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Chemical kinetics at equilibrium of an ionized mixture¹

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Abstract-This paper describes a contribution to the investigation of changes in plasma ionisation rates, caused by water injection. Concentrations were computed, assuming the existence of a state of chemical equilibrium in a mixture of perfect gases consisting of nitrogen water with 0.0001-1 mixture ratios. The most recent data on the 43 chemical species investigated were used. Temperatures ranged from 1500 to 6000°K, pressures from 10 to 10⁴ Pa.

Comparison with pure nitrogen plasma in identical temperature and pressure conditions revealed over- and de-ionization zones which are dependent on mixture ratio, among other factors.

Computations required an adaptation of the Brinkley method, due to plasma neutrality and also to the selection of water injections, which involves a specific ratio of two chemical elements. These computations were used for predicting chemical changes induced by chemical kinetics in such plasmas. One result is a classification of chemical reactions in order of significance, leading to prediction of possible freezes, which is necessary to investigate actual cases of water injection.

Introduction

The study of an ionized nitrogen/water mixture is of basic value for a better knowledge of chemical processes occurring in plasmas, and also from the standpoint of applications, as water injection into the boundary layer is a means of improving radio links with artificial satellites reentering the atmosphere. The broad range of temperatures, pressures and water content which we consider requires accounting for 43 chemical combinations and 216 chemical reactions. Hence the test mixture is complex and simplifying hypotheses are necessary.

The chemical equilibrium concentrations were initially calculated in Poissant and Prud'homme (1976). It was assumed that the thermodynamic potential of the mixture of perfect gases considered was a minimum at a given temperature and pressure. This equilibrium hypothesis can only be realized in practice in precise configurations (flow near the stagnation point, for example). It is nevertheless a valid hypothesis in such a way that major changes in the plasma caused by different water injection rates are revealed, and that valuable data can be obtained from fairly simple computations.

In order to concentrate on essentials, it is also necessary to correct the results in this light of chemical kinetics; this constitutes part two of this investigation.

Computation of equilibrium concentrations

Minimization of the thermodynamic potential of a reactive gas mixture implies writing that the reactions of formation of the combinations from chemical elements are at equilibrium.

Since any chemical combination is formed from elements in accordance with the reaction:

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$$\sum_{l=1}^L \alpha_{lj} \mathcal{A}_l = \mathcal{E}_j, \quad j = L+1, \dots, N \quad (1)$$

the element conservation relations are written successively:

$$\sum_{j=L+1}^N \alpha_{lj} n_j + n_l = \mathcal{N}_l, \quad l = 1, \dots, L \quad (2)$$

and the equilibrium equations linking the molar chemical potentials G_l :

$$G_j = \sum_{l=1}^L \alpha_{lj} G_l, \quad j = L+1, \dots, N \quad (3)$$

For perfect gases, the chemical potentials depend on the standard tabulated potentials (G_T^0); and the partial pressures p_i , so that eqn (3) can be replaced by the equivalent form:

$$\log X_j = \log K_{p,j} + (\alpha_j - 1) \log p + \sum_{l=1}^L \alpha_{lj} \log X_l \quad (4)$$

$X_j = n_j/n$ denotes the molar fraction of the species,

$$\alpha_j = \sum_{l=1}^L \alpha_{lj}$$

$K_{p,j}$ is defined by:

$$\ln K_{p,j} = -\frac{1}{RT} \left[(G_T^0)_j - \sum_{l=1}^L \alpha_{lj} (G_T^0)_l \right] \quad (5)$$

This is the pressure equilibrium constant.

The values of $\log_{10} (K_{pj})$ are tabulated for most of the 43 combinations investigated. The Janaf tables (1971) furnish data for: H, N₂, O, e⁻, N, HN, HNO, HNO₂, HNO₃, HO, HO₂, H₂, H₂N, H₂N₂, H₂O, H₂O₂, H₃N, H₄N₂, NO, NO₂, N₂O, N₂O₃, O₂, O₃, H⁺, HO⁻, NO₂⁻, O⁻, O₂⁻, H⁺, HO⁺, H₃O⁻, NO⁺, from 0 to 6000°K.

