Large Effects of Small Pressure Changes in the Kinetics of Low Pressure Glow Discharges

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Glow Discharges

- Stable over $\Delta P$ determined by the suitable conditions for $e^-$ acceleration & multiplication in collisions with gas particles (under $P \times d$ scaling).

- Gas Pressure determines $\Rightarrow T_e, N_e$:
  - $\Rightarrow$ Frequency of Gas Collisions,
  - $\Rightarrow$ Importance of Surface vs. Gas Processes
  - $\Rightarrow$ Characteristics of the Plasma Sheath.

The composition evolves often gradually with pressure, but sometimes ABRUPT CHANGES are observed within a comparatively SMALL PRESSURE INTERVAL.

In this work, we will show that these sudden changes can provide valuable clues about the variation in the relative importance of the key mechanisms determining the plasma properties!
Issues of the Present Study

Generation of Plasmas in Hollow Cathode DC Discharges from Diverse Gas Precursors

Experimental Diagnostics of these Plasmas & Their Kinetic Modeling
Low Ionization Degree + Low Pressure $\Rightarrow$ High Electron Temperature! Low Gas Temperature ($\sim 300$ K)!

**Main Interest**

Changes in the relevance of the different reaction paths induced by the change in plasma conditions
Plasma Generation in Hollow Cathode Reactors

- Cathode dimensions
  \(10 \text{ cm} \Phi \times 34 \text{ cm length}\)

- Residence times \(\sim 0.2 – 1 \text{ s}\)

- Constant Electric Current (DC)
  \(150 \text{ mA for all the experiments}\)

- \(E \approx 0\) in the Negative Glow!
  Very stable & homogeneous plasmas confined inside

- \(\Delta V \sim V_{DC} (300 – 500 \text{ V})\)
  in Cathode Sheath (\(\sim 1-2 \text{ cm}\))
  Ions are accelerated towards the cathode gaining energy, and neutrals diffuse to the walls

Tanarro & Herrero, PSST, 18, 034007 (2009)
Plasma Diagnostics

- Quadrupolar Mass Spectrometry of Neutrals, $e^-$ impact ionization (Differentially pumped)
- Quadrupolar Mass Spectrometry of Ions + Ion Energy Distributions (Differentially pumped)
- Double Langmuir Probes ($N_e, T_e$)
- Visible Emission Spectroscopy (Excited States, Plasma Temp.)

Kinetic Models

“As simple as possible to understand the main mechanisms”

• Zero Order Models (2 volumes: Negative Glow + Cathode Sheath)
• Time dependent Differential Equations for Neutrals and Positive Ions.
• $T_e$ (Maxwellian) instead of a function of $E/N$ ( $E \approx 0$ in the glow )

• Main Processes Considered
  – Ionization + Dissociation by Electron Impact in the Glow
  – Bimolecular Reactions with NO Potential Barrier ( $k \neq f (T_{gas})$ )
  – Diffusion through the Sheath + Surface Recombination or Neutralization
  – Asymmetric Charge Transfer in the Sheath (High Energetic Ions)

• Do not include three body reactions (due to the low pressure)
• Neither reactions with potential barrier (due to the low gas temperature)
Plasma Precursor Species:

- H$_2$
- H$_2$ + Ar
- N$_2$ + O$_2$ (air)
- H$_2$ + N$_2$
H₂ Discharges

\[ T_{\text{vib}} (\text{H}_2) \approx 3000 \text{ K} \]
\[ T_{\text{rot}} (\text{H}_2) \approx 300 \text{ K} \]

\([\text{H}] / [\text{H}_2] \approx 0.10 - 0.15\]
decreases slightly with growing \( P \)

Major Ion changes from \( \text{H}_2^+ \) to \( \text{H}_3^+ \)
quickly with pressure and stabilizes.

The Experimental data is well reproduced by the Model

\( \text{H}_3^+ \): key ion in the interstellar Space

Main Reactions in the H₂ Kinetic Model

<table>
<thead>
<tr>
<th>Gas Phase</th>
<th>$k \ (cm^3 \times s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2 + e \rightarrow 2H + e$</td>
<td>$1.75 \times 10^{-7} T_e^{-1.24} \times e^{-12.6/T_e}$</td>
</tr>
<tr>
<td>$H_2 + e \rightarrow H^+ + H + 2e$</td>
<td>$3.00 \times 10^{-8} T_e^{0.44} \times e^{-37.7/T_e}$</td>
</tr>
<tr>
<td>$H_2 + e \rightarrow H_{2}^+ + 2e$</td>
<td>$3.12 \times 10^{-8} T_e^{0.17} \times e^{-20.1/T_e}$</td>
</tr>
<tr>
<td>$H + e \rightarrow H^+ + 2e$</td>
<td>$6.50 \times 10^{-9} T_e^{0.49} \times e^{-12.9/T_e}$</td>
</tr>
<tr>
<td>$H_{2}^+ + H_2 \rightarrow H_{3}^+ + H$</td>
<td>$2.00 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

