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PLASMA SAMPLING - A VERSATILE TOOL IN PLASMA CHEMISTRY

H. Helm[+], T.D. Märk and W. Lindinger

Institut für Experimentalphysik der Leopold Franzens Universität, Karl Schönherrstr. 3, A 6020 Innsbruck, Austria.

Abstract - In order to determine the nature of the charged constituents of plasmas, various sampling techniques have been applied succesfully in different laboratories. It is the aim of this paper to show the limitations of these techniques due to sources of error, caused by effects occurring in the plasma sheath in front of a sampling orifice and effects within it, such as reactive collisions or collisional breakup, mass dependent transmission of the ions or the change of the energy distributions of the various types of ions in collisions during the extraction process.

INTRODUCTION

Plasma sampling had its early beginnings in experiments concerned with the nature of anode and cathode rays (Refs.1-4). Although these experiments date back to the end of the last century, it was not until the fifties that the sampling technique was recognized as a powerful tool in plasma diagnostics (5-8).During extensive investigations of combustion processes in 1953 Calcote and King measured the dependence of the ion concentration on the distance from the luminous flame zone in propane air mixtures (5). In 1957 Pahl and Weimer started systematic studies on the dependence of the wall current in a positive column on the discharge parameters and analyzed the positive ion current penetrating through a tiny orifice in the wall of the discharge vessel (Fig.1) with a magnetic mass spectrometer.

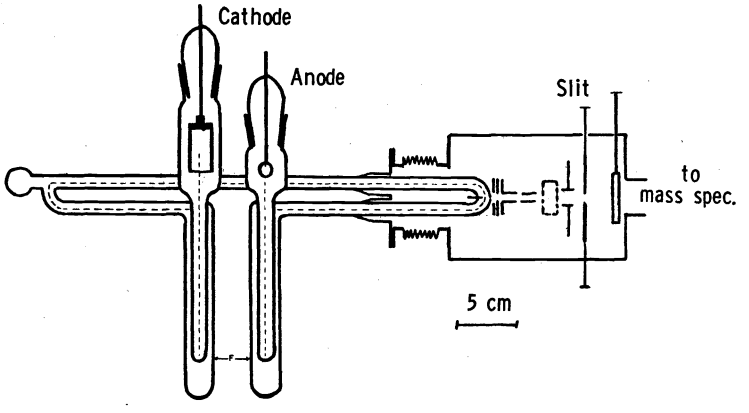


Fig. 1. Apparatus of Pahl and Weimer (Ref.8) used for the investigation of the wall current in a positive column burning in a glass tube.

[+] Present address: SRI International, Molecular Physics Laboratory, Menlo Park, Ca. 94025, USA.

This technique has proven to be of general use and has since been applied to the study of other discharge regimes as well as to decaying plasmas and flames.
The exciting prospect about the sampling technique is that one has direct access to the identity of the plasma species, and indeed many new species such as H_3^+ have first been detected in this way (9).
The sampling technique is however not free from complications. Since the ions have to be sampled remotely, a mass spectrometer cannot be placed into the plasma without interfering with the system.
In this paper we shall limit ourselves to a discussion of various problems associated with the sampling technique and show its limitations.

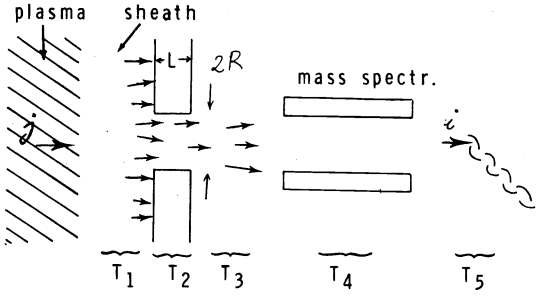


Fig. 2. Schematic drawing of a sampling system for the analysis of charged plasma constituents.

The cleanest approach to the diagnostics of the ion species present in a plasma would certainly be optical spectrometry but it is hard to see this in the near future as an easily manageable tool replacing mass spectrometers. While an optical window usually does not interfere with the state of the plasma, a sampling hole usually does and we should be aware of that. The sampling orifice should have the properties to preserve the nature of the plasma composition sampled through it (Fig.2). As long as molecular flow takes place, the composition of the beam gas is identical to that of the source gas reaching the wall of our plasma vessel in the vicinity of the orifice. While these conditions may be fulfilled in certain applications it is still not obvious in what respect the composition of the wall current is related to the composition in the bulk plasma. This relation is governed by the nature of the sheath which separates the wall from the bulk plasma.Supposing we know that relation, we may then ask for the fate of the plasma species as they travel from the orifice to the detector. The ions are now travelling through a very different environment. Generally they experience accelerating fields which may cause collisional breakup or excitation. The mass spectrometer also does not transmit and resolve all masses equally well. And finally if an electron multiplier is used,it will exhibit different relative responses for different ions. Whether the sampling orifice alters the ion composition or not is determined by the size of the orifice,that is the diameter and the length of the hole, which nearly

always is a short tube, and the pressure in the sampled plasma. In addition it will also depend on the nature of ions sampled, as we shall explain below.

The complexity of the problem, is indicated by the following relation between the current of a particular ion, i, measured at the detector and the current flowing through an imaginary plane at the edge of the plasma, j,

$$i = j \cdot T_1 \cdot T_2 \cdot T_3 \cdot T_4 \cdot T_5 \ ,$$

where T denotes the transmission and geometry factors for the various parts of our sampling system (see Fig.2). These transmission factors may be interdependent. If we accelerate ions in the sheath, we are then likely to alter T_1. Since ions will now transverse the orifice with different kinetic energies T_2 may change and so on. In most experiments it is not possible theoretically to predict the magnitude of these transmission factors and they have to be checked separately if one needs information on absolute plasma current densities.

