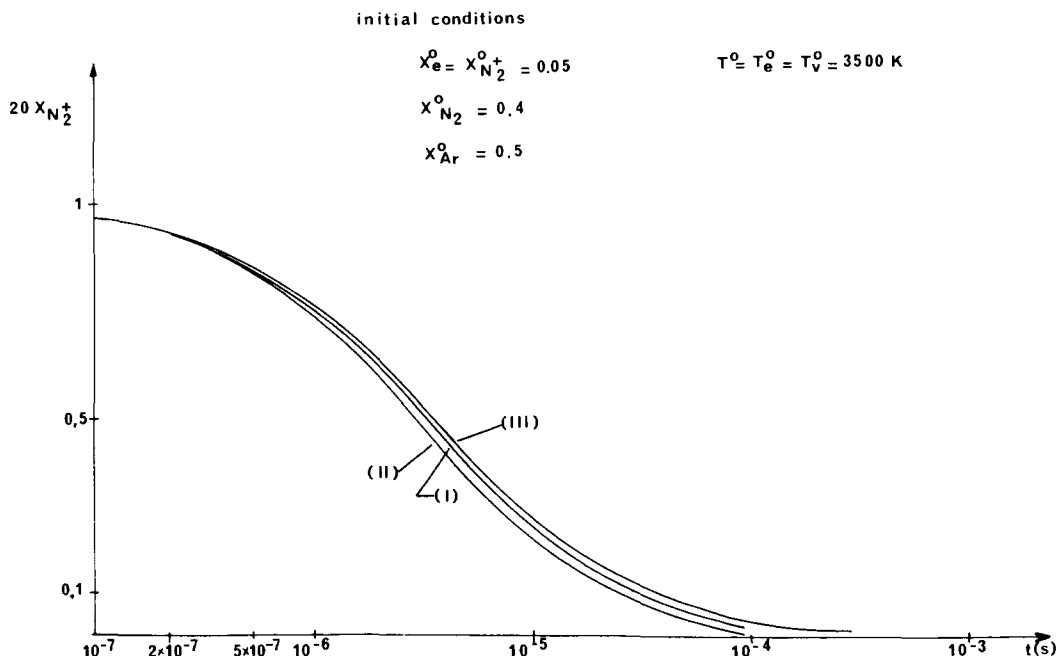


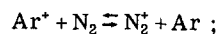
FIG. 5. Species concentrations versus time. Comparison of different models.

reaches a constant value (quasi-stationary state) Fig. 1.

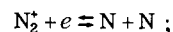
As for temperatures, if the electron density is initially high ($X_e \approx 10^{-2}$), the temperature rises because of the exothermicity of the reactions (and principally of dissociative recombination). The gap between the two temperatures first widens and then narrows to zero. This effect is clearly revealed in Fig. 2, where the three temperature evolutions are shown for a time evolution of 10^{-3} sec.

For lower values of the initial ionization ($X_e \approx 10^{-3}$), the reaction effect is less; negligible for neutral translational temperature, the effect is only substantial for the electronic temperature and to a lesser extent, for the vibrational temperature.

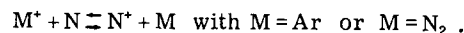
Third case: the initial ionic species is Ar^+ . The charge exchange process occurs first



followed by dissociative recombination



and charge exchange:



Since in the second case, during the plasma evolution one observes the creation of N^+ ions with a drop in electron density (Fig. 3). Note also that the N_2^+ concentration reaches a maximum and then falls (Fig. 3). The same thermal effects as in the second case are observed

