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FLUORINE NEGATIVE ION DETACHMENT KINETICS

Final Report

by

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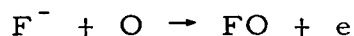
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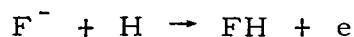
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ABSTRACT

A study of the rate of F^- detachment by O and H atoms via the reactions



and



was undertaken using a drift tube (i.e., a Tyndall tube) to produce F^- ions at various drift velocities and therefore different ion temperatures. Preliminary mobility measurements of F^- ions in Ar were made, indicating that ion temperatures in the 300 K to 5000 K range could be achieved; however due to numerous difficulties experienced in obtaining a reliable F^- ion source, the study could not be completed. This report describes the various techniques tried and recommends changes which the authors believe essential to obtain the desired measurements.

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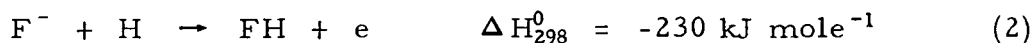
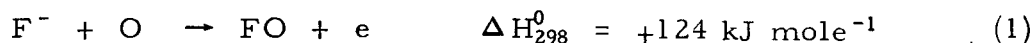
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INTRODUCTION

The use of per-fluorinated hydrocarbons and other fluorine containing compounds is of considerable interest for use in the suppression of electron concentrations in re-entry sheaths. The most stable and thus the dominant ion formed by electron attachment to these compounds in this environment is F^- .¹ In view of the importance of this ion to electron suppression, it is necessary to understand as fully as possible the kinetics of its formation and disappearance. One means by which the ion may lose its extra electron is via associative detachment reactions such as



The purpose of the present study is to measure the rates of reactions (1) and (2) in the temperature range of 2000 K to 5000 K.

A powerful tool with which to study such reactions is the drift or Tyndall tube, coupled with a mass spectrometer.²⁻⁵ Such a device consists, in essence, of a region of uniform electric field containing reactant molecules through which the ions of interest are made to drift; the pressure in the tube being such that the mean free path of the ions in the gas is much less than the tube dimensions. After drifting a certain length through gas containing reactant species (in this case H or O atoms) unreacted ions are collected. By measuring the time needed for the ions to traverse the drift length and monitoring the change in ion current as a function of reactant species pressure or drift length, a reaction rate can be determined. By varying pressure and electric field the drift velocity and thus the ion temperature can be varied. In practice, ion temperatures in the range of 300 (room temperature) to 10^4 K are achieved.

In the present study a number of attempts have been made to utilize drift tubes of various designs to obtain the needed information. The devices employed have proved to be unsatisfactory primarily because of the presence of large numbers of free electrons. These generate spurious F^- ion currents in the drift tube. Numerous other difficulties have also been encountered which have vitiated efforts to obtain the needed measurements. Time has not permitted the trouble-shooting needed to determine the causes of some of these problems. The following description of our efforts will thus be aimed at clarifying the present situation with regard to these problems in an effort to indicate what must be done to obtain the necessary data.

SYMBOLS

$\vec{D}$	diffusion dyadic, $\text{cm}^2 \text{sec}^{-1}$
D_L	longitudinal diffusion constant, $\text{cm}^2 \text{sec}^{-1}$
D_T	transverse diffusion constant, $\text{cm}^2 \text{sec}^{-1}$
$\vec{E}$	electric field vector, V cm^{-1}
E	electric field strength, V cm^{-1}
E_{cm}	kinetic energy in center of mass system, J
e	charge on ion, c
$\hat{f}_i(\vec{v}_i)$	velocity distribution of ions (not necessarily Maxwell-Boltzmann), $\text{cm}^{-3} \text{sec}^3$
$f_r(\vec{v}_r)$	velocity distribution of reactant molecules (Maxwell-Boltzmann), $\text{cm}^{-3} \text{sec}^3$
ΔH_{298}^0	heat of reaction at 298 K, J mole^{-1}
h	thickness of ion slab injected at $t = 0$, cm
$I(\ell, t)$	current collected at drift tube exit, A
$\vec{J}(\vec{r}, t)$	ion current density, $\text{cm}^{-2} \text{sec}^{-1}$
J_0	zero-order Bessel function
J_1	first-order Bessel function
K	mobility, $\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$
K_0	reduced mobility (see Eq. 4), $(\text{V sec cm})^{-1}$
$k(T_i)$	rate constant at temperature T_i (2-body), $\text{cm}^{-3} \text{sec}$
k_B	Boltzmann constant, $1.38 \times 10^{-2} \text{ J K}^{-1}$
ℓ	length of drift tube, cm

m_b	mass of buffer gas molecule, g
m_i	mass of ion, g
m_r	mass of reactant gas molecule, g
N	number of ions injected into drift tube
n	gas molecular number density, cm^{-3}
n_r	reactant gas molecular number density, cm^{-3}
$P(X)$	partial pressure of species X, N m^{-2}
$\vec{r}$	position vector, cm
r	distance from drift tube axis, cm
r_0	radius of drift tube
T_g	gas temperature, K
T_i	ion temperature, K
t	time elapsed after injection of ion slab into drift tube, sec
t_m	time elapsed between injection of ion slab to detection of maximum current, sec
t_0	time defined as $t_0 = \ell/v$, sec
$\Delta t_{1/2}$	width of ion slab after traversing the drift tube, sec
$\vec{v}$	velocity vector, cm sec^{-1}
v	drift velocity, cm sec^{-1}
$\vec{v}_i$	velocity of ions, cm sec^{-1}
$\vec{v}_r$	velocity of reactant gas molecules, cm sec^{-1}
$\overline{v_i^2}$	second speed moment of ions, $\text{cm}^2 \text{sec}^{-2}$
$\hat{z}$	unit vector along drift tube axis
z	distance from drift tube entrance along the tube axis, cm
Δz	a measure of longitudinal spread of the ion slab, $\Delta z = 2(D_L t_0)^{1/2}$, cm
α	conversion frequency of ions, sec^{-1}
β_1	first root of J_0 , $\beta_1 = 2.405$
ϵ_0	permittivity of free space, $\epsilon_0 = 8.85 \times 10^{-12}$ farad m^{-1}
μ	reduced mass

- $\rho(r, t)$ ion number density, cm^{-3}
 σ molecular polarizability, cm^{-3}
 ∇ gradient operator

I. THEORY OF DRIFT TUBE MEASUREMENTS

Drift tube apparatuses consist of three basic components: (i) an ion source, (ii) the drift tube itself (a cylindrical volume with a constant axial electric field) and (iii) an ion detector. The method used to obtain the required information (i.e. ion temperatures and reaction rates) is one of introducing a cloud of ions into the drift tube, measuring the time needed for the cloud to move through the tube and determining the change in cloud density and shape as it traverses the tube. Before describing the apparatus and results obtained in this study it will be helpful to describe briefly the theory of drift tube operation and how data obtained with such a device may be used to obtain reaction rate constants.

