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Interpretation of Ion-Mobility Experiments in Reacting Systems

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The Tyndall drift-tube experiment with a pulsed ion source has been analyzed for the case of two ions that interconvert in the drift space. Exact solutions for the relevant differential equations have been obtained. It is shown that when the time constants of the interconversion reactions become commensurate with the ion drift times, the ion velocities are given by the initial and final bounds of the ion-arrival curves for the fast and slow ion, respectively. Peaks which may occur at intermediate times are a consequence of the reacting system and must not be misinterpreted as an ion transit time. It is also shown that the reaction time constants may be extracted from the experimental data, if the analysis is extended to include diffusion and effects of the finite time resolution of the experiment. For this purpose a numerical simulation of the system is required. The relationship between this numerical approach and the analytical solution is demonstrated.

THE classical ion drift-mobility experiment has frequently yielded data which could not be interpreted on the basis of any theory for the mobility of a unique ion. Thus, while one is led to expect a mobility which is constant at low ion energy and falls off gradually as higher values of energy are approached, many systems, e.g., N_2, H_2, and Ar, yield peculiar results which do not fit this picture. One has been often forced to assume the presence of more than a single ion species whose relative abundances were energy-dependent in order to explain the experimental data.[1,2] In a number of cases attempts were made to assign identities to the various species by comparison of the measured mobilities with the predictions of classical collision theory. As later developments were to show, these attempts were not always successful, the difficulties mainly being associated with this multiple ion situation.

Improvements in experimental methods which permitted the observation of fine structure in drift current transients were accompanied by attempts at analysis of these curves in terms of two or more species which interconvert in the drift space. Burch and Geballe[3] applied such an analysis to the clustering of oxygen negative ions; the interconversion of ions in nitrogen has been investigated by Woo[4] and by Bloomfield and Hasted.[5] Waveforms observed in a pulsed Townsend discharge were treated in detail by Edelson and McAfee.[6] Beaty and Patterson[7] obtained a solution for the case of two ion species where unidirectional conversion of one ion to the other may occur in the drift region, and including the effects of diffusion. This was found to be in excellent agreement with their experimental results in helium, for which they were then able to calculate an attachment rate of He^+ to He. Other systems, notably the nitrogen experiments, have not been as successfully explained, because of the presence of more than two ion species and the necessity of taking into account the reverse as well as the forward reactions.

Within the past few years, several groups of investigators[8–10] have developed techniques for mass analysis of the ions as they arrive at the end of the drift space. Besides providing positive identification for the ions, these experiments have also served to reinforce some of the earlier conclusions as to the existence of several ionic species and their dependence on energy and pressure. Here too further complexities began to manifest themselves, with the observation of ion arrival histograms which were highly unsymmetrical and, in some cases, multiply peaked.[10,11] The inevitable conclusion was reached as before that one was observing ions which were reacting with the neutral gas through which they were drifting. The new experiments, by providing a separation of the fluxes due to the different ions, enables these processes to be seen more clearly and in greater detail than if only total current is measured. For example, the dissociation reaction in the N_2^+-N_4^+ system, which was neglected previously becomes quite obvious.[12] Analysis of these data, however, requires a more advanced treatment than heretofore; it is now necessary to include both the forward and reverse reactions in the equations. Furthermore, solutions for

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[1] R. N. Varney, Phys. Rev. **89**, 708 (1953).

[2] F. R. Kovar, E. C. Beaty, and R. N. Varney, Phys. Rev. **107**, 1490 (1957).

[3] D. S. Burch and R. Geballe, Phys. Rev. **104**, 188 (1957).

[4] S. B. Woo, J. Chem. Phys. **42**, 1251 (1965).

[5] C. H. Bloomfield and J. B. Hasted, Brit. J. Appl. Phys. **17**, 449 (1966).

[6] D. Edelson and K. B. McAfee, Jr., Rev. Sci. Instr. **35**, 187 (1964).

[7] E. C. Beaty and P. L. Patterson, Phys. Rev. **137**, A346 (1965).

[8] K. B. McAfee, Jr., and D. Edelson, Bull. Am. Phys. Soc. **7**, 634 (1962); in *Proceedings of the Sixth International Conference on Ionization Phenomena in Gases, Paris, 1963* (S.E.R.M.A., Paris, 1964), Vol. 1, p. 299; Proc. Phys. Soc. (London) **81**, 382 (1963).

