# Ambipolar Diffusion in an Isothermal Oxygen Plasma at Elevated Temperatures

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Electron removal in an afterglow discharge in oxygen was measured using microwave diagnostic techniques. For pressures below 1 mm Hg it was found that ambipolar diffusion was the principal loss process in the late afterglow which, by microwave radiation temperature measurements, was proven to be isothermal at the ambient gas temperature. A marked difference in the rate of diffusion for the low- and high-current discharge afterglow at room temperature was demonstrated with $D_a p$ values equal to $110\pm10$ and $216\pm20$ cm$^2$ sec$^{-1}$, respectively. The identity of the ions leading to the higher value is not well established since it is not clear how O$^+$ ions could be predominant in the high-current case. It is perhaps more probable that the ion O$_3^+$ is responsible based on some reported mass spectrometric studies of the oxygen afterglow. The ions responsible for the lower $D_a p$ value, however, are most probably O$_2^+$ judging from previously published results. These ions display a strongly temperature-dependent diffusion rate in the range 300 to 900°K which on the mobility versus temperature plot resulted in a maximum of about 5.0 cm$^2$ sec$^{-1}$ V$^{-1}$ around 600°K after a steep climb from the value 2.8 cm$^2$ sec$^{-1}$ V$^{-1}$ at $T=300$°K; between 600 and 900°K the decline in mobility is only slight. This behavior is discussed in terms of ion-molecule force fields and charge transfer.

## I. INTRODUCTION

IN the last few years many efforts have been made to identify the ions which can be formed in atmospheric gases by the use of laboratory mobility measurements,[1,2] and it can be said that considerable gains have been made. Thus it seems that several ionic species of oxygen can be created under various experimental conditions. The ions O$^+$, O$_2^+$, O$_3^+$, O$^-$, O$_2^-$, and possibly O$_3^-$ have been reported to exist, and most of their mobilities have been measured.[3-7] Once the mobility $K$ of an ion is well established at room temperature as seems to be the case for O$_2^+$ in its parent gas, it is of great interest to measure $K$ as a function of temperature. Obviously, such measurements in oxygen are not only of academic importance, since they can provide information of value to the study of the ionosphere. Basically, the temperature variation of $K$ can in many cases yield a better understanding of the force interaction during ion-molecular encounters.[2,8]

There are many examples illustrating the limited validity of the simple mobility theory developed primarily by Langevin,[9] however, a considerable number of observations require more realistic interaction potential models for their interpretation.[10-12] For the case of present interest, namely the motion of O$_2^+$ in its parent gas, charge transfer and possible energy-exchange collisions between ions and molecules involving rotational and vibrational states, present additional unknown problems. It seems inevitable, therefore, that information with regard to these phenomena must rely heavily on laboratory measurements. The measurement of $D_a p$ and $K$ in the temperature range presented here is, to the author's knowledge, the first of its kind.

Finally, this paper is concerned with the reported high mobility characterizing the ions present in the afterglow following a high-current density discharge in oxygen.[6] These ions were believed to be O$^+$; however, considerations involving both the creation and the survival of the atomic ions, together with some recently reported ion identification studies,[13,14] make it difficult to understand how O$^+$ can predominate in the late afterglow. It was therefore felt that a restudy of the high-current discharge would be desirable, since this at least would provide a confirmation, or lack of it, for the previously reported behavior.

## II. EXPERIMENTAL ARRANGEMENT AND PROCEDURE

The experimental arrangement and measuring procedure is basically the same as described previously.[15,16] A glow discharge in oxygen was ignited by applying a voltage pulse of about 2 μsec duration periodically between platinum electrodes. These were located just outside a cylindrical quartz container, about 80 cm long and coated on the outside with a thin layer of gold so as to serve both as a discharge tube and waveguide for the quasi-TE$_{11}$ mode at a ferquency of approximately 10 kMc/sec. This system was surrounded by a cylindrical electric oven provided with thermocouples located

