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Kinetics of Ionization in NaCl-Contaminated Argon

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Abstract

THE fact that low ionization potential contaminants can influence ionization rate experiments in inert gases is known as is the fact that shock tubes should be cleaned before attempting kinetics—particularly electron kinetics—experiments.[1-3] Usually, the determination of the impurity level of a test gas is restricted to steady-state mass spectrometry of the residue gas in a shock tube at room temperature and near vacuum condition between the actual transient experiments.[2,3] However, at this condition some impurity species are hardly detected by mass spectrometry.[4] One of these species is NaCl vapor. Contained in the ambient air, it will enter (conventional) shock tubes during the opening periods between experiments. At shocked-gas conditions, NaCl will strongly react and be able to impair the initial ionization rate of an inert test gas. In its first part, this work explores shock tube cleaning methods and experimental means to detect impurities. In the second part, a numerical simulation method predicts semiquantitatively the kinetics of ionization in NaCl-contaminated argon. The experimental results that are simulated by our reaction scheme were performed in a stainless steel shock tube with argon at initial pressure p_1 in the range from 3 to 10 Torr. Shocks of Mach numbers M_s from 7.6 to 9.5 were generated by a cold helium driver. The lowest vacuum pressure available in the driven tube section was 10^{-3} Torr.

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The first objective of this investigation was to find a cleaning method to remove a residue (produced by an electric arc driver) from the interior shock tube walls. This way, the tube was meant to be prepared for electron kinetics experiments in weakly ionized argon. As it is a nondestructive cleaning method, glass bead peening was chosen over other procedures. The cleaning was supported by several diagnostic methods. As a "steady state" testing method between experiments, mass spectrometry indicated an impurity level of less that 1 ppm consisting of 40% H_2O, 50% N_2, 5% CO_2, and 5% hydrocarbons (mostly CH_4) by volume to within 20% of the mean. As dynamic testing method, radiometry was applied to determine the density of sodium and iron.[4] After cleaning, the investigation took an unexpected turn with the discovery that the cleaning method was not perfectly effective and introduced new contaminants with non-negligible impact on the initial argon ionization. This outcome derives mainly from the fact that components of the silica glass beads (12% Na_2O, 8% CaO, and 1% Al_2O_3) participate in the ionization. Only after repeated pumping and flushing was the tube sufficiently clean to permit the desired studies. However, with our conventional-type shock tube, sodium chloride molecules contained in the ambient air could not be prevented from being absorbed on the interior wall of the driven section.[4] Thus our study required a numerical simulation program accounting for impurity effects (particularly of NaCl) in the reduction of our experimental data.

Our main experimental tool for electron density measurement was microwave equipment at frequencies of 9, 24, and 35 GHz. In Fig. 1, the initial rates of ionization in argon N_e—evaluated from microwave transmission signals—are compared to the corresponding rates of Refs. 2, 3 and 6. The rates are based on the particle reaction time t_p in contrast to the laboratory time t_L. Our lowest rates are corrected for boundary-layer effects according to the data reduction procedure of McLaren and Hobson.[3] They are derived either from the initial slope as shown in Fig. 2 or from the slope determined at $50 < t_L < 200$ μs (see Figs. 2 and 3), when—in experiments with presumably a higher content of contaminants with low ionization energy—a plateau of nearly

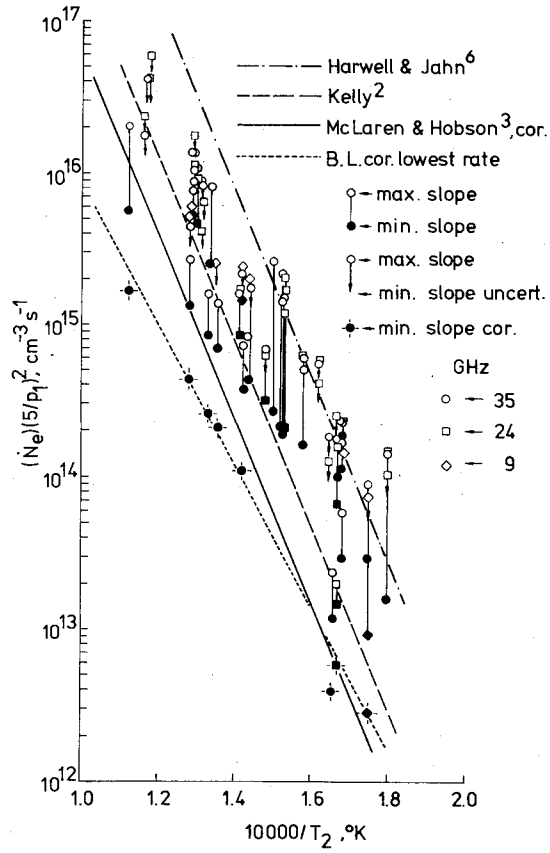

Fig. 1 Initial electron density rate normalized quadratically to $p_1 = 5$ Torr as function of $1/T_2$.