The flow of ions into the drift space is controlled using "gates" consisting of closely-spaced, gridded electrodes at the tube ends which are normally biased so as to prevent ions from entering or leaving the tube. A cloud of ions is introduced by reversing this bias with a square-wave pulse. Ideally, the cloud is thus initially disk-shaped and spreads as it moves down the tube under the influence of the electric field. The average velocity of the ions is denoted by v , the drift velocity. Wannier⁶ has shown that dimensional analysis of the Boltzmann transport equation shows that v is a function of E/n where E is the electric field strength and n is the gas density. The ion mobility is defined by the equation

$$v = K E \quad (3)$$

and the reduced mobility K_0 is given by

$$K_0 = K n \quad (4)$$

The reduced mobility is convenient for comparison of data taken at various pressures since K_0 is a function of E/n also.

For low field strengths, where ion-molecule interactions are dominated by the polarization force (Langevin polarization limit), K_0

is given by^{6-8*}

$$K_0 = 1.81 \epsilon_0 (\mu \sigma)^{-1/2} \quad (5)$$

where σ is the polarizability of the gas, μ is the reduced mass of the ion and gas molecule, and ϵ_0 is the permittivity of free space.

The ion current density of a cloud of drifting ions (non-interacting) is given by

$$\vec{J}(\vec{r}, t) = -\vec{D} \cdot \nabla \rho(\vec{r}, t) + \vec{v} \rho(\vec{r}, t) \quad (6)$$

where $\vec{J}(\vec{r}, t)$ is the ion current density as a function of position $\vec{r}$ and time t , $\vec{D}$ is the diffusion dyadic, $\vec{v}$ is the drift velocity and $\rho(\vec{r}, t)$ is the ion density. Continuity requires that

$$\nabla \cdot \vec{J}(\vec{r}, t) = -\frac{\partial \rho(\vec{r}, t)}{\partial t} + \alpha \rho(\vec{r}, t) \quad (7)$$

where α is the rate of loss of ions (ion conversion frequency). Combining Eqs. (6) and (7) gives

$$\frac{\partial \rho(\vec{r}, t)}{\partial t} - \nabla \cdot \vec{D} \cdot \nabla \rho(\vec{r}, t) + \nabla \cdot [\vec{v} \rho(\vec{r}, t)] + \alpha \rho(\vec{r}, t) = 0 \quad (8)$$

Equation (8) has been solved by a number of workers^{4,9-11} for various initial conditions and geometries. The drift tube constructed for this study (see next section) suggests the use of a cylindrical coordinate system with its origin at the drift tube entrance and with the z -axis along the drift tube axis. The ion detector (or exit aperture) is at $z = \ell$ and the radius of the tube is r_0 . At $t = 0$, we assume that a circular slab of ions of thickness h and total number N is injected into the tube. The slab ion density is assumed to drop off to zero at $r = r_0$ (i. e. the walls absorb ions reaching them) and only the zero-order radial density mode is considered. Such initial conditions have been suggested by Whealton and Woo¹¹ for the type of apparatus used in this study. The condition may be written as

*Equation (5) is given in rationalized mKs units. It is usual to quote values for K_0 in units of $(V \text{ sec cm})^{-1}$, μ in g and δ in cm^3 . Using these units, Eq. (5) is given as $K_0 = 4.8 \times 10^{-4} (\mu \sigma)^{-1/2}$

$$\rho(\vec{r}, 0) = \frac{\beta_1}{2\pi r_0^2 J_1(\beta_1)} \frac{N}{h} J_0(\beta_1 r/r_0) \times [H(z+h) - H(z)] \quad (9)$$

where J_1 , and J_0 are first and zero order Bessel function, β_1 is the first root of J_0 and H is the Heaviside step function ($H(z) = 0$, $z < 0$ and $H(z) = 1$, $z \geq 0$). Solving Eq. (8) with this initial condition gives the solution¹¹

$$\begin{aligned} \rho(\vec{r}, t) = & \frac{\beta_1}{4\pi r_0^2 J_1(\beta_1)} \cdot \frac{N}{h} J_0\left(\frac{\beta_1 r}{r_0}\right) \times \exp\left[-\left(\alpha + \frac{\beta_1 D_T}{r_0^2}\right)t\right] \\ & \times \left\{ \operatorname{erf}\left[\frac{vt - z+h}{(4D_L t)^{1/2}}\right] - \operatorname{erf}\left[\frac{vt - z}{(4D_L t)^{1/2}}\right] \right\} \quad (10) \end{aligned}$$

Here D_L and D_T are the longitudinal and transverse components of the diffusion dyadic. If the initial thickness of the ion slab, h , is small compared to ℓ (i.e., gate times are much shorter than ℓ/v) and with the current at the exit given by

$$I(\ell, t) = 2\pi \int_0^{r_a} \operatorname{er} \hat{z} \cdot \left\{ \vec{v} \rho(\vec{r}, t) - \vec{D} \cdot \nabla \rho(\vec{r}, t) \right\} dr \quad (11)$$

where $I(\ell, t)$ is the current collected, e is the ion charge, r_a is the radius of the ion detector (exit aperture) and $\hat{z}$ is the unit vector in the z direction, one obtains

$$\begin{aligned} I(\ell, t) = & \frac{e r_a J_1(\beta_1 r_a/r_0) N}{4 r_0 J_1(\beta_1)} \frac{(v + \ell/t)}{(D_L t)^{1/2}} \times \exp\left[-\left(\alpha + \frac{\beta_1 D_T}{r_0^2}\right)t\right] \\ & \times \exp\left[-\frac{(vt - \ell)^2}{4 D_L t}\right] \quad (12) \end{aligned}$$

In Eq. (12) we note the following factors: (i) the loss of current due to reaction, enters via the term:

$$\text{reaction loss} \propto \exp(-\alpha t) \quad (13)$$

(ii) the loss due to transverse diffusion is:

$$\text{transverse diffusion loss} \propto \exp\left(-\frac{\beta_1 D_T t}{r_0^2}\right) \quad (14)$$

and (iii) the decrease in magnitude due to longitudinal spreading of the slab is

$$\text{longitudinal diffusion loss} \propto \frac{v + \ell/t}{(D_L t)^{1/2}} \exp\left[-\frac{(vt - \ell)^2}{4 D_L t}\right] \quad (15)$$

It can be shown that, if a thin slab of ions is injected into the drift tube, the current recorded (at the exit) will be a maximum when the time elapsed after the entrance gate pulse is

$$t_m = t_0 \left(1 - \frac{2 \Delta z^2}{3 \ell^2}\right) \quad (16)$$

where $t_0 = \ell/v$ and Δz , a measure of the longitudinal spreading of the ion cloud during transit, is defined as

$$\Delta z = 2(D_L t_0)^{1/2} \quad (17)$$

It has been assumed in deriving Eq. (16) that losses due to diffusion and reaction are small so that

$$(\Delta z/\ell)^2 \ll 1 \quad (18)$$

and

$$\left[\left(\alpha + \frac{\beta_1 D_T}{r_0^2}\right) t_0\right] \left(\frac{\Delta z}{\ell}\right)^2 \ll 1 \quad (19)$$

In practice conditions (18) and (19) mean that the time needed for the ion cloud to traverse the tube is much greater than the duration of the detected current pulse and that the total charge detected per pulse is not highly dependent on t_m .

