QUARTERLY TECHNICAL STATUS REPORT NO. 1

PROJECT NO. A-561

MASS SPECTROMETRIC STUDY OF ION-MOLECULE
REACTIONS OCCURRING AT THERMAL ENERGIES UNDER
GAS KINETIC CONDITIONS

By

D. W. MARTIN and E. W. MCDANIEL

CONTRACT NO. AF 49(638)-1064
AIR FORCE OFFICE OF AEROSPACE RESEARCH

APRIL 1, 1961 to JUNE 30, 1961

Engineering Experiment Station

Georgia Institute of Technology

Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
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WASHINGTON 25, D. C.

TABLE OF CONTENTS

This report contains 7 pages.

I. OBJECTIVE AND METHOD

The objective of the work performed under Contract AF 49(638)-1064 is the study of ion-molecule reactions occurring at thermal energies under gas kinetic conditions by a method in which the products of such reactions are identified by a mass spectrometer. The apparatus used in this study was developed under Contract AF 18(600)-1524 (Georgia Tech Engineering Experiment Station Project No. A-251) and has been described in some detail in AFOSR Document No. TN-60-661 (June 20, 1960). Details of the development prior to the present reporting period may be found in Technical Status Reports Nos. 8-23, Project No. A-251, covering the period from May 1, 1957, to March 31, 1961. In particular, the last of these reports, which has been assigned the Document No. AFOSR-826, contains a brief summary of the entire effort and a list of all the relevant reports and publications. The work under the present contract is essentially a direct extension of the earlier work.

In many experiments in gaseous electronics there is considerable uncertainty as to the identity of the ionic species involved. Even when it is well known what species are initially formed in the primary ion creation events, there is always the possibility that the identity of the charge carriers is subsequently changed by interactions of the primary ions with neutral molecules of the surrounding gas, or with the surfaces of the enclosure. Among these possible interactions are (1) transfer of the ionic charge to a neutral molecule, (2) chemical reactions in which ionic species are formed that were not initially present, and (3) the formation of more or less stable clusters by the attachment of neutral molecules to the ion.

Uncertainties of this kind have been particularly troublesome in low-field drift experiments such as mobility measurements, in which a typical ion makes a

very large number of collisions in the course of its transit. Usually the investigator must rely on indirect evidence involving theoretical considerations to identify the ion species. It is clear that a direct experimental identification of the ions would be of great value in confirming the theoretical considerations involved. It was in fact the uncertainties of this sort in some of our own earlier mobility measurements under the preceding contract that led to the present approach.

There are well developed techniques for the mass spectrometric study of primary ionization events in a low pressure gas, particularly ionization by electron bombardment. More recently a number of laboratories have investigated reactions of the types of interest here with so-called "pressurized source" mass spectrometers. In these experiments the number of collisions an ion may take is small (typically averaging much less than one) so that the method is applicable primarily to reactions having rather large cross sections. There have been a few isolated experiments designed to analyze the ion population in some particular high pressure environments [1,2,3] which are more or less similar to the present apparatus. However, no apparatus has to our knowledge been developed with the specific objective of analyzing ions which have been caused to drift for a known and controllable distance at low energies through a relatively high pressure gas, so that a large and variable number of collisions of the ions with the gas may occur. In any case, the previous high pressure experiments referred to were each designed for a special purpose, and none of

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[1] A. V. Phelps and S. C. Brown, Phys. Rev. 86, 102 (1952).

[2] R. L. F. Boyd and D. Morris, Proc. Phys. Soc. A-68, 1 (1955).

[3] P. F. Knewstubb and T. M. Sugden, Proc. Roy. Soc. A-255, 520 (1960).

them appear to have been applied to a general study of ion-molecule reactions.

In the present experiment, ions are created in an electron bombardment source inside a large cylindrical drift tube containing gas at pressures up to 0.7 Torr. A weak axial electric field of about one volt per centimeter causes the ions to drift along the tube at low energy. At the end of the tube, a stream of the gas containing a sample of the ions present at that location passes through a small knife-edged aperture into a field-free, two-stage differential pumping chamber. From the second chamber the beam passes through a third differentially pumped slit into a Nier-type 60° magnetic deflection mass spectrometer in which the ions in the beam are accelerated and analyzed. The average number of collisions which the ions make in their transit of the high pressure region can be varied by varying the distance of the ion source from the exit aperture and by varying the gas pressure. Information about reactions that occur subsequent to the initial ionization is inferred from the resulting changes in the mass spectrum.

II. PRESENT STATUS OF EXPERIMENTAL WORK

At the time of our last report, which was the Final Summary Report of Contract AF 18(600)-1524 (Document No. AFOSR-826), the apparatus described had been operating successfully for several months. Exploratory studies had been made to determine which of several areas of possible application appeared to most promising, and a detailed systematic study of the ions present in pure hydrogen was in progress. This study had already demonstrated that the predominant ion in hydrogen under low field gas kinetic conditions was H_3^+ rather than H_2^+, and this fact had been published in a short note in Physical Review Letters.[4]

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[4] W. S. Barnes, D. W. Martin, and E. W. McDaniel, Phys. Rev. Letters 6, 110, (1961).

