MASS SPECTROMETRIC STUDY OF MOBILITY, DIFFUSION,
AND REACTIONS OF IONS IN GASES

By
Earl W. McDaniel

Final Scientific Report
Covering the Period July 1, 1971 — September 30, 1973

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October 1, 1973

School of Physics
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

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ABSTRACT

The research on slow ions in gases performed at the Georgia Institute of Technology with a drift tube mass spectrometer during the period July 1, 1971 through September 30, 1973 is described. The research dealt with the measurement of ionic mobilities, diffusion coefficients, and reaction rates. Emphasis was placed on studies of clustering of K$^+$ ions in N$_2$, H$_2$, He, Ne, Ar, O$_2$, NO, CO, and CO$_2$; on tests of the Wannier diffusion equations; on the differences in behavior of K$^+$ ions in N$_2$ and CO; and on measurements on ions, formed from CO, drifting in carbon monoxide gas. Improvements in the experimental apparatus and analytical techniques are described.
A. Statement of Activities and Accomplishments During Reporting Period

As stated to representatives of A.F.O.S.R. in Washington, D. C. during April, 1972, we have departed considerably from the objectives originally outlined in our proposal to cover this reporting period. The reasons for this departure are discussed below.

I. Departure from Original Objectives, and Research Results Obtained.

(a.) Elford's Observation of Dependence of Reduced Ionic Mobility upon Pressure. In 1971, Dr. M. T. Elford of the Australian National University sent us a preprint of a paper and asked us for our opinions concerning it. In this paper, he reported that he had observed that the reduced mobility of unclustered \( \text{K}^+ \) ions in \( \text{N}_2, \text{H}_2, \text{He}, \text{Ne}, \text{and Ar} \) shows a slight, explicit dependence on the pressure of the gas used in his drift tube for the measurements. Elford's observation, if it had been correct, would have had serious repercussions at the foundations of the transport theory for particles in gases, for it is at variance with all existing mobility theories for low-pressure gases. We did not believe his effect to be real, but we thought that his observation would probably be taken seriously by many people because of the excellent reputation that Elford enjoys. Hence we decided to undertake research directed toward testing the validity of his conclusion.

We made measurements, with our drift tube mass spectrometer, on \( \text{K}^+ \) ions in all of the gases studied by Elford, \( \text{CO}_2, \text{O}_2, \text{NO}, \text{and CO} \). In each case, we observed clustering of molecules to the ions under the conditions prevailing in Elford's experiments. The clustering in \( \text{N}_2, \text{Ar, O}_2, \text{NO, CO, and CO}_2 \) was extensive enough to vitiate measurements of the type that Elford made. In addition, Professor Gatland, of our group, made calculations that showed that diffusion
effects in all of Elford's experiments (which Elford did not take into account) could have accounted for most of Elford's effect. We are now satisfied that Elford's conclusion about the pressure effect is based on insufficient evidence, and that consequently there is no reason to believe that the transport theory of ions in gases contains the basic flaw implied by Elford's observation. Our findings are presented in references 2, 4, and 6 of Section B of this report. The last-cited reference contains a general discussion of the effects of diffusion and reactions on the measurement of ionic mobilities.

We consider the time spent on this research to have been well spent, in the light of the serious consequences that Elford's conclusion (which has now been published in the Australian Journal of Physics) would have had if it had remained unchallenged and believed true.

(b.) Tests of the Wannier Equations for Ionic Diffusion Coefficients. Early in 1971, we published a paper [E. W. McDaniel and J. T. Moseley, Phys. Rev. A, 2, 1040 (1971)] in which we compared the scanty, existing experimental data on longitudinal and transverse diffusion coefficients of ions in gases ($D_L$ and $D_T$, respectively) with certain predictions of a theory published by Wannier in 1953. This theory had never been tested in this fashion—indeed, data to do so became available only in the late 1960's. Most of the $D_L$ data at hand even today are from our laboratory, and all of the $D_T$ data for mass-identified ions published before 1972 had been obtained with our apparatus at Ga. Tech. For the test of the Wannier diffusion coefficient equations, we transformed them from a dependence upon the non-observable quantity $\tau$ (the mean free time between collisions) to the observable $v_d$ (the ionic drift velocity). We found that the Wannier equations appeared to be obeyed rather well over the range of the relatively poor quality data then available. We considered this
finding to be important from the practical standpoint for the following reason. In experimental determinations of the rate coefficients of ion-molecule reactions, it is important to assess the effects of both longitudinal and transverse diffusion in the analysis of the experiments, and we have shown how to make this assessment quantitatively. Hundreds of such reactions are of great significance in upper atmospheric physics (in the study of radar blackouts, for example), in gas lasers, in radiation chemistry, and in other fields. However, diffusion coefficients for only a few ion-molecule combinations had been directly measured in 1971. Hence, the demonstration of even the approximate validity of theoretical equations for $D_L$ and $D_T$ for the combinations that had been studied experimentally meant that one could probably use the Wannier equations with a fair degree of confidence to calculate values of $D_L$ and $D_T$ for use in applications when experimental data were unavailable.