The interpretation of drift tube data in terms of kinetic rate coefficients involves the utilization of Eqs. (12) and (16). First, with no reactant gas in the drift tube, the ion current is recorded as a function of drift time. Equation (16) is then utilized to obtain v . This is accomplished by first measuring directly the time between the entrance gate pulse and the detection of maximum current, t_m . Then, to obtain Δz , the times at which the ion current is at

half maximum are measured. Denoting the time difference between the half-maximum currents by $\Delta t_{1/2}$, we have, to a good approximation, i. e. to

$$0\left((\Delta t_{1/2}/t_m)^2\right),$$

$$\Delta z/\ell = \left[2(\ln 2)^{1/2} t_m\right]^{-1} \Delta t_{1/2} \quad (20)$$

After determining v at a variety of buffer gas pressures and field strengths, the reactant gas is introduced and the (exponential) decrease in peak ion intensity measured as a function of reactant partial pressure. Equation (12) is then used to obtain α , the ion conversion frequency. By keeping the reactant partial pressure low compared to the total pressure, v , D_L and D_T will not change appreciably and α will be given simply by

$$\alpha_p = (t_m)^{-1} \ln \left[\frac{I_0(\ell, t_m)}{I_p(\ell, t_m)} \right] \quad (21)$$

Here the subscript p refers to the reactant gas pressure and 0 to the situation with only nonreacting buffer gas.

Once α has been determined over the range of pressures and field strengths of interest, the problem of obtaining the desired reaction rate constant from α arises. For present purposes, it is necessary to obtain a rate constant which relates to a chemical system at high temperatures, rather than to a system (such as the drift tube) in which high ion energies are generated by an electric field in a cool gas.

In order to translate α , a function of drift velocity and pressure, into a rate constant expressed as function of temperature, it is necessary to obtain an effective ion temperature (i. e. the center-of-mass kinetic energy) of the ions in the drift tube. To do this we rely on the theory of Wannier,⁶ which gives us the velocity and speed moments of an ion velocity distribution in a constant electric field (this distribution cannot be written in closed form). In particular, the theory of Wannier shows that

$$\overline{v_i^2} = \left(1 + \frac{m_b}{m_i}\right) v^2 + \frac{3 k_B T_g}{m_i} \quad (22)$$

where m_i and m_b are the ion and buffer gas molecular masses, respectively, and T_g is the gas temperature. In analogy with the thermal case we write

$$E_{cm} = \frac{3}{2} k_B T_i \quad (23)$$

$$E_{cm} = \int_{\vec{v}_i} \int_{\vec{v}_r} \tilde{f}_i(\vec{v}_i) f_r(\vec{v}_r) \frac{\mu}{2} |\vec{v}_i - \vec{v}_r|^2 d\vec{v}_i d\vec{v}_r \quad (24)$$

In these expressions E_{cm} is the center-of-mass ion-molecule collision energy, k_B is the Boltzmann constant, T_i the effective ion temperature $\tilde{f}_i(\vec{v}_i)$, the ion velocity distribution (the tilde denoting the fact that this distribution is not Maxwell-Boltzmann), $f_r(\vec{v}_r)$ the reactant molecule distribution (Maxwell-Boltzmann), μ the reduced mass of ion and reactant molecule, and $\vec{v}_i$ and $\vec{v}_r$ the ion and reactant molecule velocities, respectively. From Eqs. (23) and (24) we find that

$$T_i = T_g + (3k_B)^{-1} \left[\frac{m_r (m_b + m_i)}{m_r + m_i} \right] v^2 \quad (25)$$

Therefore the determination of v for an ion at a particular field strength and pressure determines T_i . The determination of α as a function of T_i and n_r , the reactant gas density, gives us the equivalent chemical rate constant

$$k(T_i) = \frac{\alpha(v, n_r)}{n_r} \quad (26)$$

For 2-body reactions α will be proportional to n_r ; for 3-body reactions α will be proportional to the product $n_r n$. The conditions under which $k(T_i)$, determined in a drift tube, can be equated to the rate constant in a thermal (Maxwell-Boltzmann) situation at T_i have been recently discussed in great detail by Woo and Wong.¹² For present purposes, equality of these rate constants can be assumed, especially since the reacting species involved in this study are all atomic.

II. EXPERIMENTAL APPARATUS

As noted above, a drift tube apparatus consists of three basic components; an ion source, the drift tube and an ion detector. In the present study several modifications of these basic components were used.

A. Ion selection prior to the drift tube. - The first system constructed is shown schematically in Fig. 1. A microwave discharge cavity (2450 MHz) surrounds a Vycor tube through which an O_2/NF_3 mixture at $\approx 100 \text{ Nm}^{-2}$ is passed to produce F^- ions. The gas and ions are sampled through a 0.025 cm diam aperture at the apex of a conical sampling probe into a volume pumped to $\approx 5 \times 10^{-3} \text{ Nm}^{-2}$ by a 6-inch oil diffusion pump. In this section gas is skimmed off and a quadrupole lens system focuses the ions into a beam for injection into a quadrupole mass filter contained in a section which is pumped on by a 4-inch diffusion pump (to a pressure of $\approx 5 \times 10^{-4} \text{ Nm}^{-2}$). The mass filter is tuned to transmit F^- ions ($M/e = 19$) and a cylindrical lens injects the focused F^- ion beam into the drift tube through a 0.025 cm diam aperture. The drift tube itself is composed of a series of equally-spaced electrodes made of stainless steel. The electrodes are 0.079 cm thick annuli with 2.54 cm i.d. and 7.62 cm o.d. Except for two electrodes at the front and rear, electrodes are separated by 0.635 cm alumina spacers. The electrodes and spacers are supported on ceramic rods. The gating electrodes at the front and rear are separated by 0.079 cm thick Teflon spacers covered with fine (80 lines per inch) nickel mesh. These gridded electrodes form the entrance and exit gates for the drift tube (see below). The overall drift tube length is 12.3 cm. The drift tube operates at pressures in the 5 to 200 Nm^{-2} range and is pumped by a 10 cfm mechanical pump.