Fortunately most experiments do not require an absolute calibration. One is quite satisfied if a linear relationship holds between the plasma concentration and the current of the respective ion sampled. So, a basic requirement would be that the collection efficiency for various ion species were the same, even if the absolute collection efficiency is unknown. We shall see that even this much simpler requirement is often hard to achieve.

In the following we would like to concentrate on experiments which are concerned with the first three transmission factors and we begin with the choice of the dimensions of the orifice.

ORIFICE EFFECTS

It is illustrative in this context to start with the assumption of molecular flow conditions and consider the neutral gas. The neutral particles will in general fall isotropically on to the wall and unless the orifice is excessively long a cosine distribution will describe the flow of particles on the vacuum side. Obviously the number of particles penetrating the orifice will decrease as the thickness of this wall increases. What may not be obvious is how large the fraction of particles is which come into contact with the walls before they reach the vacuum vessel. Under molecular flow conditions this fraction is determined by the ratio of length to diameter of the orifice. If this ratio is one then only about 17% of the particles penetrate the orifice freely while 83% come into contact with the wall and are either backscattered or reach the vacuum side after one or several collisions (10). When sampling plasma constituents, we definitely want to avoid any contact with the walls and hence the requirement of an almost ideal thin orifice tube is mandatory. Certainly isotropic incidence is the worst possible case we may imagine and the presence of a space charge sheath helps us in the case of positive ions since the acceleration in the sheath may be close to free fall conditions in many cases hence resulting in a directed motion of the ions towards the wall. This is evident from an experiment by Holzmann (11), who measured the angular distribution of positive ions and electrons

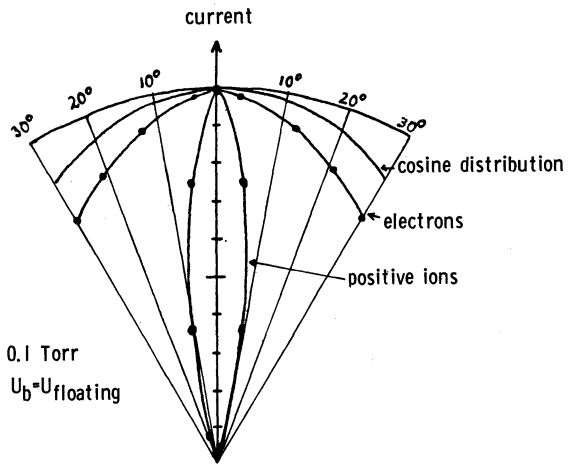


Fig. 3. Results of Holzmann (Ref.11) on the angular distribution of ions and electrons, sampled from the negative glow of a hollow cathode discharge with the sampling probe kept at floating potential.

sampled from a low pressure plasma. Fig.3 shows results on the angular intensity distribution of electrons and positive ions sampled with the wall probe being at floating potential. In contrast to the positive ions which gain considerable directed motion in the sheath, electrons have a broad angular distribution since they have to run against a potential barrier in the sheath. From this we may conclude that the effect of collisions with the orifice tube walls is less important for positive ions than for electrons under these sheath conditions.

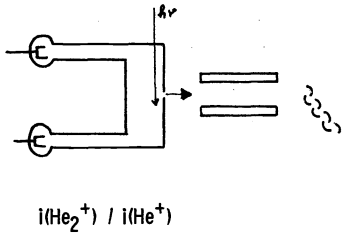
The problem of wall collisions will be more important as we sample plasmas at increased pressures since collisions in the bulk gas flowing through the tube will tend to increase the number of particles reaching the wall.

This effect has been investigated in detail and as an example we discuss here the data obtained by Wellenstein and Robertson (12).

Wellenstein and Robertson measured absolute cross sections for the associative ionization reaction

$$He^* + He \rightarrow He_2^+ + e$$

for selected states of the excited helium atom. This experiment was done in a positive column by selectively populating excited states by line absorption from metastable helium atoms present in a discharge (Fig.4). At the same time the reaction product, He_2^+ was monitored using a mass spectrometer. To determine the absolute cross sections Wellenstein and Robertson had to measure accurately the ratio of ambipolar wall currents of He^+ and He_2^+. Pahl in 1957 found that the ratio of atomic to molecular ions sampled from a positive column under similar conditions was dependent upon the length of the orifice tube and to make sure to avoid a corresponding error, Wellenstein and Robertson measured this current ratio at



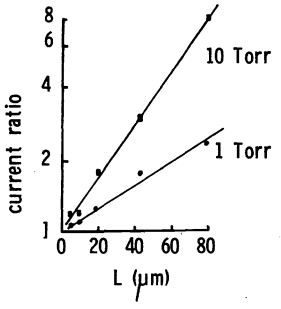


Fig. 4. Schematic drawing of (a) the experimental setup of Wellenstein and Robertson (Ref.12) for the investigation of associative ionization reactions, and (b) the normalized current ratios $i(He_2^+)/i(He^+)$ obtained with sampling orifice of various lengths.

several lengths of the orifice tube. The diameter was always 22 µ, the length varied from 5 to 80 µm. The results for two different values of discharge gas pressures are shown in Fig.4. There is a strong, exponential dependence of the current ratio on the tube length.

