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[Introduction]

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THE MOTION OF SLOW POSITIVE IONS IN GASES

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By P. G. DAVIES,* J. DUTTON and F. LLEWELLYN JONES

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IV. DRIFT AND DIFFUSION OF IONS IN HYDROGEN

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In part I the theoretical and experimental methods for the study of low energy positive ions in gases are reviewed and the available data for ions in atomic and common molecular gases are summarized.

It is shown that a large number of investigations of mobility $\mathscr{K}$ have been made, and that at low values of E/p_0 (E the electric field, p_0 the gas pressure under standard conditions), there is satisfactory quantitative agreement between theory and experiment for alkali ions in atomic and diatomic gases and for atomic ions in their parent monatomic gases. For all other cases and at high values of E/p_0, the situation is far less clear and much work remains to be done. In particular, further experimental measurements of mobility are required in which the ion species on which the observations are made are identified directly, and more theoretical quantum mechanical computations of mobility, especially when charge transfer occurs would be of interest.

As far as other quantities related to the motion of slow ions such as the diffusion coefficient D, the mean energy $\bar{\epsilon}$ and the collision cross-section Q are concerned, the review shows that there is a dearth of knowledge, and experimental determinations of these quantities would be of great value.

In parts II, III and IV an account is given of an experimental investigation of the motion of slow positive ions in nitrogen, argon and hydrogen. The principles of operation of an apparatus for the simultaneous measurement of $\mathscr{K}$ and D for ions are first discussed. The basic feature of this apparatus was the combination of a shutter-type electrode system, similar to that used by Tyndall & Powell (1930) for the measurement of $\mathscr{K}$, with an electrode system similar to that used by Townsend (1925) for the measurement of the ratio $D/\mathscr{K}$ for electrons. In the first practical construction of this arrangement it was found that large spurious currents to the ion collector of the diffusion section prevented measurements of diffusion, but that accurate measurements of mobility could be made.

This first apparatus was thus used to obtain results for the mobility of ions in nitrogen and argon and these results are discussed in parts II and III, respectively. The apparatus was calibrated by determining the mobility of potassium ions in nitrogen, since the zero-field mobility of these ions in this gas is well established; $\mathscr{K}$ was found to remain constant at its zero-field value of 2·55 $cm^2\,V^{-1}\,s^{-1}$ over the range of E/p_0 from 6 to 44 $V\,cm^{-1}\,mmHg^{-1}$. Measurements on the mobility of ions extracted from a glow discharge in nitrogen showed that there was a single ion species present, the value of $\mathscr{K}$ for which remained constant at 2·5 $cm^2\,V^{-1}\,s^{-1}$ over the range of E/p_0 from 4 to 42 $V\,cm^{-1}\,mmHg^{-1}$. Consideration of mass spectrometric evidence and comparison of the results with other recent data led to the conclusion that this value of $\mathscr{K}$ probably referred to N^+ ions.

In argon the mobility of potassium ions was found to remain constant at 2·75 $cm^2\,V^{-1}\,s^{-1}$ for $8 < E/p_0 < 28$ $V\,cm^{-1}\,mmHg^{-1}$. When we used as an ion source a glow discharge in argon, which was shown by mass spectrometric analysis to contain small quantities of hydrogen, two ions having zero-field mobilities of 2·9 and 2·05 $cm^2\,V^{-1}\,s^{-1}$ were observed. Analysis of the experimental data led to the conclusion that the slower species was formed from the faster species after a sufficient number of collisions with gas atoms. In view of the presence of hydrogen in the argon sample the faster ion with mobility 2·9 $cm^2\,V^{-1}\,s^{-1}$ was considered to be ArH^+, but the identity of the slower ion was uncertain.

In part IV a second redesigned experimental arrangement which successfully eliminated the spurious currents to the ion collector of the diffusion section is described. With this second apparatus measurements of both $\mathscr{K}$ and $D/\mathscr{K}$ were obtained for ions extracted from a glow discharge in hydrogen. A single ion species with zero-field mobility 10·8 $cm^2\,V^{-1}\,s^{-1}$ was observed. For $E/p_0 \lesssim 10$ $V\,cm^{-1}\,mmHg^{-1}$ the mobility remained constant at 10·8 $cm^2\,V^{-1}\,s^{-1}$ and the ratio $D/\mathscr{K}$ remained constant at 0·025 V. For higher values of E/p_0, $\mathscr{K}$ and the ratio $D/\mathscr{K}$ increased and for $E/p_0 \gtrsim 25$ $V\,cm^{-1}\,mmHg^{-1}$ the ratio $D/\mathscr{K}$ was found to be linearly dependent on E/p_0. The results were analysed to give values of D, of the ratio of the mean energy of the ions to that of the gas molecules ϵ, and of the collisional cross-section Q.

The results for ϵ showed that the ions remained in thermal equilibrium with the gas molecules for $E/p_0 \lesssim 10$ $V\,cm^{-1}\,mmHg^{-1}$, but that at higher values of E/p_0 the energy began to increase. As the energy increased, Q decreased rapidly and the mobility increased, both of which are consistent with the assumption of an ion species which undergoes a dissociative reaction with the gas molecules at energies slightly greater than gas kinetic. Although no direct identification of the ions was possible, the above observations were consistent with the identification of the species with zero-field mobility of 10·8 $cm^2\,V^{-1}\,s^{-1}$ as H_5^+, which has been observed in recent mass spectrometric analyses of ions produced in hydrogen discharges.