[1] L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Berkeley and Los Angles, 1960), Chap. 1.
[2] A. Dalgarno, *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), Chap. 16.
[3] R. N. Varney, Phys. Rev. **89**, 708 (1953).
[4] D. S. Burch and R. Geballe, Phys. Rev. **106**, 183 (1957).
[5] H. Eiber, Z. Angew. Phys. **15**, 103 (1963).
[6] E. Schulz-DuBois, Z. Physik **145**, 269 (1956).
[7] L. M. Chanin, A. V. Phelps, and M. A. Biondi. Phys. Rev. **128**, 219 (1962).
[8] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (The Syndics of the Cambridge University Press, New York, 1958), p. 248.
[9] P. Langevin, Ann. Chem. Phys. **8**, 245 (1905).
[10] E. A. Mason and J. T. Vanderslice, *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), Chap. 17, p. 688.
[11] E. A. Mason and H. W. Schamp. Ann. Phys. (N. Y.) **4**, 233 (1958).
[12] H. R. Hasse and W. R. Cook, Phil. Mag. **12**, 554 (1931).
[13] P. F. Knewstubb, P. H. Dawson, and A. W. Tickner, J. Chem. Phys. **38**, 1031 (1963).
[14] W. H. Kasner, W. A. Rogers, and M. A. Biondi, Phys. Rev. Letters **7**, 321 (1961).
[15] M. H. Mentzoni and R. V. Row, Phys. Rev. **130**, 2312 (1963).
[16] M. H. Mentzoni, J. Geophys. Res. **68**, 4181 (1963).

at regular intervals in the axial direction. Thus, the average temperature along the discharge column could readily be computed.

As is well known, the electron density and the effective collision frequency can be determined as functions of time in the afterglow from measurements of the propagation constant (the attenuation and the phase shift) of the probing signal after its propagation through the plasma. By the usual microwave interferometer technique the lowest measurable phase shift is 180°, which is not sufficient for measuring low-electron densities unless an extremely long discharge tube is used. This difficulty is overcome by using a pulsed probing signal and a precision phase shifter, thereby increasing the phase sensitivity by almost two orders of magnitude. The probing pulse is selected as short as possible, in this case 1 $\mu$sec, so that the pulse sees more or less a time invariable plasma. As usual, the reference signal and the signal through the plasma are superimposed at a magic $T$, and the first step is to find a very accurate cold case null, i.e., when the discharge is not ignited. This is accomplished by large amplification of the signal between the magic $T$ and the cathode-ray oscilloscope (CRO). Unfortunately, this will increase the noise level; however, with the plasma on, only the tangential sensitivity is of importance for the determination of the new null. In order to minimize the effects of random reading errors, a set of ten measurements were taken for each phase determination. It turned out that the average deviation among the ten readings was quite small (0.27 deg).

Since it is crucial to verify that isothermal conditions prevail at post-discharge times pertaining to the measurements, a pulse sampling noise radiometer[17] was incorporated with the conventional diagnostic system. This made it possible to measure the decline of the electron radiation temperature during the afterglow (see Appendix).

Linde's mass spectrometer controlled oxygen gas was used for this study. By way of special precautions the Quartz tube, gas-handling system, and electrodes were thoroughly outgassed initially until residual pressure readings were $5 \times 10^{-9}$ mm Hg at room temperature and less than $3 \times 10^{-8}$ mm Hg at all other temperatures.

## III. DATA

When ambipolar diffusion in the fundamental mode is the predominant electron removal process, the electron time decay is described by $n(t) = n(0) \exp(-t/\tau_{11})$, provided only positive ions of one kind are present. The time constant $\tau_{11}$ is related to the ambipolar diffusion coefficient $D_a$ and the characteristic diffusion length of the container $\Lambda_{11}$ by the relation $\tau_{11}^{-1} = D_a/\Lambda_{11}^2$. If the temperature of the neutral gas ions and electrons re-
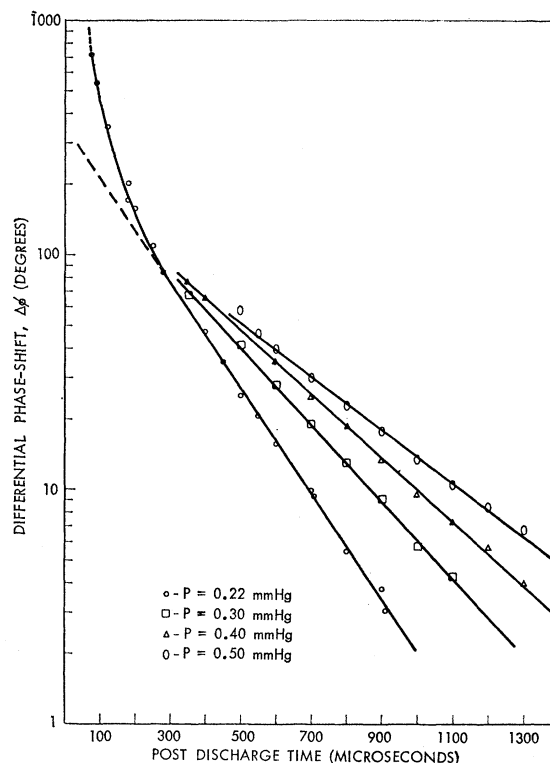