At a pressure of 10 torr the current ratio may be falsified by as much as a factor of 8 when a long orifice is used. The effect is less strong at lower pressure but still is as large as a factor of 2 at 1 torr. This effect is believed to orignate from the substantial difference in the collision cross sections of the two ion species involved here. The mean free path for He^+ will be very much smaller than for He_2^+, both in their parent gas, due to the possibility of resonant charge transfer of the atomic ions. Frank and Lüdemann (13) have derived a relation that allows to quantitatively account for this effect. The formula is based on the calculation by Walcher of the neutral gas density distribution in the vicinity of an orifice under molecular flow conditions. Frank et al. (13) assume that any ion suffering a collision in the tube or just outside it, where the neutral gas density is still appreciable, is lost from the extracted beam. Their formula relates the measured and the true ion current ratio with the dimensions of the orifice and the respective mean free path of the ions and the pressure. Plotted in Fig.5 is the ratio of the measured current ratio to the true current ratio of the two argon ion species, Ar_2^+ and Ar^+, as a function of pressure. The measurement were taken by Pahl (6) for the orifice dimensions given in the figure. The straight line represents the prediction by Frank and Lüdemann.

If one is aware of the possible source of error that can be caused by a long orifice canal one will try to eliminate it by making the orifice as thin as possible. This may not be very easy to do if a dielectric orifice is used. Thin apertures in metal orifices on the other hand, as they

$$\alpha_{meas} = \alpha_{true} \exp\left(\frac{L+R}{2}\left\{\frac{p}{\lambda_1} - \frac{p}{\lambda_2}\right\}\right)$$

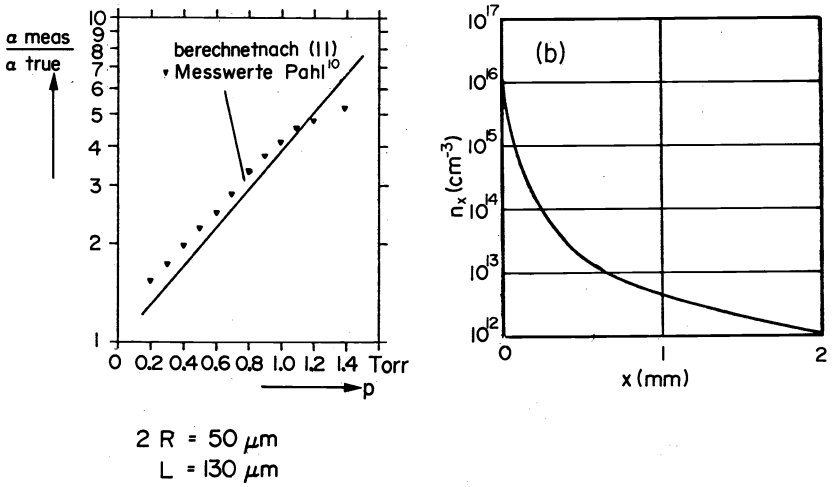


Fig. 5. Ratio of the measured current ratio $\alpha_{meas} = i(Ar_2^+)/i(Ar^+)$ to the true current ratio α_{true}, as predicated by Frank and Lüdemann (13) according to the formula shown above. The measurements were taken from Pahl (6). b) neutral gas density distribution in the vicinity of an orifice.

are used in electron microscopes are commercially available in different sizes and shapes. The foils (made of gold), have a typical thickness of 0.5 μm. The hole size may be as small as 100 μm down to 10 μm. This represents an ideal aperture (14).

For a general prediction of mass discrimination factors however parameters other than only the mean free paths have to be taken into account. This will become apparent in the discussion of an experiment performed by Milloy and Elford (15) in a drift tube system (Fig.6a). There is no space charge sheath in front of the orifice in the case of sampling from a drift tube. The flow of ions through the orifice is governed by diffusion and drift due to the external electric field and possibly due to convective motion of the neutral gas in the vicinity of the orifice. In the drift tube the ions gain energy from this external field and store it partly in motion parallel and perpendicular to the electric field vector. The distribution in these two degrees of motion is governed by the nature of the interaction between ions and neutrals and the mass ratio of ions and neutrals. A light ion in a heavy buffer gas will bounce around a lot and distribute much of the energy picked up from the field in motion perpendicular to the field while a heavy ion in a light buffer gas will more easily

remember the momentum vector it had before the collision. It will exhibit a more directed motion in the field direction than the light ion. This

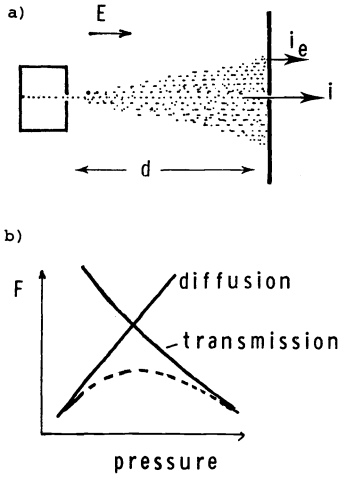


Fig. 6. a) Schematic drawing of the experimental setup of Milloy and Elford (15). b) Ratio $F = i/i_e$ as a function of buffer gas pressure in the drift tube, when the reduced electron field strength E/N is kept constant.

difference in random motion between light and heavy ion should of course influence the ability of an ion to transverse this critical region around the orifice if the mean free path is of the same order of magnitude as the orifice dimensions. And this is indeed found in the experiment of Milloy and Elford. The basic idea of the experiment is the following: if ions start in a drift tube from a point source, the ion swarm will spread out on its way through the drift tube. The ratio of ions going through a hole in the end plate of the tube, i, to the total current on the end plate, i_e, will be governed by a number of parameters, one of which is the pressure. If we keep E/N, the reduced electric field strength constant, this current ratio will increase with increasing pressure since diffusion is inhibited at higher pressure. The ratio may be predicted theoretically and the relation

$$F = \left(\frac{E}{N}\right) \cdot \frac{N}{2(D_T/K)} \left(\sqrt{d^2 + R^2} - d\right)$$

which will not be discussed here explicitly, but which is dealt with in great detail by Millay and Elford, has been verified in a large number of different experiments. The point we want to use here is that with E/N held constant one expects a linear increase in the current ratio with pressure. Any deviation from such a linear dependence will have to be attributed to a pressure dependent transmission of the orifice which falsifies the current sampled through the orifice, i., and hence the ratio $F = i/i_e$.
If collisions of ions in the orifice or beyond it cause the loss of a particular ion we may expect these effects to become more important as the pressure increases and hence the current i and therefore the ratio F might actually decrease as indicated by the dashed line in Fig. 6b when the

pressure is increased. The following results, obtained by Milloy and Elford (15) strongly support this idea. A heavy ion in a light gas, such as K^+ in H_2 shows F (Fig.7a) increasing with pressure close to what one expects in an ideal sampling case. As the mass ratio decreases however, losses become more effective and the same ion K^+ in an argon buffer where the mass ratio is about 1 already shows considerable difficulties in reaching the mass spectrometer at the elevated pressure (Fig. 7b).

