PROCEEDINGS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Mass-Spectrometric Studies of Ionization in Flames. I. The Spectrometer and its Application to Ionization in Hydrogen Flames

P. F. Knewstubb and T. M. Sugden

Proc. R. Soc. Lond. A 1960 **255**, 520-537
doi: 10.1098/rspa.1960.0084

Mass-spectrometric studies of ionization in flames

I. The spectrometer and its application to ionization in hydrogen flames

By P. F. Knewstubb[†] and T. M. Sugden
Department of Physical Chemistry, University of Cambridge

(*Communicated by R. G. W. Norrish, F.R.S.—Received* 29 *October* 1959)

An apparatus is described for the extraction of ions from flames burning at atmospheric pressure, and for the subsequent mass analysis of the ions. It consists essentially of a fine leak in a platinum or quartz diaphragm on which the flame is played, and on the other side of which a low pressure is maintained by pumping. The ions are separated by suitable disposition of electrodes in a series of expansion chambers before passing into the analyzer.

It is concluded that secondary ionization is not important in the mass spectrometer, and that charge exchange reactions and other related types of reaction, in so far as they occur inside the spectrometer, largely reflect similar reactions occurring in the external flame. Ionic concentrations as low as 10^5 per cm^3 can be measured for ions ranging in mass from 10 to 400 atomic units.

A brief account is given of the ionization observed from premixed flames of hydrogen, oxygen and nitrogen. The most evident positive ion was hydroxonium (H_3O^+), the other important ones being NH_4^+ and NO^+. The first two of these also occurred in hydrated forms, associated with up to 4 molecules of water. These hydrates occur to a large extent in the cooler parts of the flame system (just before the reaction zone), and are considered to be a secondary phenomenon, possibly formed by association just inside the entry leak into the spectrometer.

Experimental evidence is adduced for the formation of H_3O^+ in the homogeneous gas phase in and near the reaction zone, rather than by catalytic interaction with the walls of the leak. The most likely reaction is considered to be

$$H + H + OH = H_3O^+ + e^-$$

and the kinetics of this are considered. Doubts about the heat of formation of this ion, and about that of the NH_4^+ ion preclude quantitative decisions on many points. The ionization of nitric oxide is shown to be essentially a thermal phenomenon, by observations of ionization with known amounts of nitric oxide added to the flame gases.

The relatively slow rate of recombination observed beyond the reaction zone is discussed, and found to be in line with previous results.

1. Introduction

The purpose of this series of papers is to give some account of an apparatus which has been developed for the extraction of ions from flames, and their subsequent analysis, and to describe the results which have been obtained with it. Preliminary announcements of some of the results have already been made (Knewstubb & Sugden 1958*a*, *b*, 1959), but until now no complete account has been given. It is known from many previous investigations (for a review see Calcote 1957) that considerable ionization occurs in the reaction zones of many flames. This has generally been detected and studied by the large electrical conductivity produced by free electrons. The nature of the other ions, and the way in which they are produced, are not at all well understood, and the primary purpose of this work was to obtain information on these matters.

[†] Present address: Division of Applied Physics, National Research Council, Ottawa, Canada.

In the present apparatus the flame, at atmospheric pressure, impinges on a small hole in a thin foil, on the other side of which rapid pumping maintains an ambient pressure in the region of 10^{-3} mm Hg. In this way the greater part of the neutral molecules in the gas are pumped away, while the ions are focused by a series of electrodes in a train of chambers at successively lower pressures, and are then analyzed in a fairly conventional type of mass spectrometer. With any such apparatus it is necessary to consider in detail the possibilities of the observed ions being produced in the sampling device or the spectrometer, rather than existing in the flame, and this topic is discussed in detail below. A rather similar apparatus has been produced by Deckers & van Tiggelen (1957*a*, *b*, 1959), which operates with a flame at somewhat reduced pressure, and is not so sensitive from the point of view of analysis. Broad agreement obtains between results with the two instruments.

2. Design of apparatus

(*a*) *General*

The general arrangement is shown in figure 1. The sampling orifice is a small hole in a foil clamped at one end of a steel block which contains the series of expansion chambers. The pressure in the region of the third slit is *ca.* 10^{-6} mm Hg. The ions are deflected by a sector-type magnetic system with a choice of a number of accurately controlled magnetic fields, and a continuously variable accelerating potential. They are detected by a secondary electron multiplier and measured with conventional counting and electrometer devices. The whole of the vacuum system, apart from the expansion chamber block, is made of brass. The potentials shown in figure 1 are only indicative of approximate magnitudes.

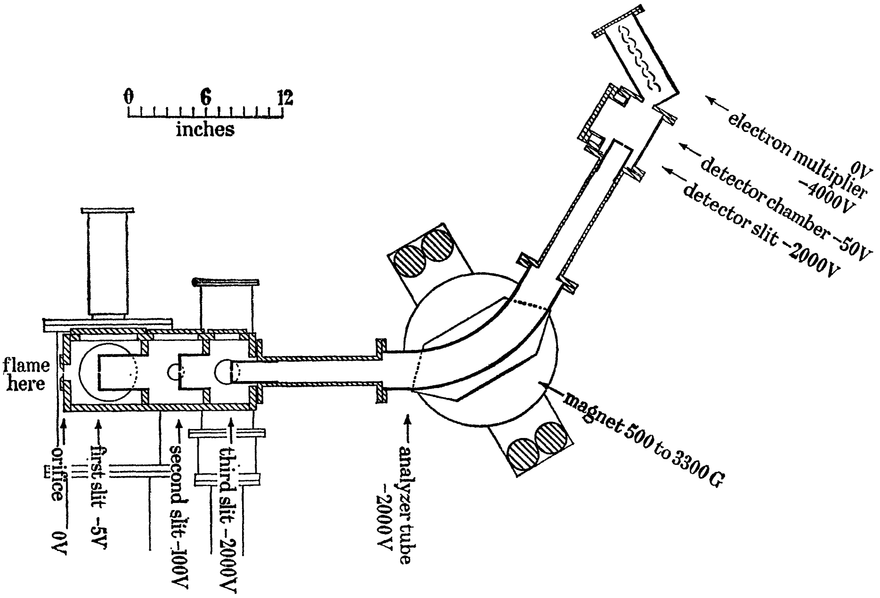


FIGURE 1. General arrangement of ion extractor and mass analyzer.

