ENERGY BALANCE IN $H_2 - N_2$ GLOW DISCHARGES

Rajesh Nagpal and Alan Garscadden

Plasma Research Group, Wright Laboratory
Wright Patterson Air Force Base, Ohio - 45433, USA

ABSTRACT

Results from energy balance calculations in glow discharges in $\%H_2-\%N_2$ mixtures are reported. The fractional power deposited in the electron impact dissociation of H_2 calculated from the Boltzmann transport analysis and a discharge model is compared with that required by the experimental data for absolute H atom densities. It is shown that the vibrational reservoir of $N_2(X^1\Sigma_g^+,\text{v})$ must directly or indirectly contribute to the dissociation of H_2 in H_2-N_2 mixtures.

INTRODUCTION

Plasma chemistry in glow discharges through molecular gas mixtures is determined by a complicated array of heterogenous interactions between atoms, radicals and internally excited molecular species. While the literature on experimental demonstrations of plasma processing through gas mixtures is flourishing, there have been very few attempts towards detailed understanding of the plasma physico-chemical processes in these systems. To enable the optimization of the throughput of plasma processing gas mixtures, it is therefore imperative to identify the key processes which determine their microscopic and macroscopic characteristics.

We have recently developed a global approach for modelling the plasma physics and chemistry in molecular gas mixtures [1, 2]. The results predicted and demonstrated the attractiveness of glow discharges in $\%H_2 - \%N_2$ mixtures as efficient sources of H atoms [1]. Following the above approach, the fractional dissociation of H_2 in $\%H_2 - \%N_2$ mixtures in a inductive mode helical resonator discharge has recently been measured in this laboratory [3]. These measurements indicate that the fractional dissociation efficiency of H_2 approaches 80% at $\approx 10\%H_2 - N_2$ mixture composition. Similar results on the high dissociation efficiency of H_2 in H_2-N_2 mixtures have also been found in *dc* discharge conditions [4]. To account for the very high fractional dissociation of H_2 measured in the above experiments, results from energy balance calculations in $\%H_2 - \%N_2$ mixtures are reported.

RESULTS AND DISCUSSION

Figure 1 presents the calculated fractional dissociation profile of H_2 in $\%H_2-\%N_2$

mixtures obtained for *dc* discharge excitation conditions of [4]. The results of figure 1 correspond to the coupled solutions of the electron collisional Boltzmann transport equation (BTE), the systems of vibrational master equations of N_2,$H_2(X^1\Sigma_g^+$,v), and a *constant current* discharge circuit equation [1]. Figure 1 clearly demonstrates that the inclusion of the following dissociation channels leads to a significant increase in the fractional dissociation profile of H_2, especially when H_2 is the minor component in the mixture.

$$N_2(A^3\Sigma_u^+) + H_2 \rightarrow N_2(X^1\Sigma_g^+) + H(1s) + H(1s) \tag{1}$$

$$N_2(a'^1\Sigma_u^-) + H_2 \rightarrow N_2(X^1\Sigma_g^+) + H(1s) + H(1s) \tag{2}$$

The measurements of H atom densities in $\%H_2 - \%N_2$ dc flowing discharges show that there is also an almost five-fold increase in the H atom number densities (over that in pure H_2) when $\approx$ 10% N_2 is added to the H_2 discharge [4]. More importantly, the measured H atom densities are relatively constant over the gas mixture composition range of $\approx$ 90-1%$H_2 - N_2$. From the estimates given in [4], the fractional dissociation in a pure H_2 discharge is $\approx$ 0.04% and that in a 1%H_2-N_2 mixture is $\approx$ 20% (an increase by a factor of $\approx$ 500 at the assumed gas temperature $T_g = 400K$).

While the results presented in figure 1 suggest significant contributions from the N_2 metastable interactions with H_2 towards dissociation of H_2, the predicted relative increases in the H_2 fractional dissociation are not as large as that measured in the experiments [4]. It is therefore instructive to compare the energy budget of the discharge with emphasis on the following:

1. The power dissipated into the discharge (P) calculated by the following expression.

$$P = j \cdot E \tag{3}$$

   where $j = ew_dn_e$ is the current density, e is the electronic charge, n_e is the electron density, and w_d is the electron drift velocity.

2. Fractional powers transferred into the different elastic and inelastic channels in pure H_2,N_2, and in their mixtures. These are readily obtained from the solution of the BTE [5] for homogeneous conditions.