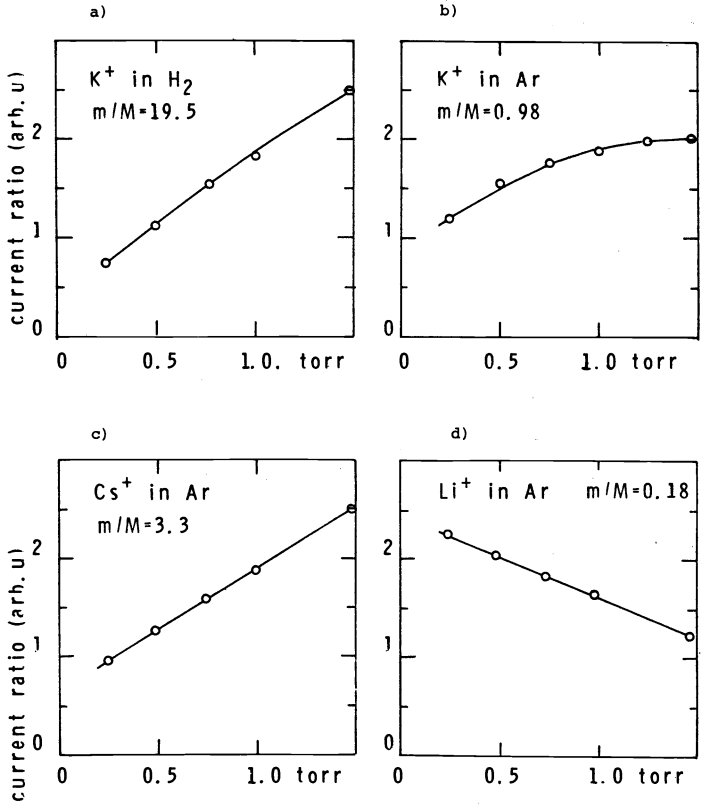


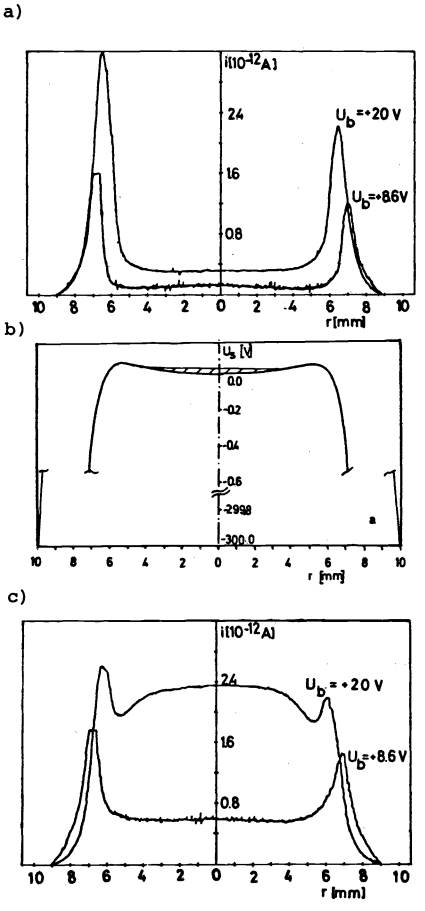
Fig. 7. Current ratio $F = i/i_e$ as a function of buffer gas pressure for the cases of a) K^+ ions drifting in H_2, b) K^+ in Ar, c) Cs^+ in Ar and d) Li^+ drifting in an argon buffer.

Similarly Milloy and Elford investigated different ions in the same buffer gas. Cs^+ in Ar which has a mass ratio of 3.3 is relatively unaffected, while Li^+ in argon, here the mass ratio is only 0.18, shows strongly decreasing transmission as the pressure increases (Fig.7c,d).

What is the message from these results? 1) Mass discrimination will be less important for heavy ions in a light buffer gas than for light ions in a heavy buffer gas (like in real life: the smaller ones often have a hard time). 2) It will also be less important the lower the pressure is held, and in addition Milloy and Elford could show that it will be less important the smaller the orifice is chosen.

Another effect which may be a serious sampling error in the case of negative ion sampling was found recently by Kuen, Howorka, and Varney (16). Sampling negative ions from a hollow cathode discharge in oxygen enabled them to detect negative ions from various radial positions in the negative glow. A typical result for the O_2^- profile over the discharge radius is

shown in Fig. 8a. The negative glow region has a diameter of about 14 mm, the cathode diameter is 20 mm. The reason why the negative ions are found preferentially at the edge of the negative glow region may be understood from the radial potential distribution in this kind of discharge. For positive ions this discharge configuration establishes a shallow potential



radial distribution of

O_2^- current

local potential

O^- current

$O_2 + e \longrightarrow O^- + O$

Fig. 8. Radial profiles of a) O_2 - and c) of O^- currents obtained by sampling a hollow cathode discharge and b) radial potential distribution within the discharge.

