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THE NEGATIVE IONS OF ATOMIC AND MOLECULAR OXYGEN

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CONTENTS

The properties, modes of formation and of destruction of the negative ions of atomic and molecular oxygen are examined in detail, using quantal theory to interpret and amplify the somewhat meagre experimental information.

A detailed examination of the $(1s)^2\,(2s)^2\,(2p)^4\,(3s)$ excited configuration of O^- is made in an attempt to decide whether it can give rise to the observed stable excited state in which the attached electron has nearly zero binding energy. This is important in attachment, detachment and electron scattering phenomena as resonance effects will occur if the configuration is on the verge of stability or instability. The Hartree-Fock equations have been solved for the deepest (^{4}P and ^{2}P)

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terms of this configuration, polarization effects being allowed for by the introduction of a term involving a polarizability p regarded as an adjustable parameter. Stable excited P terms are only found when p is two to four times as large as the polarizability of O deduced from the refractivity of O_2. This does not completely exclude identification of the excited state as belonging to the configuration considered. To examine the possible resonance effects, radiative attachment and detachment rates are calculated for a variety of values of the polarizability parameter p. The rapid variation of these quantities with p in the region where a real or virtual level of the $3s$ electron, with small energy, exists makes it unlikely that definite theoretical values can be given until more information as to the proper value of p is forthcoming. Meanwhile, the parameter p provides a convenient correlation of the probabilities of the two processes with the energy of the $3s$ electron. The other possible attachment and detachment processes involving O and O^- are also discussed.

In order to interpret experiments on attachments of electron swarms in O_2 and to decide how to extrapolate the results to low pressures, the deep electronic states of O_2^- are considered in detail, employing the empirical methods commonly used in studying molecular structure. It is found that their distribution is such as to make it most unlikely that O_2^- ions can be formed with appreciable probability by attachment of slow electrons to O_2 at low pressures, by a pressure-independent process other than direct radiative attachment. However, considerable difficulties and uncertainties are found in attempting a detailed interpretation of the experimental results at the higher pressures and more experiments are required.

In the final section the formation of pairs of oppositely charged ions from molecules by impact of electrons or light quanta is investigated in terms of the theory of the crossing of molecular potential-energy curves. The same theory is also applied to obtain information as to the possible magnitude of the cross-section for mutual neutralization of oppositely charged ions by electron transfer on impact. It is shown that a cross-section of between 10^{-13} and 10^{-12} cm.^{2} is quite likely to occur for atomic oxygen ions, but the occurrence of one as high as 10^{-11} cm.^{2} is most unlikely.

A detailed summary of results and conclusions is given.

GENERAL INTRODUCTION

The important role played by negative ions in upper atmospheric and many discharge-tube phenomena has been emphasized by various authors (Martyn & Pulley 1936; Bradbury 1938; Massey 1937; Bates, Buckingham, Massey & Unwin 1939; Emeléus & Sayers 1938). In this connexion the negative ions formed by and from atomic and molecular oxygen are of particular importance. We have therefore examined in detail the properties, modes of formation and of destruction of O^- and O_2^- ions. Even though, in the past few years, a considerable body of experimental information relating to these ions has been accumulating, it is necessary to employ quantum theory to a great extent to obtain information as to the importance, under various conditions, of the various phenomena involved. In doing this, however, we have taken account of all the experimental information available. Although it has not been possible to obtain definite results in many cases, we have attempted to enumerate all the possibilities, to point out inconsistencies, difficulties and uncertainties remaining, and to suggest further necessary lines of research. At all times applications to the theory of the ionosphere have been kept in mind, and it is hoped to consider this in detail in the light of the results and possibilities discussed in this paper. Apart from this particular aspect the conclusions are of interest in connexion with negative ions generally.

In the first section we discuss the structure, mode of formation and of destruction of the negative ions formed by and from atomic oxygen. In the second section is a corresponding analysis of the ions formed by and from molecular oxygen, while in the third section the formation and mutual neutralization of pairs of positive and negative ions is considered.

