Determination of transport and reaction swarm coefficients from the analysis of complex transient pulses from the pulsed Townsend experiment

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Abstract. We present in this paper the interpretation and analysis of transient pulses from a pulsed Townsend experiment by solving the continuity equations of the charged carriers (electrons and ions) involved in the avalanche. The set of second order partial differential equations is solved by SIMAV, a simulator designed specifically for the pulsed Townsend avalanche. Complex situations involving processes such as electron detachment, ion-molecule reactions, Penning ionization and secondary electron emission from ion impact at the cathode, virtually impossible to solve analytically, are discussed here to illustrate the capability of the simulator to help explain the various reaction processes involved in the avalanche, and also to derive some of the transport and reaction coefficients.

1. Introduction
Electron and ion interactions with gases at low energies have been studied for several decades. In essence, two kinds of experiments have been performed, namely single collision, beam experiments, aimed at measuring cross sections, and multicollisional swarm experiments from which swarm coefficients are normally obtained. Both cross sections and swarm coefficients are related to each other [1], and in many cases measured swarm coefficients are used to either derive or validate cross section sets.

Nowadays there is an increasing need for either electron and ion swarm transport and reaction coefficients or the respective cross sections in view of the ever growing low temperature plasma applications and basic research on atmospheric physics, for instance. The swarm technique has been very helpful in providing a wealth of data for many gases and mixtures, and in particular the pulsed Townsend technique (PTT), since it permits the observation of the temporal development of the discharge and the derivation of transport and reaction data from it. Nevertheless, the swarm techniques have so far provided transport coefficients such as electron and ion drift velocities, diffusion coefficients and/or reaction coefficients such as electron impact ionization and attachment. Only in very few cases electron detachment coefficients and reaction rates have been derived. The reason for this stems from the fact that modelling the Townsend avalanche is difficult since it involves the solution of continuity equations for the charge carrier species involved in the process, hence this has only been possible for relatively simple cases such as electron/ion drift, ionization and attachment.
Even simple cases such as electron detachment have been successfully solved for the electron component of the discharge, the ion part remaining unsolved thoroughly because of its analytical complexity. Thus, the need to solve the set of continuity equations numerically, taking into account the special boundary and initial conditions is called for.

A pulsed Townsend avalanche simulator, SIMAV, has been developed to solve the equations of continuity for up to six different charged carrier species (electrons and ions) moving and reacting in a gas under the action of a homogeneous electric field in a parallel plate arrangement [2-5]. SIMAV is capable of solving a set of second-order partial differential equations accounting for the drift, diffusion and reaction of all the charge carriers involved in a particular pre-breakdown condition. The solver is based on a finite difference approximation that calculates the temporal evolution of the density of each species and from these, the individual and total currents flowing in the discharge gap, the latter being accessible to measurement [3,4]. SIMAV has been successfully used and examples of this are presented in this paper. Its usefulness has been twofold since it has helped explain complex reaction schemes such as electron detachment and ion molecule reactions in SF₆, Penning ionization in C₂F₆-Ar mixtures, charge transfer in Xe-Ne mixtures, negative ion clustering in O₂, or even predict complex avalanche processes due to secondary electron emission by ion impact at the cathode.

2. The pulsed Townsend experiment
This section is dedicated to provide the essentials of the technique by means of illustrative examples that may help the reader appreciate the importance of resorting to the numerical simulation of the processes for the complex situations referred to above.

2.1. Experimental setup
The pulsed Townsend apparatus used for this research has been described fully in detail elsewhere [2]. Briefly, the experiment relies on the measurement of the displacement current due to the electron and ion swarms (positive and/or negative) drifting and reacting under the action of a highly uniform, homogeneous electric field produced by a parallel-plate capacitor. The initial photoelectrons are released from the cathode by the action of a UV flash (337 nm, 1 ns duration). These photoelectrons and their progeny drift toward their corresponding electrodes. Thus, the time-dependent total current flowing through the gap is amplified by a transimpedance amplifier and registered on a digital oscilloscope connected to a computer for data acquisition and further analysis. A sketch of the layout of the experiment is given in figure 1.