At the exit of the drift tube is another 0.025 diam aperture. Ions passing through the drift tube and out of the exit aperture enter a volume containing an 18-stage ion multiplier tube coupled to an electrometer or pulse counting equipment. This volume is pumped to $\approx 1 \times 10^{-3} \text{ Nm}^{-2}$ by another 6-inch diffusion pump.

The ions, generated at approximately ground potential in the discharge are, upon entering the ion lens section, accelerated by the +250 V bias of the ion lens. They are then decelerated to 8 eV, to optimize resolution and transmission in the mass filter. After passing through the mass filter, the ions are again accelerated with a +210 V potential on the focusing lens. Ions entering the drift tube are decelerated rapidly by collisions with the buffer gas (argon). They then drift to the first grid of the entrance gate which is biased 10 V more positive than the entrance aperture (220 V above ground).

The gridded gate electrodes are operated so that, except during the relatively short pulse times, there is a negative potential (provided by 1.5 V batteries) across them to prevent transmission of negative ions. Two pulse generators provide square pulses of 0.5 to 2 μsec duration which open the gates. A positive pulse generator opens the entrance gate and, after an adjustable delay, a negative pulse generator opens the exit gate. Pulse heights are typically 8 V. The drift tube electrodes between the gates are connected to a bridge, made of glass coated resistors strung inside the drift tube vacuum

jacket, which divides the total potential drop across the tube so that a constant axial potential gradient is obtained down the tube. Upon passing through the exit aperture the ions are accelerated toward the first dynode of the ion multiplier by a 1 kV potential.

As noted above, the ion source used with this apparatus was a microwave discharge in an O_2/NF_3 mixture at about 100 Nm^{-2} . Argon was the buffer gas employed in the drift tube. All gases were Matheson High Purity grade and were used without further purification.*

Serious problems were encountered with this apparatus and no data of value were obtained. The problems were: (i) discharges occurred in the drift tube, (ii) maximum drift tube pressures were limited to about 70 Nm^{-2} by pumping requirements in the ion multiplier section (which must be operated at less than $1 \times 10^{-3} \text{ Nm}^{-2}$ to prevent discharges between dynodes), and (iii) electron detachment by the reaction



as F^- ions enter the drift tube (with energies $\approx 210 \text{ eV}$).

The problem of discharges in the drift tube was avoided by keeping pressure in the tube at $\approx 10 \text{ Nm}^{-2}$. Keeping pressures in this range also eliminated the problem of high pressures at the ion multiplier.

The problem of electron detachment could not be solved so easily. In fact, this problem forced the redesign of the entire apparatus. That Reaction (27) was indeed the problem was demonstrated by several observations. First, detector outputs were not affected by gate potentials. This would be expected, since electrons would not respond to the narrow gates at these low pressures ($\approx 10 \text{ Nm}^{-2}$). Also, electrons would be extremely difficult to gate because their high drift velocities (~ 100 times as great as ion drift velocities) make transit times across the drift tube very short (under usual condition, $\approx 1 \mu\text{sec}$). Finally, the addition of a gas with high electron affinity (SF_6) led to increases in signal. This would be expected if electrons were the dominant negative species before introduction of SF_6 . (It should be remembered that the lack of mass analysis between the drift tube and ion multiplier makes definite species identification

*Drift tube work is notorious for problems caused by impurities. Charge transfer reactions may greatly magnify the importance of trace impurities. However, in the present case, because of the large electron affinity of fluorine, this is not expected to be a serious problem, since most impurity negative ions (in particular O^- , O_2^- and OH^-) will charge transfer to F^- .

impossible.) The negative ions formed by attachment (SF_6^- and SF_5^-) would have much smaller diffusion constants and thus more negative ions would successfully traverse the tube before diffusing to a wall.

It was decided on the basis of these negative results to change the apparatus dramatically. A new design, very similar to that used by Beatty and Patterson,⁴ was selected.

B. Ion selection after the drift tube. - The redesigned drift tube is shown schematically in Fig. 2. We do not show the mass filter and quadrupole ion lens system since no changes were made in these components except that the ion multiplier was placed directly after the mass filter. The drift tube was constructed with the same electrodes and ceramic spacers used before. The major changes in the drift tube itself were (i) a decrease in length (the distance between the gridded gate electrodes) to 3.49 cm and (ii) the introduction of a thermionic electron source.

The redesigned tube at first contained a 0.025 cm diam platinum filament with a $\text{BaZrO}_3/\text{BaCO}_3/\text{SrCO}_3$ coating to lower the work function of the filament and permit operation at temperatures of < 1400 K. This coating is reported¹³ to provide long filament life in oxidizing (oxygen) atmospheres. Unfortunately, NF_3 and SF_6 , the fluorine containing gases used here, apparently removed the coating and attacked the platinum. The result was short (~ 10 min) filament lifetimes at the temperatures needed (≈ 1600 K) to obtain emission. Failure occurred through melting of the platinum. After several attempts, the platinum was replaced by 0.038 cm diam tungsten. These filaments proved to have lifetimes of about 1 to 2 hours in SF_6 at $\approx 6 \text{ Nm}^{-2}$.

Electrons from the filament pass through a gridded electrode and enter the region referred to in Fig. 2 as the attachment region. In this section, some of the electrons attach to fluorine containing gases resulting in the production of F^- ions (among others). The negative species are drifted toward the entrance gate of the drift tube. The gates were operated as described earlier. The time between entrance and exit pulses was measured using an oscilloscope. The electrical circuitry used with the revised drift tube is shown in Fig. 3. The potentials employed were typically 10 to 30 V between the filament and electron grid, 5 to 30 V across the attachment region, 1.5 or 4.5 V across the gates (with pulse heights of 8 V) and 50 to 150 V across the drift region.

The drift tube vacuum jacket contains two gas inlets and two exhausts. One set of inlets and exhausts was on each side of the Teflon spacer (Fig. 3) which divides the drift region from the attachment region. A 1 cfm mechanical pump exhausts the attachment region and a 5 cfm pump exhausts the drift region. A capacitance manometer is used to monitor pressure in the drift tube.

III. RESULTS AND DISCUSSION

Using the device just described, F^- ions were generated in sufficient quantity to allow mobility measurements to be made. These measurements, which provide the dependence of the drift velocity and thus ion temperature on E and n , are the first step toward performing the reaction rate measurements. However, the difficulties encountered while obtaining these preliminary results were compounded by the next step; that of adding the reactant species (i.e. O- and H-atoms) to obtain reaction rate data. At this time we can only report the difficulties encountered and the results of the mobility measurements. The eventual measurement of the rate constants of interest requires the further improvement of technique and additional changes in apparatus design.