FIG. 1. Typical time curves for the differential phase shift $\Delta\phi(t) \propto n(t)$ during the afterglow of the high-current discharge (10 mA average current).

main constant during the time range of interest and the ionic species do not change in time by other processes than diffusion, ambipolar diffusion should manifest itself as a straight line on a semilogarithmic plot of $n(t)$ versus $t$ for constant pressure, provided the initial cross-sectional spatial distribution of electrons and ions is symmetrical.[18] This is seen to be the case sufficiently far out in the afterglow according to Fig. 1, which represents measurements taken for relatively high-average discharge currents ($\approx 10$ mA). Furthermore, it is seen that the time constant increases with increasing pressure, and that the computation of $D_a p$ yields a constant value of 216 cm² sec$^{-1}$ allowing for a certain scattering of the data, for pressures up to 1 mm Hg as illustrated in Fig. 2. Above 1 mm Hg the average discharge current could not be maintained at the same high level as at lower pressures; however, the power supply was adjusted for maximum current which was found to decrease gradually with increasing pressure. Exponential decay could be ascertained up to about 2 mm Hg, but there was not any longer any proportionality between $\tau$ and $p$. From 2 mm Hg and up to the breakdown limit for the system, 4.5 mm Hg, the straight line portion of the decay curve was either too limited in

[17] D. Formato and A. Gilardini, in *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1962), Vol. I, pp. 660.

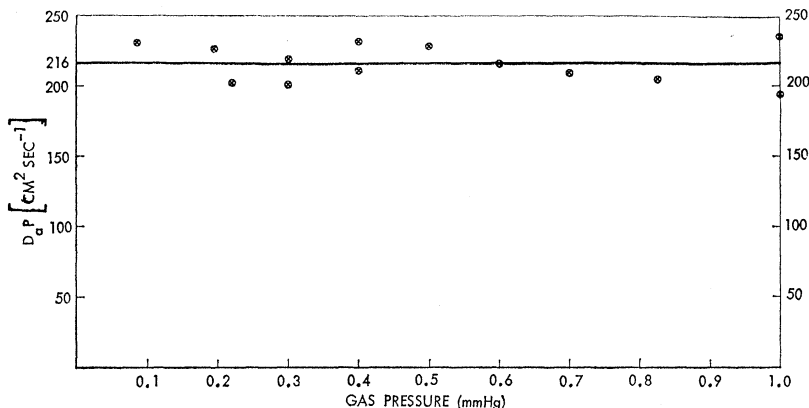[18] S. C. Brown, *Basic Data of Plasma Physics* (John Wiley & Sons, Inc., New York, 1961), p. 86.

FIG. 2. $D_a p$ values versus pressure pertaining to the high-current discharge (10 mA average current).

range to be conclusive or completely lacking. These effects are illustrated in Fig. 3.

The next set of measurements were taken with the average discharge current adjusted to a fixed, low value of 1 mA for all pressures and gas temperatures. Here, as in the case of the high-current discharge, the rate of electron decay varies exponentially with time and inversely with pressure for all gas temperatures investigated and pressures below 1 mm Hg. The composite results of these measurements are shown in Fig. 4(a).