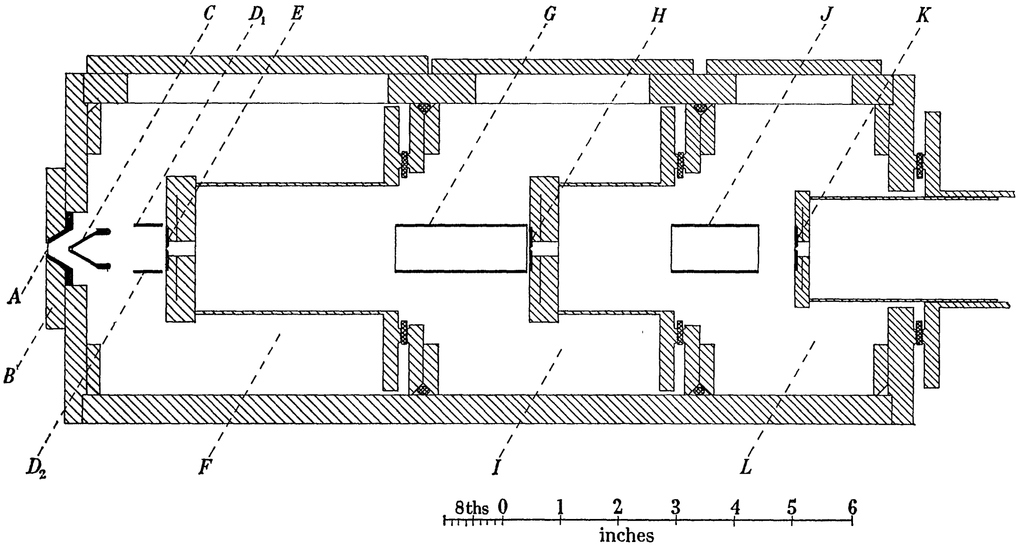
(b) *Sampling system*

In order that the sample passing through the hole should be disturbed to a minimum, it is clearly desirable that the channel should be as short and as wide as possible. Eltenton (1947) gives the average number of collisions of a molecule with the wall in passing through a short channel as 4 × (length/diameter). In most of our work the hole has a diameter of about 0·05 mm, and is pricked in platinum foil of about 0·05 mm in thickness. This was thought to be the thinnest foil which would withstand the direct and continuous impact of a hot flame at atmospheric pressure on one side with vacuum on the other. The foil, about 0·5 cm in diameter, is mounted in a massive brass holder, efficiently cooled by an internal spiral, and which is bolted to the front of the main block. The earliest experiments were made with a thin quartz diaphragm, through which a suitable hole was punctured by a discharge from a Tesla coil, but this proved to be unsatisfactory. Some work has also been done with a hole which was bored in a thicker quartz plate, the inside of which was bevelled by grinding so that the effective aperture was very similar to those used in the platinum foil. The ratio (length/diameter) has also been varied over a range of about fourfold by using holes of different size in the platinum foil, about a mean diameter of 0·05 cm. Under the average conditions Eltenton's formula suggests about four collisions of each particle with the walls of the hole; this might be somewhat reduced for ions by field penetration effects from the internal electrodes, but probably not to any marked extent. This number of collisions is larger than would be preferred, because of the possibilities of catalytic and other reactions at its surface, and it is hoped to reduce it in future work. It is very significant, however, that the patterns of ions which have been obtained are independent, within experimental error, of the diameter of the hole used in the platinum foil, and also remain unchanged when the quartz input diaphragm is used. This suggests relatively little interference by the surface.

Using a formula given by Eltenton (1947) to calculate the pumping speed necessary to reduce and maintain the pressure on one side of such a hole to 10^{-3} mm of mercury (1 μ), with atmospheric pressure on the other, we obtain a value of 190 l./s. Even with a generous allowance for loss of speed in baffles and pumping lines, this figure should be well within the reach of the 6 in. oil diffusion pump which has been used, backed by a suitable rotary pump. This is confirmed by pressure measurements on the system in operation. The calculated sampling rate for a hole of the design figure is $\frac{1}{4}$ cm^3/s, which agrees reasonably with the observed rate of 0·4 cm^3/s.

(c) *Extraction and transmission of ions*

The flame gas enters the sample as a turbulent jet, which is allowed to expand as rapidly as possible, and should attain a diameter of 5 cm, corresponding with a pressure of 1 μ, within 2 cm along the axis of the instrument. The ions pass to the analyzer through a series of three chambers, communicating by slits whose dimensions were not very critical (5 × 0·5 mm). The first chamber is held at about 1 μ pressure by a 6 in. oil diffusion pump, backed by a 7 l./s rotary pump. The second chamber is maintained at about 30 mμ by a 2 in. oil diffusion pump, and the third chamber and analyzer at about 2 mμ by a second 2 in. diffusion pump, with suitable backing. Pirani gauges monitor the backing line pressures, and the high vacua are checked with ionization gauges with a simple logarithmic display of pressure. The pressure in the first chamber is monitored by a Pirani gauge which, in the event of failure of the foil at the entrance hole, switches off all the important parts of the equipment. Magnetic valves of conventional design are fitted in the backing lines to protect against the effects of mains failure.



A, thin platinum foil } 0 V
B, water-cooled block }
C, first accelerating electrode (−24 V)
$D_{1, 2}$, beam shift plates (−2 V, −6 V)
E, first slit (−8 V)
F, first chamber (800 mμ)

G, focusing cylinder } (−90 V)
H, second slit }
I, second chamber (30 mμ)
J, focusing cylinder (+2 V)
K, third slit (−1800 V)
L, third chamber (3 mμ).

FIGURE 2. Diagram of ion extraction apparatus and electrode and slit system. The potentials given are typical, and are mutually variable over fairly wide ranges.

Although a measurable number of ions were found to traverse these chambers as shown in figure 1, without further complication, it was found possible, by using a series of ion-lenses, greatly to increase (by at least 100-fold) the intensity of the ion beam entering the analyzer. This modified system is shown in figure 2, all components having cylindrical symmetry except for the slits and the beam shift plates D_1, D_2 in the first chamber. The electrode *C*, together with the tapered inside surface of the input block, produces an accelerating field, tending to direct the ions through the central hole, while the bulk of the molecules are pumped off at the sides. Beyond this electrode further expansion can occur, while the beam is decelerated. Correct adjustment of the potentials of D_1, D_2 and *E* with respect to *C* produces a focus on the slit *E*. The two beam-shift plates are designed as a cylindrical lens to produce a line image from a point source, and to move this image to coincide with the slit. The arrangement in the next chamber is a simple two-cylinder lens, formed from *E* and *G*, which still allows a fairly high pumping speed back to the first slit. The third chamber requires a three-component lens, and since one potential (*K*) is the final accelerating voltage, slight adjustment of one other potential (*J*) is necessary to compensate for variations of the former. Two other adjustments are available in the form of a sliding motion of the first and second slits perpendicular to the axis, which can be made with the system under vacuum. All the focusing potentials are taken from batteries. The potentials shown in figure 2 represent good working conditions, but can be varied over quite wide ranges.

