

THE ROLE OF ELEMENTARY PROCESSES IN MODELLING NON-EQUILIBRIUM PLASMAS

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Abstract. The properties of non-equilibrium plasma of a low pressure d.c. discharge in molecular gases are illustrated using, in particular, oxygen as an example. Special attention is devoted to a detailed investigation of the electron distribution function, which represents a starting point for the subsequent analysis of the discharge regime. The significance of elementary processes in forming the electron distribution as well as for the resulting populations of the plasma constituents is discussed. It is hoped that these and similar computations may prove useful in search for optimum conditions in plasma chemistry experiments.

INTRODUCTION

There is a wide variety of plasmas which have been used as reaction media in various plasma chemical reactions of great practical interest. A chemically reacting plasma, whose associated problematics borders on several scientific and technical disciplines, represents a medium where the rates of known chemical reactions might be greatly enhanced, but it is also suitable in search for more exotic reactions, with reaction rates virtually nil under normal conditions. An obvious way of overcoming the activation energy barrier is a creation of plasma with high temperature, which can also serve as a heat source for endothermic reactions. The high temperature plasma is usually produced in arcs or plasma jets with the power of sometimes up to 100 MW. It is concentrated on synthesis of industrial products (C_2H_2 , HCN, nitrides, carbides etc.) and on extractive metalurgy (Refs. 1, 2). In such a plasma the temperature may reach 20 000 K and the reactions run under equilibrium conditions. The reaction rate is enhanced just due to the increased temperature and not due to any particular property of the plasma medium. But the main part of the plasma energy need not necessarily be stored in the translational degrees of freedom. In case of s.c. cold plasmas the activation energy may be drawn from the internal degrees of freedom of the constituent atoms or molecules. By using such systems, which as a rule, are far from a thermodynamic equilibrium, the necessity of heating the reactants to the exorbitant temperatures may be by-passed. In some cases only a partial activation may give rise to the reaction intermediates, which then are able to carry the reaction on to the required

result. The non-equilibrium plasma is less exacting from the point of view of energy consumption and the plasma chemistry based on it is usually confined to small-scale processes. The plasma is invariably produced by some kind of discharge, such as hf or d.c. glow discharge at low pressures, corona at the atmospheric pressure, unipolar discharge etc. The various plasma technologies comprise methods of preparatory chemistry, material cleaning, recrystallization, production of thin anorganic or polymer films, etching (Refs. 3-8), ozone production (Ref. 19) etc.; of paramount importance are those used in the rapidly developing electronic industry. Some of these reactions belong to a wider class of the s.c. transport processes (Refs. 6, 10). As in all these cases the gaseous discharge plays the role of plasma source, we think that a good understanding of the discharge physics may greatly contribute to its more efficient utilization in various branches of plasma chemistry. Below we shall attempt to expound some of its aspects.

NON-EQUILIBRIUM REACTION KINETICS

In the classical chemical kinetics the time evolution of the reacting homogeneous gaseous mixture is described by the set of equations of the following type (Ref. 11):

$$-\frac{dn_i}{dt} = \sum_j k_{ij} n_i n_j - \sum_k k_{ki} n_k n_l \quad (1)$$

These equations follow from statistical balancing of the particle production rates under the assumption of dual collisions, statistical independence etc. k_{ij} are the rate constants of the chemical reactions, n_i the concentration of the i -component. As long as the translational and the internal degrees of freedom of the reactants are in the thermal equilibrium at a given temperature, the equations (1) represent only an alternative form of the "mass action law" (Guldberg-Waage) and the reaction constants depend on the temperature, T , only (Arrhenius equation) (Ref. 12):

$$k = A(T) \exp(-E_a/kT) \quad (2)$$

E_a is the activation energy; (i.e. the energy distribution of the species is Maxwellian and the bound energy states are distributed according to the Boltzmann law). In the general case the equations of the chemical kinetics may be derived by an integration of the Boltzmann kinetic equation

$$\frac{d(n_i f_i)}{dt} = \sum_j n_j \iint [f_i(v_i') f_j(v_j') - f_i(v_i) f_j(v_j)] \sigma_{ij}(v_i - v_j, \Omega) dv_j d\Omega \quad (3)$$

over the velocity space (Ref. 13). The left-hand-side of the Boltzmann equation yields the time derivative of the pertinent particle density and the diffusion loss (omitted for a closed system), the non-vanishing terms on the right-hand-side render the reaction rates, with the reaction constants given now, quite generally, as integrals over the distribution functions of

the colliding particles and the effective cross-section, σ_{ij} , (Refs. 14,15):

$$k_{ij} = \iiint \sigma_{ij}(v_i - v_j, \Omega) |v_i - v_j| f_i f_j dv_i dv_j d\Omega \quad (4)$$