For the H₂⁺ and H₃⁺ ions, the values of standard thermodynamic potentials are given by Patch and McBride (1968) and the equilibrium constants are derived from these values and from $(G_T^0)_{H_2}$ and $(G_T^0)_e$, taken from the Janaf tables. The equilibrium constants of the N⁺, N₂⁺, O⁺, O ions are derived from Barrère (1959).

In Brinkley's method in Bahn and Zukoski (1960), the chemical elements (H, N, O, e⁻ in this case) are replaced by the preponderant combinations at equilibrium, which form a system of basic chemical species. This choice is necessary to ensure convergence of the method. The new equilibrium constants are easily computed from the former. Without changing the notations (A_i , here denotes the basic species), it is shown that eqn (2) can be replaced by the following:

$$\sum_{j=1}^N [\alpha_{lj} + (1 - \alpha_j) \bar{X}_l] X_j = \bar{X}_l, \quad l = 1, \dots, L \quad (6)$$

where:

$$\bar{X}_l = \mathcal{N}_l / \sum_{l=1}^N \mathcal{N}_l$$

The systems of eqns (4) and (6) are then resolved by taking, as starting values of X_j^0 , the raw concentrations \bar{X}_i with X_j^0 ($j = L + 1, \dots, N$) being derived from eqn (4). The corrections required to determine X_i^1 are estimated by linearizing systems in eqns (4) and (6):

$$\begin{aligned} \sum_{l'=1}^L \left\{ \sum_{j=1}^N \alpha_{l'j} X_j^0 [\alpha_{lj} + (1 - \alpha_j) \bar{X}_l] \right\} \Delta(\ln X_l^0) \\ = \bar{X}_l - \sum_{j=1}^N [\alpha_{lj} + (1 - \alpha_j) \bar{X}_l] X_j^0, \quad l = 1, \dots, L \end{aligned} \quad (7)$$

One can then write:

$$X_l^1 = X_l^0 (1 + \Delta \ln X_l^0), \quad l = 1, \dots, L \quad (8)$$

The new X_l^1 values make it possible to repeat the process to compute X_l^2 , and proceed similarly until convergence.

The problems raised by the application of Brinkley's method pertain to:

- selection of basic chemical combinations (*a priori* unknown).
- rapidity of convergence (number of iterations required),
- selection of initial values when some \bar{X}_l are nil (\bar{X}_{e^-} is always nil for a neutral plasma).

The choice of basic species is made as a rule from general considerations concerning the dissociation rate in a pure nitrogen plasma (Prud'homme and Rowe, 1976) and dissociation of water. Three groups of possible basic species are thus investigated:

- group 1: $\{\text{H}_2\text{O}_2, \text{N}_2, \text{H}_2, e^-\}$
- group 2: $\{\text{H}, \text{N}_2, \text{O}, e^-\}$
- group 3: $\{\text{H}, \text{N}, \text{O}, e^-\}$

The computation carried out at intervals of 500°K. for pressures varying in powers of 10, and for nine values of the mixture ratio $\phi = m_{\text{H}_2\text{O}}/m_{\text{N}_2}$, furnishes validity zones of specific groups, namely, zones in which convergence is ensured for a given group. It enables the highlighting of a new group: $\text{H}_2\text{O}, \text{N}_2, \text{H}, e^-$ making the transition between groups 1 as 2. This computation requires determination of the raw concentrations as well as the starting values, as indicated above. For the three groups it was found that $\bar{X}_{e^-} = 0$ and for group 1, $\bar{X}_{\text{H}_2} = 0$. The classic method was inapplicable in all cases. To determine $X_{e^-}^0$, eqn (4) was used, applied to the ions and written in the form:

$$X_j = 10^{\Gamma_j - n\alpha_j} \quad (9)$$

where

$$\Gamma_j = \log K_{p,j} + (\alpha_j - 1) \log p + \sum_{l=1}^3 \alpha_{lj} \log X_l^0$$