The main difficulty experienced is a variability of focusing and transmission which develops with time, and is evidently due to fouling of the electrodes in the early stages of the apparatus, followed by development of surface charges. This is combated by gold-plating the relevant electrodes, slit-blades, etc., and by frequent cleaning.

(*d*) *Analyzer*

The instrument was designed with a view to investigating the ionization of metal additives, including lead, thallium and barium, as well as the normal flame ions: it was therefore desirable to be able to resolve mass numbers up to above 200, and possibly up to 400 in the case of dimers, etc. To achieve this a magnetic deflexion type of analyzer, with a deflexion of about 60° and a radius of 11·6 in. was used, following the design of Kerwin (1950) for second-order focusing: this, apart from other considerations, greatly reduces the size of magnet required. With moderate accelerating voltages used (500 to 2200 V), quite low magnetic fields (400 to 3500 G) only were required, and no trouble with magnetic saturation was expected. To avoid hysteresis difficulties, the analyzer has been arranged to operate at any of six definite magnetic fields, the accelerating potential being varied to scan the mass spectrum. Manual scanning is used, although it would not be difficult to incorporate a measure of automatic scanning. These magnetic fields are measured directly by a proton magnetic resonance probe, built according to the design of Pound & Knight (1950), the frequency of the oscillator being checked against the appropriate harmonic of a 2 Mc/s crystal-controlled oscillator. By this means any of the six fields could be reproduced with sufficient accuracy ($\sim$ 0·05 %). Any residual uncertainty in the mass/charge ratio lay solely in measurement of accelerating voltage. This measurement was made on a high-grade moving-coil meter with a series resistance of high stability, the uncertainty in voltage being about 0·2 % after calibration. Uncertainty in identification of (integral) mass numbers only became serious above mass 200.

The magnet was wound with high-resistance coils (8·8 kΩ) having a total of 77000 turns of 28 s.w.g. copper wire, solidly impregnated with synthetic resin during winding. The current for it was supplied from a highly stabilized supply delivering up to 1000 V at 120 mA, based on the circuit of Graham, Harkness & Thode (1947). The accelerating voltage is variable from 250 to 2250 V, and is tapped off from a mains-operated supply of fairly conventional design, the residual ripple being about 2 in 10^4.

(*e*) *Detection system*

An Allen type ion-conversion electron multiplier has been used as a detector throughout this work; it has 14 stages, and a current gain of about 10^{-6}. For low ion currents (up to about 10^4 ions/s) the pulses are amplified as such and passed to a Dynatron scaling unit or an Ekco ratemeter, and the ion current measured as a count rate. The background count is generally negligible. With a voltage of 260 per stage on the multiplier the pulses are many times greater than noise level, and a 'counting plateau' could be found. Measurements were made in this region, so that any small dependence of the operation of the first stage on ion type, affecting the output pulse-height distribution, would have no effect.

For greater ion currents the multiplier output current is switched to a Vibron (Electronic Instruments Ltd) vibrating reed electrometer giving a reading of 1·6 mV across $10^6\Omega$ for a current of 10^4 ions/s, and a linear increase with increasing ion current. This has been used for ion currents up to about 7×10^6/s.

(*f*) *Measurement of negative ions*

The instrument may also be used to analyze negative ions from flames or similar sources. This involves reversal of the polarity of all accelerating voltages and of the direction of the magnet current. The multiplier is not so readily adaptable to the detection of negative ions, but has been used with a loss of sensitivity in the region of ten-fold multiplication. Counting techniques only can be used with this system.

(*g*) *The burner system*

All the work up to the present has been concerned with premixed flames at atmospheric pressure, although work on flames at reduced pressures is projected. To avoid over-heating of the foil, despite the fact that input block is water-cooled, rather small flames must be used. These have been obtained by burning the gas mixture at the end of a length of Pyrex capillary tubing of 1·5 mm internal diameter. This gives a flame with a reaction zone (or primary cone) of conical shape and about 2 mm in height, with a visible stream of burnt gases a few cm long. This simple burner is mounted on a retractable carriage so that it is directed horizontally towards the sampling hole, and samples can be taken at various points along the axis.

Ionic concentrations in general vary rapidly with position along the axis of the flame gases, and flames must be very stable. This is ensured by a rather elaborate system of mixing chambers. The fuel gas, oxygen, and any diluent are metered on capillary flowmeters, the selected flow rates being taken from earlier work (Knewstubb 1956), in which flame temperatures were measured for a wide variety of hydrogen and acetylene flames. In some cases a portion of the diluent, usually nitrogen, was used to operate an atomizer, so that fine sprays of solutions of metallic salts could be added to the flame supply. It was further possible to divert some of the diluent stream through a saturating device so that small quantities of substances such as chloroform could be added to the supply.

3. Instrumental Characteristics

The mass range was calibrated in the first place by adding sprays of aqueous solutions of the readily ionizable alkali metals to a hydrogen + air flame. Strong peaks due to the singly ionized metal atoms were obtained, and subsequently many others have been obtained with other metallic elements. Peaks corresponding to integral mass numbers only have been found on the scale set up in this way—as is to be expected, since the energies available in flames are insufficient to cause multiple ionization.

The instrument is capable of a resolution of 600; very clear separation is obtained between the peaks from the lead isotopes at mass numbers 206, 207 and 208. For general investigations of ions with mass numbers less than 100, it is convenient to work with rather lower resolution, and so obtain flat-topped peaks. Such peaks had steep sides and were without marked 'tailing'.