This latter subject could be partially treated in each of the preceding sections, but it is convenient to discuss, in a single section, both formation and neutralization processes.

A. Negative ions formed by and from atomic oxygen

1. *Introduction*

O^- ions have been frequently observed in the mass spectrograph, and Lozier (1934), by a study of the products of electron collision in molecular oxygen at low pressures (10^{-5}–10^{-4} mm. Hg), has determined the electron affinity of the atom as $2{\cdot}2 \pm 0{\cdot}2$ eV. He also finds evidence from similar collision experiments in carbon monoxide that an ion exists with energy nearly 2·2 eV in excess of that of the normal state, i.e. that there is an excited state of the ion with energy near that of the continuum. Further evidence in the same direction has been furnished by the collision experiments carried out by Hagstrum & Tate (1941) in oxygen, carbon monoxide and nitric oxide.

Hartree, D. R., Hartree, W. & Swirles (1939) have calculated the energy of the normal state of O^- by the self-consistent field method taking electron exchange into account as in the Fock method (1930). They find that the ion is stable relative to dissociation into a neutral atom and electron, but the calculated value (0·5 eV) of the electron affinity is rather low. From a study of the errors inherent in the theoretical method in its application to neutral atoms and positive ions, they conclude, however, that the value obtained by Lozier from his experiments is certainly not higher than might have been anticipated from the theory.

2. *Structure of* O^-

The ground state of O^- has the configuration $(1s)^2\,(2s)^2\,(2p)^5$ and is a $^2P^\circ$ term. Of this there is little doubt, but the nature of the excited state with very small binding energy observed by Lozier (1934) and by Hagstrum & Tate (1941) cannot be decided so easily. Since an answer to this question has an important bearing on the behaviour of oxygen atoms towards slow electrons, either in regard to elastic collision or attachment and detachment phenomena, we will now consider the matter in some detail.

It is well known that the effect of the short range of the effective atomic field which attracts an electron attached to a neutral atom is to limit the number of possible stationary states of the electron (Massey & Smith 1936). All early evidence indicated that any excited configuration of a negative ion would be unstable. The rare gases are known to form no negative ions of appreciable stability.† So a configuration such as $(1s)^2\,(2s)^2\,(2p)^6\,3s$ for Ne^- must be energetically unstable. One might have anticipated the same result for oxygen, but since the neon atomic field is very compact and the polarizability is low, the net field acting on an outer electron may well be smaller than for oxygen. The stable state observed by Lozier must be either one of the configurations $(1s)^2\,(2s)\,(2p)^6$ or $(1s)^2\,(2s)^2\,(2p)^4\,3s$. It is difficult to decide a priori which of these is likely to give the most stable state. Certain empirical evidence, however, favours the second possibility. In all neutral atoms in the second

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† Negative rare gas ions have never been observed in the discharge tube. Further, if a loosely bound s state exists in the field of a rare gas atom, it should be apparent in the appearance of a large elastic collision cross-section of the atom towards very slow electrons (see A 4·1 of this paper). All experimental evidence tends to show that this is not the case, at least for Ne, A and Kr (Kollath 1930).

row of the Periodic Table the first excited configuration is of this type, whereas for the corresponding singly- and doubly-ionized atoms it is of the other type. This seems to indicate that in a weak field the first excited configuration does involve excitation of a p electron to a $3s$ orbital.† This case is the one most susceptible to theoretical treatment, so we examine whether it is likely to give a stable state of O^-.

