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Properties of the positive column of a glow discharge in flowing hydrogen

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Abstract. — Results of a theoretical model for predicting the effects of gas flow on the properties of the positive column in a glow discharge are presented. A cylindrical discharge at low pressure (~ 30 torr) in a hydrogen flow is considered. The two-dimensional model couples electric and molecular properties of the discharge through E/N, the ratio of electric field to neutral gas density. It predicts the electric field and the discharge voltage as a function of pressure, flow velocity, diameter and length of the discharge and current. Molar flow rates of vibrationally excited H₂ molecules and H atoms produced by the discharge are calculated. Comparison with available experimental data is made.

1. Introduction. — The positive column of a molecular gas at moderate pressure and current discharge is characterized by high electron energies and low mean translational energies for the molecules and atoms. Because of this large ratio, the positive column is an useful source of highly non-equilibrium populations of excited molecules and atoms which has been used in a large class of molecular and chemical lasers. Numerous investigations of properties of a glow discharge in a static gas have been reported [1, 2, 3, 4]. However, there is little information on the properties of an electric discharge in a flowing gas [5, 6]. The objective of this work was to develop a model for predicting the electric, vibrational and chemical properties of a flowing hydrogen discharge at low and moderate pressures. The two-dimensional model presented in this paper extends the work of Ecker and Zoller [1] to include gas flow velocity and finite vibrational and chemical kinetics. The model is based on the fact that the electric properties of the discharge are fully correlated with the neutral gas density which is, in turn, fully correlated with the vibrational and chemical kinetics. The model predicts the field strength and the discharge voltage as a function of gas pressure, gas flow velocity, diameter and length of the discharge and current. We find that gas heating plays a major role in causing the negative voltage-current curve. The differences between the predicted and the experimental values of the electric field are usually less than 15%.

The model predicts the number densities of vibrationally excited molecules and H atoms. Species molar flow rates are presented. The theoretical predictions for the vibrational temperature are compared with the experimental values of Shirley and Hall [7]. Good agreement is obtained. Finally the predicted values of the atom flow rate are compared with our own experimental results obtained by NOCl titration. We find that the theoretical values are within a factor of 2.5 of the experimental results.

2. Discharge model. — 2.1 Equation. — We assume that the degree of ionization is low enough so that collisions between charged particles can be neglected. We also assume approximate charge neutrality \( n_e \approx n_i \) where \( n_e \) and \( n_i \) denote electron and positive ion density. For the positive ions, we assume that the ions remain in equilibrium with the gas so
that $T_1 = T$. We assume that the gas flow is uniform, i.e., the radial neutral particle velocity is zero. Therefore, the equation for the electron density may be written:

$$\frac{1}{r} \frac{\partial}{\partial r} \left[ r \frac{D_e}{T_e} \frac{\partial}{\partial r} (n_e v_{ex}) \right] + \frac{\partial}{\partial x} (n_e v_{ex}) =$$

$$= k_i N n_e - \alpha_r n_e^2. \quad (1)$$

Here, $D_a$ is the ambipolar diffusion coefficient, $T_e$ the electron temperature, $v_{ex}$ is the longitudinal electron velocity, $k_i$ the ionization coefficient, $N$ the total neutral density and $\alpha_r$ the electron-ion recombination coefficient.

The boundary condition requires that $n_e(r = R) = 0$ and from symmetry considerations $\partial n_e/\partial r = 0$ at $r = 0$.

The ambipolar diffusion coefficient is defined in the usual way by:

$$D_a = \mu_e D_e + \mu_i D_i \simeq \frac{\mu_e D_e}{\mu_i} \quad (2)$$

where $\mu_e$ and $\mu_i$ is the electron and ion mobility, $D_e$ and $D_i$ the electron and ion diffusion coefficient, respectively. The longitudinal electron velocity may be written $v_{ex} \approx u + \mu_e E$ where $u$ is the gas flow velocity, $E$ the longitudinal electric field opposite to the flow direction and $\mu_e E$ the electron drift velocity, respectively. The flow velocity is always much smaller than the electron drift velocity ($10^5$ cm/s compared to $10^7$ cm/s) so that $v_{ex} \approx v_0 = \mu_e E$ is a function only of $E/N$. All other quantities $D_a, N, T_e$ and $k_i$ are also functions only of the local $E/N$ value. It can be shown that equation (1) is strictly valid only when $\mu_e N$ is a constant and if it is assumed that $kT_e = eD_j/\mu_e$. For $E/N$ values of interest to us, the diffusion condition is approximately satisfied for product $n_0 N < 5 \times 10^{29}$ particles/cm$^6$, i.e., for pressure such that $I, P < 4000$ mA.torr.

As we are interested in the dissociation of $H_2$, we use the mole mass ratio $F_j = N_j/\rho N_A$ in place of the number density $N_j$ of particles to simplify the species conservation equations. We consider only six species, namely $H_2(v = 0$ to 4) molecules and $H$ atoms.

The governing equations for the gas flow may be written:

**Momentum**

$$p u \frac{\partial u}{\partial x} = - \frac{\partial P}{\partial x} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \eta \frac{\partial u}{\partial r} \right). \quad (4)$$

**Energy**

$$\rho u c_p \frac{\partial T}{\partial x} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \chi \frac{\partial T}{\partial r} \right) + \frac{\partial P}{\partial x} - \rho u \sum_j h_j \frac{\partial F_j}{\partial x} + \mu_e e_n e^2 E^2. \quad (5)$$

**Continuity**

$$\dot{m} = \rho u A = \text{constant}. \quad (6)$$

**State**

$$P = \rho R T \sum_j F_j. \quad (7)$$

Here $P$ is the total pressure (an uniform radial pressure is assumed so that $\partial P/\partial r = 0$), $\rho$ is the gas density, $\eta$ is the viscosity, $c_p$ is the specific heat, $\chi$ is the gas thermal conductivity, $h_j$ is the specific enthalpy of species $j$ and $N_A$ is Avogadro number. Finally, the specific heat is given by $c_p = \sum_j c_p j F_j$ where $c_p j$ is the molar heat of species $j$ and the neutral gas density is given by $N = \rho N_A \sum_j F_j$. Note also that the viscous dissipation term which is much smaller than the Joule heating term has been omitted in equation (5).
Species

\[ \text{H}_2(v = 0 \text{ to } 4) \text{ molecules} \]

\[
u \frac{\partial F_0}{\partial x} = -k_0 F_0 n_e + \frac{k_b}{\nu}(\rho \cdot \nu) \frac{2}{5} F_0^2 (F_0 + F_1 + F_2 + F_3 + F_4) 
+ \frac{k_1}{\nu} \rho \cdot \nu F_0^3 
+ (k_{10} \nu F_1 + k_{20} \nu F_2) \rho \cdot \nu F_5 
+ V-V \text{ terms} \]

(8)

\[
u \frac{\partial F_1}{\partial x} = (k_1 F_0 - k_0 F_1) n_e - (k_{10} \nu F_1 - k_{21} \nu F_2 - k_{31} \nu F_3) \rho \cdot \nu F_5 
+ V-V \text{ terms} \]

(9)

\[
u \frac{\partial F_2}{\partial x} = (k_2 F_0 - k_0 F_2) n_e - [(k_{21} \nu F_1 + k_{22} \nu F_2 - k_{32} \nu F_3) \rho \cdot \nu F_5 
+ V-V \text{ terms} \]

(10)

\[
u \frac{\partial F_3}{\partial x} = (k_3 F_0 - k_0 F_3) n_e - [(k_{32} \nu F_1 + k_{33} \nu F_2 - k_{43} \nu F_4) \rho \cdot \nu F_5 
+ V-V \text{ terms} \]

(11)

\[
u \frac{\partial F_4}{\partial x} = -k_0 F_4 n_e - k_{43} \nu F_4 \rho \cdot \nu F_5 
+ V-V \text{ terms} \]

(12)