The sensitivity of the instrument varies markedly with time, particularly with hydrocarbon flames and heavily salted ones, due to electrode fouling, but when clean it is possible to detect and measure ionic concentrations of the order of $10^5/\text{cm}^3$ in the flame gases at atmospheric pressure. This calibration was made by introduction of dilute solutions of potassium and caesium salts from a calibrated atomizer into a hot flame (*ca.* 2500 °K) of acetylene, and measuring the ion current from the alkali ions in the burnt gases about 2 cm downstream from the reaction zone. Under these conditions these metals are known to be fully ionized or very nearly so (Knewstubb & Sugden 1958*c*), so that an absolute calibration is possible. The overall collecting efficiency of the apparatus for ions appears to be about 1 in 10^4. Loss of ions within the instrument has been investigated by measurement of the potassium ion current collected on electrode *C* (figure 2), and on *E* with the slit closed, using the Vibron electrometer directly on the appropriate electrode. This showed that the ions appeared to pass the sampling hole without apparent loss, but that only about 1 in 40 succeeded in reaching the first slit. Expected losses of between five- and tenfold at the three slits of the sampling system would then account for the overall efficiency observed.

4. General consideration of the results

It is important to know whether the ions which are detected truly reflect the ionic composition of the gas entering the sampling orifice. This problem may be considered in two parts—the possibility of modification or production of ions by interaction with the walls of the orifice, and the further possibility of such changes occurring within the mass spectrometer.

Assume, in the first place, that the sample emerges unscathed from the hole. Various processes might then occur, particularly in the first chamber, where the pressure is still relatively high, involving interaction with neutral molecules. These will be considered briefly in turn.

(*a*) *Secondary ionization*

Positive ions might be accelerated towards the first electrode (C of figure 2), and acquire enough energy to cause further ionization by collision

$$A^+ + B = A^+ + B^+ + e^-.$$

Alternatively, such ions might strike the surface of C and cause emission of electrons, which would be accelerated towards the inlet, and there ionize molecules by impact

$$e^- + B = B^+ + 2e^-.$$

The evidence against these reactions is as follows:

(i) Secondary ions, unless formed in the immediate vicinity of the inlet, would either not be properly focused by the instrument and thus not reach the collector, or would give rise to marked 'tails' on the peaks, which are not observed.

(ii) The total ionic populations agree quite well with electron populations estimated by independent means, which would not be expected if massive production of positive ions was occurring inside the spectrometer.

(iii) The most significant point is that the pattern of ions formed in a particular flame remains unchanged, within experimental error, when the accelerating voltage between the inlet hole and the first electrode (C) is varied between 9 and 100 V. The collecting efficiency varies, but no new types of ion appear as this potential is raised, nor do the relative amounts of different ions alter.

It therefore appears possible to neglect secondary ionization.

(*b*) *Charge transfer*

Reactions of the type

$$A^+ + B = A + B^+$$

may have quite high efficiencies, and may occur during passage through the sampling hole or in the first chamber. After this the pressure is too low for suitable collisions. Even in the first chamber it is unlikely that collision with more than one molecule will occur. Such reactions, however, will normally be proceeding in the flame itself, which from this point of view can be regarded as extending somewhat into the first chamber.

(*c*) *Dissociation*

Spontaneous dissociation of polyatomic ions *en route* to the collector is a phenomenon quite well known in ordinary mass spectrometry (Field & Franklin 1957), and is evidenced by the appearance of non-integral peaks. No such peaks were observed with this apparatus. In normal mass spectrometry, however, the primary ionization is done with relatively fast electrons (about 100 eV), which produce ions which tend to be highly excited vibrationally and thus prone to dissociation. This is unlikely to occur under the milder conditions of ionization in flame gases.

(*d*) *Ionic clustering*

This is in some sense the inverse of dissociation

$$A^+ + B = AB^+.$$

For compound ions formed in this way to be detected, the reaction must take place very near to the inlet. There is some evidence (see below) that this can occur with molecules of water (hydration).

The evidence is thus reasonably strong that the ions observed are a representative sample of those emerging from the inlet. There remains the more obscure problem of the effect of the inlet itself, since each molecule of the flame gases collides with the wall about four times in an average experiment. This wall may be catalytically active in causing ionization. The point is best considered with respect to specific examples, the case of hydrogen flames being chosen in this paper.

5. POSITIVE IONS IN HYDROGEN + OXYGEN + NITROGEN FLAMES

Figure 3 shows the pattern of ions found in a typical fuel-rich hydrogen + oxygen + nitrogen premixed flame. This diagram gives the maximum counts recorded for each particular ionic mass, irrespective of position along the axis of the flame,

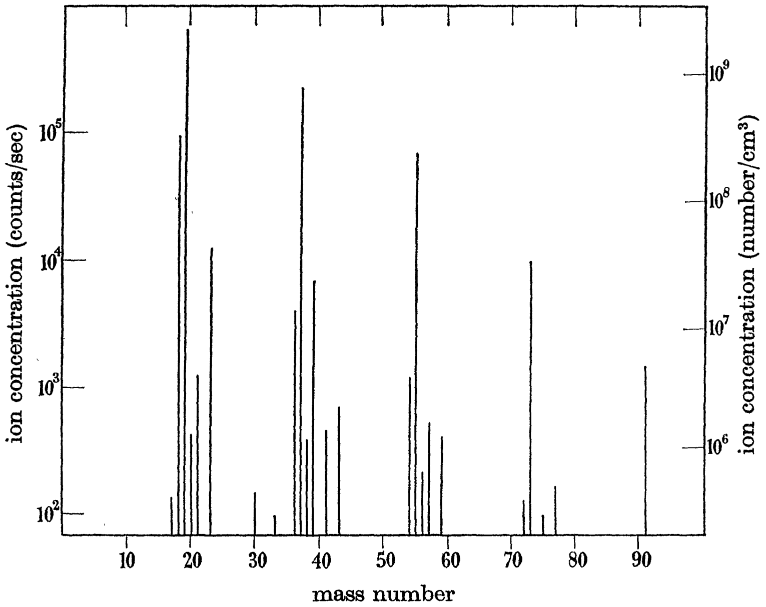


FIGURE 3. Maximum counts of the ionic masses detected in a premixed hydrogen + oxygen + nitrogen flame. The unburnt composition of the flame gases was $H_2/O_2/N_2 = 1{\cdot}0/0{\cdot}3/1{\cdot}0$ by volume giving a flame with burnt gas temperature of about 2300 °K. Most of the maximum counts were found in or near the reaction zone (see text). The right-hand ordinate gives approximate concentrations in the burnt gases. Total pressure was atmospheric.

from which all samples were taken. Variation of counts along this axis will be considered later.