Figure 2 presents the calculated steady state electric fields (E) and electron densities (n_e) for the excitation conditions of [4]. From the absolute H atom number densities reported in [4], the power dissipated in the dissociation of H_2 can also be calculated. Using the experimental data of discharge tube radius ($r_d = 0.8\ cm$), gas flow rate ($Q = 200\ sccm$), and the dissociation energy of H_2 ($D_e = 4.8\ eV$), the power dissipated in the dissociation of H_2 (P_H) is given by

$$P_H = [H]Q_vD_e \tag{4}$$

where Q_v is the volume flow rate of H_2. If dissociation occurs primarily by direct electron impact, then the fractional power $\frac{P_H}{P}$ obtained from equations (3,4) should correspond closely to that calculated from the solution of the BTE.

The values of P, P_H for pure H_2, and 1,10%H_2-N_2 calculated using the data of figure 2 are presented in table 1. Figure 3 and and table 2 present the fractional power deposited (calculated from the solution of the BTE) in the dominant inelastic modes in pure N_2,H_2, and in their mixtures respectively.

%H_2	E V/cm	E/N Td	w_d cm/s	n_e cm^{-3}	[H] cm^{-3}	P W/cm^3	P_H W/cm^3	$\frac{P_H*100}{P}$
100	23.8	49	5.4(6)	8.3(10)	2.0(13)	1.7	0.58	34.1
10	43.4	90	9.8(6)	5.2(10)	1.0(14)	3.6	2.9	80.5
1	32.0	66	7.7(6)	6.4(10)	1.0(14)	2.5	2.9	116.0

Read 5.4(6) as 5.6 × 10^6. 1 Td = 10^{-17} Vcm^2.

Table 1: Total power (P), and fractional power dissipated in the dissociation of H_2 (P_H). For normalization, the gas temperature is assumed to be 400K. The power densities are normalized as per unit volume for the discharge configuration of [4].

	1%H_2-N_2						10%H_2-N_2					
E/N	Vib.		Elec.		Diss.		Vib.		Elec.		Diss.	
(Td)	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2
10	94.7	0.7	0.0	0.0	0.0	0.0	82.5	6.8	0.0	0.0	0.0	0.0
20	97.8	0.2	0.0	0.0	0.0	0.0	93.6	2.5	0.0	0.0	0.0	0.0
30	98.6	0.1	0.0	0.0	0.0	0.0	96.4	1.3	0.1	0.0	0.0	0.0
40	98.5	0.1	0.5	0.0	0.0	0.0	96.9	0.9	0.6	0.0	0.0	0.0
50	96.8	0.1	2.2	0.0	0.1	0.0	95.2	0.7	2.7	0.0	0.1	0.1
60	92.7	0.1	6.2	0.0	0.2	0.0	90.7	0.6	7.1	0.0	0.3	0.2
70	86.7	0.1	11.9	0.0	0.6	0.0	84.1	0.6	13.2	0.1	0.6	0.4
80	79.3	0.1	18.9	0.0	1.0	0.1	76.1	0.6	20.4	0.1	1.2	0.7
90	71.2	0.1	26.4	0.0	1.7	0.1	67.7	0.5	27.9	0.2	1.8	1.0
100	63.3	0.1	33.6	0.0	2.4	0.1	59.6	0.5	34.8	0.3	2.6	1.3
150	32.9	0.0	59.3	0.1	6.4	0.2	30.1	0.3	58.5	0.8	6.6	2.4
200	18.2	0.0	69.5	0.1	9.9	0.3	16.4	0.2	67.0	1.2	9.9	2.7

Table 2: Fractional power transferred in the different inelastic channels of H_2,N_2 in H_2-N_2 mixtures. The deficit not shown is transferred into rotational and elastic collisions.

The above comparisons provide important constraints towards identification of the efficient dissociation channels of H_2 in $H_2 - N_2$ mixtures among the following:

a. Dissociation by electron impact excitation of the triplet states of H_2. In pure H_2, this is the dominant channel. The fractional power required for dissociation as calculated from equations (3,4) corresponds closely to that calculated from the Boltzmann equation analysis at the respective E/N (see table 1 and figure 3 at 50 Td for pure H_2). However, table 2 shows that due to the presence of N_2 as a huge sink of energy, there is negligible power deposition in the direct electron impact dissociation mode of H_2 and it is far less than the actual requirements of table 1. Therefore in N_2-H_2 mixtures, the direct electron impact dissociation channel does not account for the experimentally observed H atom densities. *We note that for 1%*H_2 *in table 1, the impossible power requirement of* $> 100\%$ *is an artifact that results primarily due to the uncertainty in the H atom densities, and due to normalization of the data at the same gas temperature (The results of figures 1,2 include gas heating).*