[9] D. W. Martin, W. S. Barnes, E. W. McDaniel, and D. S. Harmer, Bull. Am. Phys. Soc. **7**, 634 (1962); in *Proceedings of the Sixth International Conference on Ionization Phenomena in Gases, Paris, 1963* (S.E.R.M.A., Paris, 1964), Vol. 1, p. 295; Rev. Sci. Instr. **33**, 2 (1962).

[10] M. Saporoschenko, Phys. Rev. **139**, A352 (1965).

[11] G. E. Keller, D. W. Martin, and E. W. McDaniel, Phys. Rev. **140**, A1535 (1965).

[12] L. G. McKnight, K. B. McAfee, and D. P. Sipler, preceding paper, Phys. Rev. **164**, 62 (1967).

the ion densities rather than drift currents are required; this is inherently a more difficult mathematical task.

In this paper an analytic solution will be presented for the spatial and temporal dependence of the ion densities in a drift space in which two ions are interconverting by reaction with the neutral gas. These results are used to survey in a general manner the observations to be expected over a wide range of reaction rate and mobility parameters. They are not, however, suitable for detailed analysis of experimental data because they fail to include a number of effects by which the experiments differ from the idealized theoretical case. Including these other factors makes the problem no longer tractable by purely analytic methods and it becomes necessary to resort to a numerical solution of difference equations. The results of the two calculations are compared; in a companion paper their application to the reduction of experimental data is demonstrated.[12]

THE ANALYTIC SOLUTION

Consider a drift region in which there exists a unidirectional constant field. At zero time we introduce a δ function of ions of species 1 at the starting point $x=0$, and these will drift along the field (x direction) at a velocity v_1. At the same time they will undergo a reaction in the ambient gas to yield ions of species 2 which proceed to drift with a different velocity v_2. For the sake of generality, we assume further that these product ions may also react to give back ions of species 1, i.e., the reaction is reversible. Taking the reaction to be first order in the ion densities ρ, the continuity equations governing the drift of the ions can be simply written as

$$\frac{\partial\rho_1}{\partial t}+v_1\frac{\partial\rho_1}{\partial x}=-\frac{\rho_1}{\lambda_1}+\frac{\rho_2}{\lambda_2}\,, \tag{1a}$$

$$\frac{\partial\rho_2}{\partial t}+v_2\frac{\partial\rho_2}{\partial x}=\frac{\rho_1}{\lambda_1}-\frac{\rho_2}{\lambda_2}\,, \tag{1b}$$

where λ_1 and λ_2 are the time constants for the forward and reverse reactions, respectively. Diffusion of the ions has been neglected. The initial conditions are given by

$$\rho_1(x,0)=\sigma(x)=\delta(x)\,, \tag{2a}$$

$$\rho_2(x,0)=0\,. \tag{2b}$$

Proceeding by Laplace transformation, we obtain

$$\bar{\rho}_1=\lambda_1\left[\left(p+\frac{1}{\lambda_2}\right)\bar{\rho}_2+v_2\frac{d\bar{\rho}_2}{dx}\right], \tag{3a}$$

$$\bar{\rho}_2=\frac{e^{-(\alpha p+\beta)x}\left[e^{\gamma x[(p+\mu)^2+\nu^2]^{1/2}}-e^{-\gamma x[(p+\mu)^2+\nu^2]^{1/2}}\right]}{2\lambda_1 v_1 v_2\gamma[(p+\mu)^2+\nu^2]^{1/2}}\,, \tag{3b}$$

where

$$\alpha=(v_1+v_2)/2v_1v_2\,,\quad \gamma=|v_1-v_2|/2v_1v_2\,,$$
$$\beta=(\lambda_1v_1+\lambda_2v_2)/2\lambda_1\lambda_2v_1v_2\,,$$
$$\mu=(\lambda_1v_1-\lambda_2v_2)/\lambda_1\lambda_2(v_1-v_2)\,,$$
$$\nu^2=4v_1\nu_2/\lambda_1\lambda_2(v_1-v_2)^2\,.$$