The most obvious feature of figure 3 is the grouping of the pattern into subpatterns which repeat themselves, in essentials, at increasing intervals of 18 mass units. This is clearly a case of hydration—i.e. cluster formation by attachment of water molecules. The ion giving the largest peak is at mass 19, and can only reasonably be H_3O^+; confirmation of this is provided by the peaks at masses 20 and 21, which stand in the correct relation to that of mass 19 to correspond with isotopic forms H_2DO^+ and $H_3\,^{17}O^+$ (mass 20), and $H_3\,^{18}O^+$ (mass 21), respectively. The amounts of this ion vary little with the flame gas composition. On the other hand the peak at mass 18 decreases markedly as the flame becomes richer in fuel: it was initially assigned to H_2O^+, but experiments in which argon was substituted for nitrogen as diluent showed a decrease of the order of 1000-fold, and hence it appears rather to be NH_4^+ (as similarly mass 17 appears to be NH_3^+).

The pattern shown by masses 18 to 21 appears in successively hydrated forms at 36 to 39, 54 to 57, 72 to 75, with a further hydrated H_3O^+ at 91. The expected isotopic ratios hold, except for mass 39 which is high, and probably arises from a trace of potassium impurity as does the peak at 41. Similarly, the peak at 23 arises from sodium impurities.

An important feature, although one not very prominent in figure 3, is the peak at mass 30, which again is reduced by argon substitution, and must arise from NO^+. This peak becomes much larger towards stoicheiometry.

The only other peaks in figure 3 are the relatively small ones at mass numbers 33 (HO_2^+?), 43, 59, and 77. The last three of these are difficult or impossible to explain on the basis of compounds of H, O and N. It may be noted that the first two of these three are both found much more strongly (about 1000-fold) in hydrocarbon flames, and they are ascribed to traces of hydrocarbon in the fuel; 77 is probably the monohydrate of 59. In a subsequent paper it will be shown that their most probable formulae are $C_2H_3O^+$ (43) and $C_2H_3O_2^+$ (59).

The most notable omission is a figure for free protons, which could not be sought conveniently with this apparatus; they are not expected to be at all important in view of the high proton affinity of H_2O, which is well above 100 kcal/mole. Succeeding sections will deal with some of the ion types in more detail, with some discussion of their modes of formation.

(*a*) *The hydroxonium ion and its hydrates*

Figure 4 shows the variation of H_3O^+ and its first two hydrates along the axis of the flame. The hydrates (including the higher ones) show a very different variation with position in the flame gases from that of the parent H_3O^+ ion. The sharp rise shown by the latter occurs at the tip of the almost invisible reaction zone of the flame, and is followed by a relatively slow fall, while the hydrates give very sharp maxima *before* the reaction zone—where the flame gases have not yet reacted to any marked extent.

It is not surprising that ions such as $H_3O^+(H_2O)_n$ appear best under rather cool conditions. A very rough idea of the stability of hydrates can be obtained by assuming that $H_3O^+.H_2O$ can be represented by a point dipole of 1·6 D situated 2 Å from a point ion. The electrostatic energy of interaction then amounts to about 30 kcal/mole. If this is taken as the heat of reaction of $H_5O_2^+ = H_3O^+ + H_2O$, an equally approximate calculation of the equilibrium constant shows that the ratio $[H_5O_2^+]/[H_3O^+]$ should be of order 10^{-5} at 1000 °K and 10^2 at 500 °K. Such calculations could well be in error by a factor of 100, but serve to show the improbability of hydrates being present in the reaction zone, or the burnt gases, where the temperature is in the region of 2000 °K. Even the amounts of hydrates found downstream from the reaction zone are improbably high for burnt gas temperatures, and are probably formed under quasi-molecular beam conditions of attachment in or near the sampling hole.

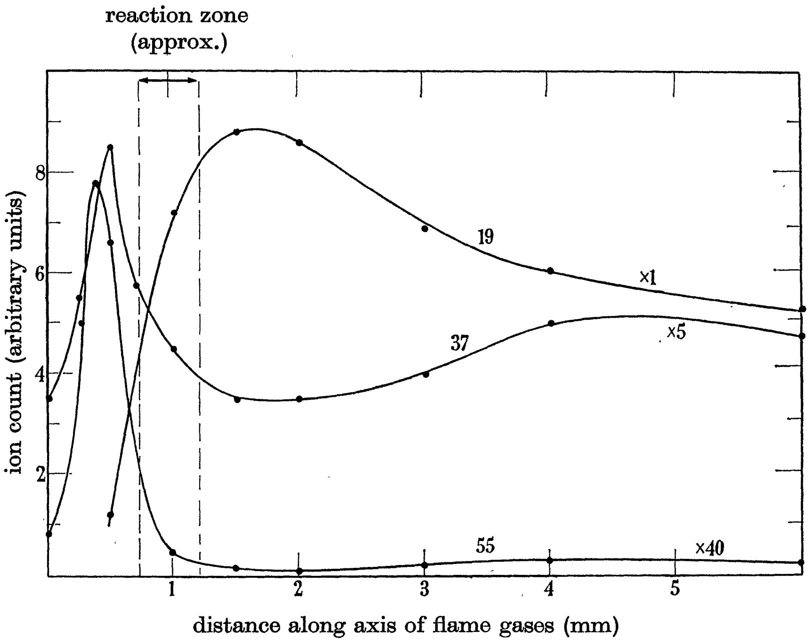


FIGURE 4. Concentrations of the ions H_3O^+ (mass 19), $H_3O^+(H_2O)$ (mass 37), and $H_3O^+(H_2O)_2$ (mass 55) as functions of distance along the axis of the flame of figure 3. The hydrated ions are scaled as shown.

In any case it appears that hydrate formation, spectacular though it is in these experiments, is a secondary phenomenon, associated with the system (flame + sampling apparatus), rather than with the flame alone, except possibly to a small extent just before the reaction zone. Ions up to the tetrahydrate of H_3O^+ (and NH_4^+) were detected, but none higher, although the sensitivity was such that at least one more might have been expected on the basis of simple extrapolation. Beckey (1958) has reported hydrates up to $H_3O^+(H_2O)_3$ in a field-emission mass spectrometer, and concludes that they are made in a 'liquid water like' phase at a tungsten surface. It is difficult to see how this would apply in our higher temperature conditions. The absence of a pentahydrate of H_3O^+ suggests a stable arrangement of four water molecules round the central ion. This seems more reasonable than a grouping of four molecules symmetrically about a proton.