3. *The* $(2p)^4\,3s$ *configuration of* O^-

This configuration gives rise to ^2S, ^2P, ^4P and ^2D terms. The electrostatic energies E of the four terms may be written down by the use of the formulae given by Slater (1929). They are

$$E(^4P) = E(^3P) + F(3s) - G_0(1s, 3s) - G_0(2s, 3s) - G_1(2p, 3s), \qquad (1)$$

$$E(^2P) = E(^3P) + F(3s) - G_0(1s, 3s) - G_0(2s, 3s), \qquad (2)$$

$$E(^2D) = E(^1D) + F(3s) - G_0(1s, 3s) - G_0(2s, 3s) - \tfrac{2}{3}G_1(2p, 3s), \qquad (3)$$

$$E(^2S) = E(^1S) + F(3s) - G_0(1s, 3s) - G_0(2s, 3s) - \tfrac{2}{3}G_1(2p, 3s), \qquad (4)$$

where $E(^3P)$, $E(^1D)$, $E(^1S)$ are of the same form as the electrostatic energies of the ^3P, ^1D and ^1S terms of the ground configuration of neutral O but include wave functions appropriate to O^- instead of to O. $F(3s)$ is the term arising from the direct interaction of the $3s$ orbital with the nucleus and with the $1s$, $2s$ and $2p$ orbitals. It is given by

$$F(3s) = I(3s) + 2F_0(1s, 3s) + 2F_0(2s, 3s) + 4F_0(2p, 3s).$$

The quantities G_0 and G_1 represent the corresponding exchange interaction. The quantities I, F, G are defined as usual, in atomic units, by

$$I(\alpha) = -\frac{1}{2}\int_0^\infty P(\alpha \mid r)\left\{\frac{d^2}{dr^2} + \frac{2N}{r} - l_\alpha(l_\alpha+1)/r^2\right\} P(\alpha \mid r)\, dr,$$

$$F_k(\alpha\beta \mid r) = \int_0^\infty P^2(\alpha \mid r)\, Y_k(\beta\beta \mid r)\, r^{-1}\, dr = \int_0^\infty P^2(\beta \mid r)\, Y_k(\alpha\alpha \mid r)\, r^{-1}\, dr,$$

$$G_k(\alpha\beta \mid r) = \int_0^\infty P(\alpha \mid r)\, P(\beta \mid r)\, Y_k(\alpha\beta \mid r)\, r^{-1}\, dr,$$

$$Y_k(\alpha\beta \mid r) = \int_0^r P(\alpha \mid r_1)\, P(\beta \mid r_1)\, (r_1/r)^k\, dr_1 + \int_r^\infty P(\alpha \mid r_1)\, P(\beta \mid r_1)\, (r/r_1)^{k+1}\, dr_1,$$

where N is the nuclear charge, l_α is the azimuthal quantum number and $r^{-1}P(\gamma \mid r)$ is the self-consistent wave function for the γth orbital. We note that, while the ^2P and ^4P terms are based on the ground ^3P term of neutral oxygen, the ^2D term is based on the ^1D, and ^2S on the ^1S terms of the ground configuration of the neutral atom.

As the screening of the nuclear field from the $3s$ electron by the electrons occupying the two-quantum orbitals is less in the excited terms, it is probable that the ^2S and ^2D terms of O^- are deeper than their basic O terms by a greater amount than the ^2P and ^4P terms. The added negative energy due to the $3s$ electron must in any case be so small, however, that the ^2S and ^2D states will be unstable through "auto-ionization", viz.

$$O^-(^2S, {}^2D) \rightarrow O(^3P) + e.$$

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† It must be remembered that extrapolation of known properties associated with positive ions and neutral atoms to apply to negative ions is always a doubtful procedure.

Therefore we need consider only the ^{2}P and ^{4}P terms as possibly responsible for the observed stable excited state of O$^-$. Of these two terms ^{4}P clearly lies deeper.