b. Dissociative excitation by interactions with the electronic manifold of N_2 (through quenching collisions). These contributions have been discussed in detail in [1], and are shown in figure 1. Let us consider 10%H_2 mixture composition. Table 2 shows that at E/N=90 Td, $\approx$ 28% of the power is deposited into electronic excitation of N_2. Even if it is assumed that all the N_2 metastable excitation results in H_2 dissociation through processes of the type (1,2) (which is very unlikely), the energy available is far less than the actual requirement of 80% (table 1).

c. Dissociative excitation by the vibrational ladder mechanism through V-V collisions with N_2. This process is very unlikely since the higher vibrational levels of $H_2(X^1\Sigma_g^+,\mathrm{v})$ are strongly quenched by H_2 and H atoms through $V-T$ deactivation collisions [6, 7].

d. Dissociative excitation by interactions with the vibrational manifold of N_2. It is well established that $N_2(X^1\Sigma_g^+,\mathrm{v})$ is an efficient reservoir of vibrational energy. An important indication towards the contribution of this channel comes from the experimental observation that irrespective of the discharge excitation mode (*dc* [4], *rf* [3], microwave [3]), very efficient dissociation of H_2 occurs in H_2-N_2 mixtures. It is therefore important to note that while the dissociation of H_2 is relatively insensitive to E/N in H_2-N_2 mixtures, the dominant vibrational excitation of $N_2(X^1\Sigma_g^+,\mathrm{v})$ is always prevalent (for operating $E/N > 10$ Td).

CONCLUSIONS

We have presented in detail, the energy balance analysis of the dissociation process of H_2 in glow discharges in H_2-N_2 mixtures. It is shown that significant amounts of power dissipations (up to $\approx$ 100%) in dissociation are required to account for the experimentally observed dissociation yields of H_2 in H_2-N_2 mixtures. The results indicate a dominant contribution of $N_2(X^1\Sigma_g^+,\mathrm{v})$ towards the dissociation of H_2. However, the detailed mechanism for such vibrational energy promotion of dissociation needs to be investigated. Efforts to bound the problem by including $V - T$ collisions between $N_2(X^1\Sigma_g^+, v)$ and H atoms are in progress.

ACKNOWLEDGEMENT

The work of R.N. has been supported by the Wright Laboratory.

References

[1] R. Nagpal and A. Garscadden, Chem. Phys. Lett. **231**, 211 (1994).

[2] A. Garscadden and R. Nagpal, Plasma Sour. Sc. & Tech. in press (1995).

[3] B. N. Ganguly and P. Bletzinger, in *47th Gaseous Electronics Conference* (Gaithersburg, MD (also in this conference), 1994).

[4] G. Baravian and A. Ricard, in *XI International Symposium of Plasma Chemistry* (Loughborough, UK, 1993), pp. 1511–15.

[5] A. V. Phelps and L. C. Pitchford, Phys. Rev. A **31**, 2932 (1985).

[6] M. Cacciatore, M. Capitelli, S. D. Benedictis, M. Dilonardo, and C. Gorse, in *Non-Equilibrium Vibrational Kinetics*, edited by M. Capitelli (Springer Verlag, Berlin, 1986), pp. 5–46.

[7] J. Loureiro and C. M. Ferreira, J. Phys. D: Appl. Phys. **22**, 1680 (1989).