well (Fig. 8b) in the axis with a small barrier against the strong field of the cathode fall region. For negative ions this potential distribution must be looked at upside down. Negative ions are trapped in these two humps of the potential. There they are either lost by recombination or they flow off in axial direction towards the anode. The distribution of O_2^- is shown here for two different values of sampling probe potential, a weak draw out field and a stronger draw out field. The radial distribution which is found is basically the same in both cases. For O^- however this is not at all true (Fig. 8c). While at low draw out fields the O^- distribution is similar to that of O_2^-, the center portion of the distribution changes critically with the magnitude of the draw out field. The reason for this is that when stronger draw out fields are used, the electrons which are drawn towards the wall together with the negative ions gain sufficient energy to produce O^- in the dissociative attachment reaction

$$O_2 + e \rightarrow O^- + O$$

This reaction has a resonance at about 8 eV electron energy, and occurs either in the sheath or in or beyond the orifice. The radial distribution of the additionally formed O^- ions reflects the radial distribution of electrons in the discharge and has nothing to do with the negative atomic oxygen ions present in the discharge. This effect may be called a very serious sampling error if one is not aware of it.

We have so far confined our discussion to systems at relatively low pressure. There is a lot of interest in sampling high pressure systems, typically at atmospheric pressure. In this case one generally has to reduce the nozzle diameter and employ differential pumping in order to keep the background pressure in the analyzer region at an acceptably low level. There are however limitations as to how small the sampling hole can be made and usually one encounters a situation where the flow is no longer molecular or close to molecular but becomes continuous. Under these conditions a new class of effects appears which are characterized by the isentropic expanding gas jet in which, at least in the early stage, the mean free path is much smaller than the diameter of the gas beam flowing through the nozzle. In practice this means that a beam molecule travelling in the beam center with a higher velocity than its neighbours will be slowed down in collisions when it tries to overtake them. Likewise slow molecules will be accelerated by these collisions and as a result a narrowing of the velocity distribution in the flow direction will occur. Moreover, since more beam molecules have larger velocity components in the flow direction than perpendicular to it, a molecule trying to escape from the beam will have a lower mean free path than one flying in the beam direction. Collisions will than occur which tend to reduce this perpendicular motion.

Consequently there is a drastic drop in the translational temperature, that is the temperature perpendicular to the beam as the beam expands. Ideally one then has a narrow translational distribution of a few degrees Kelvin superimposed on a most probable beam velocity that may be supersonic.

For polyatomic species the cooling affects internal degrees of freedom as well as translational motion and the resulting beam may exhibit $T_{vib} > T_{rot} > T_{trans}$, when the flow finally becomes molecular.

This transition occurs within less than 10 orifice diameters, so the transit time from the high pressure region to the collisionless case will be of the order of 1 μsec. To a reactive ion a lot may happen within a microsecond. If an ion X^+ spends a μsec in a high pressure environment of 10 torr and reacts with the gas Y

$$X^+ + Y + Y \rightarrow XY^+ + Y$$

with a three-body rate coefficient of 10^{-29} $cm^6 s^{-1}$, then the probability for this reaction to occur within a μsec is

$$\exp(-k_3 [Y]^2 t) \approx \exp(-1)$$

That means the ion has a good chance to be converted. This obviously occurs in the high pressure plasma under consideration and we might first think that this is of no further concern to us. What is important however is that

this reaction may also occur in the expanding free jet where the local thermodynamic conditions may be entirely different from those in the plasma sampled.

Let us assume, the reaction

$$X^+ + 2Y \rightleftarrows XY^+ + Y$$

to be in equilibrium in a high pressure plasma. As the ions X^+ and XY^+ whose equilibrium we might want to determine pass through the expansion region, the local temperature effective in collisions may drop due to the isentropic flow. As long as collisions occur the reaction equilibrium will try to accomodate to the changing thermodynamic conditions. If that happens the ion composition at the end of the expansion may be entirely different from what it is in the plasma.

About six years ago, Hayhurst and Telford (17) studied this phenomenon probably for the first time in connection with mass spectrometric sampling at high pressures.

