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Edited by **MICHAEL T. BOWERS**

DEPARTMENT OF CHEMISTRY
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PREFACE

Fifteen years ago there was a handful of research groups involved in research on the chemistry of ions in the gas phase. Today there are hundreds of groups spanning a discipline that stretches from biochemistry to theoretical chemical physics. The growth has been dramatic, almost explosive, in the past decade, and the field is currently at the point where no one can even superficially keep up with all of it. There are three journals totally devoted to ion chemistry of one sort or another, and ion chemistry papers are making major contributions to most of the main line chemical journals.

The roots of gas phase ion chemistry, perhaps more than those of some disciplines, are found in technique development. The rapid technological advances in the post-Sputnik era provided the materials and vacuum and electronic capabilities to develop the sophisticated instrumentation we take for granted today. The chapter by Gentry on molecular beams in Volume 2 is illustrative of the inventive methods used to probe microscopic reaction mechanisms. Previous editors recognized this relationship and built their books around chapters that discussed the various techniques in use at that time.

The question arose, in attempting to put the present volumes together, of what topics should be emphasized and how they should be organized. In the end, the decision was to emphasize the topics I found most interesting and relevant, and to assign the organization of these topics to the various authors who graciously agreed to write the chapters. Each of the authors is a world leader in his respective area, and each area presents different requirements of both length and style presentation. The areas I

chose to emphasize are theory (3), kinetics and mechanism (6), thermochemistry (3), and technique and applications (4). The numbers in parentheses give the number of chapters in each section. The dominant theme of the treatise is the chemical physics aspect of gas phase ion chemistry; but a broad range of chemists should find most of the chapters of interest, particularly those on thermochemistry where comprehensive compendiums of gas phase basicities, acidities, and electron affinities are given.

Finally, I would like to thank the many people who made these volumes possible. To the authors go the primary thanks for preparing high quality chapters and forwarding them promptly. Members of my research group all deserve thanks for carrying on during the editing process. The helpful, competent, and professional attitude of everyone at Academic Press minimized all of the difficulties encountered, and my thanks go to them. Last, my family, and especially my wife Diane, gave support and encouragement throughout, and I am deeply grateful and thankful for their presence in my life.

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Chapter 1
**Recent advances in flow tubes:
Measurement of ion–molecule
rate coefficients and product
distributions**

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I. INTRODUCTION

The use of flow tubes to obtain quantitative data on ion-neutral reactions dates back to 1963 with the development of the flowing afterglow plasma technique by Ferguson, Fehsenfeld and Schmeltekopf in the U.S. Department of Commerce Research Laboratories, formerly ESSA now NOAA, at Boulder, Colorado (Fehsenfeld *et al.*, 1966a; Ferguson *et al.*, 1969). The technique was developed in response to the need for critical data relating to ionospheric chemistry which demands that the ion-neutral interaction energies be very low ($\lesssim 0.1$ eV). At that time very little relevant data were available, although a start had been made in the time-resolved afterglow (often termed the stationary afterglow) by Sayers and colleagues at Birmingham University, England (Dickinson and Sayers, 1960; Sayers and Smith, 1964). In principle, the collision dominated afterglow plasma is an ideal medium in which to study both binary and ternary ion-neutral reactions at truly thermal energies since the reacting species possess a Maxwellian distribution of kinetic energies $f(E)$ characterized by the system temperature, and the internal energy states of the ions and neutrals will have the corresponding Boltzmann distribution. Thus, the rate coefficient k for the reaction can be determined under controlled temperature conditions. This contrasts with measurements made using beam techniques in which reaction cross sections $\sigma(E)$ over a much wider range of energies are determined but for which, in practice, accurate measurements are limited to interaction energies above an electron volt or so (McDaniel *et al.*, 1970). In some cases such beam data can be utilized to determine thermal energy rate coefficients by energy extrapolation and application of the appropriate mathematics ($k = \int \sigma(E)f(E)dE$), an approach which has been discussed in detail by Henchman (1972). However, ion beams are also rather prone to contain significant fractions of excited ions, which can have greatly different cross sections for reaction than the ground state ion species, and thus the uncertainty in the composition of the ion beam has led researchers requiring thermal energy reaction rate data to favor those obtained from collision dominated experiments.