A. Mobility measurements. - As noted above, problems encountered with coated Pt filaments forced a change to tungsten filaments which could operate at higher temperatures without melting. First experiments were attempted using NF_3 , but use of this gas as a source of F^- ions resulted in such short filament life that less corrosive SF_6 was finally employed. Use of SF_6 produced the ions SF_6^- , SF_5^- , and F^- , the latter two appearing in approximately equal quantities.

The following procedure was employed. After pumping the drift tube down to an ultimate pressure of 1.3 Nm^{-2} , SF_6 is introduced at a pressure of $\sim 6 \text{ Nm}^{-2}$ through the attachment region inlet. Argon is introduced through both drift and attachment region inlets at equal flow rates of $\approx 0.5 \text{ cm}^3 \text{ sec}^{-1}$ (using calibrated orifices) until the drift tube pressure reaches the desired value (in the range 27 to 133 Nm^{-2}). Potentials and gate pulses are then applied to the tube, the delay time between entrance and exit pulse varied, and ion counting rates (or currents) recorded.

The following problems were encountered:

1. Attempts to monitor F^- via ion counting failed and the signal had to be detected instead by using an electrometer to measure current from the ion multiplier. Most probably the delay between the end of work with the first design and the redesigned tube (about 4 months) resulted in some deterioration of the multiplier dynode surfaces. A quick check to see if positive ions could be counted was affirmative. Potentials in the drift tube (except between the filament and first grid) and the polarity of the ion lens and mass filter biases were reversed for this experiment. With the filament on and only Ar being introduced into the system counting rates of 10^3 sec^{-1} were observed at $M/e = 18$ (H_2O^+). This anomaly may be due to the fact that the construction of the multiplier tube and accompanying electronic equipment is such that positive ion energies are $\approx 3000 \text{ eV}$ at the first dynode, while negative ions have $\sim 1000 \text{ eV}$

energies. Thus damage to the surface of the first dynode might lead to the results observed. The possibility that F^- ions were never counted because there were no such ions present is unlikely; it was always possible to obtain large ion currents at $M/e = 19$ on an electrometer attached to the multiplier by introducing NF_3 or SF_6 to the drift tube and raising the drift region field strength until a glow discharge was generated. Even under these conditions, no F^- (or other negative ion) was observed by pulse counting. Thus time limitations forced us to proceed without the added sensitivity provided by pulse counting.

2. The drift region field strengths were limited by the occurrence of discharges to ≈ 50 V/cm. These discharges were observed by noting both changes in the drift tube electrode potentials and large F^- ion currents which did not respond to the gates. The discharges are caused by electrons passing through the attachment region and gates and cascading in the relatively high drift region field. Lowering attachment region potentials reduced the tendency to discharge, as did increasing SF_6 flows. However, both of these measures also reduced F^- (and other negative ion) signals to the point where measurements were impossible. Thus we were forced to work at attachment region potentials which resulted in high "background" F^- signals (not controlled by the gates) over which small gated signals were superimposed. The reasons for this limitation are probably twofold: (i) As described above, we may have been using a degraded ion multiplier which could detect F^- ions only in cases of high ion densities in the drift tube. (ii) We were working with low partial pressures of SF_6 . Negative ion drift tube studies by others¹⁴⁻¹⁹ have utilized pure gases (notably O_2) which have relatively high electron affinities and are undiluted by gases with zero affinities, such as Ar.

Experience strongly indicates that when acceptable F^- signals were observed, they were the result of discharges in the attachment region. For example, in many instances, a gated F^- ion current was observed which was much larger than the background ion current component (which did not respond to the gates). However, within minutes after obtaining this desirable situation the background current would become much larger than the signal, the result being a total current which did not vary measurably with delay times between the gates. Furthermore, it proved impossible to reproduce results by using potentials, pressures, and filament emission currents which, during the previous running period, gave usable signals. This lack of reproducibility strongly suggests an ion production mechanism which depends on such uncontrollable parameters as electrode surface contamination and noise levels (especially in electron emission).

In order to obtain more reliable operation of the device a number of changes were made, none of which produced significant improvements. These included: (i) placing grids over some of the attachment region electrodes to

gain better control over fields in the attachment region, (ii) lowering the potential of the entire apparatus (drift tube electrodes, ion lens and mass filter) to prevent the drift of negative species to the drift tube jacket, (iii) use of WF_6 , CCl_2F_2 , or CF_4 as a source of F^- ions instead of SF_6 , and (iv) introduction of a microwave discharge ion source by connecting a glass tube through a hole drilled in the flange on the filament end of the drift tube.

The results of mobility measurements made during the brief periods in which F^- ions were observed which responded to gating are shown in Fig. 4. The reduced mobility $K_0 = K_n$ is plotted vs. E/n . These data were obtained at three pressures with Ar as the buffer gas. The data are tabulated, along with operating conditions, in Table I. The table lists E/n and the field strength and pressure in the drift region, the drift velocity, the reduced mobility and the ion temperature (with respect to O-atoms). In all measurements the gate pulses were less than $0.1 t_m$ in duration, and the approximations in Section I apply.

A matter of concern is revealed by the use of (Eq. 5) for the Langevin zero field mobility. For the F^-/Ar system one finds a predicted $K_0 = 8.2 \times 10^{19} (\text{V sec cm})^{-1}$. The average experimental value is $4.9 \times 10^{19} (\text{V sec cm})^{-1}$. Although the measurements were made at relatively high values of E/n ($\sim 1 \times 10^{-15} \text{ V cm}^2$) where the Langevin limit is of limited applicability, the discrepancy is unexpectedly large. An even more disquieting observation is that the Langevin mobility for SF_6^- (also present in the system) in Ar is $4.95 \times 10^{19} (\text{V sec cm})^{-1}$, very close to the value measured here for F^- . Thus, there is some reason to believe that the F^- detected may in some way be generated near the exit gate by SF_6^- (or SF_5^-) ions which have traversed the drift region.

B. Other measurements. - After obtaining the mobility measurements attention was turned to the O-atom source. A microwave cavity (2450 MHz) was placed over a Vycor tube at the drift tube gas inlet. Oxygen was then introduced along with argon into the drift section. Using the NO/NO_2 light titration technique,^{20, 21} O-atom density measurements were made at the drift section inlet and exhaust ports. Only one measurement was performed. For this test $\approx 1/3$ of the O-atoms survived passage through the drift tube. Averaging the entrance and exit O-atom flows this test indicated that the following partial pressures were obtained in the drift section:

$$\begin{aligned} P(\text{Ar}) &= 67.2 \text{ Nm}^{-2} \\ P(\text{O}_2) &= 14.0 \text{ Nm}^{-2} \\ P(\text{O}) &= 1.6 \text{ Nm}^{-2} \end{aligned}$$

Oxygen flows lower than those used in this test led to O-atom concentrations too low to measure at the exit port. (The light titration method gives light

output proportional to the square of the O-atom concentration.) Larger pumps would thus be advantageous since they would permit shorter residence times in the drift tube, thus decreasing recombination losses of O-atoms.