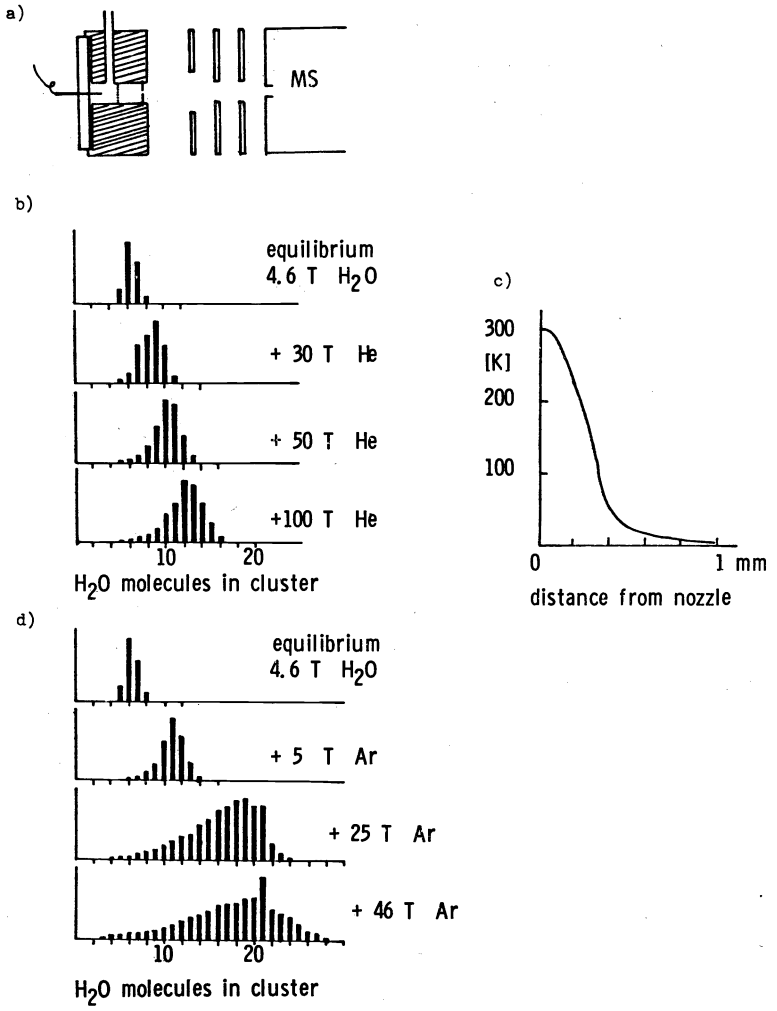


Fig. 9. a) The apparatus of Searcy and Fenn (18) b) Distribution of water cluster ions in H_2O and H_2O-He mixtures, d) in H_2O-Argon mixtures. c) Temperature profile as a function of the distance from the nozzle.

In the mean time a number of other investigations have been made which confirm the conclusions of Hayhurst and Telford and below we discuss a typical experiment, performed by Searcy and Fenn (18). The basic idea of their experiment was the following. First an equilibrium mixture of water cluster ions was prepared in a host gas of argon or helium. The ions were created by a corona discharge between a needle and the grid and then flew into a drift region where they could reach equilibrium conditions (see Fig.9a). A few of the ions reached the sampling orifice after about 100 msec. Two nozzle sizes of 100 and 200 μm were used. The water vapor pressure was kept constant at 4.6 torr. At this pressure an ion distribution was found which closely resembled the equilibrium distribution which was predicted by Kebarle's (19) data (Fig.9b). Then helium was added to the water and measurements taken at various helium pressures. Since the water vapor concentration did not change the equilibrium conditions should be unchanged. What was found in the mass spectrometer however was a strong shift towards larger cluster size as the pressure of the host gas increased. The shift towards larger cluster size was due to collisions of the ions in the expanding jet where the temperature continued to drop. Fig. 9c also shows a temperature profile along the centerline of the expanding jet as Searcy and Fenn have calculated it for the 100 μm nozzle. The experimental results have to be understood thus: the decrease in temperature of the host gas is in collisions transferred to the ions which in turn are then able to build up larger clusters. Searcy and Fenn found that cluster ion formation increases dramatically as the orifice diameter increases and also is stronger if argon is used as a gas rather than helium. One reason for the larger effect in argon is that argon has a greater cross section for collisions and that because of its lower flow velocity the time scale for the argon expansion is longer than for helium. Consequently under otherwise identical conditions the ions will suffer more collisions in the argon bath than the helium bath. How drastic the effect is in argon is apparent from Fig.9d. At a pressure of 50 torr the dominant ion is the cluster with 21 water molecules.

Ion sampling under such conditions can only be done with extreme care and should be repeated with a smaller orifice diameter, say 10 μm, in order to see how much this effect may be reduced.
Apart from the orifice another important source of error in the sampling technique is the modification of the ion composition due to the presence of the sheath between plasma and wall.

SHEATH EFFECTS

One general evidence for sheath reactions that has been observed several times is shown in Fig.10, which was taken from a paper by Lambert et al.(20). Ions were sampled from a decaying helium plasma through an orifice which may be biased with respect to one of the discharge electrodes, and the characteristic of ion current vs probe potential is shown in Fig. 10.
Both He^+ and He_2 are present in the plasma and at low probe potentials Lambert et al. observe a fairly constant current ratio until the two

currents reach saturation values. Beyond that however the current of the molecular ion decreases rapidly and correspondingly the current of He^+ increases, the total current being constant. The reason for this is that as

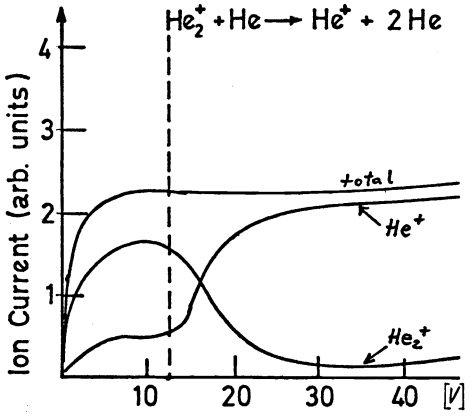
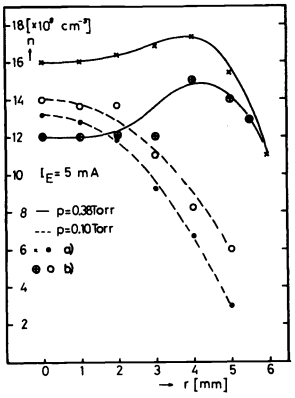


Fig. 10. Characteristics of ion currents versus probe potential obtained by Lambert et al. (20) from a decaying helium plasma.

the probe potential increases the potential across the sheath-separating the plasma from the wall increases until finally the molecular ion is accelerated to energies which are sufficient to lead to breakup of the ion in collisions. He_2^+ is a fairly strongly bound molecular ion, $D(He^+\text{-}He)$ = 2.46 eV but the effect of breakup of ions in the sheath will be more important the smaller the bond energy of the molecular ion is. This effect has been observed for a number of cases with other ions (21-24).