In the present period, our attention was at first directed to efforts to improve the reproducibility and the theoretical understanding of the experimental observations. Most of the hydrogen data had been obtained according to the following scheme, which we had found to be the most convenient: The drift tube was filled with hydrogen to the largest pressure of interest, and the inlet was then closed. One of the ion mass peaks was then monitored continuously by the mass spectrometer while the pressure slowly decreased due to pumping through the exit aperture, until the lowest pressure of interest was reached. The mass spectrometer was then set on the next mass peak and the cycle repeated. Thus it was necessary to make frequent observations of the instantaneous value of a pressure that varied slowly through the range from 0.7 Torr to about 0.001 Torr, for which purpose a commercial Pirani gauge was used. We have since added a cold-trapped mercury McLeod gauge to the system. While we still use the Pirani gauge for the actual observations, it is now checked and recalibrated against the McLeod gauge at frequent intervals. More recently, we have added electronic regulation of the electron emission in the ion source. The regulation has much reduced the random fluctuations of the mass spectrometer readings, and has improved the reproducibility. There still remain some unexplained differences between runs that should be identical. Two factors which are responsible for some of the trouble are: (1) changes in the concentrations of certain impurities in the drift tube and (2) changes in the transmission of the supposedly field-free differential pumping chambers due to charged layers of impurities on the walls. Neither of these problems can be readily disposed of in any simple manner, as our rather large and complex vacuum system is far from clean in the modern sense. We expect to continue making minor improvements as further experience may dictate.

A complete theoretical analysis of the manner in which the intensity of a given mass peak should vary with the drift tube pressure is a difficult transport problem, involving complex boundary conditions and a number of unknown parameters. Some progress with this problem has been made, but as yet no generally valid results have been obtained. Our interpretation of the hydrogen results is based on what amounts to a one-dimensional analysis of what is really a three-dimensional problem. At present we can state that we are quite certain that the most important process for the formation of the H_3^+ ion is the reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$, and can confirm qualitatively the findings of Stevenson and Schissler for the corresponding reactions with deuterium[5], that the cross section for this reaction has a very large value of the order of 10^{-15} to 10^{-14} cm^2 at low energies.

It is hoped that we will be able to improve our analysis in the future, in particular to achieve semiquantitative determinations of the energy dependence. However, we are now largely agreed that the present type of swarm experiment is probably not capable of high quantitative precision in absolute cross section determinations.

The really unique capability of our method is in providing definite answers as to the identity of the ion that is present under a given set of conditions, or with future possible improvements, to determine the identity of the ion with a given mobility. A case in point is the nature of the ions in pure nitrogen. The results of mobility experiments have been taken to indicate that one single species is found at low values of E/p (less than 35) and a different single species is found at high E/p (greater than 100). Varney[6] asserts that these species are N_4^+ and N_2^+ respectively, but there has remained some doubt as to whether this

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[5]D. P. Stevenson and D. O. Schissler, J. Chem. Phys. **29**, 282 (1958).

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

can be regarded as established. We recently began an examination of the ions in nitrogen with our apparatus. The results are only preliminary at the present time, but it appears that both N_4^+ and N_3^+ are present under low-field conditions. Since this identification is at variance with Varney's evidence for a single species, the matter will require further study before we can assert our final conclusions.

Our present plans are to conclude the nitrogen study, and then go on to some other ion identification questions of current interest, such as, for example, to look for evidence of the controversial third ion in argon.[7] Meanwhile, our efforts to improve our theoretical analysis will continue.

III. PUBLICATIONS AND TRAVEL DURING THE CURRENT PERIOD

It has come to our attention that our findings regarding the molecular ions in hydrogen may be of some importance to workers in the field of radio astronomy. A brief note concerning these findings has been submitted to The Astrophysical Journal as a letter to the editor.

A paper describing the apparatus in some detail and presenting the hydrogen results is being prepared for submission to the Journal of Applied Physics as a regular article.

D. W. Martin and E. W. McDaniel attended the Second International Conference on the Physics of Electronic and Atomic Collisions, held at the University of Colorado, Boulder, on June 12-15, 1961, and the D. A. S. A. Reaction Rate Conference held at the National Bureau of Standards, Boulder, on June 16, 1961.

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[7] E. C. Beaty, DASA Reaction Rate Conference, Boulder, Colo. (June 15, 1961), unpublished.

E. W. McDaniel has visited the Oak Ridge National Laboratory several times during the past quarter for consultations with members of the Thermonuclear and Chemistry Divisions on the subject of ion-molecule reactions and other aspects of gaseous electronics.