The stationary afterglow can be criticized for the measurement of ion-molecule reaction rate coefficients. The technique involves the ionization of a gas or a mixture of gases by a short time duration pulse of an rf or dc electric field and then the time history of the ions in the afterglow of the electrical discharge is studied by mass spectrometric sampling of the diffusive wall currents of the positive ions. The loss rate of the ions is related to the partial pressure of the reactant neutral gas. It is in the nature of the technique that the reactant molecular gas is exposed to the gas discharge which produces the afterglow plasma, and hence the possibility of significant population of internal energy states of the molecular gas arises which can result

in misleading rate coefficients. Problems of this kind can be minimized by monitoring the ion loss rates at times late into the afterglow, thus allowing the excited states to relax by collision with plasma electrons and neutral gas particles before measurements are made. This phenomenon was graphically illustrated by the stationary afterglow data relating to the reaction of O^+ ions with N_2 molecules. The "early" afterglow data (Batey *et al.*, 1965) provided a rate coefficient which was more than an order of magnitude greater than the "late" afterglow data (Copsey *et al.*, 1966), presumably due to the presence of significant concentrations of vibrationally excited N_2 molecules in the early afterglow as was suggested to us at the time by Ferguson. Subsequent flowing afterglow studies by Schmeltekopf *et al.* (1967) strongly supported this argument. Nevertheless, the stationary afterglow can provide accurate reaction rate coefficients for both binary and ternary reactions if used with care and has been exploited to provide a great deal of accurate data concerning positive-ion-molecule reactions, notably by the Birmingham University group (Smith and Fouracre, 1968; Adams *et al.*, 1972; Smith *et al.*, 1972) and the Ballistics Research Laboratory group (Lineberger and Puckett, 1969a,b). However, it is not so useful for the study of negative-ion-molecule reactions. This is because the simultaneous presence of electrons as well as negative ions in the afterglow plasma results in an appreciable ambipolar field which prevents the flow of negative ions to the plasma boundary and so the essential property that the wall current of ions should be proportional to the number density of ions in the plasma breaks down (Smith and Plumb, 1973; Smith *et al.*, 1974). However, in the presence of an appreciable concentration of an electron-attaching gas, the electron/positive-ion afterglow plasma will convert to a negative-ion/positive-ion plasma and the ambipolar field will collapse to an insignificant intensity allowing the negative ions to flow toward the plasma boundary. Under such conditions, negative-ion-molecule reactions can be studied, as has been demonstrated in the experiments of Puckett and Lineberger (1970). Similar phenomena have been observed by Kebarle (1975) in the pulsed high pressure mass spectrometer. Nevertheless, the high pressure mass spectrometer has been used very successfully in the study of ion equilibrium in positive- and negative-ion-neutral reactions (Kebarle, 1975).

Several of the disadvantages of the stationary afterglow have been overcome by the development of the flowing afterglow and with its development came a great upsurge in the amount of data relating to low energy ion-neutral reactions. A brief discussion of the principles of the technique and some of its many successes will be given in Section II and so they will only be mentioned here. The essence of the technique is that ionization is created upstream in a fast flowing carrier gas and an afterglow plasma is distributed

along a flow tube remote from the source of ionization. The ions, either positive or negative, are sampled at a point downstream in the flow and the decrease in the primary ion signal is observed as a function of the rate of flow of a reactant gas, which is introduced into the afterglow at a position remote from the ionization source. The essential point is that the neutral reactant gas is never exposed to the extreme conditions of the ionization source but only to the thermalized afterglow plasma, and so significant internal excitation is prevented. Several other important advantages are apparent. By the sequential addition of gases at different positions along the length of the afterglow column, a wide variety of ion types can be generated and their reactions studied. The method of ion sampling ensures that negative-ion reactions can also readily be studied (Section II.B).

Following its development and exploitation to study a wide range of reactions at the Boulder laboratories, flowing afterglow apparatuses have been built and are being used in several laboratories throughout the world, notably by Schiff and Bohme at York University, Toronto (Burt *et al.*, 1970; Bohme, 1975), Fite and Kaufman at Pittsburgh University (Farragher *et al.*, 1969; Howard *et al.*, 1971), Twiddy at the University College of Wales at Aberystwyth (Bolden and Twiddy, 1972), Bierbaum and DePuy at Colorado University, Boulder (Bierbaum *et al.*, 1976), and Freeman and McEwan at the University of Canterbury, Christchurch, New Zealand (Liddy *et al.*, 1977) for the study of ion-neutral reactions, and by Smith and colleagues at the University of Birmingham, England for the study of ion-ion mutual neutralization (Smith and Church, 1976; Smith *et al.*, 1976) and electron temperature relaxation (Smith and Dean, 1975).