The solution is found to be[13]

$$\rho_1=\frac{1}{v_1}e^{-\mu t}e^{-(\beta-\mu\alpha)x}\left\{\delta\left(t-\frac{x}{v_1}\right)+\frac{(v_2-v_1)}{2|v_1-v_2|}\left(t-\frac{x}{v_2}\right)\times\frac{\nu I_1\{\nu[\gamma^2x^2-(t-\alpha x)^2]^{1/2}\}}{[\gamma^2x^2-(t-\alpha x)^2]^{1/2}}\times H[(\alpha+\gamma)x-t]H[t-(\alpha-\gamma)x]\right\}, \tag{4a}$$

$$\rho_2=\frac{e^{-\mu t}e^{-(\beta-\mu\alpha)x}}{\lambda_1|v_1-v_2|}I_0\{\nu[\gamma^2x^2-(t-\alpha x)^2]^{1/2}\}\times H[(\alpha+\gamma)x-t]H[t-(\alpha-\gamma)x], \tag{4b}$$

where I_0 and I_1 are the hyperbolic Bessel functions. H is the Heaviside step function $H(+)=1$, $H(-)=0$. An equivalent solution has been published by Frommhold.[14]

Several things are immediately obvious from examination of these solutions. The initial δ function of ions of species 1 persists and moves with velocity v_1; the number of ions in this δ function is reduced in time and space by the exponential factors appearing at the left. As ions of species 1 disappear, a distribution of ions of species 2 grows; some of these ions are converted back into species 1, etc. The resultant distributions of derived ions are given by (4b) and the second term in (4a). The step functions cut off these distributions so that no ion arrives sooner than the transit time of the faster ion nor later than that of the slower ion, a result which would be necessarily expected.

To give some insight into the experimental observations which would be predicted by this model, plots are presented (Figs. 1–4) for a number of representative cases over a wide range of parameters. Plotted is the ion density at an imaginary electrode representing the end of the drift space x_t; this is proportional to the actually measured quantity which is the flux through the electrode, $v_i\rho_i(x_t,t)$. The δ functions are shown as heavy lines whose heights are proportional to their integrated ion density. No normalization has been made, the object merely being to indicate the general features of curves. The upper and lower time bounds have been slightly offset for the sake of clarity.

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[13] A. Erdelyi, *Tables of Integral Transforms* (McGraw-Hill Book Company, New York, 1954), Vol. 1, p. 282, formula 26.

[14] L. Frommhold, Fortschr. Physik. **12**, 597 (1964).

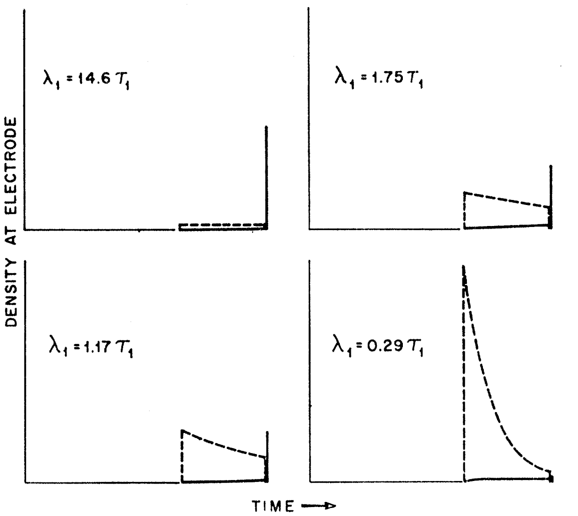

FIG. 1. Calculated ion densities at electrode surface for an initially injected slow ion decaying to a faster ion, with a very slow reverse reaction $\lambda_2 = 1000\tau_2$. Reaction time constant λ and transit time τ, in the ratio indicated. Initial ion, solid line; secondary ion, dashed line.

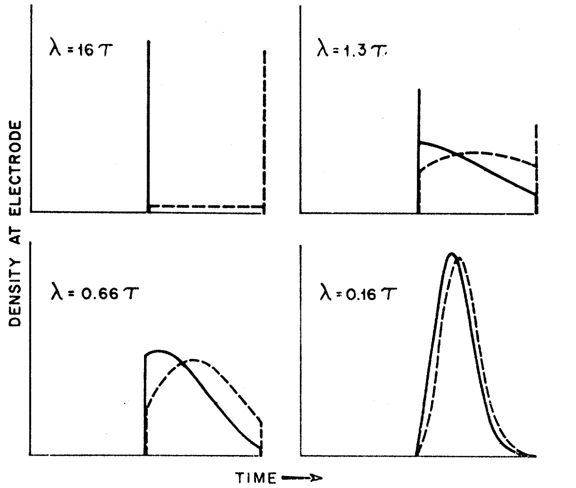

FIG. 3. Initial injection of a mixture of equal amounts of slow and fast ion; equal forward and reverse reaction times. Fast ion, solid line; slow ion, dashed line.