## IV. DISCUSSION

As can be seen by studying Figs. 2 and 4, two very different values of the diffusion coefficient exist at room temperature, namely, $D_a p = 216 \pm 20$ cm$^2$ sec$^{-1}$ and $D_a p = 110 \pm 10$ cm$^2$ sec$^{-1}$ for the case of high- and low-average discharge currents respectively. The corresponding values reported by Schulz-DuBois,[6] who observed the same marked distinction between the high- and low-current oxygen discharges, are $D_a p = 225$ cm$^2$ sec$^{-1}$ and $D_a p = 87$ cm$^2$ sec$^{-1}$ with estimated accuracies

of 20% and 10%, respectively. Thus one finds complete agreement between the present and the earlier study with regard to the higher $D_a p$ value which was attributed to atomic ions, mainly because, apart from $O_2^+$ associated with the lower $D_a p$ value, no other positive ions had been reported to exist in oxygen. It was also suggested that the energy-enriched high-current discharge would cause more ionization of O since the ionization potential of the latter is 1.4 eV higher than that of $O_2$.

Unfortunately, however, judging from some previous mass-spectrographic[13,14] and spectroscopic measurements[19] of oxygen discharges, the ion $O^+$ does not seem to be very important. On the other hand, these identification studies may not pertain exactly to the discharge conditions appropriate for the high-current, pulsed discharge of interest here. In any case, if $O^+$ is the predominant ion, it is natural to ask how this can be brought about. The same question arose when the ions in a beam extracted from an rf ion source, using hydrogen, were found to be mainly atomic.[20] For this
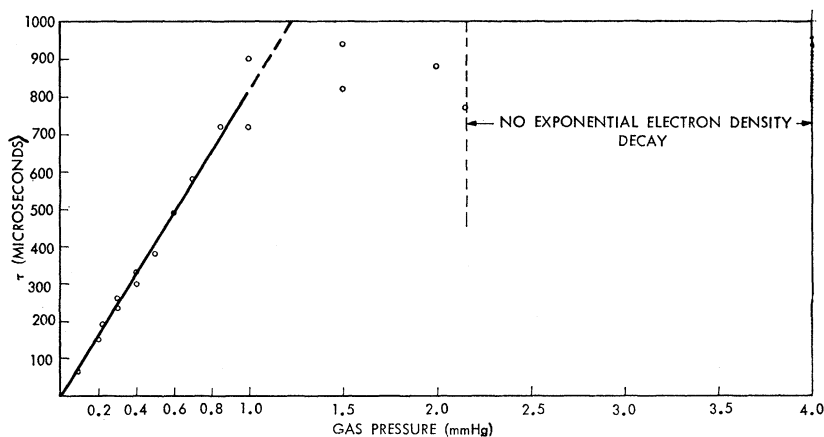


FIG. 3. The time constant $\tau$ for the exponential decay versus pressure for the high-current discharge. Deviation from linearity becomes apparent beyond 1 mm Hg, indicating that attachment becomes important. For pressures higher than 2.2 mm Hg, an unambiguous exponential decay did not occur.

[19] R. B. Bryan, R. B. Holt, and O. Oldenberg, Phys. Rev. 106, 83 (1957).
[20] C. C. Goodyear and A. Von Engel, in Proceedings of the Fifth International Conference on Ionization Phenomena in Gases (North-Holland Publishing Company, Amsterdam, 1962), Vol. I. pp. 203.

case it was concluded that the two-stage processes of dissociation and subsequent ionization of the atoms could compete favorably with direct electron ionization of the hydrogen molecule, considering ground-state processes only. The important difference when this argument is carried over to the problem at hand is that the onset potential for ionization of O is higher than for $O_2$, as already mentioned, whereas the opposite is true for hydrogen. Since the ionization cross sections for O and $O_2$ immediately beyond onset do not differ significantly,[21,22] it appears that such a two-stage process would still favor molecular ionization. It is also unlikely that metastable atoms, either as dissociation products ($'D$ and $'S$ states) or via separate electron excitation processes, should play such important roles as to drastically alter this situation. Furthermore, if one for a moment assumes that atomic ions predominate during the active discharge, the survival of these ions until post discharge times of the order of a millisecond requires much smaller charge transfer cross sections to prevail in the thermal range than those reported at higher energies.[23] While it is plausible to expect the afterglow to contain a binary mixture of the positive ions, this, in turn, would lead to a time-dependent diffusion coefficient,[24] which is contrary to observations. Thus, for the time being, no simple explanation can be given for attributing the observed high $D_a p$ value to the atomic ions. On the other hand, in what appears to be the only mass spectroscopic study of an oxygen *afterglow*[14] the ion $O_3{}^+$ has been reported to be the dominant ion at higher pressures. It seems therefore very possible that this ion is responsible for the higher mobility.