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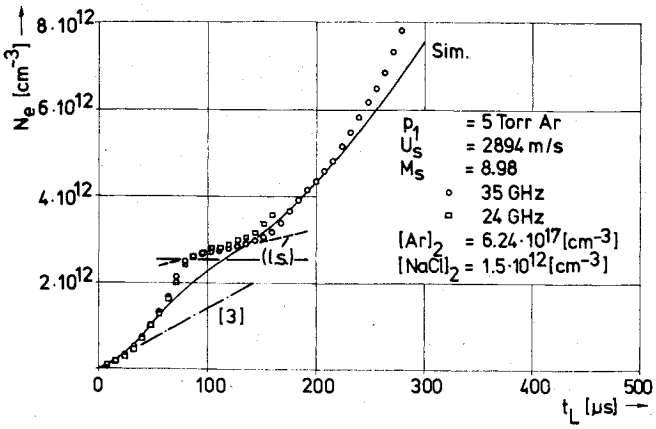

Fig. 2 Electron density as function of t_L. Comparison of experimental to analytical results, and of lowest slope (l.s.) to Ref. 3 without boundary-layer correction.

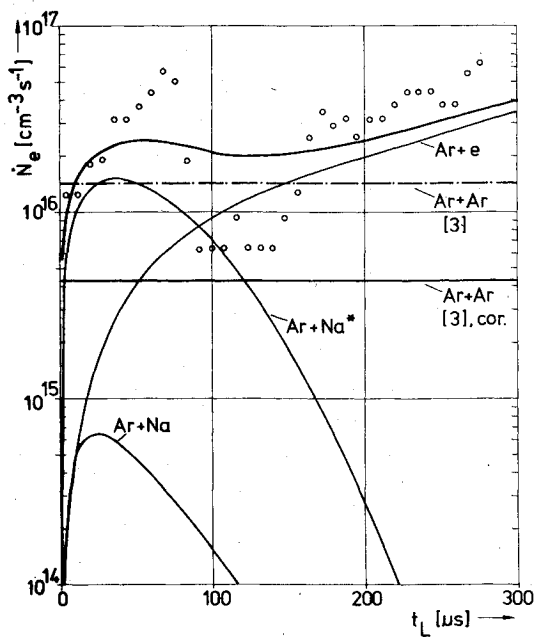

Fig. 3 Electron density gradient based on t_L as function of t_L. Experimental result in comparison to the sum of the simulated gradients and to the argon-argon rate of Ref. 3 with an without boundary-layer correction.

constant electron density appears. Here, the rate increase of electron density N_e drops to values much lower than at any time after the shock begins. This is shown in Fig. 3, where N_e derived from Fig. 2 is plotted vs t_L.

The participation of NaCl in the ionization process is included in our analytical simulation of the electron density (Fig. 2) and its time derivative (Fig. 3). Fourteen collisional and five radiative processes are taken into account, the most important of which are $Ar+Ar+15.76\ eV \rightarrow Ar+Ar^+ +e$, $Ar+e+15.76\ eV \rightarrow Ar^+ +e+e$, $Ar+NaCl+4.27\ eV \rightarrow Ar+Na^o+Cl$, $Ar+Na^o+2.1\ eV \rightarrow Ar+Na^*$, $Ar+Na^*+3.04\ eV \rightarrow Ar+Na^+ +e$, $Ar+Na^o+5.14\ eV \rightarrow Ar+Na^+ +e$, and $Na^* \rightarrow Na+h\nu$.

The superscripts (o, *, +) denote energy levels, i.e., the ground state, the excited state, and the ionization of particles, respectively. Our simulation approximates only roughly the experimental data of our test. Possible explanations of not reproducing the "bump" of Fig. 2 exactly may be missing impurity reactions such as those of Na_2O, for instance, or a time-dependent number of desorbed NaCl vapor molecules after shock passage. Also, in spite of repeated revisions of our reaction model,[4,5] some of our reaction rates may still be coarse approximations.

For comparison of our data, only Kelly's results are relevant as he applied a microwave diagnostic similar to ours. Kelly's measured electron density has an inflection point (see Ref. 2, Fig. 6), indicating a weak plateau as well, which we infer to mean the presence of similar reactions in Kelly's shock tube experiment as in ours. However, Kelly, as well as McLaren and Hobson, did not account for possible impurities in data reduction.

As a result of our analytical simulation and because of the activation energy of 9.1 eV [rather than 11.5 eV as expected (Ref. 2)] we conclude that previous investigators have unjustifiably neglected the influence of low ionization potential contaminants on the reaction rates in shock-heated argon. We suggest that for electron kinetics studies such as those of Refs. 2-4, experimental efforts must tend toward improved cleanliness (0.01-0.001ppm) of the shock tube and improved test equipment for the detection of impurity species.

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