<div align="right">Respectfully submitted:</div>

<div align="right">D. W. Martin
Project Director</div>

Approved:

A. L. Bennett, Chief
Physical Sciences Division

QUARTERLY TECHNICAL STATUS REPORT NO. 2

PROJECT NO. A-561

MASS SPECTROMETRIC STUDY OF ION-MOLECULE
REACTIONS OCCURRING AT THERMAL ENERGIES UNDER
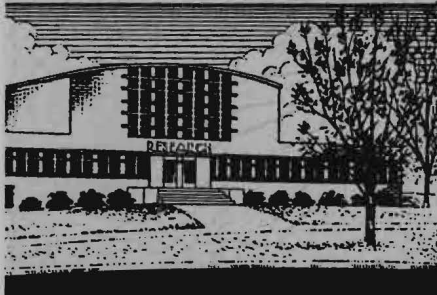GAS KINETIC CONDITIONS

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QUARTERLY TECHNICAL STATUS REPORT NO. 2

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Uncertainties in identification have been particularly troublesome in low-field drift experiments such as mobility measurements, in which a typical ion makes a very large number of collisions in the course of its transit. Usually the investigator must rely on indirect evidence to identify the ion species observed. The present study seeks to obtain direct experimental identification of the ions present under low-field conditions.

Studies of reactions of the types of interest here performed with conventional "pressurized source" mass spectrometers are of necessity limited to reactions having rather large cross sections. There have been a few special purpose experiments, designed to analyze the ion population in a particular high pressure environment,[1,2,3] which are somewhat similar in concept to the

[1] A. V. Phelps and S. C. Brown, Phys. Rev. 86, 102 (1952).

[2] R. L. F. Boyd and D. Morris, Proc. Phys. Soc. A-68, 1 (1955).

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present apparatus. However, no apparatus has to our knowledge been developed with the specific objective of analyzing ions which have been caused to drift for a known and controllable distance at low energies through a relatively high pressure gas, so that a large and variable number of collisions of the ions with the gas may occur. In any case, none of these previous experiments appear to have been applied to a general study of ion-molecule reactions.

In the present experiment, ions are created in an electron bombardment source inside a large cylindrical drift tube containing gas at pressures up to 0.7 Torr. A weak axial electric field of about one volt per centimeter causes the ions to drift along the tube at low energy. At the end of the tube, a stream of the gas containing a sample of the ions present at that location passes through a small knife-edged aperture into a field-free, two-stage differential pumping chamber. From the second chamber the beam passes through a third differentially pumped slit into a Nier-type 60° magnetic deflection mass spectrometer in which the ions in the beam are accelerated and analyzed. The average number of collisions which the ions make in their transit of the high pressure region can be varied by varying the distance of the ion source from the exit aperture and by varying the gas pressure. Information about reactions that occur subsequent to the initial ionization is inferred from the resulting changes in the mass spectrum.

II. PRESENT STATUS OF EXPERIMENTAL WORK

In the last previous report there were described certain improvements made in the apparatus in order to improve the reproducibility of the observations. Since these changes did achieve a great reduction in the short term random fluctuations of the observed ion currents, the results could be more sensibly interpreted. Nevertheless, it was still found that the day to day reproducibility

of the observations was not adequate to lend much confidence in the results of any detailed analysis. Additional steps taken in the present period have resulted in further improvement in this respect.

It had been noted that the total ion yield observed in the mass spectrometer tended to deteriorate progressively with time, but could usually be largely restored by buffing the surfaces of the brass rod anodes of the ion sources. The latter were then gold plated by immersion in a plating bath, and this was found to increase the useful life of the surface markedly. It is now possible to obtain an extensive body of data over a period of many days without interruption. It is still necessary to clean these anode surfaces periodically, and it will probably be necessary to renew the gold plating from time to time.

In the earlier observations on hydrogen, all attention had been concentrated on the low end of the mass spectrum at masses 1, 2, and 3. In the nitrogen studies, on the other hand, there was wide examination of the spectrum in the course of searching for ions at masses 14, 28, 42, 56, and also higher multiples of 14. It had long been known that there were a number of spurious peaks in the spectrum that must be associated with impurities in the system, in particular peaks at masses 18 and 19 that are associated with water vapor. In addition, there was found to be a cluster of small peaks around each of the higher multiples of 14 that are evidently attributable to hydrocarbon fragments from the diffusion pump oil. Previous addition of a large liquid nitrogen trap inside the drift tube, and of dry ice traps in the gas filling lines, had sharply reduced the sizes of many of these peaks. However, in the nitrogen studies it was noted that certain peaks were still of an intensity comparable to some of the peaks of direct interest. In addition, as the drift tube pressure was varied systematically to observe the effects on the relative sizes of

the several nitrogen peaks, it was soon evident that certain of the impurity peaks must be associated with ion-molecule reactions between nitrogen ions and impurities. In particular, a peak at mass 29 was observed, at low pressure, to be much smaller than the adjacent mass 28 peak of N_2^+. However, as the pressure was increases it increased in intensity to become one of the dominant peaks of the spectrum. We interpret this peak to be the ion N_2H^+, formed by a reaction between N_2^+ ions and molecules of pump oil or water vapor. This process competes with the processes for formation of N_3^+ and/or N_4^+ for the available supply of N_2^+ ions. Thus it is evident that in the study of any reaction, it is unwise to restrict attention solely to the peaks of direct interest, since a side reaction such as this can be a serious perturbation and have a marked effect on the apparent rate of the process of interest. A broad search of the spectrum at pressures throughout the range of interest must always be made, and in fact repeated as often as there is reason to think that there might have been significant changes in the impurity level in the drift tube.