Some energy variation can be obtained in the flowing afterglow by varying the flow tube wall temperature and preheating or precooling the carrier gas (Dunkin *et al.*, 1968; Lindinger *et al.*, 1974) but a more successful and quite recent development is the inclusion of a drift-tube section downstream in a flowing afterglow tube. This so-called flow-drift tube experiment, again developed at Boulder, allows the study of ion-neutral reactions over an interaction energy range from thermal to a few electron volts (McFarland *et al.*, 1973a,b,c). This new development is discussed in more detail in Section III, and so it is sufficient to note here that it combines all the flexibility of the flowing afterglow with the essential features of drift tubes and as such extends the study of ion-neutral reactions into an important energy regime.

A restrictive feature of the flowing afterglow as used conventionally is that the ions to be studied have to be generated in the flow tube (see Section II). Although it has been possible to study many hundreds of different ionic species by thoughtful choice of suitable systems, many other species for which data are urgently required, for example radical-ion species such as CH^+ and CH_2^+ , have defied the attempts of the best flowing afterglow

researchers to generate them without simultaneously generating other ions, which renders the mass spectrometer data intractable. The presence in the flow tube of the gas from which the required ionic species is generated also complicates the interpretation of the mass spectrometer data and these factors render the technique unsatisfactory for the study of many species. In response to the desire to study ion-neutral reactions thought to be of importance in the synthesis of the molecules observed in interstellar clouds (e.g., Dalgarno and Black, 1976), the authors conceived of, and have recently constructed and exploited at Birmingham University, the selected ion flow tube (SIFT) (Adams and Smith, 1976a,b). This most recent development in flow tube instrumentation, which is discussed in some detail in Section IV, essentially involves the injection of a mass selected ion beam at low energy into a flowing gas where the method of studying the ionic reactions is very similar to that of the flowing afterglow technique. Thus, in principle with the SIFT, the reactions at thermal energies of any ion which can be generated in an ion source and injected into a relatively high pressure gas without undergoing collisional fragmentation can be studied. This has greatly extended the versatility of the flow tube technique. At the time of writing, the rate coefficients and product ion distributions of several hundred positive-ion reactions have been determined using the SIFT (Section IV.C). We wish to stress at the onset that the SIFT reactive medium is *not* an afterglow plasma, no electrons are present, only a low concentration of ions convected along the flow tube by the carrier gas.

In summary, having placed the topic of flow tube studies of ion-neutral reactions in perspective, the following sections involve a brief description of the well-established flowing afterglow technique (Section II), mentioning some of its more noteworthy successes, in order to prepare the ground for a discussion of the flow-drift technique (Section III) and of the SIFT technique (Section IV). Finally in Section V, we allude to our most recent development, the temperature variable SIFT-DRIFT apparatus, which combines the essential features of the SIFT and the flow-drift tube and which promises to provide a great deal of critical data concerning ion-neutral reactions at thermal energies.

II. THE FLOWING AFTERGLOW

The more recent developments in flow tube technology rely heavily on the now standard flowing afterglow technique which has been reviewed in detail by the originators (Ferguson *et al.*, 1969) and has also been the subject of several more recent reviews (McDaniel *et al.*, 1970; Twiddy, 1974; Fehsenfeld, 1975a; Meisels, 1975). In this short discourse only those aspects

of the technique which are relevant to the more recent developments are discussed in any detail.

A. General Description of the Apparatus and Technique

A schematic diagram of a typical flowing afterglow apparatus is shown in Fig. 1. A carrier gas, usually helium (flow rate about 200 torr liter s^{-1}), is made to flow along a glass or stainless steel tube (about 8 cm internal diameter, 1–2 m long) at a velocity of about 10^4 cm s^{-1} by the action of a large Roots pump. Typical flow tube pressures range from ~ 0.3 to several torr limited by the requirements for an adequate ion number density, an established flow pattern, and a tolerable pressure in the ion detection system. Ionization is produced either in the pure carrier gas alone or in the carrier gas containing a small admixture of an ion source gas, usually by a hot cathode electron emitter, although microwave (Farragher, 1970) and cold cathode (Bolden *et al.*, 1970a) discharges have also been used. The resulting plasma of electrons and positive ions (and often negative ions and metastable neutrals) is then constrained to flow with the carrier gas and the charged particles thermalize as they move away from the ion source and along the flow tube. The ion source gas is often added downstream of the ionization region, and thus into the afterglow of the discharge, creating the desired primary ion species by reaction with ions or metastable atoms or electrons rather than by direct electron impact in the upstream ion source. By these various reactions, a great variety of primary ions can be produced. More than one primary ion is often present and although this does not generally influence the determination of reaction rate coefficients, it does complicate and, in some cases, prevent the identification of the ionized reaction products. Also, the presence of energetic metastable species such as 2^3S helium atoms