We may now pass from a discussion of hydration, which appears to be a subsidiary phenomenon as far as flames are concerned, to the production of H_3O^+ itself. The study of appearance potentials leads to a heat of formation of 195 kcal/mole for this ion (Field & Franklin 1957; Mann, Hustrulid & Tate 1940; Cummings & Bleakney 1940). On the other hand, lattice energy calculations

(Sherman 1932) give a proton affinity for H_2O of 182 kcal/mole, which puts the heat of formation of the ion at 136 kcal/mole. This large discrepancy remains for the present unresolved, the actual value probably being between these two figures.

$$\tfrac{3}{2}H_2+\tfrac{1}{2}O_2 = H_3O^+ + e^-; \quad \Delta H = 195 \text{ to } 136 \text{ kcal.}$$

Only two homogeneous reactions seem worth considering as sources of H_3O^+ in hydrogen flames

$$H_2O+H = H_3O^+ + e^-; \quad \Delta H = 205 \text{ to } 146 \text{ kcal,} \tag{1}$$

$$H+H+OH = H_3O^+ + e^-; \quad \Delta H = 86 \text{ to } 27 \text{ kcal.} \tag{2}$$

The heat of reaction based on appearance potentials of H_3O^+ is always written first in these equations. The first of these reactions is quite unreasonable for production of H_3O^+ in the observed concentrations except at the lower limit of the heat of reaction (assumed equal to the energy of activation), unless the associated cross-section is abnormally large. Reaction (2) is of a type very unusual in reaction kinetics—a ternary reaction which is also endothermic. This is not so improbable, however, if it is remembered that the concentration of radicals (hydroxyl and atomic hydrogen) is of the order of 1 % of the total gases in the reaction zone (Padley & Sugden 1959). If we assume a reasonable frequency factor for reaction (2), 10^{-31} cm^6 molecule^{-2} s^{-1}, and energy of activation equal to the heat of reaction, the rate of production of H_3O^+ ranges from 10^{12} cm^{-3} s^{-1} for $\Delta H = 86$ kcal to 10^{18} cm^{-3} s^{-1} for $\Delta H = 27$ kcal. Thus the reaction is feasible from a kinetic standpoint for the observed amounts of H_3O^+, which are produced in the reaction zone in about 10^{-4} s. A rough estimate of the equilibrium constant of reaction (2) suggests values of the concentration of H_3O^+ ranging over 10^7 to 10^{13} cm^{-3} for ΔH ranging from 86 to 27 kcal.

Hence, provided the heat of formation is only slightly below the appearance potential value, the production of H_3O^+ by reaction (2) is quite feasible. An alternative is reaction (1) under catalytic conditions, when the atomic hydrogen is chemisorbed on to the platinum, and the electron is released into the metal. In this case the heat of adsorption must be added to ΔH, and the work function of platinum subtracted.

$$H_2O+H(\text{ads.}) = H_3O^+ + e^-(\text{Pt}). \tag{1a}$$

The heat of reaction of (1*a*) will be about 100 kcal/mole less than that of reaction (1), which therefore makes it a serious competitor for H_3O^+ production. It may be pointed out, however, that H_3O^+ appears to be formed equally well with a quartz inlet, and also that the electron concentration in clean hydrogen flames, estimated by quite different means (Knewstubb & Sugden 1958), is of the same order as the concentration of H_3O^+ ions found here. A fairly definite conclusion in favour of the homogeneous formation is provided by the following experiment.

The addition of a fine spray of aqueous potassium salt to the gas supply produces the effect shown in figure 5*a*, the amount of H_3O^+ detected rising in the normal way in the reaction zone, but then decreasing rapidly with distance, while the number of K^+ ions increases. Sprays of this type are well known to be completely decomposed in the reaction zone, so that potassium atoms should be operating in full concentration from the reaction zone onwards. The disposition of the flame with respect to the inlet at positions *x* and *y* (figure 5*a*) is shown in figure 5*b* and *c*. It seems most improbable that similar amounts of H_3O^+ produced at the inlet would show such profoundly different responses to the same amount of potassium in the short period of passing through the hole. On the other hand the charge transfer reaction

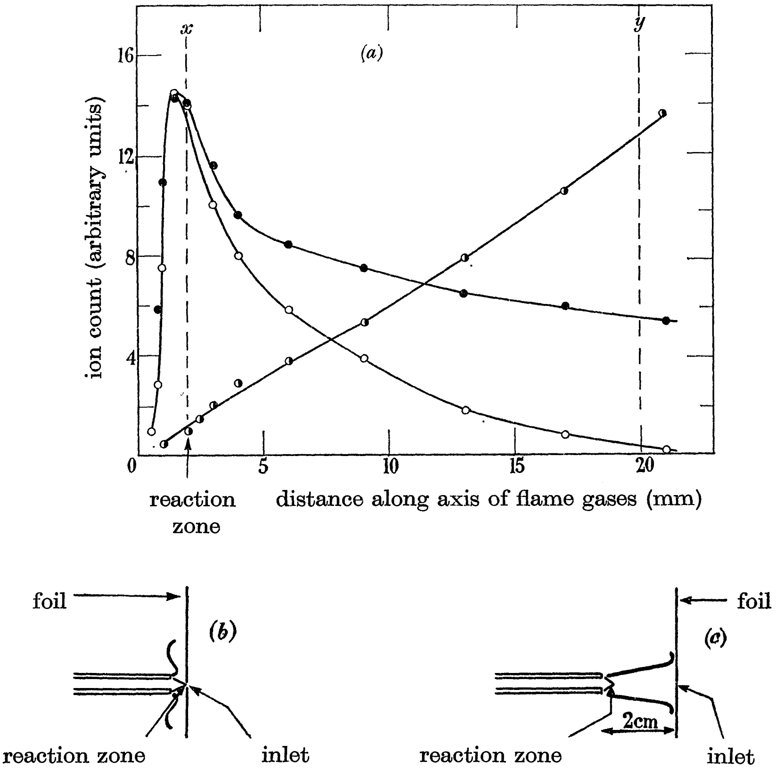


FIGURE 5. (*a*) shows the variation of the H_3O^+ ion (●) with distance along the axis of the flame gases for the flame of figure 3, for the 'clean' flame, and the flame with M/50 KCl solution (○) sprayed into the supply. The variation of potassium ions (mass 39) with position (◐) is also shown for the salted flame. (*b*) and (*c*) show the disposition of the flame with respect to the inlet of the mass spectrometer at the positions denoted by *x* and *y* respectively, in figure 5(*a*).

$$K + H_3O^+ = K^+ + H_2O + H; \quad \Delta H = -105 \text{ to } -46\,\text{kcal}$$

has much more time to operate if the hydroxonium ions are produced in the reaction zone. Under the conditions of figure 5, about 1 in 10^5 of the burnt gas molecules is atomic potassium, so that an H_3O^+ ion, making a normal number of about 10^9 collisions per second with burnt gas molecules, would make about 10 collisions with potassium atoms in 10^{-3} s, which is the order of the time taken by the gas to travel from *x* to *y*. The observed rate of disappearance of hydroxonium ions and the appearance of potassium ions is then understandable.