Following these observations steps were taken to reduce the impurity level further. The previously mentioned large liquid nitrogen trap in the drift tube was located directly above the outlet to the diffusion pump, but did not provide complete "optical closure" of this outlet. Therefore a set of interleaving baffle rims extending upward from the outlet and downward from the trap was added to accomplish such closure. This step produced some improvement, but it appeared that there was still an appreciable level of oil vapor in the drift tube.

An additional cold trap directly in the pumping line seemed to be the next logical thing to try, but this could not be accomplished without fairly extensive mechanical reconstruction because of spatial limitations. As a purely

exploratory step, the 4" diffusion pump, baffle, and gate valve were removed altogether, and replaced by a 3/4" line having a ball valve and trap, but going then directly to the forepump. Despite the greatly reduced pumping speed for permanent gases, this arrangement appears to have achieved a significant improvement in the cleanliness of the drift tube by eliminating the backstreaming of pump oil. For the time being we have continued to use this arrangement in the conduct of the experiment. However, it is felt that eventually this diffusion pump will have to be restored, with a line trap and also a trapped bypass that will permit direct fore-pumping when desired.

In the past, the diffusion pump fluid used has been "Octoil", chosen because according to the pump manufacturer it provides the greatest pumping speed. In the future we will probably try another fluid such as "Convoil-20" or one of the silicones. Although these provide less speed, the backstreaming is lower and the ultimate vacuum is better. A disadvantage of the silicone oils is that if any of it does get onto sensitive surfaces in the apparatus, it is much more difficult to clean off than are the hydrocarbon oils.

In view of what had been learned about side reactions with impurities, it was decided to repeat the hydrogen observations with due attention to the possibility of side reactions. Even with the improved experimental conditions, it was immediately found that there is indeed at least one side reaction of sufficient prominence that its effects cannot be ignored in analyzing the data, namely the formation at the higher pressures of an ion of mass 29, which is interpreted to be the same N_2H^+ ion that was observed in nitrogen. The manner in which the relative abundance of this ion increases with an increase in pressure indicates clearly that it is formed by reactions involving both H_2^+ and H_3^+ ions, presumably:

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$$H_2^+ + N_2 \rightarrow N_2H^+ + H$$

$$H_3^+ + N_2 \rightarrow N_2H^+ + H_2$$
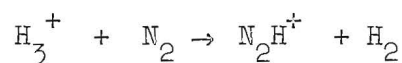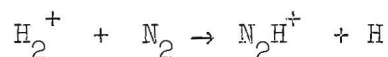
In both of these equations, the N_2 reactant represents residual nitrogen gas in the drift tube, which may come from atmospheric leaks or may in part be due to the slow evolution of occluded gas from surfaces. The relative abundance of the N_2H^+ ion appears to be relatively constant with time under constant conditions, but the relative abundance at a given pressure was sharply reduced when a constant flush of fresh hydrogen was maintained during the observations. These facts lend support to the idea that atmospheric leaks are responsible. However, no leaks of such a size as to be found readily with a helium leak detector have been found. Further, the drift tube pressure will drop to less than 10^{-3} Torr when it is pumped only by the 1/32-inch diameter exit pinhole to the differential pumping chamber. Therefore the remaining leaks cannot be very large, and the residual nitrogen pressure must be quite small. Thus it is indicated that the nitrogen reactions have rather large cross sections. At the highest hydrogen pressures the N_2H^+ peak becomes the dominant one of the spectrum, to the destruction of all of the H_2^+ and H_3^+. At the lower pressures where the conversion of H_2^+ to H_3^+ is occurring, the nitrogen interference is appreciable and must be taken into account in a quantitative analysis of the data. However, allowing for the nitrogen interference does not change our earlier qualitative conclusions about the basic nature of the hydrogen reactions.

Ideally, data should be taken on the relative abundances of the several ion species of interest for constant pressure with varying drift distances. For a number of reasons, involving the fact that we have four separate sources

rather than a single movable one, and that the number of different drift distances available is small, most of the data taken to date have been obtained under a scheme in which only one source was used at a time, and the pressure was varied. At very low pressure the currents of all species are small because the ion production of the source is small. All species will at first increase with increasing pressure, reach a maximum, and then decline again because of increasing loss of ions to the walls due to diffusion, diminishing transmission of the differential pumping section due to scattering in the first chamber, and also, of course, to depletion of some of the species due to the ion-molecule reactions of interest. The situation is sufficiently complicated that we have not devised any way to infer much information from the absolute intensity of any single species alone. The information we have was obtained from plots of the ratio of the current of each species to the total current at the same pressure of all ion species involved in the reaction system.

The first product of the new data series on hydrogen was a rather definite confirmation of our earlier belief that H^+ ions are not involved to any appreciable extent in the formation of H_3^+. When the H^+ current had been included in the total utilized in the normalization scheme above, the relative abundance vs. pressure curves obtained had certain confusing and unexplainable features; these disappeared when the normalization was repeated leaving out the H^+ current. Finally, inclusion of the current of the N_2H^+ peak in the normalization produced curves that for the first time appeared to make sense and be reasonably consistent.