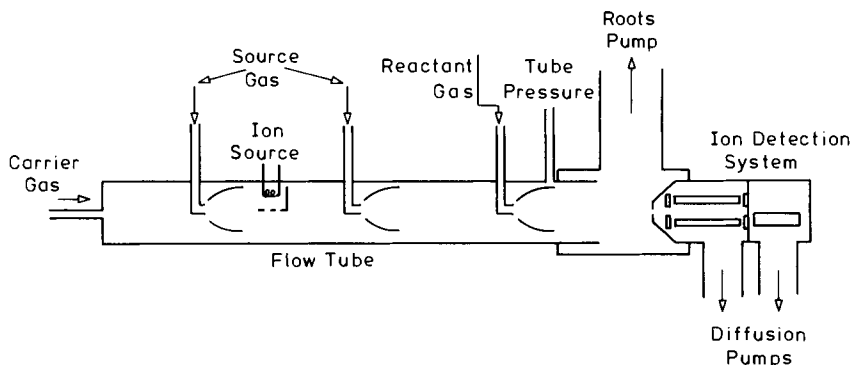


FIG. 1 Schematic diagram of a typical flowing afterglow apparatus.

can greatly add to the "product" ion spectrum as a result of Penning ionization and also complicate product identification. However, the presence of metastable atoms in the flowing afterglow has been very successfully exploited to determine many Penning ionization rate coefficients (Bolden *et al.*, 1970b; Schmeltekopf and Fehsenfeld, 1970).

On their passage along the flow tube, the ions pass an axially positioned entry port through which the reactant gas is added (Fig. 1). This method of reactant gas injection contrasts with that employed in the flow drift and SIFT (Sections III and IV, respectively). The flow rate of the reactant gas is usually determined using pressure transducers in conjunction with calibrated capillaries (Ferguson *et al.*, 1969), although in a few cases the rate of pressure drop in a known volume of reactant gas has been used (Bolden and Twiddy, 1972). The former method is also usually used to determine the much larger flow rates of the carrier gas. At the end of the reaction zone (typically 25–75 cm long), the ions are sampled through an orifice (typically 0.5–1.5 mm diameter) in a disk located at the tip of a truncated nose cone, passed into a differentially pumped quadrupole mass filter, and are detected by a particle-multiplier/ion-counting system. The orifice disk is usually constructed of molybdenum since only with this metal is reliable sampling consistently obtained, especially when reactive neutrals like O and H are present (Ferguson *et al.*, 1969). The particle multiplier is located off axis to reduce the background count rate due to photons from the ionization source, due to metastable atoms and—in the case of negative-ion studies—due to electrons which are not efficiently filtered out by the quadrupole spectrometer. Rate coefficients are determined and ionized products identified from observations of the primary and product ion count rates as a function of reactant gas concentration by the procedure outlined below (Section II.C). In one apparatus, the position of the entry port is varied at constant reactant gas flow rate in order to obtain the rate coefficient (Farragher, 1970; Howard *et al.*, 1970). Using either method, binary rate coefficients of the order of 10^{-9} – 10^{-13} $\text{cm}^3 \text{s}^{-1}$ can be accurately determined for reactant gas flow rates varying from typically 10^{-4} to several torr liter s^{-1} .