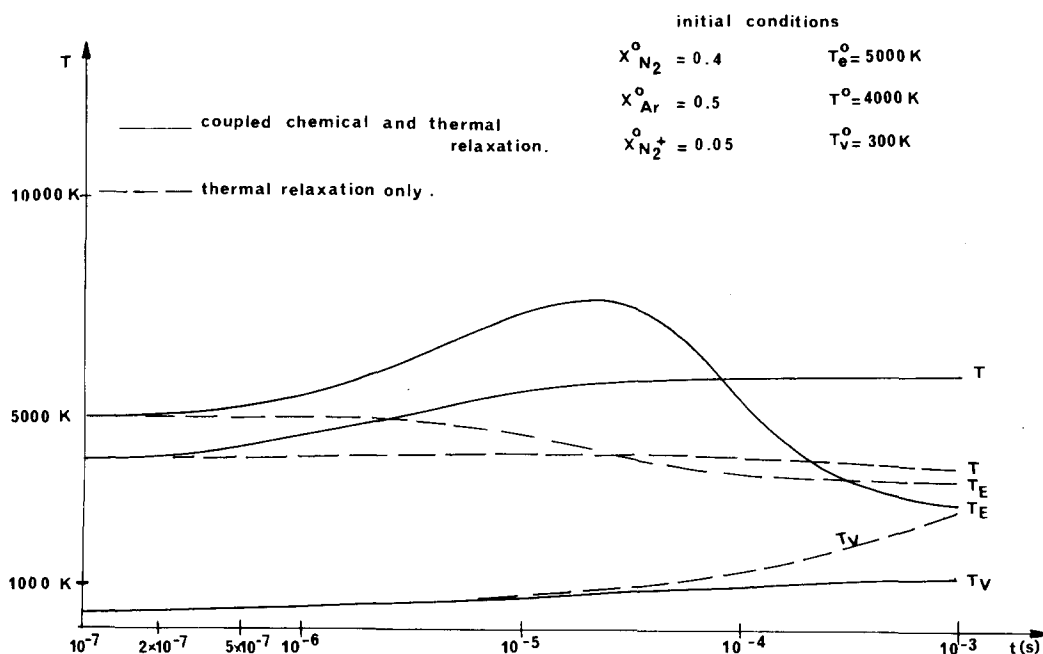


FIG. 6. Temperature versus time; comparison of different models. The initial ionic species is N_2^+ .

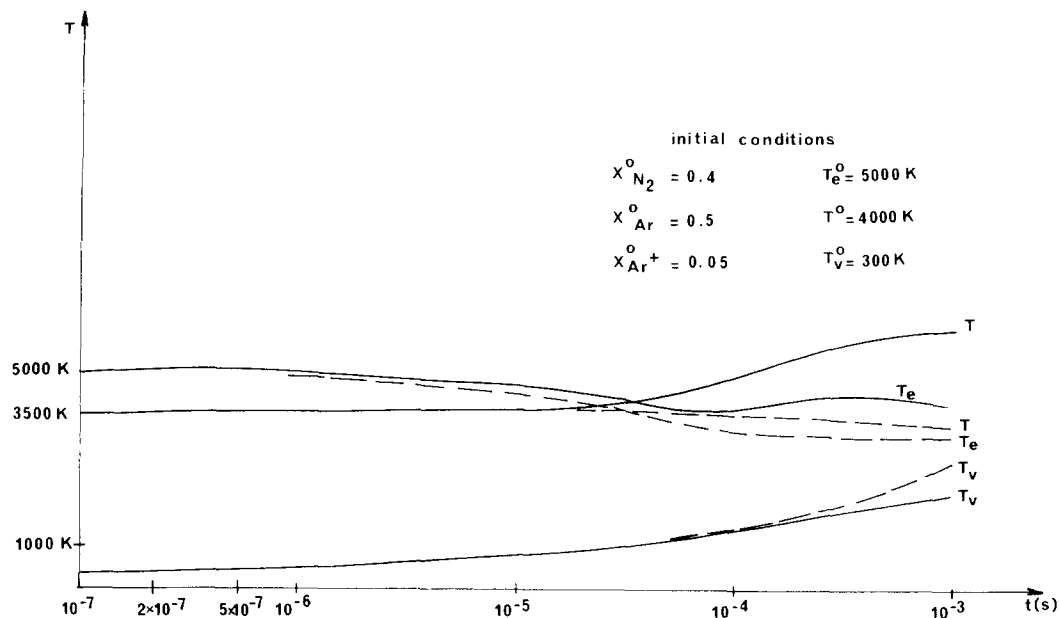


FIG. 7. Temperature versus time: comparison of different models. The initial ionic species is Ar^+ .

but less strongly for the same initial electronic density (Fig. 4). For the last two cases a comparison was made of the results obtained for thermal relaxation with and without chemical reactions. Similarly, the results for chemical relaxation were compared as a function of the thermal evolution model.

XVI. INFLUENCE OF THERMAL RELAXATION ON CONCENTRATION EVOLUTION

A computation was made with the same initial temperature values $T = T_e = T_v = 3500$ K, not only for the complete system of equations seen previously (model I), but also for two other models.

Isothermal evolution was first assumed (model II) followed by evolution with temperature evolution but with a single temperature T (thermal equilibrium, model III).

Figure 5 shows the typical evolution of X_e , X_{Ar^+} , and $X_{\text{N}_2^+}$ for the three models. As can be seen, the differences between the three models are very slight, especially for models I and III. It can be concluded that thermal relaxation, in fact, has little effect on chemical evolution.