Analysis of curves of relative ion abundance vs. pressure is complicated by the fact that change of the pressure changes the ratio E/p and therefore the average collision energy, as well as changing the average number of collisions. For the $H_2^+ \rightarrow H_3^+$ reactions considered, the cross section is so large that the

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conversion is essentially complete at all pressures greater than about 15×10^{-3} Torr, for the smallest drift distances we can use at present. The study is therefore confined to pressures in the range 1×10^{-3} Torr to 15×10^{-3} Torr. With a drift field that is nominally one volt per centimeter, E/p is in the range from 1000 to 70. This is in the region in which the average collision energy varies with E/p.

Therefore the slope of the H_2^+ relative abundance curve is not simply proportional to the cross section at one energy, but also depends on how the cross section changes with energy and therefore with p. Attempts to deduce the pressure dependence of the cross section from the slope of the H_2^+ curve at each pressure have not produced any self-consistent results.

On the other hand, the magnitude of the H_2^+ relative abundance for a given drift distance at a given pressure can be used to compute a value for the apparent cross section at that pressure, provided that the effective drift distance is known, if the assumption is made that the current is 100% H_2^+ at the beginning of the drift region. Unfortunately, this scheme does not provide any means of eliminating the need for end corrections, which are difficult to estimate with the existing ion sources. Nevertheless a large body of our best hydrogen data to date has been analyzed in this way, yielding curves of an apparent cross section as function of the pressure.

The results were encouraging in some respects and disappointing in others. The computed cross section in every case approached a constant value for increasing pressure, consistent with the fact that the average collision energy must approach thermal energy at low E/p. The magnitudes of this limiting value obtained from different runs with different sources and drift distances were self consistent within a factor of two. They averaged about 2 or

3×10^{-16} cm^2, considerably less than the value obtained by Stevenson and Schissler[4] for the corresponding reaction in deuterium.

A disappointing feature of the results was that the computed cross section was found to increase for pressures approaching zero, contrary to the expectation that it should decrease with the increase in E/p and therefore in the average collision energy.

It is not very likely that this apparent energy dependence can be correct. An obvious weakness in the normalization procedure outlined above is that it fails to take account of the fact that the several ion species involved in the reaction system have different diffusion coefficients, and are therefore lost by diffusion to the drift tube walls at different rates. The relative abundance of a given species will be affected by this factor as well as by the creation or destruction of the species by ion-molecule reactions. As yet we have not devised any procedure to correct for this difference, but this problem is currently under further study.

In summary, several further improvements in the apparatus were made to correct deficiencies of the experiment that had become apparent in our attempts to make detailed analyses of the data. Attention was returned to the case of hydrogen, for which the earlier more crude measurements had already provided several qualitative conclusions. The new results confirmed the qualitative features of the old, and greatly strengthened the prior belief that there is no direct reaction of importance creating H_3^+ directly from H^+. It was further shown that both H_2^+ and H_3^+ will react with nitrogen gas, if present, to produce N_2H^+ as the final terminal species at low E/p. Methods so far devised to

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[4] D. P. Stevenson and D. O. Schissler, J. Chem. Phys. 29, 282 (1958).

evaluate the reaction cross section from the data do not appear to be adequate, particularly with regard to the energy dependence at higher values of E/p.

III. PROGRAM FOR THE IMMEDIATE FUTURE

We intend to make yet another series of observations on hydrogen in which the relative abundance of each type of ion will be measured in rapid chronological succession for two or more different drift distances at constant pressure; an apparent cross section will then be computed from the differences between these values. This procedure will eliminate part of the problem of end corrections. While such observations already exist in the earlier data, normally the measurements from two different sources that would have to be compared were separated by at least several days, during which the pressure in the tube had been cycled from high to low values many times. During this time the impurity situation and other factors could have changed appreciably and would probably produce a large error in the results. The new observations will be conducted so as to minimize uncertainties in this respect.

IV. TRAVEL AND PUBLICATIONS DURING THE REPORT PERIOD

The short letter giving the qualitative information on the conversion of H_2^+ to H_3^+ submitted to The Astrophysical Journal has been accepted for publication as a Note, and is scheduled to appear shortly.

The previously mentioned manuscript which describes the apparatus in some detail and presents the early hydrogen results was completed and submitted to the Journal of Applied Physics. The editors have returned it with generally favorable comment, but with the recommendation that the content of the paper would be more appropriate for The Review of Scientific Instruments. A new version revised somewhat in accordance with the reviewers' suggestions was

prepared and submitted to the latter journal. Notice has been received that it has been accepted for publication.

E. W. McDaniel has continued to make periodic visits to the Oak Ridge National Laboratory for consultations with members of the Thermonuclear and Chemistry Divisions on the subject of ion-molecule reactions and other related aspects of gaseous electronics.

Respectfully submitted:

D. W. Martin
Project Director

Approved:

A. L. Bennett, Chief
Physical Sciences Division

INTERIM FINAL REPORT

PROJECT NO. A-561

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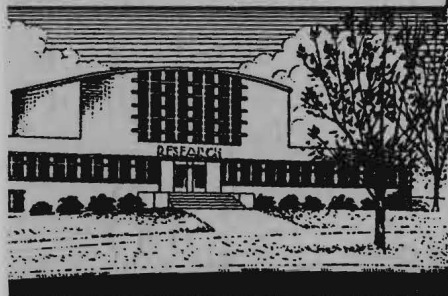GAS KINETIC CONDITIONS

By

D. W. MARTIN
and
W. S. BARNES

CONTRACT NO. AF 49(638)-1064
AIR FORCE OFFICE OF AEROSPACE RESEARCH

MARCH 31, 1962

Placed by
PHYSICS DIVISION
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WASHINGTON 25, D. C.