A schematic diagram illustrating many of the features often obtained in flowing afterglow data is shown in Fig. 2 for the reaction in which two primary ion products result, viz,



The ion count rates are plotted logarithmically as a function of the flow rate of reactant gas B. Numerous examples of actual flowing afterglow data are available in the literature. The decay of the primary ion A^+ , from an initial count rate of typically 10^5 – 10^6 counts s^{-1} , is usually linear over one

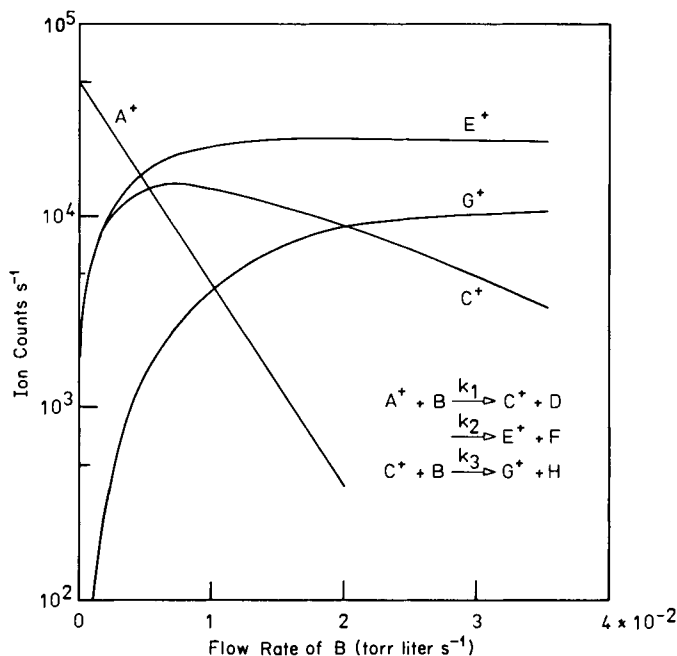


FIG. 2 Diagram illustrating features commonly observed in flowing afterglow mass spectrometer data. Here the A^+ ion reacts with molecule B and the ions C^+ and E^+ are primary products. C^+ then reacts with B to produce G^+ . The rate coefficient for the primary reaction is obtained from the exponential loss of A^+ . Mass discrimination in the detection system is evident since the total count rate ($E^+ + G^+ + C^+$) for large flow rates of B is less than the initial A^+ count rate.

to several orders of magnitude. The count rates of C^+ and E^+ are shown to increase with that of C^+ reaching a maximum and the declining due to further reaction with B producing a secondary ion G^+ . The total primary ion count rate at zero flow and the total product ion count rate at maximum flow are deliberately made unequal to illustrate the inevitable mass discrimination in the ion sampling system. It is difficult (Govers *et al.*, 1974) to accurately account for mass discrimination in the flowing afterglow. Such is however readily possible when a SIFT apparatus is used, as is described in Section IV.A.3, and thus enables the relative proportions of the product ions to be accurately determined.

B. Plasma Properties and Ion Sampling

In determining rate coefficients from flowing plasma experiments, it is important to have an appreciation of other ion loss processes and of the method of ion sampling from a plasma. In a flowing afterglow plasma

containing positive ions and electrons, the overall ion number density decreases with distance along the flow tube mainly as a result of ambipolar diffusion to the walls, but also at the higher charge densities ($\geq 10^8 \text{ cm}^{-3}$) due to electron-ion recombination (Smith *et al.*, 1975). Thus in rate coefficient measurements, it is necessary to operate with small charge densities in the reaction zone to minimize ion loss by recombination to simplify the interpretation of the mass spectrometer data. Under such conditions, the ion density is typically 10^7 cm^{-3} at the sampling orifice. In this plasma situation, the space charge sheath at the orifice is such as to accelerate positive ions through the orifice. A detailed discussion of positive-ion sampling with orifice probes has been given by Smith and Plumb (1973).

When negative ions are also present the situation is very different. For small relative concentrations of negative ions to electrons, the potentials within the plasma are still controlled by the electrons and so the radial ambipolar field is retarding to negative ions, reducing their diffusive loss much below that of the positive ions and effectively preventing them from reaching the flow tube walls. This type of plasma situation has been studied experimentally in the stationary afterglow using electrostatic probes to map out the distributions of the charged particle densities and the potential (Smith *et al.*, 1974). However, the problem which this presents to negative-ion sampling from stationary afterglows is overcome in the flowing afterglow by sampling on axis in the region where the negative-ion number density and the gas velocity are greatest and by using large sampling orifices. For electron densities $\geq 10^7 \text{ cm}^{-3}$ and electron temperatures of about 300 K, the Debye screening length is $\leq 0.5 \text{ mm}$, resulting in a sheath thickness of the same order as the orifice diameter. Under these conditions, some distortion of the sheath must occur allowing at least the high energy tail of the negative-ion energy distribution to penetrate the sheath and pass through the orifice with the convective assistance of a small fraction of the carrier gas. The details of this sampling process are still not completely understood.