The purpose of this argument is simply to show that there is an homogeneous mechanism by which H_3O^+ can be made in flames of hydrogen, and that homogeneous mechanisms are more probable than heterogeneous ones involving interaction with the input system of ions and gas into the apparatus. The particular reaction suggested may not be the best one, in particular the role, if any, played by negative hydroxyl ions not having been considered; neither does it follow that the charge transfer reaction is the only one by which potassium or other metallic ions are produced.

It is now possible to comment on the other two ions of interest occurring in hydrogen flames, the ammonium ion NH_4^+ and the nitric oxide ion NO^+.

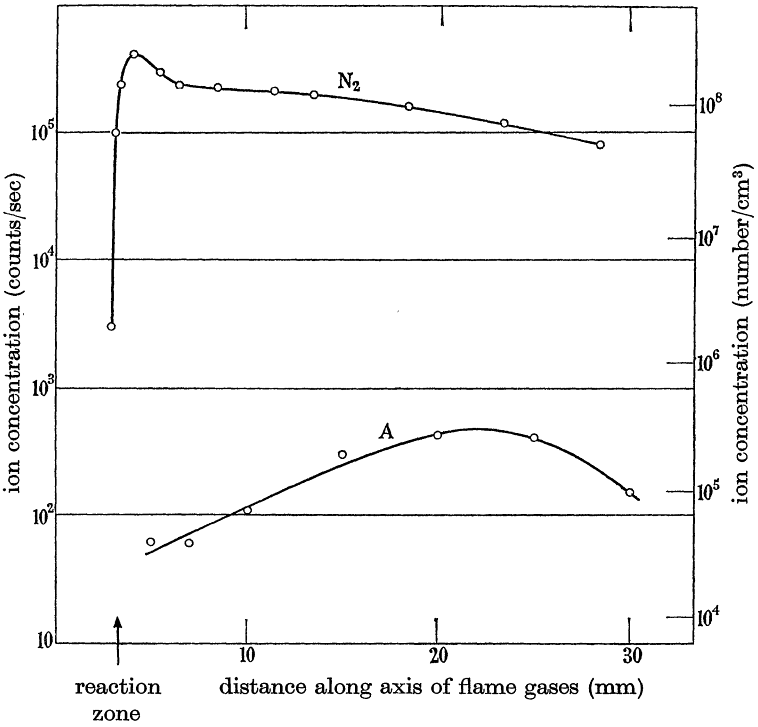


FIGURE 6. The ammonium ion NH_4^+: concentration along the axis of the flame gases for (upper line) the flame of figure 3, and (lower line) the same flame with argon substituted for nitrogen in the gas supply and the flame sheath.

(*b*) *The ammonium ion*

This is closely related to the hydroxonium ion, both in electronic structure and in the way in which it gives rise to hydrates in the hydrogen/air type of flame. Figure 6 shows its behaviour with position in the flame gases along the axis, and its identification by argon substitution. A subsidiary point of interest here was the noticeable smell of ozone near the flame in the argon case, but not in the nitrogen one.

As in the case of H_3O^+ there is a discrepancy between the heat of formation of the ion as estimated from appearance potentials and from the proton affinity based on lattice energies. The former gives 210 kcal/mole (Field & Franklin 1957; Collin 1953), while the latter gives 154 kcal/mole, based on a proton affinity of 209 kcal/mole (Sherman 1932). Provided there is a little ammonia in the gases emerging from the reaction zone there is little difficulty about formulating a proton exchange reaction

$$H_3O^+ + NH_3 = H_2O + NH_4^+$$

for its production. It is pointless to attempt to estimate the equilibrium constant of this reaction while there is so much doubt about the heat of reaction, although the entropy change will be very small. The NH_4^+ ion shows very similar behaviour to that of H_3O^+ with position in the flame and with respect to added alkali metal, so it may be presumed that its mechanism of formation is either similar to or directly dependent on that of H_3O^+, and the latter seems the more probable. At the same time it must be said that there is little or no information about the breakdown of molecular nitrogen (requiring at least 225 kcal/mole) in these flames to give hydrides and oxides of nitrogen. Padley (1959) has detected the NH spectrum in emission very weakly in the reaction zones of hydrogen/air flames. The unexcited compound could be made by

$$N_2 + OH^*(^2\Pi) = NO + NH,$$

but there is no spectroscopic evidence for more heavily hydrogenated nitrogen in these flames. Extrapolation of equilibrium constant data for the nitrogen + hydrogen reaction suggests about 1 part of ammonia in 10^6 under flame conditions used here, which is not impossibly low to give the observed ratios of $[H_3O^+]/[NH_4^+]$ of 10 to 100. The point seems not worth pursuing until a detailed investigation of this ion and the compounds related to it has been made in the gas phase.