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The objective of the research performed under Contract AF 49(638)-1064

is the study of ion-molecule reactions occurring at near-thermal energies

in a gas by a method in which the products of such reactions are identified

by means of a mass spectrometer. Special apparatus for this study was developed

under an earlier contract, AF 18(600)-1524. Activity under the present contract

has consisted of exploration of the potentialities of this apparatus, making

modifications and improvements where desirable, and application of the apparatus

to studies of certain ion-molecule reactions of basic general interest. This

research is being continued beyond the term of the present contract under an

Air Force Basic Research Grant, AFOSR 62-306. The present report covers activi-

ties to the close of the term of Contract AF 49(638)-1064, and for that reason

has been designated as an Interim Final Report. A more complete account of the

scientific results obtained will be presented when the matters under current

investigation are brought to a satisfactory conclusion. It is expected that a

report of results can be prepared for journal publication by the late summer of

1962, upon completion of that part of the program which will constitute the

doctoral dissertation of Mr. W. S. Barnes, presently a graduate student in the

School of Physics.

There are a number of experimental situations involving ions in gases in

which any of several types of reactions between the original ions and the

molecules of the gas may play an important role. Possible types of reactions

include transfer of the ionic charge to a neutral molecule, chemical reactions

to form ions of new molecular composition, and the formation of more or less

stable clusters by attachment of neutral molecules to the ion. Among the

products of such reactions, a number of types of stable molecular ions are

known for which no neutral counterparts exist. In situations where an ion may make a large number of collisions during its lifetime, reactions involving impurities of even very low concentration may have an appreciable or even dominant effect on the experiment.

The present experiment is concerned with studies of ion-molecule reactions occurring under the conditions of a low-field mobility measurement. The apparatus consists of a large, cylindrical drift tube which communicates, through a series of small, differentially pumped apertures, with a mass spectrometer. Gas pressures as large as about 1 Torr may prevail in the drift tube without noticeable loss of high vacuum in the spectrometer. A set of electrodes in the drift tube permit the establishment of a weak, axial electric field; the regions between the successive differentially pumped apertures are carefully shielded so as to be as nearly free of either electrostatic or magnetic fields as possible. Ions may be created in the drift tube gas by any of 4 simple sources located along the axis of the tube at different distances from the end ranging up to 35 cm. The ions are caused to drift toward one end by the electric field, making a large number of collisions with gas molecules along the way. A sample of the ions then passes through the apertures into the spectrometer, where they are accelerated and analyzed. Thus the nature of the species present at equilibrium after a large number of collisions can be positively determined. Further, the number of collisions can be varied by changing either the drift distance or the pressure, permitting study of the reaction or system of reactions by means of which the terminal species is produced.

Many previous studies of the types of reactions of interest here have been performed with "pressurized source" mass spectrometers. These studies have necessarily been limited to reactions of quite large cross section, and

could not approach equilibrium conditions. In addition, there have been a few special purpose experiments, designed to analyze the ion population in a particular high-pressure environment,[1,2,3] which are somewhat similar in concept to the present experiment. However, our apparatus remains unique in two major respects: (1) the differential pumping region is fieldfree, so that the ions in the sample extracted from the gas are not accelerated appreciably until they have reached a region of sufficiently high vacuum that any further collisions are unlikely. This feature assures that the mass spectrum obtained is truly representative of the thermal equilibrium situation in the gas; (2) the drift distance in the gas is known and controllable, which permits a systematic study of the reactions occurring.

II. STATUS OF THE EXPERIMENTAL WORK AND RESULTS OBTAINED

For completeness, brief mention is made of early ion identification results that have been described in previous reports. The terminal, or equilibrium, ion species in pure hydrogen was shown to be H_3^+ rather than H_2^+. Further, both H_2^+ and H_3^+ will react strongly with trace amounts of nitrogen to form the stable ion N_2H^+ at mass 29. H_3^+ appears to be formed chiefly by reactions of H_2^+ with H_2, and not to any great extent by reactions of H^+.

In "pure" nitrogen, both N_3^+ and N_4^+ are observed at moderately high pressures. Both appear to be formed from N_2^+ in competing processes, and the possible existence of a tertiary process by which one can convert to the other is still uncertain. Analysis of the situation has been greatly complicated by

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[1] A. V. Phelps and S. C. Brown, Phys. Rev. <u>86</u>, 102 (1952).

[2] R. L. F. Boyd and D. Morris, Proc. Phys. Soc. <u>A-68</u>, 1 (1955).

[3] P. F. Knewstubb and T. M. Sugden, Proc. Roy. Soc. <u>A-255</u>, 520 (1960).

the fact that N_2^+ reacts very strongly, apparently with very minute amounts of water or hydrocarbon vapor, to form the same mass-29 ion N_2H^+ observed in "pure" hydrogen. A part of the effort in the present contract year has been devoted to improvements of the vacuum system designed to reduce the interference from this side reaction. Although a considerable improvement has been effected, this process continues to be a major factor.