The possible modification of the ion comparison in the sheath is the second serious problem in the sampling technique.
Ideally one would like to sample ions with a probe at plasma potential. In this case wall current and ion density would be related by the simple relation $j = N\bar{v}/4$. In general it will however not be possible to construct a sampling probe that is small compared to the Debye length and usually one is forced to use an arrangement where a small metal probe is imbedded in the dielectric plasma wall or where the orifice is part of a large discharge electrode or the wall of the plasma vessel. In each case the regime between orifice and the bulk plasma will be dominated by wall effects, plus effects due to an external bias of the orifice with respect to a distant discharge electrode. With the presence of the sheath and the presheath, the region where this simple equation $j = N\bar{v}/4$ holds is shifted away from the probe to where the bulk plasma goes over into the presheath. The relation between the current density at the probe surface with the plasma current density will be governed by ion optical effects in the sheath and presheath. Obviously these effects will very much depend on the geometry of our sampling device. Only in special cases these optical effects are negligible, e.g. in the investigations of Howorka et al. (25). A comparison of the radial density distribution in a hollow cathode discharge measured by Langmuir probes and obtained by the sampling of ions using a hole probe led to nearly identical results (Fig.11), indicating that optical effects do not strongly disturb the ion currents passing through the sampling orifice. Despite

this, the possibility of a modification of the ion composition in this transition region has to be of concern in every diagnostic experiment. In this context some results are shown in Figs. 14-16 obtained in an experiment by Gieseke (14) recently. His experimental system is shown schematically in Fig. 12. Ions extracted from a hollow cathode discharge are first



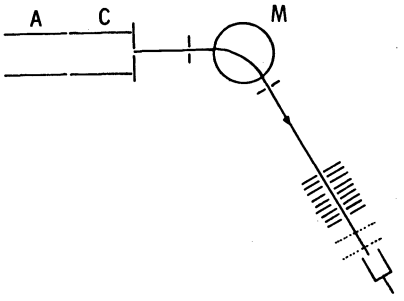


Fig. 11. Radial dependence of the total carrier density determined by two different methods. a) from mass-spectrometric measurements of ion currents, and b) from Langmuir-probe measurements of electron saturation currents.

Fig. 12. Schematic drawing of the experimental arrangement of Gieseke (14).

mass analyzed in a 60° magnetic mass spectrometer, then decelerated by a series of lenses and finally a retarding potential analysis is made to determine

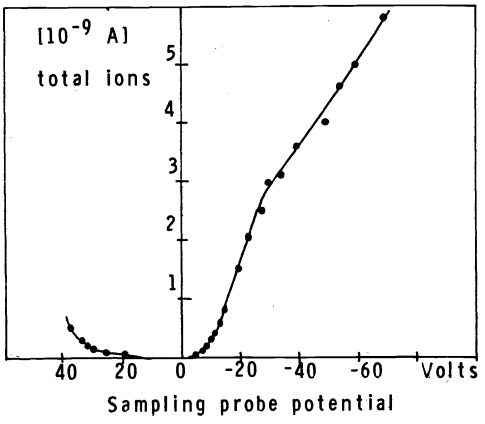


Fig. 13. Typical characteristics of total ion current versus probe potential obtain by Lindinger (26) from a hollow cathode discharge.

the energy of ions escaping from the sampling orifice. The system was first calibrated with a thermionic ion source and then applied to the discharge. A typical ion current probe voltage characteristic as it is known from the experiments of Lindinger (26) is shown in Fig. 13. Ions from the discharge are extracted with the probe being biased negatively with respect to the anode. The characteristic looks close to that of an ideal Langmuir probe: an ion retardation region followed by a small plateau indicating saturation, followed by a steeply rising section which is associated with an ion optical effect, the sheath blowing up and collecting more ions towards the sampling probe surface. Gieseke measured the energy distribution of a large number of ions at various probe voltages. Let us look at the behavior

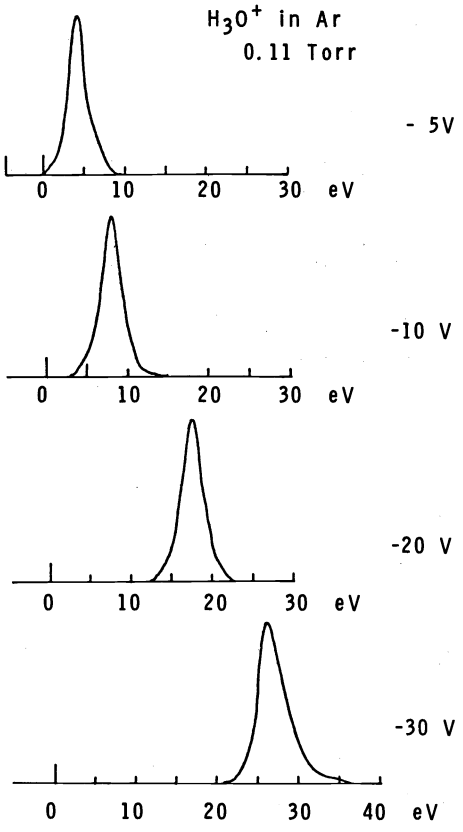


Fig. 14. Energy distributions of H_3O^+ at various probe potentials.

of some of the ions in an argon discharge. Fig. 14 shows the energy distribution of H_3O^+ at various probe potentials. As the draw out field is increased,the energy distribution merely shifts towards larger energies. There is no indication of inelastic energy losses of the H_3O^+ ions as they transverse the sheath region. The parent ion Ar^+ on the other hand (Fig.15) behaves remarkably differently under the same discharge conditions. The argon ion is unable to reach the high energies the H_3O^+ showed. Rather it always shows a low energy portion of ions which have suffered resonant charge exchange and at high energies a yet unexplained structure which is probably

associated with inelastic energy losses occurs. The structure observed in the distribution is specific for different ions as may be seen from Fig.16.