Supported by the findings from measurements of the microwave electron noise radiation temperature (see Appendix) one is justified in assuming ions and electrons to be Maxwellian and isothermal with the same temperature as the ambient gas. Consequently, the Einstein-Townsend relation can be used together with the approximation $D_a \approx 2D_+$, where $D_+$ is the diffusion coefficient of the positive ions, and the ionic mobility can be computed. The value thus found pertaining to the high-current discharge afterglow is 5.5 $cm^2$ $sec^{-1}$ $V^{-1}$ at room temperature.

For the low-current case it is seen from Fig. 4 that the mobility at room temperature is higher than the generally accepted value for $O_2{}^+$ in $O_2$ which is $K(O_2{}^+)$ = 2.25 $cm^2$ $sec^{-1}$ $V^{-1}$. The discrepancy is not too serious, however, considering the estimated total error involved. It is therefore reasonable to assume $O_2{}^+$ to be primarily responsible for the ambipolar diffusion observed in the low-current discharge afterglow. It should be mentioned

[21] E. W. Rothe, L. L. Marino, R. H. Neynaber, and S. M. Trujillo, Phys. Rev. **125**, 582 (1962).

[22] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, England, 1956), p. 265.

[23] R. F. Stebbings, B. R. Turner, and A. C. H. Smith, J. Chem. Phys. **38**, 2277 (1963).

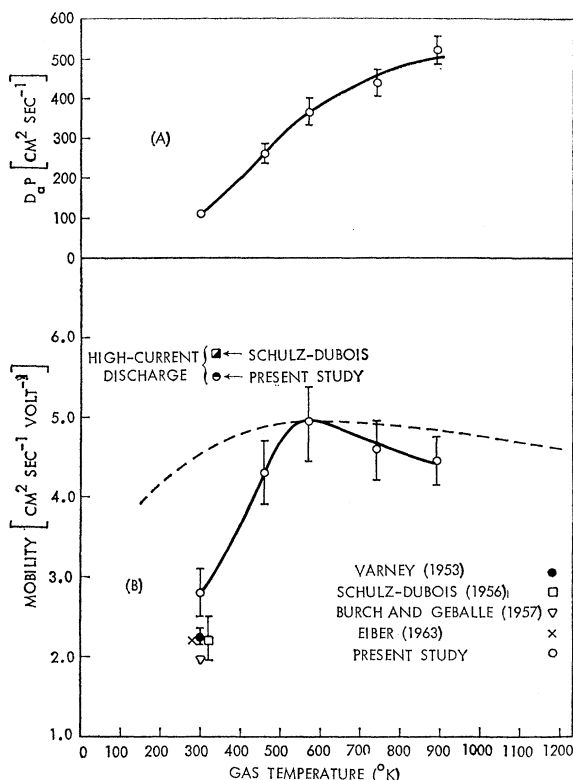[24] H. J. Oskam, Philips Res. Rept. **13**, 335 (1958).

FIG. 4. (a) Curve showing the temperature variation of $D_a p$ ($p$ refers to 300°K) pertaining to the low-current discharge afterglow (1 mA average current). (b) Results from Fig. 4(a) converted into mobilities $K$ together with some previously reported values for $K(O_2{}^+)$. The $K$ values pertaining to room temperature for the high-current discharge afterglow are also indicated. The strongest temperature variation to be expected using Mason and Schamp's potential $V(r)$ takes place when $\gamma = 0$ (see text); this case is reproduced by the dashed curve, the maximum of which is made to coincide with the experimental curve.

that Schulz-DuBois' result[6] was obtained indirectly from data that followed a curve of the form $p/\tau_{11}$ = $D_a p/\Lambda_{11}{}^2 + const \times p^2$, yielding the desired $D_a p$ value by extrapolation to zero pressure. This curve implies that the attachment process is of the two-body type which seems to be symptomatic for most microwave afterglow studies,[25] in contrast to the findings of Chanin et al.,[7] who reported an unambiguous three-body attachment process up to electron energies of 1 eV. As for the present results, the apparent proportionality between $\tau_{11}/p$ and $p^2$ (as seen from Fig. 5) indicating concordance with previous microwave afterglow studies may be somewhat fortuitous, due to the limited pressure range and scattering of the data.