Concentrations X_1^0, X_2^0, X_3^0 were assumed to be known and X_4^0 denoted the concentration of the electrons, which is set equal to 10^{-n} . The equation giving the electrical neutrality of the plasma was also used:

$$X_{e^-} = -\sum_j \alpha_{4j} X_j \quad (10)$$

which, by setting:

$$\beta_j = 10^{\Gamma_j - (\alpha_{4j} - 1)n} \quad (11)$$

becomes:

$$1 + \sum_j \alpha_{4j} \beta_j = 0 \quad (12)$$

The principle of the method consists of accepting that a very low number of ions are predominant. For example, if a single positive ion j^* is taken ($\alpha_{4j^*} = -1$), one directly finds:

$$n = \frac{\Gamma_{j^*}}{2} \quad (13)$$

In cases in which one can no longer accept the uniqueness of the preponderant ion, the method is still applicable (Poissant and Prud'homme, 1976).

The initial values of X_{H_2} were determined by trial and error using the digital program, and an approximate formula was established. The digital program is completely automatic.

The equilibrium concentrations at the 43 chemical combinations investigated were computed for 450 values of the triplet (T, p, ϕ) . The overall results are given in the report by Poissant and Prud'homme (1976). The influence of water injection on the pure nitrogen plasma is examined here.

These results are summarized in Figs. 1 and 2. Figure 1 shows the effect of water injection on the dissociation of molecular nitrogen represented by the values:

$$\log \left(\frac{X_N}{X_{N_2}} p^* \right).$$

Figure 2 shows the effect of water injection on the electron concentration, characterized by the deionization ratio:

$$I_e = \frac{X_{e^-}(\phi = 10^{-4}) - X_{e^-}(\phi)}{X_{e^-}(\phi = 10^{-4})} \quad (14)$$

as a function of temperature for different values of the injection ratio and pressure.

Chemical kinetics

The chemical kinetics data available deal with 216 reactions involving the 43 chemical combinations of the mixture. The chemical reactions which may be written:

$$\sum_{j=1}^N v'_{jq} E_j \xrightarrow{k(T)} \sum_{j=1}^N v''_{jq} E_j, \quad q = 1, \dots, K \quad (15)$$