Heterogeneous | $\gamma \ (Recomb. \ Prob.)$ |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$H + \text{wall} \rightarrow 1/2 H_2$</td>
<td>0.03</td>
</tr>
<tr>
<td>$H^+ + \text{wall} \rightarrow H$</td>
<td>1</td>
</tr>
<tr>
<td>$H_{2}^+ + \text{wall} \rightarrow H_2$</td>
<td>1</td>
</tr>
<tr>
<td>$H_{3}^+ + \text{wall} \rightarrow H_2 + H$</td>
<td>1</td>
</tr>
</tbody>
</table>
Large Changes in Ion Concentrations & the Inversion of Major Ion at \( P \approx 1 \text{ Pa} \) from \( \text{H}_2^+ \) to \( \text{H}_3^+ \).

**WHY?**

Initial concentrations of the Two Colliders are Similar in Both Reactions: \( \text{H}_2^+ \) is the Primary Major Ion.
Evolution of Ions with Time in H₂ Model

0.8 Pa, 8 eV

H₂

H⁺

H₃⁺

2 Pa, 5 eV

H₂

H⁺

H₃⁺

Steady State Experimental Values
Why $[H] / [H_2] \approx 0.1$?

$H_2 + e \rightarrow 2H + e$

$2H + \text{wall} \rightarrow H_2$

\[ k(T_e) \]

\[ \gamma_{ss} \]

\[ \gamma_{ss} = 0.03 \text{ s}^{-1} \]

Model Predictions $\Rightarrow$

Agrees with $\gamma_{ss}$ of Tserepi & Miller, Appl. Phys. 75, 7231 (1994)

Experimental Result

By Comparing Model With / Without Ions:

<table>
<thead>
<tr>
<th>P (Pa)</th>
<th>2</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contribution of Ions to $[H]$</td>
<td>7%</td>
<td>40%</td>
</tr>
</tbody>
</table>
**H₂ + Ar discharges**

- Crossing of H₂⁺ vs H₃⁺ major ion, analogous to that of pure H₂ plasmas, at 1 Pa.
- Remarkable concentration of ArH⁺ >> Ar⁺.
- Ar⁺ decreases with increasing pressure.
- Relatively high concentration of Ar²⁺, even exceeds those of Ar⁺ at 2 Pa.

**BUT measured T_e ≈1/2 those for pure H₂ !**

Very Important in the Model

Simulation at 2 Pa…
Essential Reactions in H\textsubscript{2} + Ar Kinetic Model

Those of H\textsubscript{2}, and ⇒ …

<table>
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<tr>
<th>Gas Phase</th>
<th>( k ) ( (\text{cm}^3 \times \text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar + e ( \rightarrow ) Ar\textsuperscript{+} + e</td>
<td>( 2.53 \times 10^{-8} T_e^{0.5} e^{-16/Te} )</td>
</tr>
<tr>
<td>Ar + e ( \rightarrow ) Ar\textsuperscript{++} + 3e</td>
<td>( 2.58 \times 10^{-9} T_e^{0.5} e^{-47/Te} )</td>
</tr>
<tr>
<td>Ar\textsuperscript{+} + H\textsubscript{2} ( \rightarrow ) H\textsuperscript{2+} + Ar</td>
<td>( 1.78 \times 10^{-11} )</td>
</tr>
<tr>
<td>Ar\textsuperscript{+} + H\textsubscript{2} ( \rightarrow ) ArH\textsuperscript{+} + H</td>
<td>( 8.72 \times 10^{-10} )</td>
</tr>
<tr>
<td>ArH\textsuperscript{+} + H\textsubscript{2} ( \rightarrow ) H\textsubscript{3}++ + Ar</td>
<td>( 6.30 \times 10^{-10} )</td>
</tr>
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<th>Heterogeneous</th>
<th>( \gamma ) (Recomb. Prob.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar\textsuperscript{+} + wall ( \rightarrow ) Ar</td>
<td>1</td>
</tr>
<tr>
<td>ArH\textsuperscript{+} + wall ( \rightarrow ) Ar+H</td>
<td>1</td>
</tr>
<tr>
<td>Ar\textsuperscript{++} + wall ( \rightarrow ) Ar</td>
<td>1</td>
</tr>
</tbody>
</table>

Large Discrepancies
Experiment vs. Model in
H\textsuperscript{2}+ & Ar\textsuperscript{++}

It is just because the measured $T_e$ is Too Low

$H_2^+ + H_2 \rightarrow H_3^+ + H$

$H_2 + e^- \rightarrow H_2^+ + 2e^-$

$Ar + e^- \rightarrow Ar^{2+} + 3e^-$

$2 \ Pa \Rightarrow 2.5 \ eV$
To solve the discrepancy Experiment - Model, we assume:

a) Small % of Electrons (> 47 eV)
Not detectable with the Langmuir Probe.

