ON PLASMA COMPOSITION AND PARAMETERS
OF PULSED DISCHARGE IN ELECTROLYTE

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ABSTRACT
The equilibrium plasma composition for system containing H, O, N and Na is
determined for the temperature range between 5000 and 20000 K. This corres-
ponds to the pulsed discharge in liquids of the following characteristics;
discharge voltage - 1,2 kV, current - 2 to 4 kA, pressure - 20 bars, pulse
duration - 20 100 µs. \( T_e \) is evaluated from the Boltzmann plot of the OII
lines and \( n_e \) from the MII ionic line profiles.

1. INTRODUCTION
Thermodynamical properties of pulsed discharge plasmas in electrolytes
have recently been investigated by several authors. It was shown that these
plasmas are multicomponent (1-3) but their composition was only theoreti-
cally determined (2,4). The calculations were based on complex models often
not adequately representing the physical conditions of the discharge. In
this experiment the plasma is characterised by relatively low temperature
(-1-2 eV), high concentration of charge carriers (-1·10¹⁶ cm⁻³) and moderate-
ly high pressure which the plasma channel exerts on the surrounding media.
The spectrum of such a dense and cold plasma consists of atomic and ionic
lines and molecular bands superimposed on an intense continuum. Most of the
lines are broadened and highly absorbed. The emitted spectrum depends on
the discharge conditions, composition and conductivity of the electrolyte,
electrode configuration and on the applied energy. These in turn define the
composition, density and temperature of the plasma.
In the present paper, based upon a detailed spectroscopic analysis, the
equilibrium plasma composition was computed by the method of minimization
of free energy (5). The calculated electron densities were compared with
experimentally obtained values. The results for pure water were compared
with the calculations of Burhorn and Wienecke (6) who applied the mass ac-
tion law and the Saha equation to \( H_2O \) plasma for the same pressure and tem-
perature range.

2. EXPERIMENTAL
The experimental setup is described in detail in Ref. (3).
The discharge in a 1% NaNO₃ electrolyte was observed end-on through the
electrode, shot by shot, by a Zeiss PGS-2 spectrograph (first order inverse linear dispersion, 0.8 mm/mm, measured instrumental full halfwidth, 0.024 nm at a 15 μm slit) followed by an EMI 9659B photomultiplier.

The electron concentration \( n_e \), was determined from the Mg line profiles. For investigating of the MgII UV multiplet (Table 1.) magnesium was added to the solution in a concentration of 1–4 \( 10^{-3} \% \). For these lines, at these concentrations, the plasma can be considered optically thin. The deconvolution of the Voigt profile (7–9) has been applied to derive the Stark component from the total observed width.

Both experimental and theoretical data for the broadening of these lines are available (10).

Table 1. Experimentally determined full-halfwidths and the ratios of measured and calculated halfwidths \( W_m/W_{th} \)

<table>
<thead>
<tr>
<th>Ionization stage</th>
<th>Transition array</th>
<th>Designation (mult no.)</th>
<th>( T_e ) (K)</th>
<th>Wavelength ( W_m ) (nm)</th>
<th>( W_m/W_{th} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgII</td>
<td>3s–3p</td>
<td>( ^2S_2p^o ) 1,6×10^4</td>
<td>279.55</td>
<td>0.068</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ^2S_2p^o ) (1)</td>
<td>280.27</td>
<td>0.064</td>
<td>12.8</td>
</tr>
</tbody>
</table>

Experimentally determined \( n_e = 1.3×10^{18} \) cm\(^{-3}\).
The estimated error of these line widths is ±24%.

The electron temperature \( T_e \) was determined from the Boltzmann plot of relative intensities of nine OII lines (Table 2.).

Table 2. OII lines used for the Boltzmann plot method

<table>
<thead>
<tr>
<th>Ionization stage</th>
<th>Transition array</th>
<th>Designation (mult no.)</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OII</td>
<td></td>
<td>( 2p^2^3S_2p^2(3P)3p ) ( ^2P_0^2P_0 ) (3)</td>
<td>371.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ^4S_2p^2(3P)3d ) ( ^4D_2p^0 ) (6)</td>
<td>372.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ^4D_2p^0 ) (6) ( ^4F ) (10)</td>
<td>374.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 2p^2^3p^2(3P)3d ) ( ^4D_2p^0 ) (36)</td>
<td>397.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 2p^2^3p^2(3P)3d^2 ) ( ^4D_2p^0 ) (6)</td>
<td>395.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ^4D_2p^0 ) (6) ( ^4F ) (10)</td>
<td>394.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 2p^2^3p^2(3P)3d ) ( ^4D_2p^0 ) (36)</td>
<td>408.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ^4F_2p^0 ) (36) ( ^4F ) (10)</td>
<td>418.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ^4F_2p^0 ) (36) ( ^4F ) (10)</td>
<td>418.55</td>
</tr>
</tbody>
</table>

Experimentally determined \( T_e = 1.6×10^4 \) K.

Finally, the optical depths of all lines were checked by measuring the ratio of line intensities within multiplets and comparing the results with the values calculated from the known transition probabilities.

3. PLASMA COMPOSITION CALCULATIONS

For computing the equilibrium composition of the system based on the mini-
Fig. 1. Particle densities of the atomic (a) and ionic (b) components in H$_2$O plasma at 20 bars.
Fig. 2. Particle densities of the atomic (a) and ionic (b) components in aqueous solution of 1% NaNO$_3$ at 20 bars.
mization of free energy, the method of steepest descent was used. The plas-
ma under investigation was considered to be in LTE, in a quasi-stationary
state and a single phase system with a constant ratio of the main atomic
components H/O. As there was a temperature gradient in the whole volume
of the plasma, the calculations were performed in the temperature range of
5000 to 20000 K.
The free energy data were either taken from Refs. (11,12) or computed (13).

4. RESULTS AND DISCUSSION

Equilibrium particle densities were calculated for an eleven component
system for pulsed discharge in H₂O (Fig. 1a and 1b) and a sixteen component
system of a water solution of 1% NaNO₃ (Fig. 2a and 2b).
The calculated equilibrium composition is in agreement with the results
obtained by spectroscopical analysis.
i) Experimentally determined \( n_e \) (Table 1.) at measured \( T_e \) (Table 2.)
on the plasma axis is in accordance with the value of \( n_e \) obtained by the
method of steepest descent.
ii) At lower temperatures the electron density is three orders of ma-
gnitude higher than in pure water, which is the consequence of the ionization
of Na. Practically all electrons at temperatures between 5000 K and 8000 K
are due to the ionization of Na. Therefore the degree of ionization at these
temperatures is increased as compared to pure water, this being of impor-
tance for the initiation of the breakdown period.
iii) At higher temperatures, when the maximum radius of the plasma is
achieved, Na has little influence on \( n_e \) in comparison to \( H^+ \) and \( O^+ \) which
are the dominating ions. So the plasma composition, particularly at higher
temperatures, is not significantly influenced by the presence of an electro-
lyte.

iii) The equilibrium composition for this discharge agrees well with
the calculation using the mass action law and Saha equation (14). In addi-
tion, the same calculations for the H₂O plasma (Fig. 1.) are in accordance
with the results of Burhorn and Wiesecke (6).
The obtained plasma composition, which follows from the thermodynamic cha-
racteristics of the plasma, is in agreement with experimental results and
thus confirms that the plasma is in LTE under the stated conditions.
Since, H, O, H⁺ and O⁺ are the main components of the system, this plasma
could be used on research of chemical reactions with these components.

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REFERENCES