The final step was the attempt to obtain F^- detachment rates by O-atoms. The presence of O_2 led to shortened filament life (~ 30 minutes). This new problem, coupled with those described previously, plus time and financial limitations, forced an end to our efforts.

IV. SYNOPSIS AND RECOMMENDATIONS

A. Synopsis. - Drift tubes of two different designs were used to study the reactions



Attempts to measure reaction rates were frustrated principally by (i) a lack of a reliable F^- ion source, (ii) an inability to prevent hot electrons from passing through the drift tube entrance gate, and (iii) a suspected lack of sensitivity caused by possible degradation of the ion multiplier dynode surfaces during the period of construction of the redesigned tube.

With considerable effort, preliminary mobility measurements of F^- in Ar were made. As required, K_0 , the reduced mobility, is a function of E/n and is nearly constant. However, for E/n as low as 4.4×10^{-16} V cm², the measured value of K_0 (5×10^{19} (V sec cm)⁻¹) is appreciably lower than would be expected, the Langevin polarization mobility (zero-field) being 8.2×10^{19} (V sec cm)⁻¹. This discrepancy requires further study before the mobility measured here can be taken at face value.

B. Recommendations. - In order to obtain the desired measurements the following steps should be taken:

1. Faster pumping rates are needed to obtain higher O-atom/ O_2 ratios in the drift tube.

2. There would seem little hope of obtaining the needed data with the simple thermionic electron source used here. The presence of both O_2 and fluorine compounds is too corrosive. One can remedy this problem by two means: (i) enclose the filament in a compartment flushed with argon with a small gridded aperture through which electrons pass into an attachment

region containing NF_3 , F_2 or SF_6 , or (ii) construct a system more suitable for use with a microwave discharge ion source. Such a system would contain the needed light trap (to prevent ultraviolet light from reaching the ion multiplier) and would need more rapid pumping (which is available) to increase flow rates so that ions would reach the drift tube before recombining.

3. If, with these improvements, there is still a problem with hot electrons creating spurious ion currents an "electron filter"^{14, 22} could be introduced. This device is a double grid across the drift tube (in the attachment region) with which a transverse rf electric field is applied at frequencies of ~ 10 MHz. The rf field sweeps out electrons but does not appreciably perturb the more massive ions.

4. Degradation of the ion multiplier used with the drift tube may have caused much of the difficulty. This problem could be easily eliminated with a new or reconditioned unit. A standby unit would be very desirable.

It is the authors' belief that these modifications would be sufficient to permit the successful completion of the detachment coefficient measurements. Time and financial limitations prevented their implementation during this effort.

AeroChem Research Laboratories, Inc.,
Sybron Corporation,
Princeton, N.J., 4 November 1971.

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TABLE I MOBILITY MEASUREMENTS

$E/n, 10^{-15} \text{ V cm}^2$	$E, \text{ V cm}^{-1}$	$P, \text{ Nm}^{-2}$	$V, 10^4 \text{ cm sec}^{-1}$	$K_0 10^{19} (\text{V sec cm})^{-1}$	$T_i 10^3 \text{ K}$
0.44	14.1	135	2.32	5.22	0.41
0.94	14.6	66.6	3.67	3.92	0.50
0.95	30.4	135	4.11	4.29	0.53
1.34	42.7	135	6.35	4.72	0.79
1.38	21.5	66.6	5.82	4.21	0.72
1.89	29.2	67.5	7.94	4.32	1.0
2.28	36.5	67.8	10.9	4.80	1.6
2.80	44.7	67.8	14.5	5.20	2.6
2.81	18.3	27.8	12.7	4.50	2.1
2.90	19.2	28.4	14.2	4.91	2.5
3.17	21.2	28.7	19.5	6.05	4.5
4.17	27.2	26.8	23.3	5.56	6.2