In Figs. 3 and 4 we have started with equal quantities of ions of both species present. Since the differential equations are linear this is easily done by superimposing two solutions, one for each species of initial ion.

Several features are common to all the curves. Foremost is the obvious one that all are bounded by the transit times of the two ions. It is therefore always possible, in principle at least, to simply extract the individual ion mobilities from the data, provided the edges of the distributions are sufficiently far out of the noise to be clearly discernable. A corollary conclusion is that the arrival time of a maximum in ion intensity can be used to assign a mobility if, *and only if*, it can be shown that it is truly the remains of the initially introduced δ function. When it is considered that the δ function will be drastically transformed by the effects of diffusion and the finite resolution of the instrumentation, it becomes apparent that this assignment may be not at all obvious. Some of the curves show two peaks; others show highly misleading sharp and symmetrical peaks which are in fact due to a rapidly reversible reaction and which appear at some intermediate time. One must be careful even when treating the δ function, especially if it bounds a sharply rising or falling distribution. Diffusion will not only broaden the composite

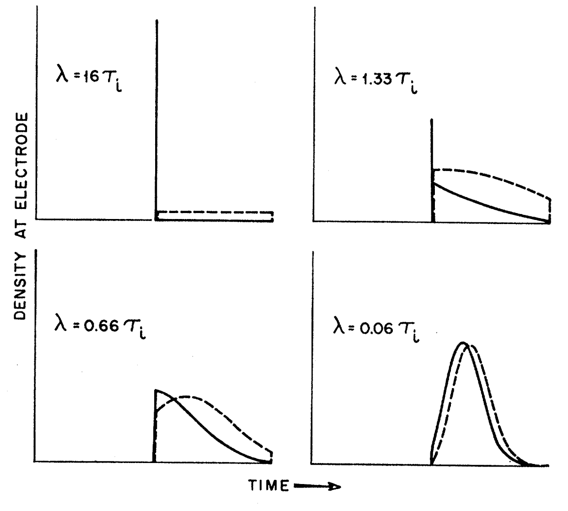

FIG. 2. Initial fast ion decaying to a slower ion, with an equal reverse reaction time.

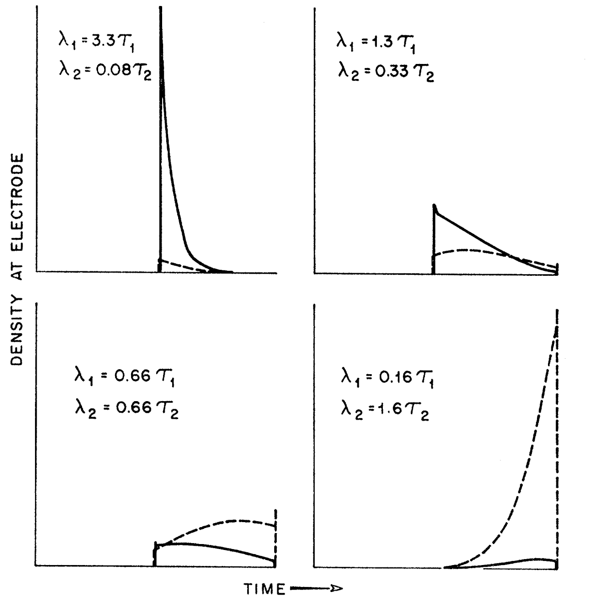

FIG. 4. Initial injection of a mixture of equal amounts of slow and fast ion; equilibrium constant shifting from predominantly fast to predominantly slow ion.

waveform, but will shift its maximum, so that while a correct interpretation of the peak is made, the mobility calculated from it is in error. In summary, one must conclude that a careful scrutiny of the curves and their variation with such factors as pressure, field, and flight distance is necessary to avoid incorrect conclusions. Unfortunately this has not always been done in the past, and many errors and inconsistencies in published values has been the result.