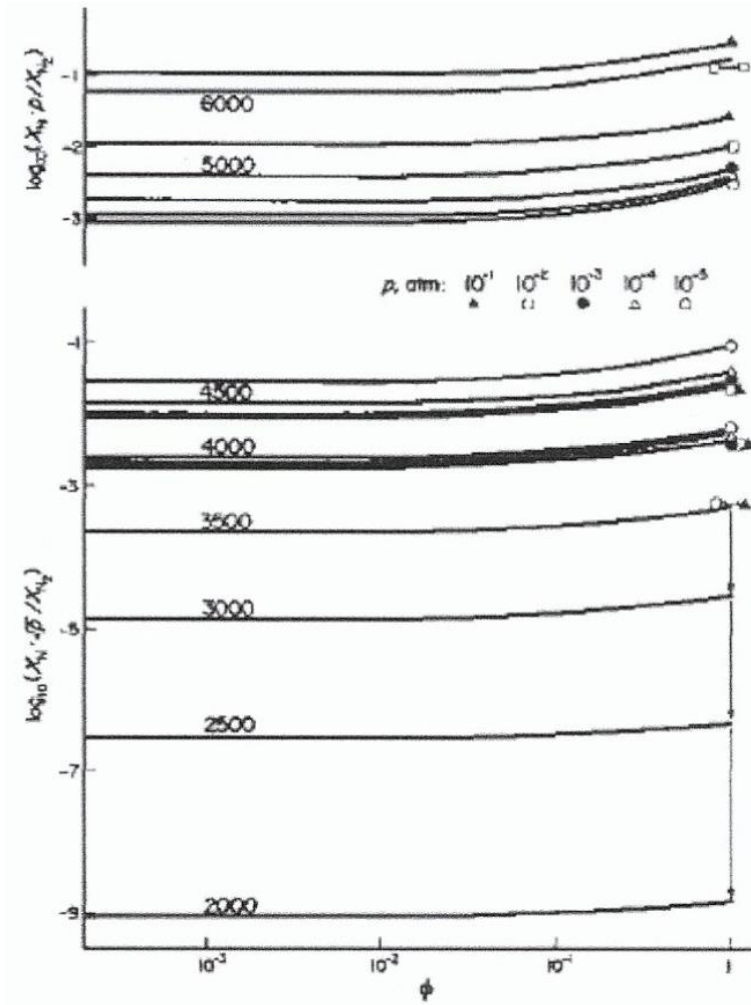


Fig. 1. Influence of the injection parameter ϕ on dissociation of nitrogen

have the reaction rate:

$$\dot{w}_q = k(T) \prod_{j=1}^N C_j^{v'_{jq}} \quad (16)$$

The production rate of species j in reaction q is:

$$\dot{C}_{jq} = a_{jq} \dot{w}_q, \quad a_{jq} = v''_{jq} - v'_{jq} \quad (17)$$

and for all reactions:

$$\dot{C}_j = \sum_{q=1}^K \dot{C}_{jq} = \sum_{q=1}^K a_{jq} \dot{w}_q \quad (18)$$

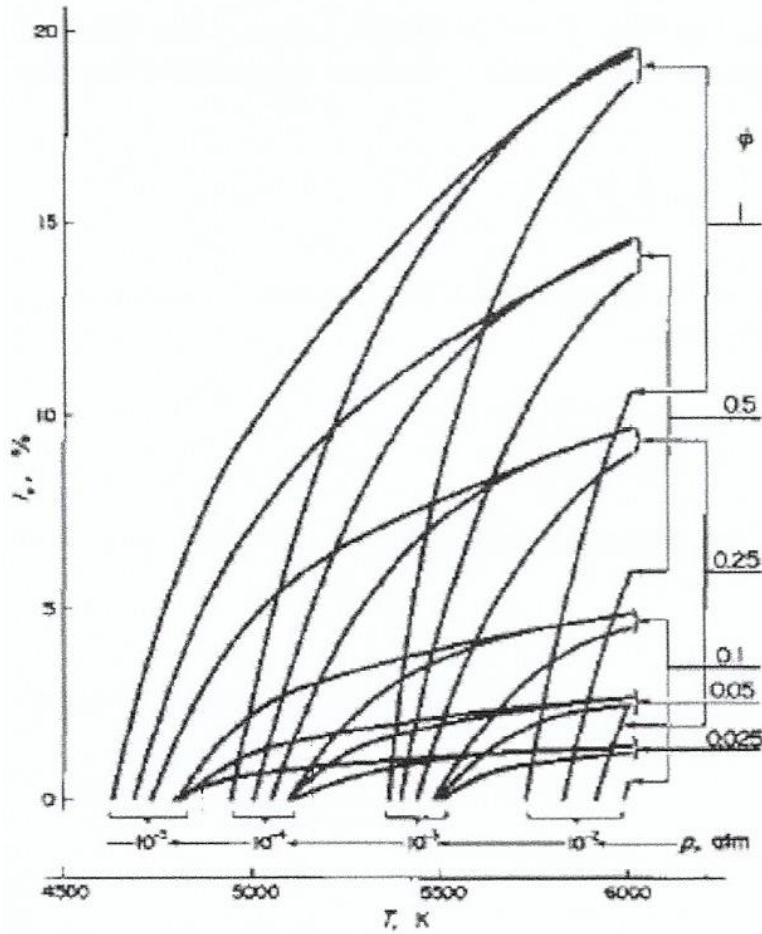


Fig. 2. Percentage of deionization vs de parameters p , T and $\phi = m_{H_2O}/m_{N_2}$.