Every chemical reaction going on in the system introduces a disturbance, which in principle can influence the solution of the Boltzmann equation and thus to change the particle distribution function. However, if the characteristic time of the reaction is sufficiently long, if compared to the time of momentum transfer, energy relaxation or the redistribution of the internal degrees of freedom, a perturbation scheme due to Enskog may be applied to solve the Boltzmann equation (Ref. 16). The distribution functions entering the integral (4) are then to the zero order independent of the reaction affinity itself, by which the mass action law is again recovered. To a higher order, the rate constants may depend on the affinity and also on the time. Consequently, the constant on the right-hand-side of the mass action law may become time dependent. The Enskog perturbation scheme, which is essentially based on the assumption of the equal temperatures of all the mixture components, is inherently not suitable for a description of highly non-equilibrium systems - such as electric discharges (Ref. 17). In a discharge plasma, owing to the tiny mass ratio, the energy exchange between the electron component of the discharge plasma and the heavy particles is so slow that the electron temperature (or the mean electron energy) may be much higher than the temperature of the heavy plasma components. The plasma of a low pressure, direct current, electric discharge represents from a microphysical point of view a complicated mixture of atoms and molecules in the ground as well as excited states and at least one kind of ions, whose charge is compensated by an adequate amount of electrons. The electron gas, even if its concentration is by several orders of magnitudes lower than that of the neutrals, is the most active component of the plasma. It draws kinetic energy from the electric field, by which the discharge is sustained, and simultaneously this energy is dissipated mainly in the excitation of the neutral particles and in the elastic collisions with the background gas. The action of the electric field on the electron gas is in no way small, in the sense, that it might be included among the first order thermodynamic forces disturbing the equilibrium. This together with the smallness of the electron-atom mass ratio, which is responsible for the poor energy transfer between the electrons and the heavy particles of the plasma, causes the electron gas to be maintained in a state which is far from thermodynamic equilibrium to the extent that even the methods of irreversible thermodynamics are inapplicable. Non-equilibrium of the electron gas also implies non-equilibrium of the electronic and vibrational state populations of the atoms and molecules, as these populations are governed by the inelastic collisions with the electrons. It is just this property of the discharge plasma, which makes it attractive for the plasma chemistry.

ELECTRON GAS IN THE DISCHARGE PLASMA

The starting point in description of the electron gas in the plasma of a

d.c. discharge is the electron Boltzmann equation for the electron distribution function (EDF), $f(\vec{v})$. Although the imposed electric field accelerates the electrons in a single direction the elastic collisions have the effect of fast randomization of any directed electron motion. The EDF must be thus nearly isotropic in the velocity space, on which a method of solution is based. The distribution function is expanded in a series of spherical harmonics in the velocity space and the expansion is cut off at the second term. In this way, the "two-term approximation" contains only the leading isotropic part and a small axial correction. More details of the procedure can be found in (Refs. 17,18). While the momentum scattering is invariably mainly due to the elastic collisions, several elementary processes compete in the energy redistribution of the electrons. Although, in principle, any collisional process modifies the distribution, there are, depending on the discharge conditions only few of them that must be included in the Boltzmann equation to get a realistic EDF. The list of elementary processes participating in formation of the isotropic part of the distribution function usually comprises

- 1) elastic and inelastic impacts
- 2) superelastic processes
- 3) electron-electron Coulomb collisions
- 4) photon-electron (free-free) processes
- 5) attachment and recombination
- 6) ionization by secondary electrons
- 7) an external electron source (beam).

The large routines available at the programming libraries are, as a rule, capable to cope with any of the above listed terms on the right-hand-side of the Boltzmann equation (Ref. 21). With a weak external field and a high ionization degree the electron-electron Coulomb collisions manage to establish a Maxwell distribution of the electrons, which, however, at the high energy end is depleted by the inelastic collision (Refs. 19,20). The ensuing shortage of the energetic electrons results in an essential reduction of the production rates. At still lower ionization degrees the distribution starts to deviate from a Maxwell distribution even in the low energy interval and finally it assumes a form which is given in each elementary energy interval by a balance between the electron acceleration in the field and the energy loss in the elastic and inelastic impacts, the second kind (superelastic) collisions, if included, representing an alternative energy supply. Such a stationary, non-equilibrium distribution is strictly individual for each gas and it is essentially given only by the form of cross-sections of the considered elementary processes. Since the production rates depend critically on the exact form of the distribution function, especially on its high energy part, the distribution must be found by a numerical solution of the Boltzmann equation (Ref. 21,22), which requires a prior knowledge of the impact cross-sections. These are scattered over the literature and often data given by various authors greatly differ from each other. Luckily, for a reasonably accurate calculation of the electron distribution function just a few processes play a vital role and usually a compromise can be made in using the available data. At the same time, a