THE NUMERICAL SOLUTION

While the discussion of the previous section has been devoted largely to consideration of transit time and mobility determinations, it is evident that a detailed analysis of experimental data should be capable of yielding the reaction rates as well. Here, however, one runs into difficulty with the analytic solution because it does not include diffusion or the finite time and space resolution of the measurement, which drastically alter the shapes of the observed curves. Any attempt to include such effects, except as very small perturbations, would render the differential equations intractable. We have therefore resorted to a numerical approach to simulate the actual experiments. Comparison with the data should then yield the desired parameters.

Briefly, the simulation program is started with two square pulses representing the density of the ions entering the drift space in the x direction through the Tyndall gate. The drift distance was divided into cells of width Δx which was small enough so that the initial pulses would occupy several of these cells. The program then simulated the effect of drift, diffusion, and reaction by applying them to each individual cell in the drift space at time intervals Δt, where Δt was short enough to ensure that waveform distortion due to the finite time intervals was small. Movement of the ions in the cell was accomplished by movement of the total charge distribution for each ion through the correct number of spaces n for the ion drift velocity v_d and the space and time intervals chosen:

$$n\Delta x = v_d \Delta t.$$

Interaction of the ions was simulated after every time interval Δt by subtracting the proper fraction of ions of one type in the cells and adding them to the corresponding cells of the other ion. The reverse reaction was treated in the same way. Diffusion was effected for each ion by calculating and subtracting the amount of charge in each cell which would appear in neighboring cells in Δt and then adding to the charge left in the cell the amounts which would diffuse in from neighboring cells. The whole process of charge movement, reaction, and diffusion was repeated at intervals Δt until the ion distributions reached a distance $x = L$ which corresponded to the length of the drift space. Here the density in the cell at L was converted into a relative flux through the electrode by multiplying the density by the drift velocity of the ion. This current was recorded for both ions at each time t until virtually all of the ions had passed the distance L at which time the calculation was terminated. The time-versus-current curves generated in this way represented the ion current transients which would be observed for each ion for the given input parameters. Computation time for the current transients for each set of experimental parameters was about 12 sec on an IBM 7094.

Some modifications were made in the above outline for programming convenience. The principal one was the use of a moving x' axis which moved in a positive direction with the velocity of the slow ion; that is,

$$dx_0'/dt = v_d \text{ (slow ion)},$$

where x_0' represents the abcissa of the origin of the new system. Using this moving axis, the velocity of the slow ion becomes zero and the ion simply diffuses and reacts from a stationary distribution. The drift velocity of the fast ion along the x' axis is then

$$v_d' \text{ (fast ion)} = v_d \text{ (fast ion)} - v_d \text{ (slow ion)}.$$

The cell size $\Delta x'$ and the time interval Δt are then chosen so that

$$\Delta x'/\Delta t = v_d' \text{ (fast ion)},$$

which corresponds to moving all the ionic charge of the fast ion one cell, $\Delta x'$, for each time interval Δt. In this way the cell size could be kept the same for the fast and slow ions, and the different drift velocities for the two ions did not move the cells of one ion relative to those of the other. In addition, it was easy to confine the calculation to the space in which the ion charge density was appreciable.

The fraction of ions of one type converted to the other during time interval Δt was calculated from the relationship

$$\frac{\Delta Q_1}{Q_1} = \frac{\Delta(\rho_1 \Delta x')}{\rho_1 \Delta x'} = 1 - e^{-\Delta t/\lambda_1},$$

where Q_1 is the ion charge for species 1 in a given cell, ΔQ_1 the amount converted to species 2, and λ_1 the time constant for the reaction. ΔQ_1 was then subtracted from the charge of species 1 in the cell and added to that of species 2 in the corresponding cell. The reverse process, using the time constant λ_2, similarly moved ions from species 2 back to species 1.

The diffusion process after each time Δt treated each cell separately and was based on the diffusion of a square pulse containing density ρ and of width $\Delta x'$, corresponding to one cell. After each Δt, the envelope of the charge diffusion from the cell was computed from the relationship

$$\rho=\frac{dQ}{d\xi}=\frac{\rho_0}{2}\left[\operatorname{erf}\left(\frac{\Delta x'+2\xi}{4(D\Delta t)^{1/2}}\right)+\operatorname{erf}\left(\frac{\Delta x'-2\xi}{4(D\Delta t)^{1/2}}\right)\right],$$

where D is the diffusion constant and ξ is the distance from the center of the diffusing cell along the x axis. ρ_0 is the original charge density within the cell.