When the interaction potential is of the form $V(r) \propto r^{-n}$, $D_a p$ should vary with temperature according to $T^{2/n} T^{1/2}$.[8] For the rigid sphere model ($n = \infty$), one would therefore have $D_a p \propto T^{1/2}$ and $K \propto T^{-1/2}$, whereas when only the induced dipole interaction is of importance ($n = 4$), $D_a p \propto T$ and $K$ should be temperature-

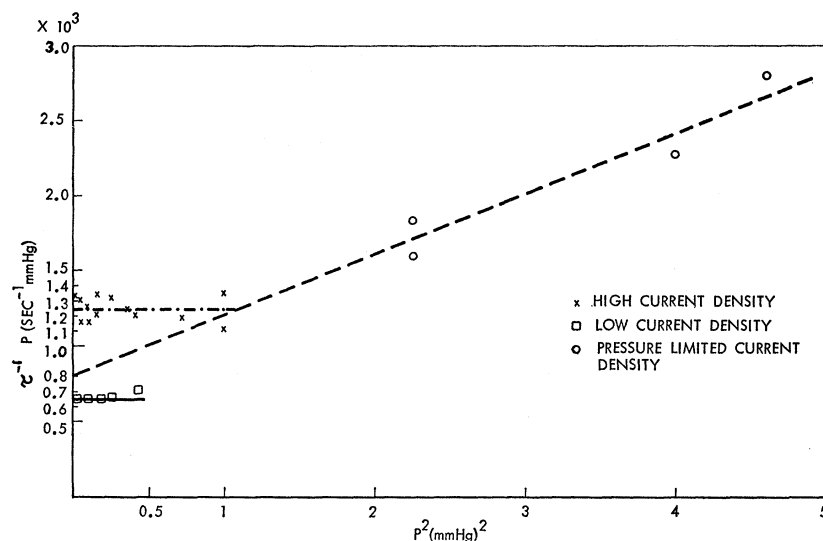[25] See Ref. 7 for an extensive list of references.

FIG. 5. $P/\tau$ plotted versus $p^2$ for the high-current discharge indicating a two-body attachment process to be important above 1 mm Hg with an attachment frequency $\nu_a = 400$ $p(\text{sec}^{-1})$.

independent (Langevin's formula). As expected none of these models can explain the temperature dependence illustrated in Fig. 4, since the interaction potential between ions and polyatomic molecules can be anticipated to be more complex depending upon the molecular orientation. The most important term in the case of a homonuclear molecule should vary as[2] $r^{-3}$ resulting in $D_a p \propto T^{1.166}$ and $K \propto T^{0.166}$, which again leads to a much too mild temperature variation. Obviously, no central force model consisting of a single term can explain the observed temperature dependence. However, if one adopts a force interaction model consisting of short-range repulsive as well as the long-range attractive terms, some cancellation may take place at a certain temperature, leading to a maximum in the mobility versus temperature curve, as has been demonstrated previously.[11,12]

The interaction potential used by Mason and Schamp, Jr., reads[11]

$$V(r) = \epsilon/2 \left[ (1+\gamma)\left(\frac{r_m}{r}\right)^{12} - 4\gamma\left(\frac{r_m}{r}\right)^{6} - 3(1-\gamma)\left(\frac{r_m}{r}\right)^{4} \right],$$

with $\epsilon$ the value of the potential energy minimum which occurs at $r=r_m$, and $\gamma$ a parameter which takes into account the charge-induced quadrupole interaction and the London dispersion.[26] By an elaborate computational analysis, collision integrals were tabulated for this model and used in a curve-fitting procedure in which the adjustable parameters $\epsilon$, $r_m$, and $\gamma$ were selected so as to give the best possible agreement with reliable experimental mobility data pertaining mainly to alkali ions in rare gases. The rather remarkable agreement thus obtained certainly shows that the Mason-Schamp potential is more universal than previous models. How-

ever, an inspection of the available collision integral tables seems to indicate that it would be difficult to obtain a fit with the present data because of their strong variation with temperature.