measurement of the EDF is a possible check on the realism of the choice of cross-sections, but the measured EDF cannot replace the calculated one, since the high energy part is usually inaccessible by a direct measurement (Ref. 23). An indirect check on the correctness of the distribution function is to compare the calculated and measured values of the electron drift velocity and of the characteristic energy for various values of E/N (E - longitudinal electric field, N - total particle concentration). A similar procedure involving the ionization coefficient enables us to improve the high energy part of EDF. In fact, on the same principle the indirect method of finding the cross-sections of the most important elementary processes advanced in (Refs. 24,25) is based. The Boltzmann equation is repeatedly solved with trial values of the cross-sections till a satisfactory fit of the integral quantities (mobility and diffusion coefficient, Townsend ionization coefficient) is obtained with the experimental curves over the whole range of E/N values. The method usually yields fairly reliably the correct form of the elastic and of some inelastic cross-sections.

Electron distribution function in molecular gases. In the following a few examples of the calculated EDF will be given (see also Refs. 26,27). We shall mainly be concerned with molecular gas discharges as these are most common in plasma chemistry applications. It is interesting to compare the EDF in a molecular oxygen discharge with that calculated for molecular nitrogen for the same value of longitudinal field E/N in Fig. 1 (Refs. 28, 29,30).

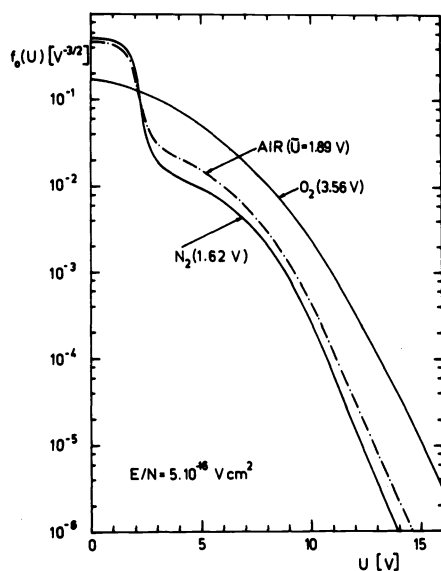


Fig.1. Electron distribution functions in N_2 , O_2 and the air.

Fig.2,3 demonstrate how far the elementary processes included in the Boltzmann equation participate in the formation of the EDF at various values of E/N (Refs. 28,30). The measure of that participation is expressed as the energy loss incurred by the process considered. It is seen that with the rising E/N the proportion of vibrational losses, always much higher than the elastic losses, markedly diminish, whereas the significance of the energy pumping in the molecular electronic levels increases. It is also worth noticing that the electronic levels of oxygen start to absorb energy at a value of E/N which is one order of magnitude below the corresponding value in case of nitrogen. Whereas in oxygen the sequence of the elementary processes (arranged with respect to the rising threshold energy) is almost equally spread over the low energy part of the energy axis, in nitrogen there is a distinct gap between the highest significant vibrational level of the ground state and the onset of the first electronic vibrational state. Consequently, on the distribution function a kink arises, by which the low and high energy parts are joined.

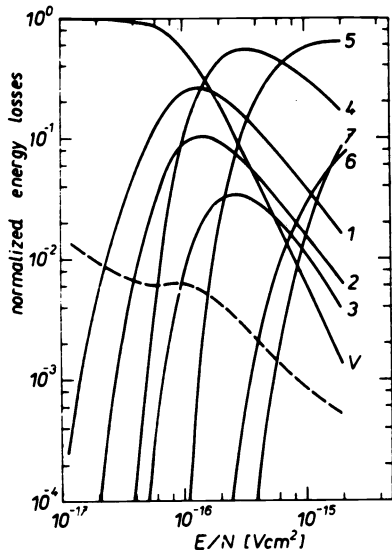


Fig.2. Normalized electron energy losses due to elastic (dashed) and inelastic (solid) collisions with O_2 molecules. 1 - 7 - excitations of the states with the threshold energies 0.98, 1.63, 4.2, 4.5, 8.0, 9.7 and 12.2 eV (ionization), V - excitations of the vibrational levels of the ground state.