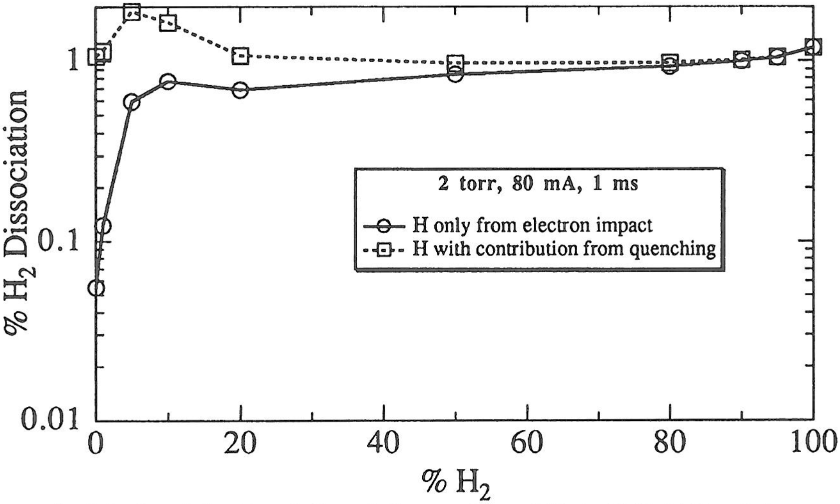

Figure 1: Calculated fractional dissociation profiles of H_2 in $\%H_2$-$\%N_2$ mixtures. Full line represents the results only from direct electron impact dissociation process. Dashed line represents the results when dissociation channels from quenching of excited electronic states of N_2 are also included. Measurements indicate a similar profile but a peak dissociation of ≈ 20% [4].

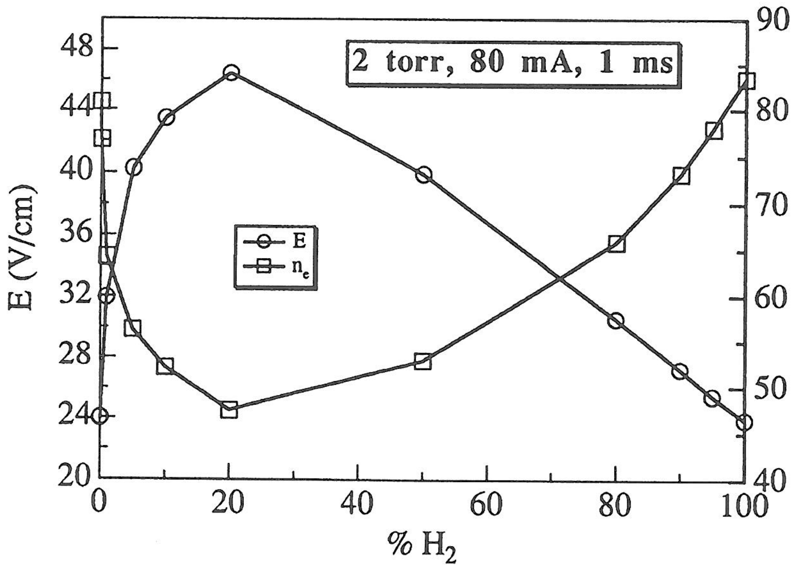

Figure 2: Calculated steady state profiles of electric fields and electron densities in $\%H_2$-$\%N_2$ mixtures for the excitation conditions of [4].

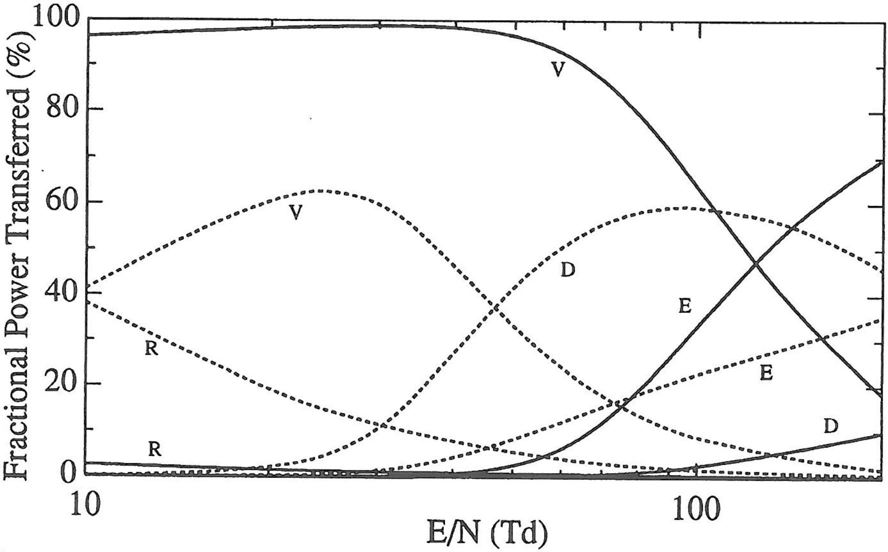

Figure 3: Fractional power deposited into the different inelastic modes of pure N_2 (full lines) and pure H_2 (dashed lines) as a function of E/N. The labels V,D,E,R correspond to vibrational, dissociation, electronic, and rotational processes respectively. The deficit not shown is transferred into elastic and ionization collisions.