H atoms

\[
u \frac{\partial F_5}{\partial x} = 2(F_0 + F_1 + F_2 + F_3 + F_4) k_0 n_e - 2[k_0^b (F_0 + F_1 + F_2 + F_3 + F_4) + k_1^b F_5] (\rho \cdot \nu F_5)^3 \]

(13)

Here \( k_1 \), \( k_2 \) and \( k_3 \) are the electronic vibrational excitation rates, \( k_0 \) is the electronic dissociation rate, \( k_{m,n}^V (m = j - 1, j - 2) \) is the vibrational deactivation rate by collisions with H atoms [9, 10], \( k_b^V \) and \( k_i^V \) is the H-atom recombination rate with H\(_2\) molecule and H atom as third body, respectively. Therefore the depopulation rate of the \( v = 0 \) level is the sum \( k_0 = k_1 + k_2 + k_3 + k_0 \).

The self relaxation rates of H\(_2\)(v) molecules are very low compared to those by H atoms and consequently they were neglected.

The V-V terms are expressed in the usual way for species \( j = 0 \text{ to } 4 \):

\[
\left( \nu \frac{\partial F_j}{\partial x} \right)_{V-V} = \rho \cdot \nu \sum_m (K_{j,j-1}^{m+1} F_m 
+ K_{j,j-1}^{m+1} F_{m+1} \nu F_j 
+ \rho \cdot \nu \sum_m K_{j-1,j}^{m+1} F_{m+1} F_{j-1} 
+ \rho \cdot \nu \sum_m K_{j+1,j}^{m+1} F_{j+1} F_{j+1} \right). \]

(14)

The vibration-vibration transfer probabilities were calculated using the Sharma-Brau theory [11] for the long range interaction whereas the Jackson-Mott transition probability (as adapted for V-V transfer by Herzfeld and Litovitz [12]) was used for the short-range interaction. For the latter interaction, the range parameter was taken to be \( l = 0.23 \text{ Å} \). Our V-V rate constants, in good agreement with those calculated by Billing and Fisher [13], are shown in figure 1.

2.2 INPUT DATA. — The input transport coefficients and the electron excitation rates are those reported by Brunet and Vincent [14]. The ion mobility is taken from the measurements of Chanin [15]. Thus,

\[
\mu_i N = 3.3 \times 10^{20} \text{ V}^{-1} \text{ cm}^{-1} \text{ s}^{-1}. \]

The thermal conductivity \( \chi \) and the viscosity \( \eta \) are taken from reference [16] and are assumed to vary
with \( T \) according to the Sutherland relation. Thus,

\[
\eta = 0.85 \times 10^{-4} \frac{273 + 83}{T + 83} \left( \frac{T}{273} \right)^{3/2} \text{ g cm}^{-1} \text{s}^{-1}. \]

Although we consider relatively high average flow velocities (100 to 300 m/s), the Reynolds number of the flow is less than 2000 and therefore the flow is laminar at the entrance of the discharge. Then, the velocity profile is given by

\[
u(r, 0) = u_0 \left[ 1 - \left( \frac{r}{R} \right)^2 \right]
\]

where \( R \) is the discharge radius.

For most calculations, we assume that the discharge takes place in a pyrex tube inside which a Teflon jacket is inserted (see Sec. 3). The Teflon thermal conductivity is low, namely

\[
\chi = 2.4 \times 10^4 \text{ erg cm}^{-1} \text{ deg}^{-1} \text{s}^{-1},
\]

so that the gas temperature at the wall is variable. The external wall of the Teflon jacket is taken at a fixed temperature, namely \( T_w = 293 \text{ K} \).

2.3 Method of Solution. — For the numerical integration equations (1), (4) and (5) are cast into an implicit constant grid-finite-difference formulation. A grid of 16 radial points (13 inside the gas and 3 inside the wall) and 1000 axial points is used. Calculational procedure is as follows: starting with the initial neutral gas density at the upstream end of the discharge, the local \( E/N \) value is calculated by iterating on \( E \) and \( n_e \) until the current continuity is preserved. Once \( E/N \) and \( n_e \) are found equations (4), (5) and (8) to (13) are solved to give a new value for the neutral gas density. This new value is then used to calculate the electric field and the electron density at the next axial step. The procedure is repeated until the downstream end of the discharge is reached. The computational time is typically 30 min. on a PDP 11/70 computer.