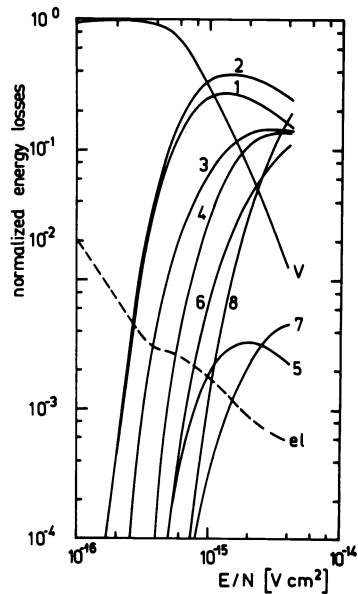


Fig.3. Normalized electron energy losses due to elastic (dashed) and inelastic (solid) collisions with N_2 molecules. 1 - 8 - excitation of the states with the threshold energies 6.2, 7.3, 8.5, 11.0, 11.9, 12.6, 12.8, 15.6 (ionization), V - excitations of the vibrational levels of the ground state.

Superelastic collisions and other elementary processes. The gap, mentioned in the previous section, represents, simultaneously, the energy interval into which the electrons would be scattered by the superelastic collisions from higher vibrational levels of the electron ground state. It is therefore instrumental in assessing the part played by the second kind collisions to incorporate these effects just in case of nitrogen (Refs. 31,32). The calculations were not performed self-consistently in the sense that the realistic EDF determining the vibrational level population is, in turn, itself determined by the vibrational level population. Instead, a certain population of the vibrational levels is assumed to exist in advance corresponding to a given vibrational temperature, and for that particular vibrational level population the EDF is then calculated. The computations show that there is an enrichment in the energetic electrons due to the additional heating by the superelastic impacts. In fact, a similar effect is achieved by including a small amount of electron-electron Coulomb collisions. These collisions tend to restore the Maxwell distribution and therefore they replenish the electrons in the high energy interval, which have been removed by the inelastic collisions. In a hydrogen discharge the number of dissociated molecules reaches usually a very appreciable amount and the finite dissociation degree can no longer be ignored. A distribution in partially dissociated hydrogen, Fig. 4 (Ref. 33), points out that with the falling number of the molecules the vibrational energy losses are reduced and the distribution is again shifted towards higher energies, especially for low values of the longitudinal field E/N . A similar picture is obtained if the EDF is calculated in a mixture of a molecular with a noble gas. Complicated mixtures of molecular gases turn up in laser work and as gaseous dielectrics. In case of gas lasers the calculation of the electron distribution function is usually only a part of the complicated plasma chemistry model of inversion pumping (Refs. 34,35,36). The gaseous dielectrics are molecular gases with a high electron attachment ability to quench any developing electron avalanche and at the same time with a sufficiently complicated molecular

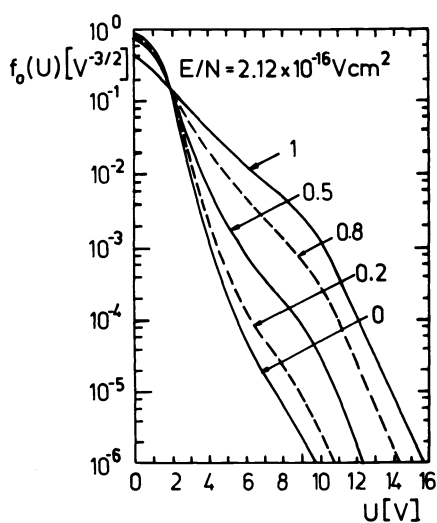


Fig. 4. Electron distribution function in H_2 . The parameter is the dissociation degree.

structure capable of absorbing a high portion of the electron kinetic energy and thus keeping the ionization coefficient low (Refs. 37-41). The attachment mechanism has, as a rule, a negligible influence on the form of EDF and normally it is not included in the Boltzmann equation.

Electron beam produced plasma. A special kind of discharge suitable for plasma chemical applications is the electron beam discharge (Ref. 42), which can also be used for laser pumping (Ref. 43). A high power electron beam penetrates into a discharge chamber and drives there a Langmuir turbulence. The chaotic electric field heats the electrons to a higher temperature than the steady state field, while leaving the heavy gas components comparatively cold. The non-equilibrium is thus enhanced. With the level of the turbulent energy per electron known and for a given ionization degree, which is generally very high, it is possible to evaluate in this case the EDF. It shows that in some cases the number of the high energy electrons exceeds that of the steady state discharge, approaching in such a way closer the Maxwell distribution (Refs. 44,45).