To determine whether a reaction is frozen or near equilibrium, the chemical times can be computed and compared with the mechanical flow times. This computation was made for the nitrogen plasma, but will not be made for the nitrogen/water mixture. Computation of the 39 proper values of the relaxation matrix will be replaced by a simple estimate of each reaction rates occurring in the production of each component.

To do this, sets $\{E_x\}$ of chemical combinations \mathcal{E}_j , are defined such that one has $\mathcal{E}_j \in E_x$ if $X_j \geq 10^{-X}$ and sets $\{A_y\}$ of chemical reactions R_q , such that $R_q \in A_y$, if $\dot{w}_q \geq 10^{-y} \dot{w}_q^*$ with $\dot{w}_q^* = \sup_{(q)} \dot{w}_q$. For any value of X , a maximum value $Y^*(X)$ is thus defined such that: $0 \leq Y \leq Y^*(X)$.

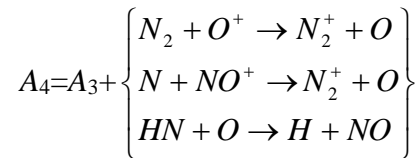
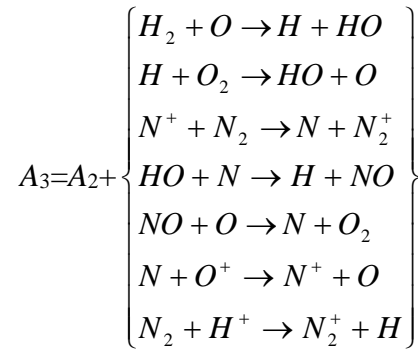
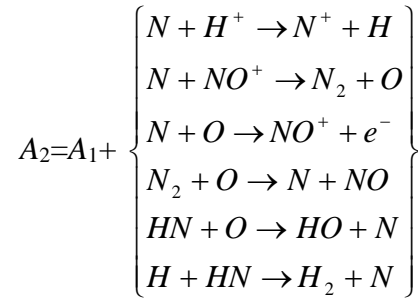
The production rates \dot{w}_q are estimated by means of the equilibrium computation.

For example, in the case of the triplet: $T=4000$ K, $\phi=1$, $p=10^{-5}$ atm, by taking $X=8$, a set of 15 chemical combinations is found:

$$E_8 = \{H, N_2, O, e^-, N, HN, NO, H_2, NO, O_2, H^+, NO^+, N^+, N_2^+, O^+\}$$

and sets of successive reactions, $A_0 \subset A_1 \subset A_2 \subset A_3 \subset A_4$:

$$A_0 = \{O+H^+ \rightarrow O^+ + H\}; A_1 = A_0$$



These results are obtained by means of an automatic computer program which also gives the λ_{jq}^y components, in the space of the reacting species, or the chemical invariants of the reactive system A_y :

$$\sum_{j=1}^N \lambda_{jq}^y C_j = I_q^y, \quad (I_q^y = \text{const.})$$

Hence, in addition to the element conservation equations, one obtains the following invariance equations:

- for A_0 and A_1 $C_{H^+} + C_{O^+} = I_1^0 = I_1^1,$
- for A_2 $C_{H_2} + C_{NO} - C_{N^+} - C_{H^+} - C_{O^+} = I_1^2, \quad C_{HN} + C_{HO} + C_{H_2} = I_2^2$
- for A_3 and A_4 $C_{N_2} + C_{NO} + C_{HN} + C_{HO} + C_{H_2} + C_{O_2} - C_{N^+} - C_{H^+} - C_{O^+} = I_1^3 + I_1^4$

Conclusions

This study shows that at chemical equilibrium, the presence of water in nitrogen lowers or raises the plasma ionization rate, hie tendency depending on the parameters T, ϕ, p . It also specifies the chemical kinetics et the medium and provides a basis for computations of partial equilibrium which are more accurate than hitherto reported.

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