3. Experiment. — Measurements were carried out on a pyrex tube inside which a 0.96 cm i.d., 1 mm wall thickness Teflon jacket was inserted. This jacket was used to limit H atom recombination on the walls. The pyrex tube was, in turn, surrounded by a water-cooling jacket. The mass flow rate was fixed by a sonic throat located upstream the discharge and the pressure was regulated by a gate valve placed on the downstream.

Experimental discharge voltage data in the positive column were obtained by measuring the voltage between a movable anode and an auxiliary electrode located 2 cm upstream the water-cooled cathode. The probe current was about 10 \( \mu \)A. Usually, the gas flow was from anode to cathode but reversing the flow made little difference to the observations.

Hydrogen atom concentration was determined by adding NOCl and following the red light intensity from HNO* [17].

4. Results and discussion. — Calculations were carried out over the range \( 5 \leq P \leq 30 \text{ torr} \), \( 20 \leq I \leq 100 \text{ mA} \) and \( 5 \leq \dot{m} \leq 20 \text{ millimoles/s} \). Figure 2 shows the variation with discharge length of the electric field and the discharge voltage in the positive column. For the same conditions, figures 3, 4 and 5 show the variation of temperature, neutral gas density and electron density, respectively. As shown in figure 2, the electric field decreases rapidly along the discharge axis. This characteristic feature is correlated with the decrease of the neutral gas density and can be explained as follows: whether is the value of \( N \), the production rate of electrons must be sufficient to balance the loss of electrons due to ambipolar diffusion. Since this latter is inversely proportional to \( NR [18] \), product of the neutral gas density by the discharge radius, the balance between ionization and
Fig. 4. — Calculated neutral gas density profiles as a function of length.

Fig. 5. — Calculated electron density profiles as a function of length.

diffusion requires the higher $E/N$ values the lower the $NR$ products (see Fig. 6). Now since the neutral gas density decreases along the discharge axis, the local $E/N$ value increases but much less rapidly than $N$ decreases so that the electric field finally decreases. Therefore, at fixed entrance pressure, the discharge voltage should decrease as the current increases or the mass flow rate decreases. This actually is verified both by the experiment and the theory. Comparison of figure 7 with figure 2 permits to see the effect of the gas flow velocity (i.e. mass flow rate) on the discharge voltage. Figure 7 shows the voltage-current curve for typical conditions.

It should be noted that, at first sight, this electric field variation is not compatible with the assumption of quasi-neutrality of the plasma. However, it can be easily verified that a very small charge separation, namely $n_e/n_i = 1 \times 10^{-6}$ is sufficient to produce the variation of the electric field. Therefore, there is no intrinsic contradiction between the quasi-neutrality assumption and the Poisson law.

As is shown in figures 2, 7 and 8 the model predicts with good accuracy the variations of the discharge voltage. For most cases of interest, the theoretical absolute values are about 15% higher than the measured ones. The largest differences (about 20%) between theory and experiment occur at high current or at high mass flow rate.

The most likely source of these discrepancies is the use of an underestimated ionization coefficient in equation (1). At high current, the ratio of excited-state to ground-state populations is large and therefore the ionization coefficient is significantly enhanced by superelastic collisions and two-step ionization processes. The superelastic collisions with vibrationally excited molecules lead to a rise of the tail of the electron distribution function and therefore to an increase of the ionization rate at a fixed $E/N$ value. Preliminary results obtained from our modified Boltzmann code show that both the dissociation and the ionization rates are increased by about 50% when the fractional...
population $H_2(v = 1)/H_2(v = 0)$ reaches 0.3. Detailed results will be published in the future.

The effects of two-step ionization processes are difficult to estimate since the ionization cross-sections from excited states are unknown. Therefore these processes have not been investigated yet.

Another source of discrepancy is our failure to accurately predict the pressure distribution into the discharge at high flow velocities. The model slightly under-estimates the pressure drop and consequently over-estimates the electric field.