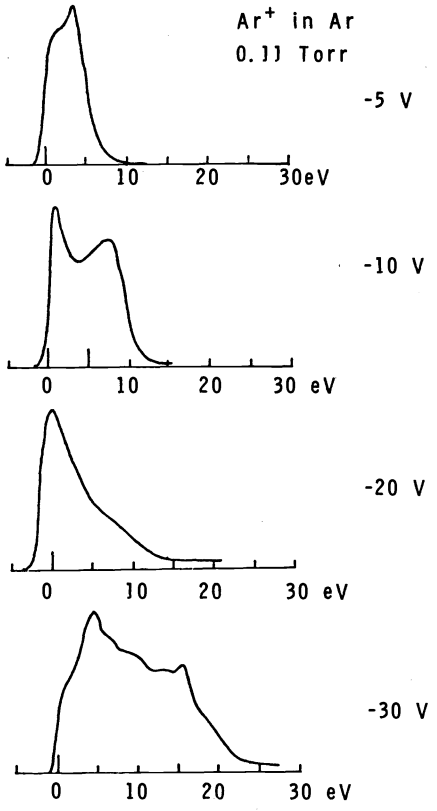


Fig. 15. Energy distributions of Ar^+ at various probe potentials.

All these ions are measured with the probe being at floating potential. The three argon associated ions all show a structure in the energy distribution at lower energies that corresponds to the sheath potential. And this structure is likely to come from the fact that Ar^{++} may exchange charge, Ar_2^+ may suffer ion atom interchange and ArH^+ may suffer proton exchange as it moves through the sheath. These results are shown here to point out two aspects. Firstly, if a mass analyzer is very sensitive to the ion energy it will have to be readjusted for different ions, since their energies will be different, and secondly, it may happen that one does not see some ions at all if the potential across the sheath is too large (breakup).

Earlier we mentioned the different transmission of Ar^+ and Ar_2^+ through the orifice. The large difference in the energy distribution clearly shows us the origin of this effect. In general reactions in the sheath are very serious when we search for weakly bound cluster ions. The mass spectrometric sampling technique has recently shown a new area of application where cluster ions are important namely in the measurements of ion density profiles in the earth atmosphere. At high altitudes satellites or rockets carry the sampling device and the low background pressure makes it somewhat easier

to gather data one may trust. In the lower D region however the background pressure reaches several torr and since cluster ions are the most abundant ones

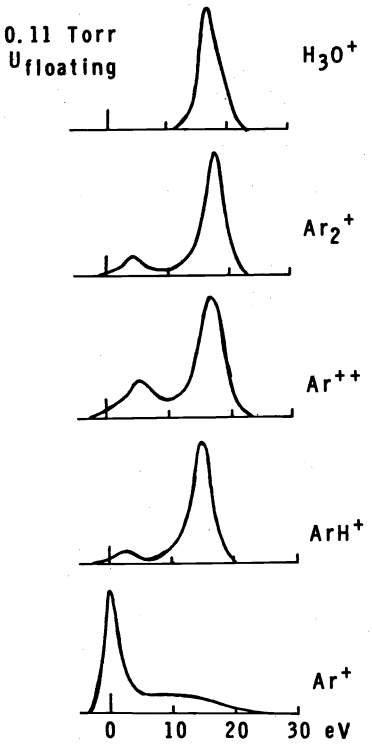


Fig. 16. Energy distributions of H_3O^+, Ar_2^+, Ar^{++}, ArH^+ and of Ar^+ at floating potential.

there the layout of the sampling device requires careful consideration of possible sampling problems. The sensitivity of cluster ions is probably

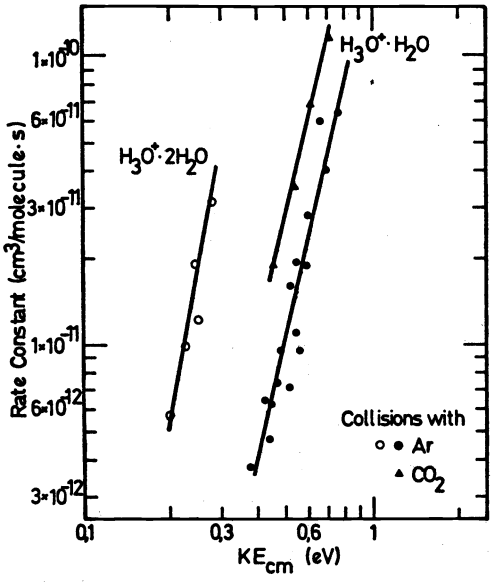


Fig. 17. Rate coefficients for the destruction of $H_3O^+ \cdot nH_2O$(n=1,2) in collisions with Ar and CO_2, obtained by Dotan et al. (27).

best demonstrated with some data which Dotan et al. obtained in the flow drift tube in Boulder (27) recently. This finally leads us back again to water cluster ions, which are so abundant in many plasmas that are not thoroughly outgassed, and which occur as well in the upper atmosphere. Plotted in Fig.17 is the rate coefficient for the destruction of two cluster ions of H_3O^+ as a function of the mean kinetic energy of these ions in the center of mass system. A rate constant of about 1.10^{-9} would mean the breakup in every collision. So we may conclude from this data, that for collision energies of only 300 and 600 meV respectively already one out of 10 ions would break up. A breakup probability of unity will be reached for both ions at energies around as little as 1 eV, an energy that is easily reached even when low draw out potentials are used in sampling systems.

IV CONCLUSIONS

It was impossible in this short review to cover all papers in this field. However we want to draw the readers' attention to a series of other papers which also describe the current state of the sampling technique. A series of review articles on the sampling technique were published in volume 16 of Int. J. Mass. Spec. Ion Phys. (1975) p.1 - 223. A series of papers by the group of Müller are dealing with the ion energy distributions at the wall of non thermal plasmas (28).
A compilation of sampling effects and techniques has also been given in our previous review article (29).

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