Clustering of Negative Ions in Oxygen*

D. S. BURCH† AND R. GEBALLE
Department of Physics, University of Washington, Seattle, Washington
(Received October 8, 1956)

Observed transient ion currents in oxygen below breakdown at low *pd* deviate from those predicted by use of the assumption that ions are formed during the initiating electron pulse and retain their identity while drifting in the electric field. The deviations, ascribed to clustering reactions that generate O_2^- and O_3^- from initially formed O^-, are analyzed to obtain values for the clustering rates. These rates have orders of magnitude comparable with ionization and attachment rates under the experimental conditions. Their variation with E/p and p are discussed and possible clustering reactions are suggested.

1. INTRODUCTION

THE application of transient techniques to Townsend discharges provides a means for studying certain low-energy ionic reactions. In such discharges mean ion energies do not exceed the order of an electron volt and mean free paths for inelastic collision can be comparable with the dimensions of the discharge region. Collisions which result in an altered mass of the charge carriers are susceptible to transient analysis because various drift velocities can be distinguished and because transient current shapes are dependent on reaction cross sections. A previous paper[1] describes transient discharges in oxygen that required an explanation in terms of two clustering reactions which generate two product ions, evidently O_2^- and O_3^-, from initially formed O^- ions drifting in an electric field. In the present paper we attempt a further analysis of those data to obtain values for the clustering rates and to provide information regarding the reactions responsible for clustering.

2. EQUATIONS OF CLUSTERING

In a gas at pressure p between two plane parallel electrodes separated by a distance d let there be a density $n_1(x,t)$ ions of Type 1 per cm. The rate at which these ions generate a different species, Type 2, by collision as they drift in the electric field is given by

$$-dn_1/dt=+dn_2/dt=\mu n_1 v_1, \tag{1}$$

where μ is defined as the clustering coefficient and where n_2=density of Type 2 ions per cm, v_1=drift velocity of Type 1 ions. In order to solve Eq. (1), we rewrite the total derivatives as follows:

$$\partial n_1/\partial t+v_1\partial n_1/\partial x=-\mu n_1 v_1, \tag{2}$$

$$\partial n_2/\partial t+v_2\partial n_2/\partial x=\mu n_1 v_1, \tag{3}$$

where v_2 is the drift velocity of Type 2 ions. These are to be solved with initial and boundary conditions appropriate to the state of the discharge immediately after transit of the initiating electron burst, as described in the preceding paper.[1] Once n_1 and n_2 are known, they may be integrated over the discharge region to obtain an expression for their contribution to the total transient current.

In case ions of Type 1 can also generate a third type, an additional clustering coefficient and further equations may be necessary. The manner in which analysis is altered depends on the mode of formation of the third species; i.e., "parallel clustering," the formation of Types 2 and 3 independently, or "series clustering," in which Type 2 is an intermediate step leading to Type 3. In the previous paper it was necessary to invoke the former kind in order to explain certain observations. Accordingly, we introduce a second clustering coefficient, ω, and an additional equation with obvious notation,

$$\partial n_3/\partial t+v_3\partial n_3/\partial x=\omega n_1 v_1, \tag{4}$$

while adding a term $-n_1 v_1\omega$ to the right-hand side of Eq. (2). If the parent ions are negative, the initial conditions for Eqs. (2), (3), and (4) are then

$$n_1(x,0)=\eta n_0 \exp[(\alpha-\eta)x]=\eta n_0 \exp(\beta x),$$
$$n_2(x,0)=0,$$
$$n_3(x,0)=0,$$

where η is the electron attachment coefficient, α is the first Townsend coefficient, and n_0 is the number of

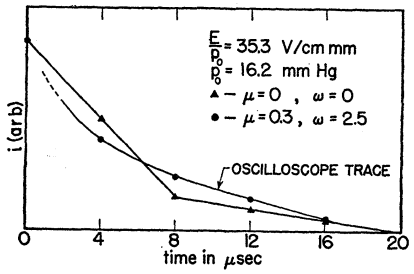

FIG. 1. Drawing made from an ion transient to illustrate the effect of clustering. Triangular points are computed on the assumption of no clustering. Circular points are computed with clustering coefficients as indicated. The curve on which they lie has been traced from a transient.