Simple qualitative results such as these can sometimes be obtained relatively easily. In most of our work so far, the raw data consists of plots of the intensity of each of the mass peaks of interest as a function of the drift tube pressure. All peaks are of low intensity when the pressure is low, because the total ion production of the source is low. As the pressure increases, the peak intensities at first rise to a maximum, primary ions most rapidly and secondary ions next. Eventually the intensities of all species decline, due to increased diffusion losses to the walls, to increasing scattering losses in the differential pumping chambers, and of course to depletion of some of the species through ion-molecule reactions. When there is a simple parent-daughter relationship between two species with a moderately large cross section for the reaction, and no important side or competing reactions, the relationship may be evident in the raw data. The intensity of the parent ion reaches a maximum at the lowest pressure, and then falls rapidly in the same pressure region where the intensity of the daughter ion is rising most rapidly. If there are no further reactions, the daughter intensity has a very broad maximum, and declines slowly toward higher pressures. This was essentially the situation in the case of the $H_2^+ \rightarrow H_3^+$ reaction.

Considerable analysis of the data may be required to obtain even qualitative results when the reaction cross section is not so large or when there are competing

side reactions. Also, some analysis is necessary to infer anything quantitative about the reaction cross sections. A reasonably exact treatment of the events in the drift tube would be an impossibly difficult problem, involving simultaneous solutions of the transport equations for the several species, all with complex and somewhat uncertain boundary conditions. Even if otherwise feasible, such a solution would require knowledge of, or guesses at, the values of a number of scattering and reaction parameters, virtually amounting to knowing all the answers before you start. Thus, one must necessarily resort to drastic theoretical simplifications whose validity can be tested by comparison of the results obtained with the experimental data.

The first and simplest scheme used follows: First a preliminary guess is made as to which of the ions observed in the spectrum are related to each other through reactions. Then the intensity of each is replotted against the pressure, but normalized at each pressure to the sum of all their intensities at that pressure. This scheme cancels out, to first order, all of the diffusion and other loss effects, under the simple assumption that these effects are the same, percentagewise, for all of the species involved. In favorable cases, parent-daughter relationships can be quite unmistakable in these normalized plots. Primary ions have their greatest relative intensity at the lowest pressures, and the intensity falls monotonically with increasing pressure. The relative intensity of a secondary ion rises as its parent falls; if there are no further reactions, it remains high for further pressure increase. If an ion species has been included in the normalization which in fact has nothing to do with the others, this may also be readily evident. This was the case with the H^+ ion in hydrogen. Including it in the normalization simply caused incongruous dips in all of the other curves at the pressure where the H^+ intensity

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was maximum. Omitting this ion from the normalization produced the sort of curves that were expected for the H_2^+, H_3^+, and the final N_2H^+ ions. Thus it was concluded that reactions involving H^+ did not contribute materially to the formation of H_3^+.

Obtaining at least semiquantitative values for the cross sections of the observed reactions has proved to be a far more intractable problem; on this much effort has been expended. In the case of hydrogen, the cross section for the $H_2^+ \rightarrow H_3^+$ reaction is known from pressurized source mass spectrometer studies[4], and has value of the order of 5×10^{-15} cm^2 at low energies. The enormous size of this cross section actually makes the reaction rather unsuitable for quantitative study with this apparatus. Our present simple ion sources produce primary ions with substantial initial energies. This reaction goes to completion in so few collisions that the assumed thermal equilibrium on which our analysis is based is probably never achieved. Indeed, we observed that the conversion from H_2^+ to H_3^+ was over 99% complete, for our shortest practicable drift distance, for all pressures above about 1.5×10^{-2} Torr. Even if the considerable effect of the ion source anode is ignored, and it is assumed that the only electric field present is the applied drift field of about 1 volt/cm, the value of E/p at which the bulk of the reactions occur corresponds to high field rather than low field conditions.

Despite these factors, apparent values of the reaction cross section were deduced from the normalized hydrogen data described above, by a method that was compatible with the approximation inherent in the normalization. The method has been described in somewhat more detail in Technical Status Report No. 2. It provided a cross section that was a function of pressure, and approached a

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[4] D. P. Stevenson and D. O. Schissler, J. Chem. Phys. 29, 282 (1958).

constant limiting value toward high pressures. This limiting value was an order of magnitude smaller than the value expected for thermal energies. In addition, the apparent cross section consistently increased toward lower pressures, where it should have decreased with the accompanying increase in E/p and in the average collision energy. It could be concluded from these results that the simple normalization analysis was far from adequate to handle the existing real situation.