As was mentioned in the beginning, the main purpose of this work was to determine the mass flow rates of vibrationally excited $H_2$ molecules and $H$ atoms. These rates are important for designing energy transfer and chemical lasers. The excited molecule and $H$ atom densities were calculated at each point of the grid. Then the mass flow rates were obtained by multiplying the local density by the local flow velocity and integrating across the flow field.

Figure 9 shows the molar flow rates of excited $H_2(v = 1$ and 2$)$ molecules and $H$ atoms as a function of distance for typical conditions. Table I resumes the results obtained. For the purpose of comparison of theory with experiment, the vibrational temperature was calculated for the conditions of Shirley and Hall[7]. For a power loading of 7.5 kJ/mole, the vibrational temperature at the exit of the discharge tube was found to be 2 190 K on the axis. Due to the $V-T$ deactivation by $H$ atoms ($H/H_2 \approx 0.1\%$), the vibrational temperature decreases to 1 830 K at 11.5 cm downstream of the discharge exit in excellent agreement with Shirley results. It is interesting to note that 40\% of the discharge power is put into the vibration. The remaining power is shared between gas heating (43\%), power transferred to the walls (13\%) and heat of formation of $H$ atoms (3.5\%). Here we would like to point out that this decrease of the excitation level is not due, as suggested by Shirley, by the strong dependence of $H_2 V-T$ self deactivation rates on gas temperature but to the deactivation by the atoms produced into the discharge. Measurements of $H$ atom flow rates were carried out by gas phase titration using NOCI [17]. As indicated in section 3, a Teflon jacket was used to reduce $H$ atoms recombination on the wall. Typically, for $P = 10$ torr and $\dot{m} = 16$ mg/s ($\overline{u} = 200$ m/s) the $H$ atom flow rate was

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<th>$P$ (torr)</th>
<th>$\dot{m}$ $10^{-3}$ mole/s</th>
<th>$I$ (mA)</th>
<th>$V_p$ (V)</th>
<th>$H$ $10^{-3}$ mole/s</th>
<th>$H_2(1)$ $10^{-3}$ mole/s</th>
<th>$H/H_2$ (%)</th>
<th>$T_m$ (K)</th>
<th>$WE$ (W)</th>
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found to be 0.25 mg/s and therefore $H/H_2 \approx 3\%$. For the same conditions, the value predicted by the model is 1.1%. For all other conditions, the model also under-estimates the degree of dissociation and the predicted values were found to be about 2.5 times lower than the experimental ones.

Thus our model cannot accurately predict the degree of dissociation. However, it is capable to give a reasonable estimate of the dissociation without involving mechanisms which are not well-known. For instance, we verified (using an unidimensional model including 15 vibrational levels) that the laser-type mechanism reported by Capitelli et al. [19] is most unlikely because H atoms deactivate very rapidly the highest vibrational levels. It should also be emphasized that the calorimetric results of Capezzuto et al. [20] are uncorrect because they neglected the vibrational energy of the gas flow in their analysis.

On the other hand, it is expected that superelastic collisions as well as dissociative collisions with vibrationally excited molecules would greatly enhance the electronic dissociation rate. Unfortunately these processes cannot be correctly investigated since relevant electron cross-section data are not available.

5. Conclusion. — On the basis of this comparison of theory with experiment we conclude that gas heating has the major influence on causing the electric, vibrational and chemical properties of the flowing hydrogen discharge. Two-step ionization processes and superelastic collisions play only a minor role.

The model presented here for analysing the flowing discharge is quite general and can be applied to various gases and various discharge configurations and conditions. However, its application to discharges where collisions with excited species are important, namely the pure rare gases and molecular gases such as nitrogen, requires the knowledge of realistic excitation and ionization rates. In principle these latter can be obtained from a solution of the Boltzmann equation which includes the inelastic cross-sections for the excited species weighted by the excited species fractional populations. Unfortunately there is in general little or no data available on inelastic cross-sections from excited states and therefore the effect of electron collision with excited species can be only semi quantitatively investigated at best.

References