During the first nine months of the period covered by this report, we made many significant improvements in our apparatus and analytical techniques, some of which will be discussed in Section II. These improvements have enabled us to make refined measurements of $D_L$ which are about a factor of 10 more accurate than most of our previous measurements. We expect to be able to realize a comparable improvement in our determinations of $D_T$. Hence we are now in a vastly improved position to make sensitive tests of the Wannier predictions of diffusion coefficients. We have now completed such tests of $D_L$ for $K^+$ ions in $N_2$, CO, Ar and He. The agreement of our experimental $D_L$ data with our modification of the Wannier equation for $D_L$ is impressive. For $N_2$, our thermal energy experimental value agrees with the theory to within 0.6%; for CO, Ar, He, the agreement is within 2%. We are in extremely close agreement with the predictions of the modified Wannier theory up to $E/N = 155$ Td for $N_2$ and $E/N = 200$ Td.
for CO. The average ionic energies at these values of E/N are 0.55 and 0.79 eV, respectively. The agreement with the original form of the Wannier equation for \( D_\parallel \) (expressed in terms of \( \tau \)) is not as good for ionic energies above thermal, and we consider this fact to be significant.

Shortly after our work on \( K^+ \) ions in \( N_2 \) and CO was concluded, Professor E. A. Mason sent us the results of a new theory that he and Dr. J. H. Whealton had developed. This theory provides a second-order correction to the usual diffusion theory which is negligible at low \( E/N \) but which can be very important at high \( E/N \). The Whealton-Mason correction to our modified Wannier equations gives even better agreement between theory and our experimental data on \( K^+ \) ions in \( N_2, CO, Ar, \) and He. Our conclusion is that for the purpose of estimating diffusion coefficients when experimental values are unavailable, one should probably use our modification of the Wannier equations but with the Whealton-Mason correction applied. Our work on \( K^+ \) ions in \( N_2, CO, \) and Ar has been published in refs. 6 and 9 of Section B. The measurements on \( K^+ \) ions in He will be described in ref. 1 of Section C, which will also deal with research on Ne which is almost completed.

(c.) Comparison of Transport Properties of \( K^+ \) Ions in \( N_2 \) and CO. A third activity that has occupied a significant amount of our time has been the accurate measurement and detailed comparison of mobilities (as well as longitudinal diffusion coefficients) of \( K^+ \) ions in \( N_2 \) and CO. The molecules of these gases are extremely similar; e.g. they are both diatomic, have the same mass, are composed of similar atoms, have similar atomic spacings, and are isoelectronic. The only major difference is that CO has a small, permanent electric dipole moment, whereas \( N_2 \) has none. We were interested in making a detailed assessment of the effect of the dipole moment of CO upon the transport properties of the ions. This work has been completed and is discussed at length from both the experimental and theoretical standpoints in ref. 6 of Section B. In our opinion, our results may be of considerable interest in terms of improving the basic understanding of the transport of ions through gases.
(d.) **Measurements on Ions of CO in CO Gas.** In addition, we have made measurements of the mobilities of \( \text{CO}^+ \), \( \text{CO}^+ \cdot \text{CO} \), and \( \text{C}^+ \) ions in CO, longitudinal coefficients of \( \text{CO}^+ \) ions in CO, and the rate coefficient of the reaction \( \text{CO}^+ + 2\text{CO} \rightarrow \text{CO}^+ \cdot \text{CO} + \text{CO} \). All of the measurements were made over a significant range of \( E/N \). These results appear in the report by Schummers, et al. (ref. 1 of Section E) and in references 7 and 8 of Section B. No accurate measurements of these quantities appear to have been made previously.

We believe that the research described here and in the sections above has been more significant and useful than that which we originally proposed to do, in that it relates more immediately with the theoretical developments now taking place in the field.