One particularly important physical change in the apparatus has been made since Technical Status Report No. 2 was written. A grid of 0.004-inch diameter stainless steel wires spaced 0.20 inches apart was strung across the central opening of the annular drift field electrode immediately "downstream" from each of the ion sources. Its purpose is to shield the drift space downstream from the relatively high positive potential of the anode of the source. Introduction of the grids produced a sharp reduction in all of the ion currents obtained in the mass spectrometer under given conditions, rather dramatic evidence that perturbation of the drift field by the anodes had been a factor of major importance. In the case of hydrogen, the currents were reduced to such low values that we could no longer use an integrating count rate meter to obtain an average counting rate from the detector. We had to resort to actual counting with a scaler for timed intervals. Despite this inconvenience, it is believed that the grids are absolutely essential, as long as the present sources continue to be used, to keep the actual geometry of the experiment close to something that can be handled theoretically.

During the last half of this contract year, considerable effort has been put into the development of a theoretical treatment that takes a more realistic account of diffusion effects in the drift tube than does the simple normalization procedure described earlier. Only a brief statement of the central ideas will be given here. It is assumed that the spatial distribution of each ion species obeys

a steady state diffusion equation, which includes a term involving the drift field, pseudo-absorption terms for each of the reactions by which it is thought that ions of the species are destroyed, and nonhomogeneous source terms for each of the reactions by which they are believed to be created. The several equations for the several species thus are simultaneous. However, the equations for the primary ions are homogeneous and can be integrated, with the assumption of suitable boundary conditions. The results are then substituted into the source terms for the supposed secondary ions, so that these equations can be explicitly integrated in turn. The process is repeated for the supposed tertiary ions. Possible space-charge effects must be ignored, since their inclusion would make the equations non-linear and completely intractable. Even without them, each equation with its boundary conditions is an eigenvalue problem, have in principle an infinite number of solutions or "modes". It is necessary to assume that it is sufficient to consider only the first or principal mode of each solution. With these assumptions, the system of equations can be solved, giving in general a linear combination of exponentials for the dependence of the abundance of each species on axial distance z along the tube. The exponents may contain several terms which depend on the pressure in various ways, depending on the nature of the reactions assumed to occur.

If it can be argued that certain terms in each exponential will be dominant for certain ranges of the pressure, then the ratio of the solutions for two related ion species will be predicted to have some particular type of pressure dependence in that range, which may be compared directly with the ratio of the experimental abundances of the two species. If the pressure dependences agree, it is strongly indicated that the assumed reactions and other supporting

assumptions are correct, and the implied values of the various diffusion parameters and reaction cross sections involved may be determined. If the pressure dependences do not match, the assumed set of reactions may be incorrect, and it will be necessary to examine other possibilities.

A large body of experimental data has been accumulated for all of the important ions found in "pure" nitrogen, including N^+, N_2^+, N_3^+, N_4^+, N_2H^+, and even H_3O^+, and the ratios of the abundances of various pairs of these ions have been plotted as functions of pressure. We are seeking, by trial and error and the analysis procedure described above, to find a set of assumed reactions that is compatible with the results. The situation is quite complicated, and no final results can be anticipated at this time.

Before attention was turned to nitrogen, the same kind of theoretical treatment was applied to the case of hydrogen, where the situation is consider-- ably simpler. In fact, the primary question of which possible reactions do actually occur had already been settled to our satisfaction by earlier methods. The unsuitability of the $H_2^+ \rightarrow H_3^+$ reaction for detailed study with this apparatus, because of its enormous cross section, had been made even more evident by the addition of the grids. The increased difficulty of obtaining good measurements, because of the low counting rates, added to the fact that the cross section was already known from other sources, caused us to abandon further attempts to determine the cross section quantitatively. However, one interesting feature of the theoretical results was given some attention. The solutions for the spatial dependence of the abundance of a given ion should hold "upstream" from the source as well as downstream. For a primary ion, the ratio of the abundance at a given point downstream to that at a point an

equal distance upstream, at the same pressure, was shown to be independent of the presence of reactions, and to yield explicitly a value for the important parameter K/D, where K is the mobility and D is the diffusion coefficient. Accordingly, a series of observations were made with the direction of the drift field alternately with and against the direction of drift toward the spectrometer. Unfortunately, the results had such large uncertainties due to the low counting rates that almost nothing new was determined. These are the reasons why hydrogen was finally put aside, and attention turned to nitrogen.

III. PROGRAM FOR THE IMMEDIATE FUTURE

An all out effort is being made to understand the system of reactions occurring in nitrogen, and to settle finally the question of the identities of the ions which are present at equilibrium under low-field conditions. At the same time, the design of the new ion source, which was proposed in our proposal for the extension grant under which the work will continue, will be pressed by Mr. George Keller. Mr. Keller is a graduate student in the School of Physics, who as assisted the project for the past two summers. He is now at the point where he is ready to begin thesis work, and he will rejoin the project in the summer of 1962 for this purpose.

IV. PUBLICATIONS DURING THE PRESENT CONTRACT YEAR

A note entitled "On the Possible Occurrence of H_3^+ in Interstellar Space" appeared in The Astrophysical Journal 134, 1012 (1961).

A paper entitled "Drift Tube-Mass Spectrometer for Studies of Low-Energy Ion-Molecule Reactions" has been published in The Review of Scientific

Instruments 33, 2, (1962). This paper contains a fairly detailed description of the apparatus and of its projected uses. We have already received over 75 requests for reprints of this article from all parts of the world.

Respectfully submitted,

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