* Supported in part by the Office of Ordnance Research, U. S. Army.
† Now at Atomic Physics Section, National Bureau of Standards, Washington 25, D. C.
[1] D. S. Burch and R. Geballe, preceding paper [Phys. Rev. **106**, 183 (1957)].

electrons which initiate the discharge. We find for $i(t)$, the total current including that of the nonclustering positive ions, the expression

$$\begin{aligned} i&=i_+ +i_1+i_2+i_3 \quad \text{for} \quad 0<t<d/v_1,\\ i&=i_+ +i_2'+i_3' \quad \text{for} \quad d/v_1<t<d/v_2,\\ i&=i_+ +i_3' \quad \text{for} \quad d/v_2<t<d/v_3, \end{aligned} \tag{5}$$

where

$$i_+=C\alpha v_3 e^{\beta d}(1-e^{-r}),$$

$$i_1=C\eta v_1(e^{p}-1)e^{-at},$$

$$i_2=C\eta v_2\left\{\frac{\gamma}{\beta+\zeta}(e^{q}-e^{p-at})-\frac{\gamma}{\zeta}(1-e^{-at})\right\},$$

$$i_2'=C\eta v_2\left\{\frac{\gamma}{\beta+\zeta}(e^{q}-1)+\frac{\gamma\beta}{\zeta(\beta+\zeta)}(e^{\zeta q/\beta}-1)\right\},$$

$$i_3=C\eta v_3\left\{\frac{\xi}{\beta+\rho}(e^{r}-e^{p-at})-\frac{\xi}{\rho}(1-e^{-at})\right\},$$

$$i_3'=C\eta v_3\left\{\frac{\xi}{\beta+\rho}(e^{r}-1)+\frac{\xi\beta}{\rho(\beta+\rho)}(e^{\rho r/\beta}-1)\right\},$$

and where

$$C=en_0/\beta d, \quad p=\beta(d-v_1t), \quad q=\beta(d-v_2t),$$
$$r=\beta(d-v_3t), \quad a=(\mu+\omega)v_1t, \quad \gamma=\mu v_1/(v_1-v_2),$$
$$\zeta=(\mu+\omega)/(v_1-v_2), \quad \xi=\omega v_1/(v_1-v_3),$$
$$\rho=(\mu+\omega)/(v_1-v_3).$$

The clustering coefficients μ and ω can be determined by fitting Eq. (5) to oscillographic records of the transient current.

3. EXPERIMENTAL RESULTS

Figure 1 shows a comparison between a drawing made from a photograph of an ionic transient in oxygen at $E/p=35$ v/cm mm, and two sets of computed points. The triangular points represent the current to be expected if no clustering occurs. The circles are calculated from Eq. (5) with $\mu=0.3$ and $\omega=2.5$. Values of other parameters are taken from Harrison and Geballe[2] and from the preceding paper.[1] Equation (5) fits all observed transients within 5% throughout the ranges of E/p, p, and d covered by the investigation. A certain few of the photographs seem to deviate in a systematic manner from Eq. (5) but within the above limit. In such cases the computed curves are low in the initial portion of the time interval and high in the central portion.

Figure 2 presents the variation of coefficients μ and ω with E/p. The first of these is proportional to p^2, indicating that collisions generating O_3^- from O^- involve three bodies. At low E/p, where μ becomes very large, only a lower limit can be determined. Above $E/p\sim 40$, μ/p^2 has decreased to an extremely low value, consistent with the nonappearance of transit times corresponding to O_3^-. In contrast to the rapid variation of μ/p^2 in the region of E/p covered by Fig. 1, ion energies vary by no more than a few tenths of an electron volt. This rapid fall of μ/p^2 with energy can be understood in terms of a simple model of three body collisions similar to that employed in the Thomson recombination theory.[3] Major differences between the two processes are

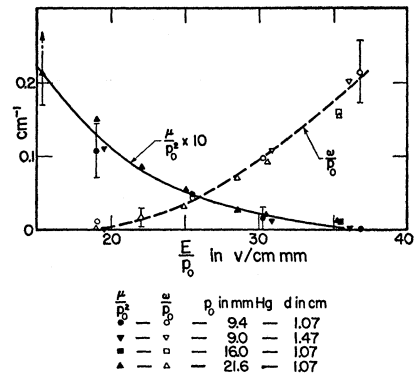

FIG. 2. Behavior of the clustering coefficients with E/p_0 and pressure. Values of μ/p_0^2 at low E/p_0 are lower limits only. Estimated limits of error are shown for a few points.

(1) Polarization replaces Coulomb attraction.

(2) All three bodies, rather than just two, are subject to the attraction force.

(3) The effective cross section for polarization scattering as given by Wannier[4] is used in Eq. (1) rather than the kinetic theory value.

Wannier[4] also has given an expression for the mean ionic energy, when polarization scattering dominates, in terms of temperature and drift velocity. Incorporating these changes into the framework of the Thomson theory, we find

$$\mu/p^2 \propto V^{-5/4}[(2V+V_0)/(V-V_0)]^{\frac{1}{2}}, \tag{6}$$

where V and V_0 are mean energies of the ions and the molecules, respectively. As E/p increases from 15 to 35 v/cm mm, Eq. (6) predicts a decrease in μ/p^2 by a factor of about 6, approximately as observed.

The second clustering coefficient, ω, is directly proportional to pressure, which indicates that a two-body reaction generates O_2^- from O^-. The adiabatic nature[5] of low-energy collisions requires that cross sections for inelastic processes rise rapidly with increasing energy as long as $a\Delta E \ll h\nu$, where a is a length of

[2] M. A. Harrison and R. Geballe, Phys. Rev. **91**, 1 (1953).