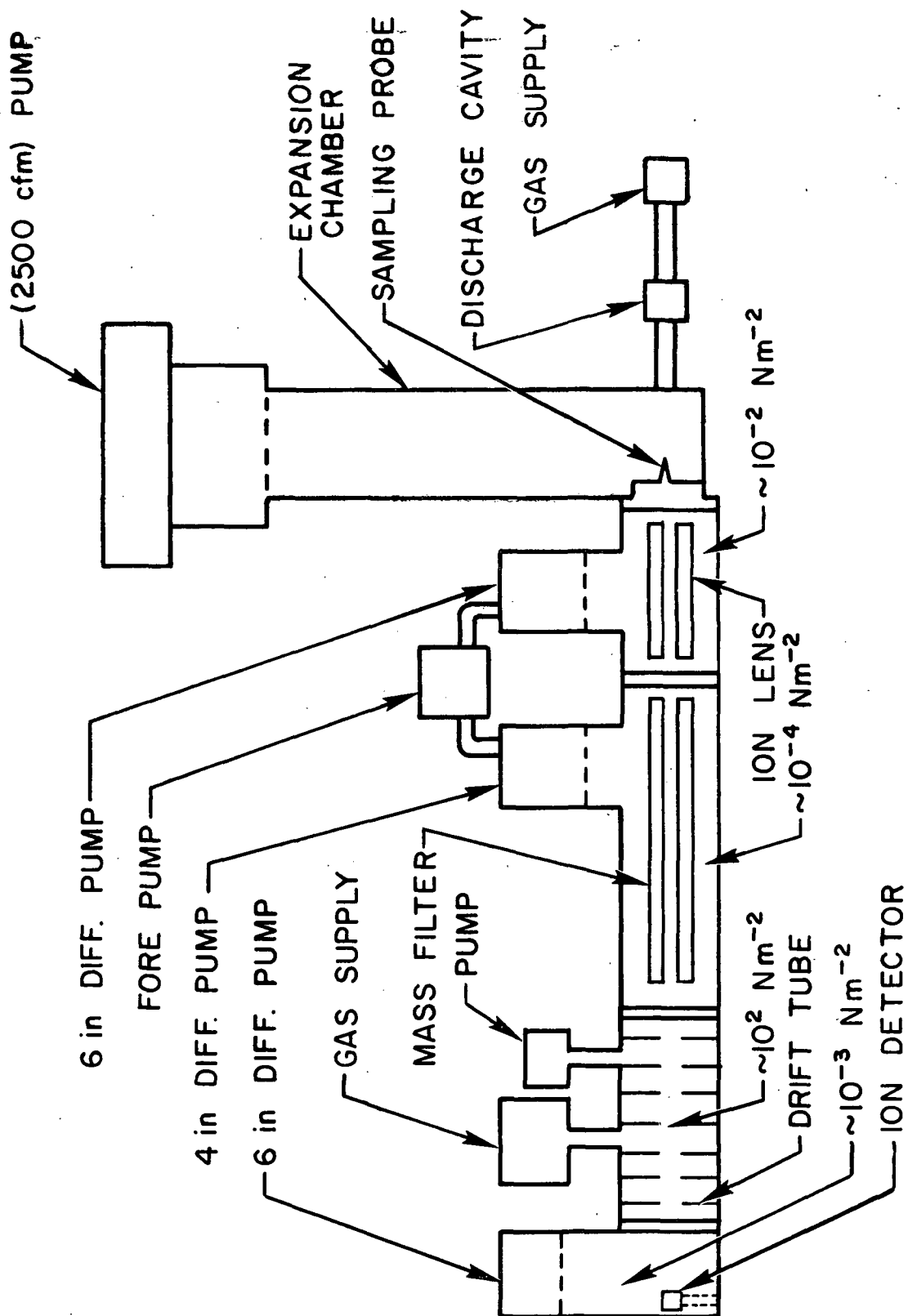


FIG. 1 DRIFT TUBE APPARATUS--ION SELECTION PRIOR TO THE DRIFT TUBE

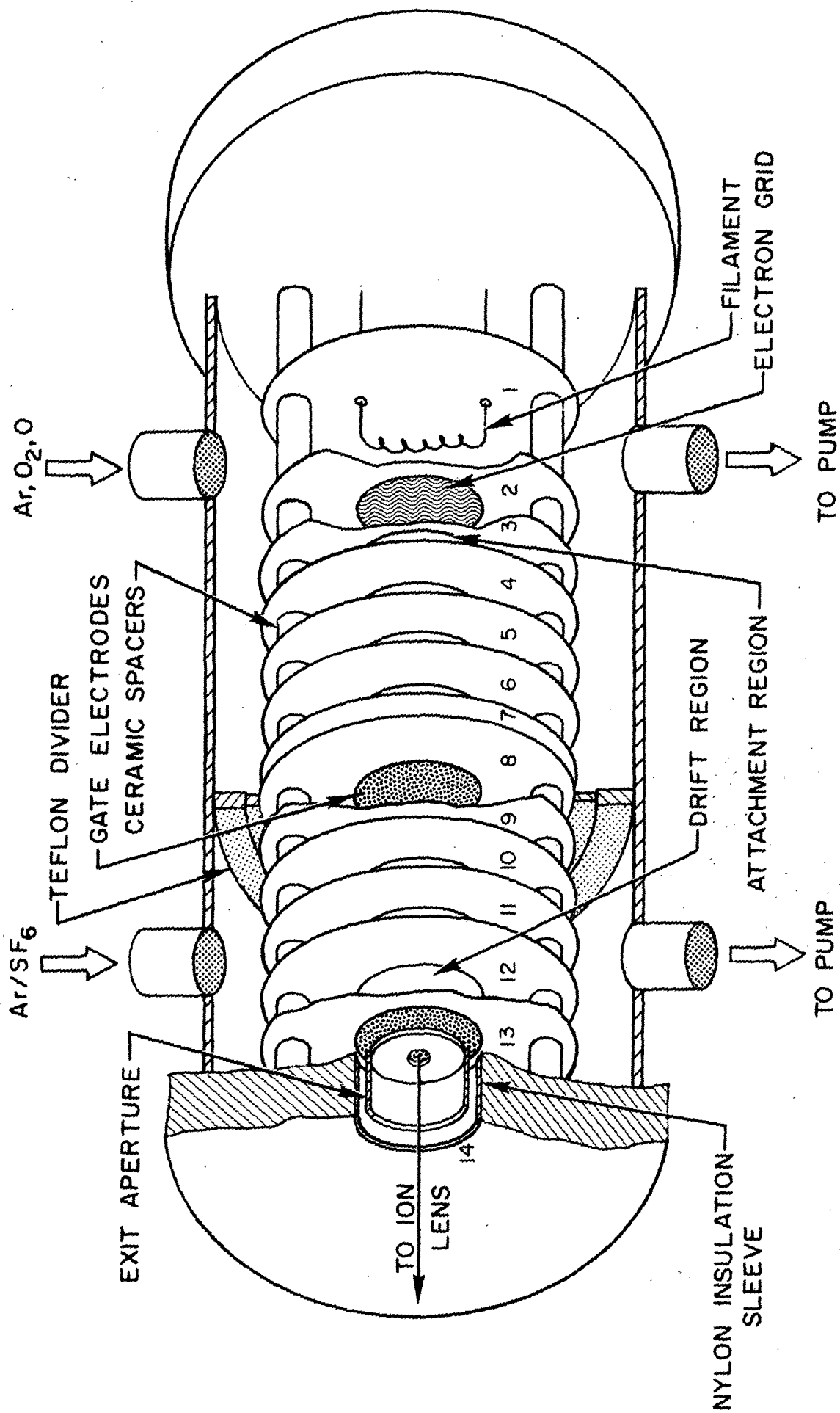


FIG. 2 DRIFT TUBE