II. Modifications of Apparatus and Analytical Techniques.

Among the more important changes made in our apparatus and analytical techniques during this reporting period were the following:

(a.) **Removal of Ion Source Magnet.** The ion source which had been in use since the construction of our drift tube mass spectrometer contained a permanent magnet whose function was to confine, to a narrow ribbon, the beam of electrons producing the ionization in the gas when the source was operated in the electron-impact mode. This magnet was known to produce a fringe field in the neighboring region of the drift tube. Late in 1971, during work on the \( \text{CO}^+ \) reaction, this fringe field was found to distort certain arrival time spectra of secondary ions formed early during the drift of the parent species. (Apparently it had not affected our previously published data to a significant extent.) Upon removal of the magnet, the distortion of the arrival time spectra disappeared, and discrepancies which had been occurring in our research on the \( \text{CO}^+ \) reaction were eliminated. With the magnet removed, there is sometimes a
very slight leakage of ions into the drift space when the Tyndall gate at the exit of the ion source is closed, but this leakage has not been a problem to date.

(b.) **Installation of Refrigerating Vapor Bath.** The conventional cold trap in the gas feed line of our apparatus was replaced by a "refrigerating vapor bath". The gas to be admitted to the drift tube can be stored in this device at any temperature between 0°C and -196°C, and this technique results in much more efficient trapping of impurities in some cases than was possible with the conventional cold trap. The RVB proved essential in our study of clustering of $K^+$ ions in NO, and in all of our work on CO.

(c.) **Improvement of Electronics.** A variable delay and "multipulsing" scheme was developed which permits the sampling of one ion cloud arriving at the bottom of the drift tube while as many as six other ion swarms are in transit down the drift space. This technique is feasible whenever the drift time is much greater than the span of arrival times of the ions in a given cloud. A major advantage of multipulsing is that it allows data to be accumulated at a much faster rate, and the variable delay feature significantly increases the effective time resolution of the measurements. The multipulsing feature apparently is unique to our apparatus.

(d.) **Relocation of Detector.** An improved, off-axis detector arrangement was introduced, wherein the electron multiplier detector is mounted off the axis of the apparatus and tilted at an angle. This new arrangement markedly reduces the number of noise pulses which are recorded and improves the pulse height distribution of the counts.
(e.) **Installation of Aperture Stop.** An aperture stop was placed over the hole through which the ions enter the drift region from the ion source. This aperture stop makes it possible to approach more closely the condition of a radially uniform input of ions which is assumed in our mathematical model of the apparatus.

(f.) **Studies of the Onset of Electrical Discharges in the Drift Tube.** We would like to be able to make measurements at high values of $E/N$ without having to operate at extremely low pressures in the drift tube, because at low pressures the mean free paths of the ions may not be sufficiently small for our analysis to be accurate to a high degree. However, we are limited in this respect because if we operate at pressures higher than about 50 micron at very high $E/N$, we must apply such high potentials to the drift field electrodes that an electrical discharge develops. In order to investigate this problem, we removed the drift tube from the main vacuum chamber and fitted it with a thick lucite top so that we could pump it down, directly watch the discharge onset, and see where it occurred. We had hoped that it would occur at some location where a reworking of the electrical connections would eliminate the difficulty, but it turned out that the discharge took place from the top drift field electrode to ground. Hence we are unable to make the desired improvement without substituting a smaller-diameter set of drift field electrodes, which would result in lateral diffusion loss of ions to the walls. The net effect of such a substitution would be disadvantageous, so we decided to retain the original configuration.

(g.) **Studies of the Effects of Varying the Skimmer Voltage on the Arrival Time Spectra.** At high $E/N$ and hence short drift times, a noticeable spurious spread in observed arrival times may result if the ions are not accelerated rapidly to the detector after they emerge from the drift tube. We made an extensive series of tests to assess this effect by operating with skimmer voltages
ranging from zero to 75 volts. We did indeed observe the effect, but determined that a skimmer voltage of about 50 volts is adequate to eliminate it. Consequently, whenever possible we now use a skimmer voltage of this magnitude.

(h.) Development of Surface Ionization Ion Source. In order to obtain more flexibility in the choice of ions to use in our diffusion studies, we have developed a low power, miniature surface ionization ion source for our drift tube. Initial runs using a quadrupole mass analyzer to identify the ions were successful with indium and barium metal charges. The barium run lasted for 80 hours, yielding a current in the $10^{-9}$ ampere region before the metal charge was exhausted. The source power requirements and dimensions are less than 20 watts and $\frac{1}{2} \times \frac{1}{2} \times 1^\prime$, respectively.