XVII. INFLUENCE OF REACTION ON THERMAL RELAXATION

Two models were considered, the complete model I and another model for which it is assumed that no chemical reaction occurs (model IV). Figure 6 and 7 show that the difference between the two models when thermal relaxation is very large. In the case of model I, the widest gap between T_e and T , for equal initial temperatures $T = T_e = T_v = 3500$ K, can be seen in Fig. 8 as a

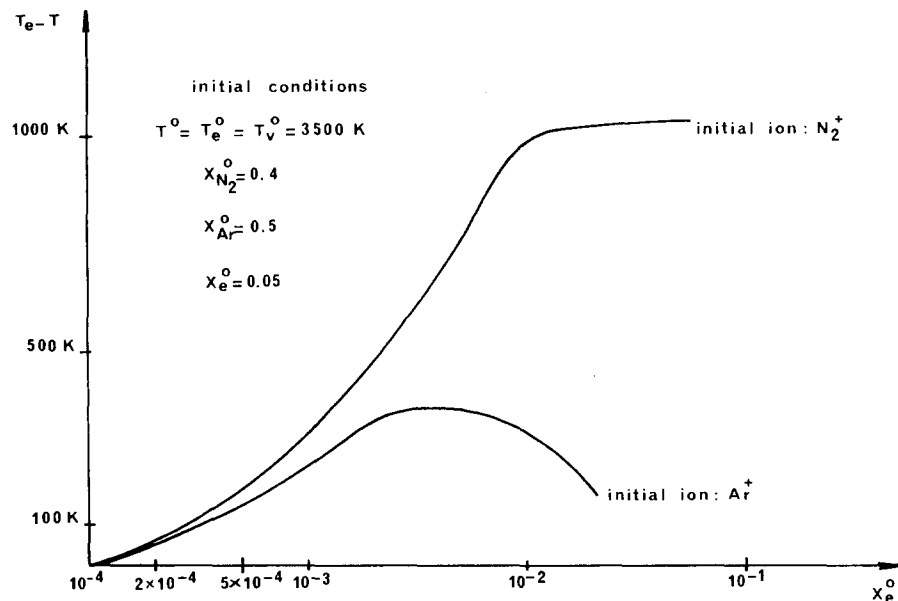


FIG. 8. Maximal gap between heavy species temperature and electronic temperature versus electronic density.

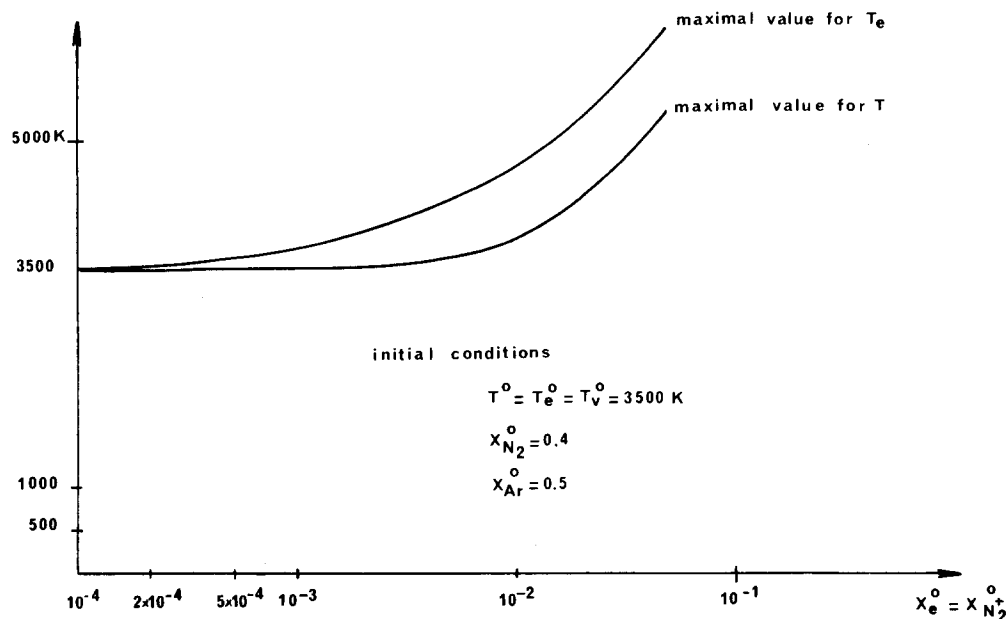


FIG. 9. Maximal value for electronic temperature and heavy species temperature versus electronic density. The initial ionic species is N_2^+ .

function of the initial electron concentration. This gives the electron concentration values for which dissociative recombination can induce great thermal nonequilibrium.

On the other hand, the maximum value reached by T_e during the time evolution, and the final value (maximum value), reached by T , are plotted in Fig. 9 as a function of the initial electron concentration X_e^0 . It can then be seen that even for low values of electron concentration, the electronic temperature can be strongly influenced by dissociative recombination.

XVIII. CONCLUSIONS

This computation has been done with a view to a better understanding of phenomena which can influence the chemical rate measurements. It has been shown that for a case in which a chemical rate is to be determined without kinetic dependence on each kind of temperature, the coupled thermal effects on the reaction are low enough to permit a rate measurement without taking thermal nonequilibrium into account. In the case of a thorough study of kinetics, where rate dependence on T , T_e , T_v is taken into account, the coupled effect between chemical reaction and temperature must be investigated. The same remarks apply to the case of a pure thermal relaxation experiment if some bimolecular reactions can occur.

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