PLASMA CHEMISTRY MODEL OF DISCHARGE

The heavy particles in the discharge have their proper distribution in the translational as well as internal degrees of freedom. Whilst the translational distribution is always more or less Maxwellian, independent of the electron distribution, the internal degrees of freedom populations are closely connected with the production and destruction processes. These are predominantly due to the collisions with the electrons and the production rates are thus given as integrals over the electron distribution. The separate quantum levels of the molecules or atoms must, within the frame of the model, be regarded as separate particle species and for each of them a separate statistical balance equation (rate equation) formulated. Their solution then yields the populations of the corresponding quantum states.

Choice of particles and elementary processes. When formulating an appropriate model of the discharge plasma the first task is to recognize which kinds of particles may play an essential role in the discharge household. The usual selection consists in the choice of the neutral molecules and of the dissociated atoms in the ground state, of the lowest metastable molecular state and several kinds of ions. Generally speaking, this choice is usually quite satisfactory, unless we are interested in some special kind of particles, as yet not incorporated in the model. Their populations could be then obtained only from an extended version including the pertinent particle species to supplement the original simple choice. Each of the balance equations entering our model may contain several kinds of chemical reactions, by which the particles are either produced or destroyed. Their number determines the complexity of the problem and it is a matter of experience to be able to assess in advance, which of the reactions is vital for the discharge regime and which is relatively unimportant.

Exclusion of spatial inhomogeneity. The balance equations, which are derived as continuity equations for the examined particle species, include also the spatial divergence terms, describing the particle flow between the volume elements. Thanks to these divergence terms the starting problem is essentially three-dimensional and its solution would require to solve partial differential equations. To avoid this difficulty a spatial averaging is carried out (in case of cylindrical symmetry over the tube radius), by which effective first-order reactions are introduced replacing the spatial divergence terms, with the reaction rate given by particle wall life time, τ_i^{eff} (Ref. 46). To effect the averaging the spatial dependence of the particle densities should be known in advance. This is usually not the case and the dependence must be guessed. In the cylindrical geometry of a normal discharge tube zero order Bessel function is the common choice. In this case $1/\tau_B^{\text{eff}} = \lambda_1^2 D_1/R^2$ (λ_1 is the first root of the Bessel function $J_0(r)$, D_1 diffusion coefficient). The averaging introduces also certain correction factors of order one in the second order reaction terms, which are usually not very sensitive to the choice of the radial dependence. This is, however, not the case if the physical conditions on the wall cause large departures from the Bessel profile. This may happen, for instance, if the wall is partially reflective for the considered particle species, as it is for dissociated atoms or molecular metastables, or if there is a strong electrostatic repulsion of the negative ions present in the plasma, which may even lead to a column constriction (Ref. 47). Both these cases require then a special treatment. Besides the normal collisional processes the terms describing the particle interaction with resonant light quanta (spontaneous emission and diffusion of resonant radiation (Refs. 48,49)) may occur. If these terms become important (as in narrow tubes) the similarity representation of the discharge parameters (Ref. 50) breaks down.

Split-up solution: EDF and balance equations. As mentioned above, the Boltzmann equation for electrons need not necessarily include all the processes which are contained in the set of the balance equations. This is rather fortunate, since then it is possible to separate the solution of the Boltzmann equation from the solution of the balance equations. In fact, a one component discharge is determined by two parameters (usually current and pressure or I/R and $N.R$ in the similarity representation (Ref. 50)). It is thus obvious that the solution can be accomplished in two steps as long as the Boltzmann equation itself does not depend on more than two unknown parameters. One of them is E/N and the second may be either the ionization or dissociation degree. All the other unknown quantities enter the set of balance equations only and may be gained by its solution. A more general case, with the Boltzmann equation involving many unknown densities, the separation is no longer allowed and both the Boltzmann equation for electrons and the set of the balance equations must be solved simultaneously. In the following we shall illustrate the solution method on the example of a discharge in oxygen.

Elementary processes in oxygen plasma. There are several constituents that form the oxygen discharge plasma: O , O_2 , O_3 (which can exist in the ground

as well as excited state), O^+ , O_2^+ , O_3^+ , O_4^+ , O^- , O_2^- , O_3^- , O_4^- and the electrons. About 60 mutual reactions are possible among these particles. It is assumed that a realistic model can be constructed by means of six chosen species: O , O_2 , $O_2^*(^1\Delta_g)$, O_2^+ , O^- and the electrons. A more extensive choice has been made in (Ref. 51). The considered mutual reactions are quoted in Table 1.