![Figure 1. Schematic layout of the pulsed Townsend experiment. HV: high voltage power supply; L: pulsed laser; A: anode; K: cathode; AMP: transimpedance amplifier.](image)
2.2. Simple analysis

The analytical expressions useful to derive the electron drift velocity \( v_e \), the effective ionization coefficient \( \alpha - \eta \) (\( \alpha \) and \( \eta \) are the ionization and attachment coefficients, respectively), and possibly the negative and positive ion drift velocities \( v_p \) and \( v_n \) are obtained readily from a simple solution of the continuity equations for the above species [3-5] provided that the ions are non-reactive. Even the longitudinal diffusion coefficient \( D_L \) can be obtained from a curve fitting procedure to the measured electron component of the avalanche [6]. Because of their much higher mobility than that of the ions, the electron signal can be completely differentiated from the ionic one, and therefore the analysis of the former component proceeds readily by means of a curve-fitting procedure to the expression

\[
I_e(t) = I_0 \exp \left[ (\alpha - \eta) v_e t \right] \quad \text{with} \quad I_0 = \frac{n_o q_o}{T_e} \tag{1}
\]

where \( I_0 \) is the initial current produced by the release of photoelectrons from the cathode, \( n_o \) is photoelectron number, \( q_o \) is elementary charge, and \( T_e = d/v_e \) is the electron transit time through the discharge gap of width \( d \). When longitudinal diffusion is considered, a more complex expression [4,6] to analyze the measured electron component of the avalanche current is

\[
I_e(t) = I_0 \exp(\alpha_{eff} v_e t) \left( 1 - \frac{\exp\left(\frac{v_e + \alpha_{eff} D_L t}{D_L} - d\right)}{\exp\left(\frac{v_e + \alpha_{eff} D_L t}{D_L} - d\right) \cdot \left(\frac{\exp\left(\frac{v_e + \alpha_{eff} D_L t + d}{D_L} - 1\right) + \exp\left(\frac{v_e + \alpha_{eff} D_L t - d}{D_L} - 1\right)}{2}\right)} \right) \tag{2}
\]

where

\[
\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-u^2)du \tag{3}
\]

is the error function of argument \( x \). Examples of the calculated waveforms are given in figure 2 for the cases \( (\alpha - \eta) > 0 \), \( (\alpha - \eta) = 0 \), and \( (\alpha - \eta) < 0 \). Also illustrated in figure 2 is the assessment of the electron transit time \( T_e \) from which the electron drift velocity is obtained. For further details of the analysis the reader is referred to earlier work [3-5].

The equations for the positive and negative ionic components are, respectively [3,7]

\[
I_p(t) = \frac{q_o}{T_p} n_o \frac{\alpha}{\alpha_{eff}} \left[ \exp(\alpha_{eff} d) - \exp(\alpha_{eff} v_p t) \right] \tag{4}
\]

\[
I_n(t) = \frac{q_o}{T_n} n_o \frac{\eta}{\alpha_{eff}} \left[ \exp(\alpha_{eff} (d - v_n t)) - 1 \right] \tag{5}
\]

where \( T_p = d/v_p \) and \( T_n = d/v_n \) refer respectively to the positive and negative ions transit time, i.e. \( v_p \) and \( v_n \) refer respectively to the drift velocity of positive and negative ions.

A sketch of the whole avalanche containing the fast electron component and the slower ionic ones is shown in figure 3.
Figure 2. Calculated electron current $I_e(t)$ (including diffusion) for the cases (a) $(\alpha-\eta)>0$, (b) $(\alpha-\eta)=0$, and (c) $(\alpha-\eta)<0$. The assessment of the electron transit time $T_e$ is indicated.

Figure 3. A sketch of the whole avalanche containing the fast electron component and the slower ionic one is shown in figure 3, calculated with equations (1), (4) and (5). Note that the time scale is logarithmic and that the ionic currents have been enlarged by three orders of magnitude.

3. The avalanche simulator (SIMAV)
In this section we briefly discuss the essential features of the simulator that solves a set of partial differential equations, first and second order, using a first order finite difference approximation. The one-dimensional (1D) simulation code calculates the density of all charged particle species and the current in the external circuit that can be used directly for comparison with the transient waveforms obtained from the pulsed Townsend experiment. For a thorough description the interested reader is referred to [2].

The general form of the continuity equations of the charged carrier species of density $n$ is [2,8]

$$\frac{\partial n_i(z,t)}{\partial t} + \frac{d j_i(z,t)}{d z} = \sum_{k=1}^{N_i} a_{i,k} j_k(z,t)$$

where
is the current density. The terms $a_{i,k}$ refer to the spatial coefficients of species $i$ due to charge carrier $k$, $z$ is the drift coordinate, $v_i$ and $D_i$ are the drift velocity and longitudinal diffusion coefficients of species $i$.

The total current which corresponds to the measurable one is given by

$$I_{tot}(t) = \sum_i I_i(t) = \sum_i \frac{q_i}{T_i} \int_0^t n_i(z,t) dz$$

where $T_i = d/v_i$ is the transit time and $v_i$ the drift velocity.