However, if the electron density n_e to the negative-ion density, n_- decreases below a critical ratio ($n_e/n_- \leq 10^{-2}$), the electron-positive-ion ambipolar field collapses and the remaining electrons are rapidly lost to the walls, resulting in a positive-ion/negative-ion plasma completely devoid of electrons. Such a transition has been observed both in stationary afterglows (Lineberger and Puckett, 1969a; Smith *et al.*, 1974) and flowing afterglows (Smith and Church, 1976). Under these conditions, the positive and negative ions can both be readily sampled by the orifice since the sheath potential difference is much less than the average ion energy (equivalent). The orifice sampling problems discussed above do not arise in SIFT ion sampling (Section IV.A.1) since there are no electrons in the reaction zone. In the study of ion-neutral reactions in flowing afterglows containing negative ions it is necessary to ensure that a transition from electron-ion to ion-ion

plasma does not occur in the reaction zone otherwise anomalous rate coefficients may be obtained because of the resultant variation in the diffusion loss rate of the ions. In some negative-ion reaction studies, this has been prevented by deliberately creating an ion-ion plasma upstream of the reaction region by the addition of a rapidly attaching gas such as SF₆ (Howard *et al.*, 1974). Clearly, this approach is only useful if the electron scavenging gas does not interfere with the reactions under study.

C. Plasma Dynamics and Determination of Rate Coefficients

In order to obtain a rate coefficient from the experimental decrease in the reactant ion count rate (Fig. 2), it is necessary to appreciate the fluid dynamics of the flowing carrier gas and afterglow plasma. For typical flow tube dimensions and carrier gas throughputs Q and pressures p , the developed carrier gas flow will be almost laminar with only a few percent slip at the walls. Under these conditions, the radial velocity profile $v_g(r)$ of carrier gas is given by

$$v_g(r) = 2v_0 \frac{(1 - (r^2/a^2) + (2s/a))}{(1 + (4s/a))}, \quad (1)$$

where a is the radius of the tube, v_0 the carrier gas bulk velocity which equals $Q/\pi a^2 p$ and $s = s'/p$, where s' is the pressure independent slip coefficient. Pitot tube measurements (Ferguson *et al.*, 1969) have shown that the form of the velocity profile is as predicted by Eq. (1). Also using this equation, Q can be expressed as

$$Q = \frac{\pi a^4}{8\eta} \left(\bar{p} + \frac{4s'}{a} \right) \Delta p, \quad (2)$$

where η is the carrier gas viscosity, Δp the pressure drop per unit length of flow tube, and \bar{p} the average pressure. From experimental measurements of \bar{p} and Δp as a function of Q , this relationship has been shown to be valid down to helium pressures of ~ 0.1 torr where the effects of molecular flow begin to dominate (Adams *et al.*, 1975). For predominantly viscous conditions and making the reasonable assumption that the instantaneous ion-velocity radial profile is identical to that of the carrier gas, the continuity equation for a given ion type of number density $[A^+]$, which is lost only by ambipolar diffusion and binary reaction with a neutral of concentration $[B]$, is given (see, e.g., Bolden *et al.*, 1970a) by

$$v_g(r) \frac{\partial[A^+]}{\partial z} = \underbrace{\frac{D_a}{r} \frac{\partial}{\partial r} \left(r \frac{\partial[A^+]}{\partial r} \right)}_A + \underbrace{D_a \frac{\partial^2[A^+]}{\partial z^2}}_B - \underbrace{k[B][A^+]}_C, \quad (3)$$

where the terms A , B , and C are the radial diffusive, axial diffusive, and reactive contributions, respectively, D_a is the ambipolar diffusion coefficient, k the reaction rate coefficient, and r and z are the radial and axial coordinates, respectively. This equation can readily be solved analytically if term B is neglected (this results in only a small error, e.g., 2% at a carrier gas pressure of 0.3 torr), giving the solution (Bolden *et al.*, 1970a; Adams *et al.*, 1975)

$$[A^+]_z = [A^+]_0 \exp - \left(\frac{\Delta D_a}{a^2} + \Gamma k[B] \right) \frac{z}{v_0}, \quad (4)$$