TABLE 1. Elementary reactions in oxygen

| Denotation | Reaction | Threshold energy U_0 [eV] | Rate coefficient k_i [cm ³ /s] |
|------------|---|-----------------------------|---|
| P1 | $e + O_2^*(^1\Delta_g) \rightarrow O_2 + e$ | 0 | $f(E/N)$ |
| P2 | $e + O_2^*(^1\Delta_g) \rightarrow O_2^*(^1\Sigma_g^+) + e$ | 0.74 | $f(E/N)$ |
| P3 | $e + O_2 \rightarrow O_2^*(^1\Delta_g) + e$ | 0.98 | $f(E/N)$ |
| P4 | $e + O^- \rightarrow O + 2e$ | 1.46 | $f(E/N)$ |
| P5 | $e + O_2^*(^1\Delta_g) \rightarrow O + O^-$ | 3.5 | $f(E/N)$ |
| P6 | $e + O_2 \rightarrow O + O^-$ | 4.2 | $f(E/N)$ |
| P7 | $e + O_2 \rightarrow O + O$ | 4.5 | $f(E/N)$ |
| P8 | $e + O_2^*(^1\Delta_g) \rightarrow O_2^+ + 2e$ | 11.2 | $f(E/N)$ |
| P9 | $e + O_2 \rightarrow O_2^+ + 2e$ | 12.2 | $f(E/N)$ |
| P10 | $O^- + O \rightarrow O_2 + e$ | | 2×10^{-10} |
| P11 | $O^- + O_2 \rightarrow O + O_2 + e$ | | $f(E/N)$ |
| P12 | $O^- + O_2^*(^1\Delta_g) \rightarrow O_3 + e$ | | 3×10^{-10} |
| P13 | $O^- + O_2 \rightarrow O_2^- + O$ | | $f(E/N)$ |
| P14 | $O^- + O_2^+ \rightarrow O_2 + O$ | | 1×10^{-7} |

Of the six balance equations one can be replaced by the quazineutrality condition and another one by the total particle number conservation (Refs. 52, 53). We thus end up with four balance equations, which are averaged over the radius, as described above, τ_i^{eff} being the effective life times of O , $O_2^*(^1\Delta_g)$ and of the electrons respectively. The negative ions do not reach the wall due to the electrostatic repulsion and the corresponding radial terms thus vanish:

$$N_k \sum_l Q_{kl} Z_{kl}^P N_l = N_i / \tau_i^{\text{eff}} + N_i \sum_j Q_{ij} Z_{ij}^L N_j \quad (5)$$

$$N = \sum_i N_i \quad (6)$$

(N_i - concentrations of the species, $Q_{ij} = \lambda_1^2/4 = 1.45$ - correction factor for Bessel radial distribution). The above set of equations was solved numerically. The results are shown in Figs. 5-7. Apart from the usual dependence on the pressure and current, influence is shown of the varying wall reflection of O and $O_2^*(^1\Delta_g)$, Figs. 6,7.

Other molecular gases. A similar analysis for a d.c. discharge in H_2 was carried out in (Refs. 54,55). Analogously, (Refs. 30,56) deal with the case of N_2 . For discharges in mixtures the model become extremely involved. A formidable example is the s.c. plasma chemistry model of CO_2 laser (Ref. 34) involving 40 balance equations with 300 reactions. But even in mixtures the models need not be always that much complex and a practical answer can be

sought within the frame of a much simpler scheme. The case of the atomic iodine laser pumped by excited O_2 molecules (Ref. 57) may serve here as a good example.

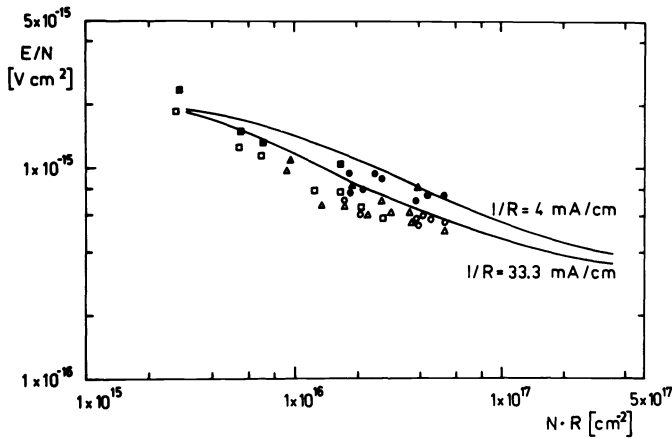


Fig. 5. Volt-Ampere characteristics in O_2 . Full marks - experimental points at 4 mA/cm, empty marks 33.3 mA/cm (Ref. 52). Full lines - computations (Ref. 53).