The reason for this may very well be due to charge transfer and other inelastic processes. The system $O_2^+$, $O_2$ should display symmetric resonance with a large charge transfer cross section, which for the similar atomic system $X^+$, $X$ is known to completely dominate the diffusion cross section[27,2] and consequently the temperature variation of the mobility. Unfortunately, measurements of charge transfer for $O_2^+$, $O_2$ in the thermal range is not known to the author, even though the cross section is reported to decrease with ionic energy beyond 25 eV.[28] If charge transfer primarily determines the diffusion one can make the conjecture that the charge transfer cross section must decrease very rapidly with temperature initially to conform with the present data. Such a conjecture can only be tested by measurements of $Q_{ch}$ in the thermal range, since even estimates of the behavior of resonance charge transfer of molecular ions in their parent gas are uncertain at low energies.[28]

### ACKNOWLEDGMENT

[26] F. London, Z. Physik **63**, 245 (1930).

[27] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, England, 1956), p. 409.

[28] A. Dalgarno, Ann. Geophys. **17**, 16 (1961).

## APPENDIX

Electrons scattered in the internal fields of molecules and ions as well as external electric fields emit incoherent radiation, the intensity of which is related to the mean electron energy. This can be utilized to measure the radiation temperature emitted from a plasma, which is equivalent to the electron temperature, provided thermodynamic equilibrium prevails and the electrons obey a Maxwellian velocity distribution function. Both the physical principles and technique for microwave measurements of plasma radiation temperature together with many results pertaining to dc glow discharges have been thoroughly presented by Bekefi and Brown.[29]

When one is interested in the decay of the electron temperature following a *pulsed* dc discharge the microwave noise sampling technique is used which makes it possible to measure the radiation temperature at any time during the afterglow. Since this technique also has been described thoroughly previously,[17,30] and is becoming more or less standard, it will not be discussed further here. Let it suffice to say that one is always faced with the vexing restriction of a Maxwellian electron distribution, in the absence of which the concept of radiation temperature becomes rather obscure and its relation to the actual mean electron energy unclear. These problems are perhaps most serious in molecular gases, and under active discharge conditions as compared with the quiescent afterglow. However, the advantage of having some experimental verification of the most commonly made assumption, namely that of isothermal conditions in the afterglow, certainly outweighs the reservations just mentioned. The present radition temperature measurements (see Fig. 6) shows that the afterglow in oxygen becomes isothermal quite rapidly.

Due to the finite width of the sampling pulse, 5 μsec, and the rapid thermal decay, the measurements for

[29] G. Bekefi and S. C. Brown, J. Appl. Phys. **32**, 25 (1961).
[30] D. Formato and A. Gilardini, in *Proceedings of the Fourth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1960), Vol. I, p. 101.
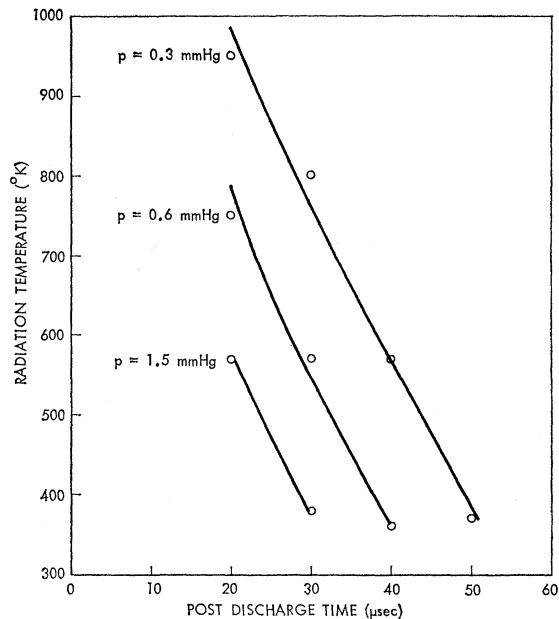


FIG. 6. Microwave radiation temperature measurements in oxygen. The voltage pulse igniting the discharge occupies the two first microseconds on the time scale.

oxygen are quite crude with an estimated error of about 15% so that any possible fine structure in the curves would be completely masked. It was beyond the scope of these measurements, however, to study the electron relaxation *per se*. The main objective was to obtain assurance that the time range of the afterglow dealt with during this study was represented by isothermal conditions; this objective one can safely say, has been achieved.

In conclusion it should perhaps be mentioned that the microwave radiometer was tested initially for an afterglow discharge in neon admixed with 5% oxygen. The results of these measurements yielded total thermal decay times exceeding those relevant to pure oxygen by roughly a factor of 20.