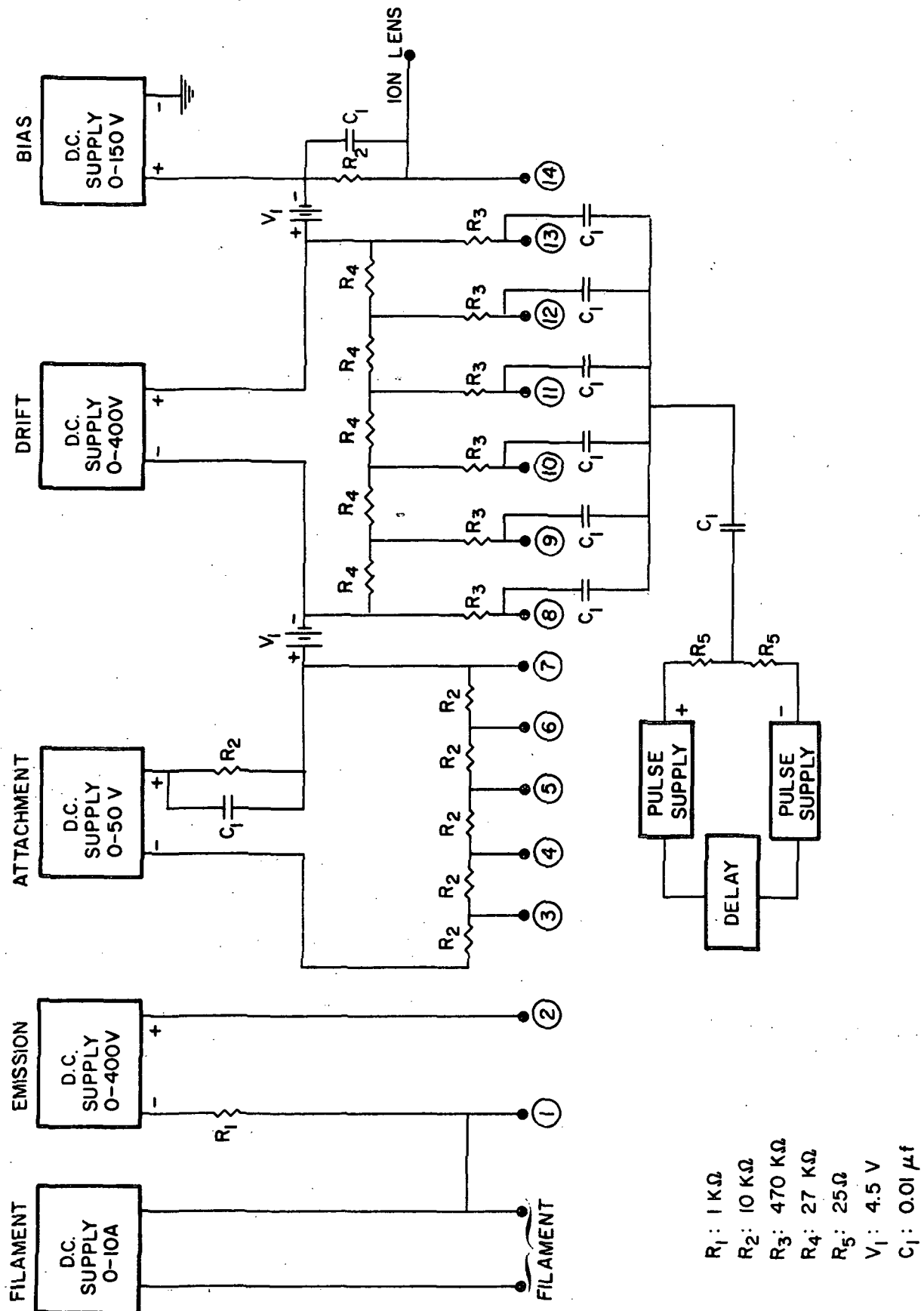
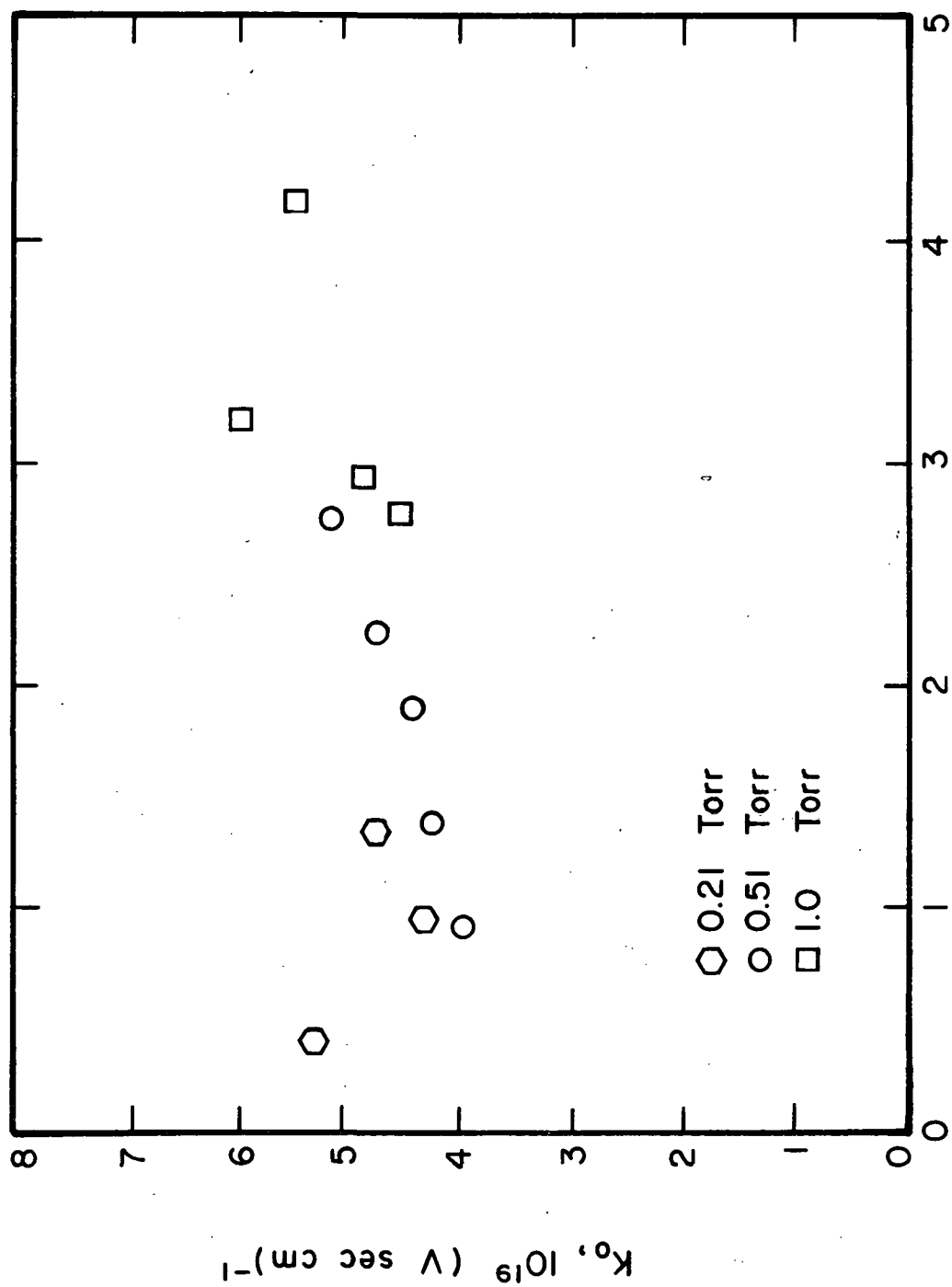


FIG. 3 DRIFT TUBE CIRCUITRY



$E/n, 10^{-15} \text{ V cm}^2$

FIG. 4 REDUCED MOBILITY OF F^- ION IN ARGON