The source is made from two cylindrical tubes. A $\frac{1}{4}$" stainless steel tube serves as the boiler, where the charge is placed, and is heated by a surrounding nichrome wire heater. A $\frac{3}{8}$" diameter molybdenum tube protrudes from the boiler and serves as a gas transfer line and ionization filament chamber. The innovative part of the source consists of a three-inch rhenium ribbon, spiral wound, ionization filament which is placed inside and at the end of the molybdenum tube opposite the boiler. The low power requirements are satisfied by direct electrical heating of the filament. Current flows between the center of the spiral, to which a .010" tungsten wire is spot welded, and the outside of the spiral which is in contact with the molybdenum tube. Good gas economy is achieved because all the gas produced in the boiler must flow through the ionizing filament. This feature is an important qualification for a thermionic drift tube source since it will be operating in a foreign gas which should not be contaminated appreciably. The remainder of the initially stated dimensions are made up by a ceramic potting material which serves as a gas seal around the boiler, thermal insulation and electrical insulation for the boiler filament.
(i.) **Analytical Studies.** A great deal of time was spent studying the effects of the eight parameters determining the shape of the arrival time spectrum of a product ion. This study was of great value in our determination of the rate coefficient of the CO\(^+\) reaction.

In addition, much time was invested in finding the best approach to fitting the analytical spectra to the experimental arrival time spectra for accurate determination of the longitudinal diffusion coefficient. The basic problem is that of normalization. Peak matching involving the raw data does not appear to be satisfactory because of statistical fluctuations in the counting, so a smoothing technique near the peak was introduced in the analysis. This technique has resulted in much improved determinations of \(D_L\).

Professor Gatland is preparing a summary of his ion swarm analysis for the journal "Case Studies in Atomic Physics". This review will be approximately 100 pages long and will be the first detailed and unified treatment of the subject.
B. Journal Articles and Books Published During Reporting Period


C. **Journal Articles in Press or to be Submitted**


D. **List of Papers Presented at Meetings**


8. Russell Akridge, Graduate Student, M. S. in Physics (no thesis), still with our group.

G. Committee Appointments, Consulting Activities, Etc. for E. W. McDaniel

1. Consultant for Controlled Thermonuclear Division, Oak Ridge National Laboratory.


5. Member of Editorial Advisory Board of journal "Atomic Data".


7. Member of General Committee, Int. Conf. on Physics of Electronic and Atomic Collisions, July 1965-July 1971.


H. Use of Our Research by Others

1. Twenty laboratories in the United States, England, Australia, Japan, Hungary, and Norway are using experimental techniques of drift tube mass spectrometry which were developed here. Several of these laboratories are applying these techniques to the measurement of ion-molecule reaction rates of direct aeronomic interest.
2. The mathematical ion swarm analysis developed by Professor I. R. Gatland of our group is being used extensively by others in the analysis of their drift tube data. (This analysis is summarized in ref. 2 of Section E, and portions of it appear in previous papers and reports published by our group.)

3. Our rate coefficient for the reaction \( \text{CO}^+ + 2\text{CO} \rightarrow \text{CO}^+ \cdot \text{CO} + \text{CO} \) will be used at Redstone Arsenal in the mathematical model of the high-power CO laser.

4. The Franklin GNO Corporation has developed and is marketing an instrument called the "Plasma Chromatograph" which is based, in part, on our drift tube mass spectrometer design. Their instrument is an extraordinary sensitive detector for many classes of contaminants in air and liquids. It has many important applications, some of them military.

5. Our rate coefficients for the reactions \( \text{N}^+ + 2\text{N}_2 \rightarrow \text{N}_2^+ + \text{N}_2 \) and \( \text{N}_2^+ + 2\text{N}_2 \rightarrow \text{N}_4^+ + \text{N}_2 \) have been used at Redstone Arsenal in the mathematical model of the high-power CO\(_2\) laser.
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13. ABSTRACT
The research on slow ions in gases performed at the Georgia Institute of Technology with a drift tube mass spectrometer during the period July 1, 1971 through September 30, 1973 is described. The research dealt with the measurement of ionic mobilities, diffusion coefficients, and reaction rates. Emphasis was placed on studies of clustering of K⁺ ions in N₂, H₂, He, Ne, Ar, O₂, NO, CO, and CO₂: on tests of the Wannier diffusion equations; on the differences in behavior of K⁺ ions in N₂ and CO; and on measurements on ions, formed from CO, drifting in carbon monoxide gas. Improvements in the experimental apparatus and analytical techniques are described.
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