[3] J. J. Thomson and G. P. Thomson, *Conduction of Electricity Through Gases* (Cambridge University Press, Cambridge, 1931), third edition, Vol. 1, Chap. I.

[4] G. H. Wannier, Bell System Tech. J. **32**, 170 (1953).

[5] H. S. W. Massey, Repts. Progr. Phys. **12**, 248 (1949).

TABLE I. Affinities and dissociation energies of oxygen species.

Species	Electron affinity, ev	Dissociation energy, ev
O	1.45[a]	...
O_2	<0.8[b]	5.09[c]
O_3	3.0[d]	1.05[e] ($O+O_2$)

[a] S. J. Smith and L. M. Branscomb, J. Research Natl. Bur. Standards **55**, 165 (1955).
[b] S. J. Smith and L. M. Branscomb, Bull. Am. Phys. Soc. Ser. II, **1**, 287 (1956).
[c] A. G. Gaydon, *Dissociation Energies* (Dover Publications, New York, 1950), p. 212.
[d] Nikolskii, Kazarnovskaya, Bogdasar'yan, and Kazarnovskii, Doklady Akad. Nauk S.S.S.R. **72**, 713 (1950). We thank Dr. L. M. Branscomb for calling our attention to this reference.
[e] B. Lewis and G. von Elbe, J. Am. Chem. Soc. **57**, 612 (1935).

atomic dimensions, ΔE is the energy defect of the process, and v is the relative velocity of the interacting particles. The shape of the curve for ω is in accordance with this interpretation. In spite of its large magnitude at $E/p \sim 35$, ω/p cannot be measured at higher values because such rapid conversion of the parent O^- ions precludes observation of their transit time and drift velocity, essential for Eq. (5).

4. DISCUSSION

At the present time, any discussion of reactions involving negative oxygen ions must procede from a basis of meager available data. Table I gives the most recent values of pertinent energies. Among reactions that generate O_3^- from O^- and O_2, the simplest are:

$$\text{(a)}\ O^- + O_2 = O_3^-,$$
$$\text{(b)}\ O^- + 2O_2 = O_3^- + O_2,$$
$$\text{(c)}\ O^- + 2O_2 = O_3^- + 2O.$$

Reaction (a) is ruled out for the usual difficulty in satisfying conservation rules. Let $A(O_3)$ denote the electron affinity of O_3. If $A(O_3) > 0.4$ ev, as seems likely from the values of Table I, reaction (b) is exothermic. Reaction (c) requires 5.09 ev more than (b) and is not likely to contribute to O_3^- production as effectively. However, both (b) and (c) have the pressure dependence which the coefficient μ is found to obey.

The following reactions are the simplest possibilities for generation of O_2^-:

$$\text{(d)}\ O^- + O_2 = O_2^- + O,$$
$$\text{(e)}\ O^- + 2O_2 = O_2^- + O_3,$$
$$\text{(f)}\ O^- + 2O_2 = O_2^- + O_2 + O.$$

From Table I we conclude that reaction (d) is endothermic to the extent of at least 0.6 ev. Reaction (e) is exothermic provided that $A(O_2) > 0.4$ ev. Reaction (f), on the other hand, would be exothermic only if $A(O_2) > 1.4$ ev, a value considerably above that listed in Table I. Although these considerations make Reaction (e) appear most favorable, the observed pressure dependence is consistent only with Reaction (e). The energy deficit, several tenths of an electron volt, must be supplied from the kinetic energy of colliding ions. At the upper limit of E/p in Fig. 2 the mean ionic energy is within a factor of about three of the deficit.

The coefficient ω/p can be converted to a probability P per cm at one mm Hg pressure through multiplication by v_1/c_1, where c_1 is the mean random speed of Type 1 ions. A curve of P *vs* V then can be compared with extrapolations of curves given by Hasted and co-workers[6–8] for probabilities of inelastic collisions of various ions in several gases. The slope and magnitude of P are not dissimilar with such extrapolations although no detailed comparison is possible in view of the following differences: (1) Hasted and co-workers used a monoenergetic beam of ions in contrast to the distribution of energies in the present experiment; (2) Hasted and co-workers were not able to extend their work below about 10 ev whereas the mean ionic energies in the present work do not exceed about 0.5 ev; (3) Hasted and Smith[8] have recently published a curve of a probability per cm for O^- ions in O_2 which they interpret as due only to electron detachment whereas the curve for ω describes a charge exchange reaction. If the present results are to be consistent with those of Hasted and Smith, P must remain small in comparison with their curve as V increases to several electron volts.

[6] J. B. Hasted, Proc. Roy. Soc. (London) **A212**, 235 (1952).
[7] J. B. Hasted, Proc. Roy. Soc. (London) **A222**, 74 (1954).
[8] J. B. Hasted and R. A. Smith, Proc. Roy. Soc. (London) **A235**, 349 (1956).