Integration to a distance α from the center of the cell gives

$$\int_0^\alpha \rho d\xi=\tfrac{1}{4}\rho_0\left\{(2\alpha+\Delta x')\operatorname{erf}\left(\frac{2\alpha+\Delta x'}{4(D\Delta t)^{1/2}}\right)+(2\alpha-\Delta x')\operatorname{erf}\left(\frac{\Delta x'-2\alpha}{4(D\Delta t)^{1/2}}\right)+4\left(\frac{D\Delta t}{\pi}\right)^{1/2}\exp\left[-\left(\frac{\Delta x'+2\alpha}{4(D\Delta t)^{1/2}}\right)^2\right]-4\left(\frac{D\Delta t}{\pi}\right)^{1/2}\exp\left[-\left(\frac{\Delta x'-2\alpha}{4(D\Delta t)^{1/2}}\right)^2\right]\right\},$$

where

$$\int_0^\infty \rho d\xi=\tfrac{1}{2}\Delta x'\rho_0=\tfrac{1}{2}Q.$$

The fraction of charge remaining in the original cell is twice the integral from 0 to $\frac{1}{2}\Delta x'$, the factor of 2 occurring because the origin of the charge distribution function is at the center of the cell. Integration through the proper limits will give the fraction diffusing into the cells once and twice removed from the original cell. The fraction of the original charge which had diffused beyond the second cell from the original was lumped into the third cell. In the event that this fraction exceeded 0.06, the program rejected the calculation and it was necessary to rerun the program with a different cell size. If the fraction in the third cell was less than 0.02, the program added the fraction to the second cell and set diffusion to the third cell equal to zero. The diffusion constants D were adjustable parameters, but the ratio of the diffusion constants for ions drifting under the same conditions were kept in the ratio of their drift velocities.

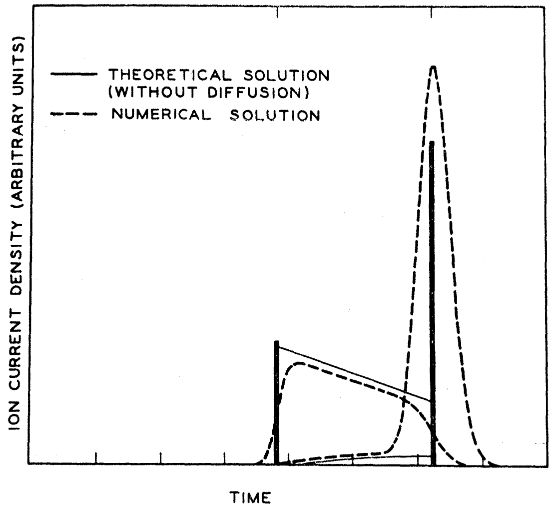

FIG. 5. Comparison of analytic and numerical solutions.

The initial pulse shapes were chosen to correspond as closely as possible with the actual entrance condition. The pulse widths were taken as the product of the individual ion drift velocities times the gate open time, usually 1 μsec. The heights of the initial pulses were adjustable to allow for variation of the relative amounts of the two interacting ions. The effect of radial diffusion was not considered since the geometry of the source and the cell combined with the use of a centrally located exit slit would make the effect negligible under our experimental conditions. No effort was made to account for possible end effects due the presence of the slit and the absorbing plate of the end of the drift space, and the calculation was simply continued until the last of the ions had covered the total distance.

Figure 5 presents a comparison of the analytic and numerical solutions for a particular case involving an initial mixture of two ions. Examination of the curves shows that the inclusion of the diffusion effect leads to the expected broadening of the transients, and in this case, even obscures the δ function of the more mobile ion. It is equally apparent that, were one to start with experimental results of the form of these curves, it would be necessary to consider in detail all these effects to properly interpret the data. Even assignment of a drift velocity to the faster ion, for example, becomes ambiguous unless this is done. In the preceding paper,[12] the use of these results in the interpretation of experiments is treated in greater detail.