The processes thus far included in the simulator are electron/ion drift and diffusion, electron impact ionization and attachment, electron detachment from negative ions, ionic conversion, Penning ionization, and secondary electron emission by positive ion impact at the cathode.

4. Case studies
In this section we shall discuss the capabilities of the simulator to solve complex reaction schemes dealing with electron detachment, ionic conversion, Penning ionization and secondary emission.

4.1. Ion clustering in O$_2$

The measurement of an ionic avalanche in O$_2$ such as that shown in figure 4 (wriggled, gray curve), bearing a peculiar trailing edge, falling vertically, led us to suspect the presence of at least a second ionic species. Further inspection of the pulse suggested that this would be a third species since a straightforward measurement of the transit time (broken curve ending at about 660 $\mu$s) rendered a negative ion drift velocity compatible with that of O$_4^-$ [9]. Thus we were led to assume that the third ionic species was O$_6^-$. The full reaction scheme leading to the formation of this species is electron attachment (three body) leading to the formation of O$_2^-$

$$e^- + 2 O_2 \rightarrow O_2^- + O_2$$

followed by ionic conversion leading to the formation of O$_4^-$ from O$_2^-$ and O$_6^-$ from O$_4^-$,

$$O_2^- + 2 O_2 \rightarrow O_4^- + O_2$$

$$O_4^- + 2 O_2 \rightarrow O_6^- + O_2$$

The number of parameters needed to calculate the avalanche pulses is large, namely four drift velocities (electrons and three ion species), the attachment coefficient for reaction (9) and two more reaction rates for processes (10) and (11). Fortunately, all drift velocities were known, as well as the electron attachment coefficient and the reaction rate for process (10), thereby leading us to fit the measured curve with only one free parameter. The absence of O$_2^-$ in the ionic component of figure 4 is due to the very fast conversion process leading to the formation of O$_4^-$ during the first 200 ns of discharge development, as it is shown in figure 5.

A plot of the reduced mobilities of O$_4^-$ and O$_6^-$ in O$_2$ is given in figure 6, together with the calculated mobility curves resulting from using the cross section sets of figure 7, where the momentum transfer cross section $Q_m$ for O$_4^-$ and O$_6^-$ in O$_2$ was derived by using the measured mobilities to estimate its value over the low energy collision range.
Figure 4. A measured ionic avalanche pulse in O₂ (gray, wriggled curve) with its total current, calculated curve (solid line) and the contribution of the individual components of O₄⁻ and O₆⁻ (see text). The conditions of the experiment were \( p = 600 \) Torr and \( E/N = 8 \) Td (1 Townsend = \( 10^{-17} \) V cm²) [9].

Figure 5. The temporal development of charge carriers in the O₂ avalanche during the first 200 ns. Note that at this time practically the only ion in the discharge gap is O₄⁻ since the current due to O₆⁻ is over four orders of magnitude smaller. (\( p = 600 \) Torr and \( E/N = 8 \) Td) [9].
4.2. Charge transfer in Xe-Ne mixtures
Our second case deals with the formation of \( \text{Xe}^+ \) by charge transfer from \( \text{Ne}^+ \) in the Xe-Ne mixture. This study was due to prove that this process had minimal influence on the measured, total current so that the measured transit time, out of which the drift velocity and mobility were derived, was that of
Xe⁺, which was previously formed by electron impact. The conditions of the experiment were such that no more than 1% Ne⁺ was present in the discharge [8].

Both Ne⁺ and Xe⁺ are initially formed by electron impact by the processes

\[ e^- + Xe \rightarrow Xe^+ + 2 e^- \]  \hspace{1cm} (12)  

\[ e^- + Ne \rightarrow Ne^+ + 2 e^- \]  \hspace{1cm} (13)  

with ionization coefficients that are well known. The charge transfer reaction

\[ Ne^+ + Xe \rightarrow Xe^+ + Ne \]  \hspace{1cm} (14)  

was also considered. The values of the ionization coefficients and drift velocities involved in the calculation are given in [8].