- $[\text{Ar}^{++}]$ & $[\text{H}_2^+]$ grow markedly
- $[\text{H}_3^+]$, $[\text{H}^+]$, $[\text{ArH}^+]$ change slightly

But $[\text{Ar}^+]$ increases too much!

$T_e = 2.5 \text{ eV} + 0.7\% \text{ High Eng.}$
To solve this 2nd discrepancy, we also propose:

b) Asymmetric Charge Transfer of High Energetic Ions in the Sheath

\[ \text{Sheath } \sim 2 \text{ cm width } \Rightarrow \text{75% decrease in } \text{Ar}^+ \text{ at 2 Pa} \]
Air Discharges

$T_e$ grows from $\sim 3 \text{ eV}$ to $4 \text{ eV}$ with decreasing pressure

$N_e \approx 2 \times 10^{-10} \text{ cm}^{-3}$ ⇒ as pressure decreases a factor 10, ionization grows from $\sim 10^{-5}$ to $10^{-4}$

Disassociation Rates $\text{N}_2$, $\text{O}_2$, $\text{NO}$

$$
\begin{align*}
\text{O}_2 + e^- &\rightarrow \text{O} + \text{O} (^1 \text{D}) + e^- \\
\text{NO} + e^- &\rightarrow \text{N} + \text{O} + e^- \\
\text{O}_2 + e^- &\rightarrow 2 \text{O} + e^- \\
\text{N}_2 + e^- &\rightarrow 2 \text{N} + e^-
\end{align*}
$$

Ionization Rates $\text{N}_2$, $\text{O}_2$, $\text{NO}$

$$
\begin{align*}
\text{NO} + e^- &\rightarrow \text{NO}^+ + 2e^- \\
\text{O}_2 + e^- &\rightarrow \text{O}_2^+ + 2e^- \\
\text{N}_2 + e^- &\rightarrow \text{N}_2^+ + 2e^-
\end{align*}
$$
Air discharges

NO produced mainly in wall reactions, with recombination coefficients tested in other reactor geometries and pressure ranges.

Change of tendencies as pressure decreases

**Lowest Pressures:**

a) ⇒ NO >> O₂

Larger dissociation of precursors by growth in \( T_e \) & Ionization Degree

b) ⇒ Ionic composition dominated by \( N_2^+ \) and NO⁺.

Encouraging Agreement

Experiment vs. Model…

Except for ions at the Higher Pressures

Sheath process?
Might it be 
\[ \text{N}_2^+ + \text{O}_2 \rightarrow \text{NO}^+ + \text{NO} \] ??

Literature: Cross Sections up to 20 eV.

But they should be \(~\sim\) 20 times larger in \(E_{\text{ion}}\sim100 - 400\) eV to explain the observed [\text{NO}^+] , [\text{N}_2^+].
**Preliminary Results: H$_2$ + 7% N$_2$**

Very large variations of Ion Concentrations with small pressure increase.

N$_x$H$_y^+$ very important in Astrophysics

**Main Ion Reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>k (cm$^{-3}$ s$^{-1}$)</th>
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<tbody>
<tr>
<td>N$_2$ + H$_2^+$ → N$_2$H$^+$+H</td>
<td>2.00x10$^{-9}$</td>
</tr>
<tr>
<td>N$_2$ + H$_3^+$ → N$_2$H$^+$+H$_2$</td>
<td>1.86x10$^{-9}$</td>
</tr>
<tr>
<td>H$_2$ + N$_2^+$ → N$_2$H$^+$+H</td>
<td>2.00x10$^{-9}$</td>
</tr>
<tr>
<td>NH$_3$ + H$_2^+$ → NH$_3^+$+H$_2$</td>
<td>5.70x10$^{-9}$</td>
</tr>
<tr>
<td>NH$_3$ + H$_3^+$ → NH$_4^+$+H$_2$</td>
<td>4.40x10$^{-9}$</td>
</tr>
<tr>
<td>NH$_3$ + N$_2$H$^+$→ NH$_4^+$+N$_2$</td>
<td>2.30x10$^{-9}$</td>
</tr>
</tbody>
</table>

and Surface Reactions ⇒ NH$_3$

**Model being developed**
SUMMARY & CONCLUSIONS

• Glow discharges are studied in the low pressure range (~ 0.5 – 5 Pa).
• Large changes are found in their $T_e$ & Neutral & Ion composition that may be very important in plasma applications and in explaining some phenomena in natural plasmas.
• The kinetic models developed allow to assign the main processes responsible of such behaviors:
  • Relevance of gas phase non barrier reactions.
  • Relevance of charge transfer reactions in the sheath.
  • Relevance of surface reactions.
• In general, the models fit quite well the experimental results.
The Team at Present

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The Excellent Technicians of our Department

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Miguel A. Moreno

Javier Rodríguez
Thank you very much for your attention