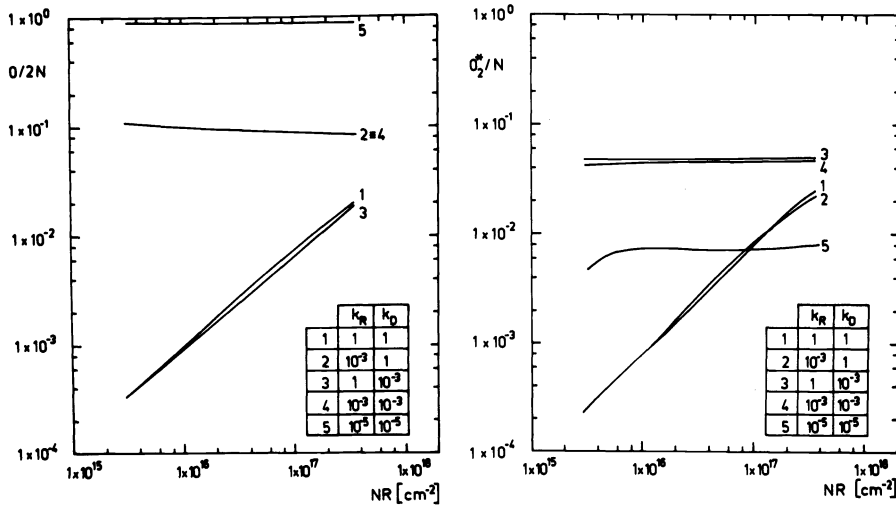


Fig. 6. Dissociation degree in Fig. 7. The relative metastable O_2 at $I/R = 33.3$ mA/cm for $O_2^*(^1\Delta_g)$ concentration in O_2 at different combinations of the $I/R = 33.3$ mA/cm for different wall recombination and deactivation coefficients k_R and k_D .

Radial dependence. In studying the plasma interaction with a solid surface it is useful to know how many active particles arrive at the surface from the plasma volume. The particle currents at the wall depend on the detailed configuration of the density profile inside the plasma, which can, in turn, be obtained by a direct solution of the radial problem (Refs. 58, 59, 60). In practice, it means to abandon the averaging procedure and to solve the balance equations, with the radial terms retained, as differential equations with the corresponding boundary conditions. Again, we shall resort to the oxygen plasma to exemplify this more complex solution procedure. The existence of the negative ions in the oxygen plasma presents a serious complication. Although the radial electric field can be eliminated as in the Schottky theory for a plasma with a single kind of ions, the effective diffusion coefficients are now density dependent (Ref. 51). It is therefore expedient not to use the full set of equations as in (Ref. 53), but to simplify the model as much as possible. In the following it has been assumed that the concentration of the atoms remains constant across the tube radius. The metastables are omitted. Then we are left with two second order equations for the electrons and negative ions:

$$\frac{1}{r} \frac{d}{dr} (r J_e) = k_9 N_2 N_e + k_{10} N_1 N_- - k_6 N_2 N_e + k_4 N_e N_- + k_{11} N_2 N_- \quad (7)$$

$$\begin{aligned} \frac{1}{r} \frac{d}{dr} (r J_-) = & k_6 N_2 N_e - k_{10} N_1 N_- - k_4 N_e N_- - k_{14} N_- (N_- + N_e) - \\ & - k_{11} N_2 N_- - k_{13} N_2 N_- \end{aligned} \quad (8)$$

$$J_e = - \frac{d}{dr} (D_e^a N_e) - b_e N_e E_r \quad (9)$$

$$J_- = - \frac{d}{dr} (D_-^a N_-) - b_- N_- E_r \quad (10)$$

These equations must be supplemented by the adequate boundary conditions. On the axis it must be for symmetry reasons:

$$\frac{dN_e}{dr} = \frac{dN_-}{dr} = 0 \quad (11)$$

At the tube wall it is set

$$J_- = 0, \quad N_e = 0 \quad (12)$$

The vanishing negative ion flux near the wall means that there is no negative ion source at the wall and that the negative ions are born and destroyed exclusively in the discharge volume (Ref. 59). It also implies that the negative ion density is negligible at the wall due to the electrostatic repulsion. The results of numerical solution of Eqs. 7 - 12 are in Figs. 8a,b. The solution points out that the approximation of the radial profiles by a simple Bessel function turns out to be rather inaccurate and that none of the effective diffusion coefficients yield realistic particle fluxes, especially near the wall. A fairly similar procedure would also

render the effective life times for the oxygen atoms and molecular metastables. The boundary conditions on the wall would now have to describe a possible partial reflection of both the particle species from the wall surface. Already very simplified radially dependent balance equations for the free atoms and metastables (assuming the radial Bessel profile for the electrons) yield order-of-magnitude departures of the effective life times from the Bessel value (Ref. 62).

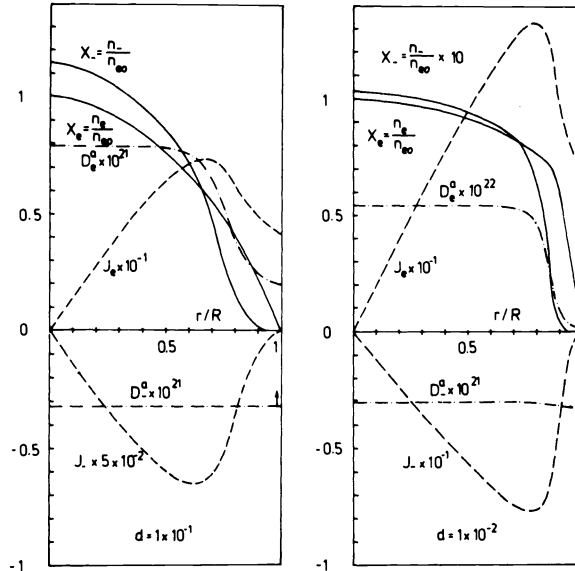


Fig. 8. Radial profiles of various plasma parameters in O_2 for two different values of dissociation degree $d = N_1 / (N_1 + 2N_2)$ (N_1, N_2 - concentrations of atoms and molecules, respectively). X_-, X_e - relative concentrations (with respect to the axial value of the electron concentration) of negative ions and electrons; J_-, J_e - radial flows (arbitrary units) of negative ions and electrons; D_-^a, D_e^a - the effective coefficients of the ambipolar diffusion. $E/N = 9 \times 10^{-16}$ V cm^2 , $NR = 1.26 \times 10^{16}$ cm^{-2} , ionization degree 1×10^{-7} (Ref.61).

CONCLUDING REMARKS

In the models discussed so far it has always been possible to separate the solution of the Boltzmann equation from that of the balance equations. The situation in molecular gases is, unfortunately, more complicated, so that this simple procedure does not always apply. At higher currents and at appreciable dissociation degrees, when it is necessary to take into account both the Coulomb interaction and the atomic component of the discharge plasma the electron distribution is dependent on three plasma parameters (longitudinal field, ionization degree, dissociation degree) and it would be thus necessary to solve the electron Boltzmann equation and the set of particle balance equations simultaneously. A still more complicated case arises if the influence of the vibrational levels in the electronic ground state on the electron distribution is considered and the population of the vibrational levels is regarded as unknown. This situation frequently occurs in mole-

cular gases where the vibrational levels may represent an energy reservoir comparable with the energy supply from the longitudinal field, and an approximation of the level population by a Boltzmann exponential may prove rather inaccurate. In this case, too, both the electron distribution and the vibrational level population must be found simultaneously. The first step in this direction has been made by Capitelli and coworkers, who computed the time evolution of the electron distribution and, at the same time, of the vibrational level populations after switching-on of the discharge (Ref. 63) with the aim of finding the stationary value of the dissociation degree. Their solution, is however, not yet complete, for the other molecular and atomic levels would have to be accounted for in the same way to obtain a full answer. A successful application of the above models depends on detailed knowledge of effective cross-sections of the considered elementary processes. They usually involve a considerable error, which can sometimes be removed by checking the results against the experimental data. With some of the cross-sections safely known, it is even possible to determine the unknown ones by fitting the computational results to the measured curves (Ref. 64). If a reasonable agreement in directly measurable quantities is achieved within the frame of a given model, it is a fair chance that the other quantitative results supplied by the model, namely the concentrations of the active particles, and their wall fluxes will be given correctly. That is why the plasma chemistry may find some interest in this kind of work.

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