Figure 8 shows the smallness of the Ne⁺ component makes it practically negligible so that the drift velocity measured from the end of the total current is that of Xe⁺. Once more, the usefulness of SIMAV was established by letting us model the reaction scheme represented by equations (12)-(14), thereby leading us to state that the ion in question was, undoubtedly, Xe⁺. To illustrate this further, the density-reduced mobilities \( \mu N \) are shown plotted in figure 9 as a function of \( E/N \). Note that the measured values (points) fit very well with an independent calculation using cross section data [8].

\[ \begin{array}{c}
\text{Time (\( \mu s \))} \\
10^{-1} \hspace{1cm} 100 \hspace{1cm} 10^1 \hspace{1cm} 10^2 \\
\text{Current (Arbitrary units)} \\
10^{-6} \hspace{1cm} 10^{-5} \hspace{1cm} 10^{-4} \hspace{1cm} 10^{-3} \hspace{1cm} 10^{-2} \hspace{1cm} 10^{-1} \hspace{1cm} 10^0 \hspace{1cm} 10^1 \hspace{1cm} 10^2
\end{array} \]

Figure 8. Calculated currents of Xe⁺ and Ne⁺ in the Xe-Ne mixture and the total current. Note that the scale is logarithmic. The conditions of the simulation are a 20% Xe-80% Ne mixture, \( p = 5 \) Torr and \( E/N = 55 \) Td.
4.3. Penning ionization in C\textsubscript{2}F\textsubscript{4}-Ar mixtures

Perhaps one of the least studied phenomena in Townsend discharges is that of Penning ionization in spite of its importance when molecular gases with a relatively low ionization threshold (IT) are mixed with rare gases (or some other) the level of metastable states of which exceed the IT of the molecular gases. Then positive ions from the molecular gas are formed, thereby constituting a second source of ionization in the realm of the discharge. It has already been shown that this extra source of ionization can be influential over certain E/N regions. This is hardly ever taken into account when modelling discharges mainly because of the lack of data such as metastable and Penning ionization rates.

Our case study deals with the ionization of C\textsubscript{2}F\textsubscript{4} both by electron impact and Penning effect in the C\textsubscript{2}F\textsubscript{4}-Ar mixture. Measured electron transients indicated a marked pressure dependence of the electron drift velocity, a fact that is hard to understand. Thus we resorted to the following discharge scheme to consisting of direct ionization and attachment

\[
e^- + \text{Ar} \rightarrow \text{Ar}^+ + 2 \text{e}^- \quad (15)
\]

\[
e^- + \text{C}_2\text{F}_4 \rightarrow \text{F}^+ + 2 \text{e}^- + \text{C}_2\text{F}_3 \quad (16)
\]

\[
e^- + \text{C}_2\text{F}_4 \rightarrow \text{F}^- + \text{C}_2\text{F}_3 \quad (17)
\]

followed by the formation of metastable \(\text{Ar}^*\)

\[
e^- + \text{Ar} \rightarrow \text{Ar}^* + \text{e}^- \quad (18)
\]

and, finally, Penning ionization

\[
\text{Ar}^* + \text{C}_2\text{F}_4 \rightarrow \text{F}^+ + \text{e}^- + \text{Ar} + \text{C}_2\text{F}_3 \quad (19)
\]
Figure 10 displays the measured and calculated electron currents in the 1% C₂F₄-Ar mixture at several pressures in the range 6-50 Torr, where the effects of Penning ionization are clearly distinguished by an enhancement of the apparent electron transit time in the measured curves (solid), and the simulated curves (dotted) that fit the measurements very closely. A single electron drift velocity was used. The enhancement of the apparent electron transit time is due to the presence of Ar* metastable that in turn produce a further positive ion cloud along the discharge gap. A film showing the evolution of the densities is available by writing to the authors.

4.4. Electron detachment and ion conversion in SF₆

Our next case deals with a study of the relative importance of electron detachment and negative ion conversion in the SF₆ avalanche [10]. The reaction scheme of SF₆ is very complex since it involves both positive and several negative ion species and electron detachment from F⁻. Figure 11 shows the reaction scheme used in the simulations to be discussed further on.

![Figure 10](image_url) Measured electron transients (solid curves) in the 1% C₂F₄-Ar mixture and their fitting (doted curves) after using SIMAV with the discharge scheme of reactions (15) to (18). Conditions of the measurements are indicated on the inset of this figure.

One can see that there are 10 reactions and 6 charged species, thereby making it again impossible to model such scheme analytically. The calculated ionic avalanches are shown in figure 12. Looking at figure 12 one can see how the agreement between measurement and calculation improves as one includes more processes in the simulation. Note, in particular, the influence of electron detachment from F⁻ on the positive ion current and that of SF₆⁻ on the formation of the cluster species SF₆-SF₆⁻ that accounts very well for the latter portions of the measured curve. All swarm data necessary for the simulations were already available in the literature with the exception of β, which was the only free parameter. Also, all parameters used for the simulations were the same with the exception of the electron detachment coefficient for which some pressure dependence was observed. A film showing the evolution of the densities is available by writing to the authors.
Figure 11. The discharge scheme used to simulate ionic avalanches in SF₆. α is the ionization coefficient, η₁ to η₃ are attachment coefficients, μ₁ to μ₄ are ion conversion coefficients (two-body), β is a three-body ion conversion coefficient, and δ is the detachment coefficient.