(c) *The* NO^+ *ion*

This is an interesting ion in that it is the only one occurring in hydrogen flames whose parent neutral molecule is a stable substance. Figure 7 shows its variation along the axis of a hydrogen-rich flame. It can be seen that it does not appear in the reaction zone, and in fact appears first a few mm downstream, at a point where the excess hydrogen is burning in entrained air from the surroundings. In the case of a stoicheiometric flame the NO^+ appears rather earlier, and attains concentrations about 20 times as great. The diagram also shows the effect of introducing 1% of nitric oxide into the flame gas supply—NO^+ appears in large quantity in the reaction zone itself, and thereafter remains roughly constant in amount. Previous work (Bulewicz & Sugden 1958) has shown that nitric oxide passes effectively unchanged through the reaction zones of hydrogen flames, and thus it is reasonable to suppose that what is being observed in the case of added nitric oxide is not far from its equilibrium ionization. The ionization potential of NO is 213 kcal/mole (9·25 eV) (Watanabe, Marmo & Inn 1953). Application of the equation of Saha (1920) gives an equilibrium constant for ionization to NO^+ and electrons of 3×10^{-1} cm^{-3} at 2200 °K, which for 1 % of nitric oxide in the flame, and an electron population of 10^9 cm^{-3} (roughly equal to the concentration of H_3O) leads to about

10^7 NO^+ ions per cm^3. This is of the correct order of magnitude given in figure 7. Such a calculation serves to indicate that nitric oxide is probably thermally ionized in the flames. The charge-transfer reaction

$$NO + H_3O^+ = NO^+ + H_2O + H$$

is about 40 kcal endothermic if the proton affinity of H_2O is 180 kcal/mole (lattice energy) or 100 kcal/mole if the proton affinity is 120 kcal/ mole (appearance potential). With a frequency factor of 10^{-10} cm^3 s^{-1} (molecular units) this reaction becomes a possible one for the mechanism of production of NO^+ if the higher value of the proton affinity applies, but not for the lower value.

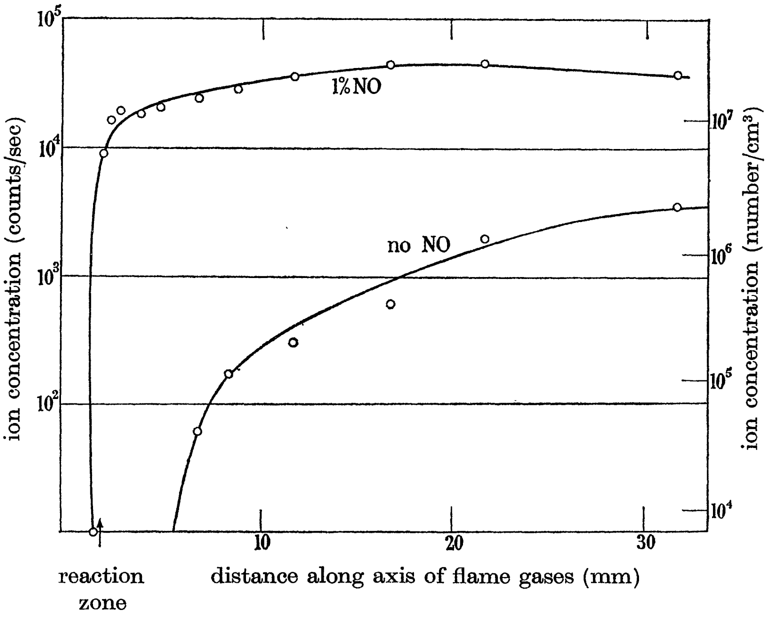


FIGURE 7. The nitric oxide ion NO^+: concentration along the axis of the flame gases for (lower line) the flame of figure 3, and (upper line) the same flame with 1 % of nitric oxide added to the gas supply.

The behaviour of flames without added nitric oxide now becomes clear. Even the equilibrium amounts of nitric oxide which can be produced in the reaction zones of hydrogen-rich flames in the region of 2000 °K are quite negligible (less than 0·01 %), and the absence of any very marked NO—O continuum in even hotter and more oxygen-rich flames (Bulewicz & Sugden 1958) suggests that this equilibrium quantity is not produced. Traces will appear, however, under very oxygen-rich conditions, such as occur when sufficient air has diffused into the flame gas from the surroundings. It is these which give the observed ionization. Figure 7 indicates that up to about 0·1 % of nitric oxide may be produced as a result of secondary combustion.

(*d*) *The variation of ionization with position*

Figure 4 shows that the number of positive ions (since these are very largely H_3O^+) falls off relatively slowly with increasing distance downstream from the reaction zone. If the reaction

$$H + H + OH = H_3O^+ + e^-$$

were equilibrated, then a much faster decrease would be expected, since both the concentration of atomic hydrogen and that of hydroxyl fall off approximately inversely as the distance from the reaction zone (Bulewicz, James & Sugden 1956; Padley & Sugden 1958). Little is known about the rates of dissociative recombination of positive ions and electrons, but it is reasonable (Massey & Burhop 1952) to allot a gas-kinetic value of 10^{-8} cm^{-3} s^{-1} to the back-reaction above. If this holds, then in a system containing 10^9 positive ions and electrons per cm^3, the rate of disappearance of positive ions will be 10^{10} cm^{-3} s^{-1}. Thus, in 10 ms the ion population will only decrease by one-tenth of its value. This is broadly in line with what has been observed—that ions, once formed, only disappear rather slowly. A similar observation has been made by Knewstubb & Sugden (1958*c*) in connexion with alkali ions in flames, where, however, the concentrations were larger and the flames longer, so that the establishment of near equilibrium could be observed.

6. CONCLUSION

Two remaining points may briefly be considered. The first is that the rather unexpectedly high concentration of positive ions in hydrogen flames (of the order of 10^9 cm^{-3}) is in general agreement with a value found by us previously (Knewstubb & Sugden 1958*c*) for free electrons. This latter was obtained in radio-frequency measurements of the conductivity of the burnt gases of hydrogen flames, in which the electrons produced by alkali metals were studied. The irreducible background which appeared to be steady, and not due to traces of alkali or other impurity, was in the neighbourhood of 10^9 electrons cm^{-3}.

The other point is that no mention has been made of the hydroxyl ion OH^- in any of the foregoing. If its electron affinity is as high as has been thought to be the case, 63 kcal/mole (Page 1955), then it should be present in amounts in general exceeding the numbers of free electrons, and thus might play a very important part in the general mechanisms and equilibria of ionization. Branscomb & Smith (1958, private communication), however, give experimental evidence in favour of a much lower value (40 kcal/mole), in which case it will certainly be much less important in flames. Measurements which we have made on negative ions in hydrogen flames on the whole support the lower value, in that only very small amounts of OH^- were found. It was therefore considered desirable to discuss the positive ions in hydrogen flames with respect to free electrons only as negative ions.

We wish to record our gratitude to our colleagues for discussions and advice, in particular to Dr K. F. Smith of the Cavendish Laboratory, and to Drs Page, Bulewicz and Padley of this department. This work has been made possible by a grant from the Research Laboratory of the General Electric Company, Schenectady, New York, to whom we extend our thanks.

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