where $[A^+]_0$ and $[A^+]_z$ are the ion densities at the reactant gas entry point and at the sampling orifice, respectively, and Δ and Γ are pressure dependent factors also related to the slip coefficient s' . That the fluid dynamics and diffusive ion loss have been correctly treated, has been confirmed experimentally by Smith *et al.* (1975) who monitored the ion density as a function of axial position for a pure helium flowing afterglow plasma in which ambipolar diffusion was the only ion loss process and deduced a value of D_a within a few percent of the accepted value. Measurements of plasma flow velocities (Ferguson *et al.*, 1969; Adams *et al.*, 1975) are also consistent with the above analysis.

In the above analysis, it has been assumed that the reactant gas is introduced uniformly into the flow tube at a plane $z = 0$, an obvious approximation since the gas is usually introduced at a point. However, this can largely be corrected for by using an effective reaction length ($z + \epsilon$) which is greater than the physical reaction length. The value of ϵ , the "end correction", has been obtained experimentally by measuring a given ion-neutral reaction for several different reaction lengths (Bohme *et al.*, 1973). ϵ has also been determined from optical absorption measurements of the concentration of helium 2^3S metastable atoms as a function of distance along the flow tube for a given reactant gas addition (Bolden *et al.*, 1970b). These experiments yield a pressure-dependent end correction which typically varies from 4 to 11 cm over the pressure range 0.2–1.5 torr (Bohme *et al.*, 1973). The corrections necessary to account for the addition of the reactant gas at a point (and other smaller corrections) have been treated numerically in detail by Ferguson *et al.* (1969). Thus from the experimental decay in the primary ion count rate with reactant neutral addition, the reaction rate coefficient can be calculated. Various workers associate differing error figures with their measured rate coefficients ranging from ± 15 to $\pm 30\%$ for a straightforward measurement. Comparison of the values obtained by flow tube techniques and by other well-established techniques such as stationary afterglows, high pressure mass spectrometry, and ion cyclotron resonance (ICR) indicates that these error figures are generally conservative and that the flow tube data analysis for reaction rate coefficients has been correctly applied.

This analysis for determining reaction rate coefficients from flowing afterglow data can equally well be applied to the analysis of SIFT data if certain minor modifications are made. The minor modifications to this analysis for application to the SIFT are discussed in Section IV.B.

D. Some Recent Successes of the Flowing Afterglow

Since its inception, the flowing afterglow has been established as a first rate, extremely versatile technique and has been used to study many hundreds of thermal energy, binary, and ternary reactions of both positive and negative ions many of which cannot at present readily be investigated by other than flow tube techniques. The rate coefficients and ionized products so measured are included in compilations by Fehsenfeld *et al.* (1969b), Ferguson (1973), and Albritton (1978). The advantages and versatility of the flowing afterglow technique are also possessed by the more recently developed flow tubes, and therefore it seems only fitting to mention some of its successes which will act as a standard against which the recent advances should be compared. These successes have been reviewed in some detail in the literature (see, e.g., Ferguson *et al.*, 1969; Ferguson, 1972).

A great virtue of the flowing afterglow technique is its ability to produce a wide variety of primary ion species in their ground electronic state and with a Boltzmann distribution of rovibronic states in thermal equilibrium with the background carrier gas. The reactant neutral is also in thermal equilibrium with the background gas. However, in a few favorable cases it has also been possible to determine rate coefficients for ions reacting with excited state neutrals, e.g., vibrationally excited N_2 (Schmeltekopf *et al.*, 1968) and $O_2(^1\Delta_g)$ (Fehsenfeld *et al.*, 1969a). The striking increase in the rate coefficient for the reaction



of one and a half orders of magnitude for a factor of six increase in the nitrogen vibrational temperature shows the virtue of knowing the excitation states of the reactants. Another aspect of the versatility is the capability for studying the reactions of ions with chemically unstable neutral species such as H, N, O, OH, and O_3 (see, e.g., Fehsenfeld and Ferguson, 1968; Howard *et al.*, 1974; Fehsenfeld *et al.*, 1975a; Fehsenfeld, 1976). The study of negative-ion reactions at thermal energies has been almost solely the province of the flowing afterglow (Fehsenfeld, 1975b) and indeed it was using this technique that the process of associative detachment was first experimentally observed (Fehsenfeld *et al.*, 1966b). For example, reactions such as