4.5. Secondary ionization by positive ion impact at the cathode

Secondary electron emission processes in gases either by ion impact at the cathode or from photoionization are very important in controlling, among other processes, gas breakdown. The techniques most commonly used to study these phenomena are steady state experiments. Important efforts were made in the decade of 1960 [3] to study transient phenomena due to both secondary ionization processes. Unfortunately, for some reason these studies were not continued and, perhaps one of the reasons was, once more, the analytical difficulty in modelling these complex processes. Figure 13 shows an excellent oscillogram of a series of ionic avalanches produced in Ar by ion impact at a Ni cathode.

We have started simulating the process of secondary electron emission by ion impact at the cathode in N₂ gas. The pulses shown in figure 14 correspond to simulations with secondary emission coefficients of γ=3×10⁻⁷ and γ=5×10⁻⁷, showing a strikingly different behavior. While the avalanche for γ=3×10⁻⁷ shows a decaying series of positive ion successors, that for γ=5×10⁻⁷ indicates an upward behavior suggesting conditions close to breakdown. Also displayed are the contributions of electrons and positive ions. A film showing the evolution of the densities is available by writing to the authors.

5. Discussion

By means of five examples, four of them contrasting measurement and simulation, we have shown the extraordinary ability and usefulness of the avalanche simulator. Undoubtedly, SIMAV has let us gain more insight into collision processes hitherto not attempted because of the formidable analytical difficulties to solve the continuity equations of charge carriers subject to complex reaction schemes in which the equations became coupled, let alone the very particular initial and boundary conditions imposed by the experiment. Thus far SIMAV can only deal with situations in which space charge effects are either negligible or absent, such as those prevailing in the experiments herein described. Further attempts to simulate processes close to breakdown would demand full consideration of the additional contribution of local fields.
Figure 12. Measured (wriggled, red curves) and calculated (solid curves) currents in the SF₆ ionic avalanche at \( p = 15 \) Torr, \( E/N = 360 \) Td, \( d = 2 \) cm, showing the evolution in the calculation as the discharge scheme becomes more complex [10]. (a) Only ionization and attachment are considered; (b) ionization, attachment and ion conversion; (c) ionization, attachment, ion conversion and electron detachment from F⁻, and (d) the full scheme of figure 11 with ionization, attachment, ion conversion and electron detachment from F⁻ and the three-body clustering reaction leading to SF₆-SF₆⁻.

Figure 13. An ionic avalanche and its successors in Ar produced by positive ion impact at a Ni cathode with \( p = 1.25 \) Torr, \( E/N = 483 \) Td, \( d = 1 \) cm, and a time base of 5 \( \mu \)s/div. The small vertical bars at the lower axis indicate the positions of the ion transit times of secondary avalanches as well as the start of the whole discharge. Taken from [3].
Figure 14. Ionic avalanches with successors in N_2 with secondary ionization coefficients of γ=3×10^{-7} (left) and γ=5×10^{-7} (right). Conditions of the simulations are p = 780 Torr, E/N = 130 Td, and d = 1 cm.

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References
[1] Christophorou L G 1984 in Electron-Molecule Interactions and their Applications (Orlando: Academic Press)
[2] de Urquijo J, Juárez A M, Rodríguez-Luna J C and Ramos-Salas J 2007 IEEE Trans. Plasma Sci. 35 1204
[3] Raether H 1964 Electron Avalanches and Breakdown in Gases (London: Butterworths)
[4] Hernández-Ávila J L, Basurto E and de Urquijo J 2002 J. Phys. D: Appl. Phys. 35 2264
[5] de Urquijo J, Alvarez I and Cisneros C 1999 Phys. Rev. E 60 4990
[6] Brambring J 1964 Z. Physik 179 532
[7] de Urquijo J, Arriaga C, Alvarez I and Cisneros C 1999 J. Phys. D: Appl. Phys. 32 41
[8] de Urquijo J, Basurto E and Bekstein A 2011 J. Physics D: Appl. Phys. 44 325202
[9] de Urquijo J, Bekstein A, Ducasse O, Ruiz-Vargas G, Yousfi M and Benhenni M 2009 Eur. Phys. J. D 55 637
[10] Bekstein A, Rodriguez-Luna J C, Ducasse O and de Urquijo J 2011 Proc. XXX ICPIG Belfast, UK