To determine whether the total energy of O$^-$(^{4}P) or O$^-$(^{2}P) is likely to be below that of O(^{3}P) we set up the Fock equation, which includes exchange, for the $P(3s\,|\,r)$ wave function by the method developed by Hartree, i.e. formal differentiation of the energy with respect to the wave functions (Hartree, D. R. & W 1935). Using the energy expressions (1), (2) we find the equation

$$\left\{\frac{d^2}{dr^2}+2V-2v_p+k^2\right\}P(3s\,|\,r)+2Q/r=\eta_{1s}P(1s\,|\,r)+\eta_{2s}P(2s\,|\,r), \tag{5}$$

where $V=\{N-2Y_0(1s,1s\,|\,r)-2Y_0(2s,2s\,|\,r)-4Y_0(2p,2p\,|\,r)\}/r,$

$$Q=\begin{cases}P(1s\,|\,r)\,Y_0(1s,3s\,|\,r)+P(2s\,|\,r)\,Y_0(2s,3s\,|\,r)+P(2p\,|\,r)\,Y_0(2p,3s\,|\,r); & {}^4\mathrm{P}\\ P(1s\,|\,r)\,Y_0(1s,3s\,|\,r)+P(2s\,|\,r)\,Y_0(2s,3s\,|\,r); & {}^2\mathrm{P}.\end{cases}$$

The terms Q are those arising from exchange effects and v_p is the polarization potential discussed below. η_{1s}, η_{2s} are parameters which must be so adjusted that $P(3s\,|\,r)$ is orthogonal to $P(1s\,|\,r)$ and $P(2s\,|\,r)$. k^2 is equal to twice the energy of the electron measured in atomic units.

For the numerical calculations the functions $P(1s\,|\,r)$, $P(2s\,|\,r)$, $P(2p\,|\,r)$ were taken to be those given by the self-consistent field calculations of Hartree *et al.* (1939) for oxygen. This amounts to neglecting the perturbation of the core by the 3s electron, and as a partial correction for this the polarization potential is included. If p is the polarizability of the oxygen atom in its ground state, in atomic units, the correct asymptotic form for v_p is $-\frac{1}{2}pr^{-4}$. Extrapolation to smaller values of r need not be done accurately as polarization effects are relatively unimportant at such distances and the procedure adopted was to divide p into contributions from the different electron shells, so

$$p=\sum_{n,\,l}p_{nl}.$$

v_p was then written
$$v_p=-\tfrac{1}{2}\sum_{n,\,l}p_{nl}/(r_{nl}^2+r^2)^2, \tag{6}$$

where r_{nl} is the radius of the nl shell. The fractional contribution from each shell was estimated theoretically from the simple formulae given by Kirkwood (1932) and from the more exact formulae given by Buckingham (1937). These formulae were also employed to estimate the absolute magnitude of the polarizability, and the values found were 9·16 and 5·69 a.u. from the Kirkwood and Buckingham formulae respectively. An 'observed' value can also be derived by using the rule (van Vleck 1932) that the refractivity of a molecule is obtained by summing those of the constituent atoms. As the molar refractivity of O_2 is 3·87 (Zahn & Miles 1928) this gives a polarizability of 5·1 a.u. for O, in good agreement with that derived from the Buckingham formula. It was soon found that even the theoretical value of the polarizability given by the Kirkwood formula did not give rise to a long-range attraction of sufficient magnitude to introduce a stable ^{4}P term. In view of this it was decided to treat the quantity p as a variable parameter. Calculations of wave functions were therefore carried out for a range of p, including values great enough to lead to stable ^{4}P and ^{2}P terms. The method used was to calculate the 3s wave function for both terms with $k=0$ and various values of p. The solution of the appropriate equation (5) was carried out in each case by methods of successive approximation, starting from a good basic function to calculate the initial values of the quantities Q. Owing to the important role played by the parameters η_{1s}, η_{2s} this involved a good deal of preliminary work in each case before a satisfactory start could be made.

To determine, for each term, the value of p at which an energy level first appears it is convenient to plot the asymptotic value of the slope of the proper solutions $P(3s\,|\,r)$ for various values of p, each function being normalized to behave in the same way at the origin. The value of p for which the slope vanishes gives the appropriate 'resonance' polarizability which just leads to a stable term.

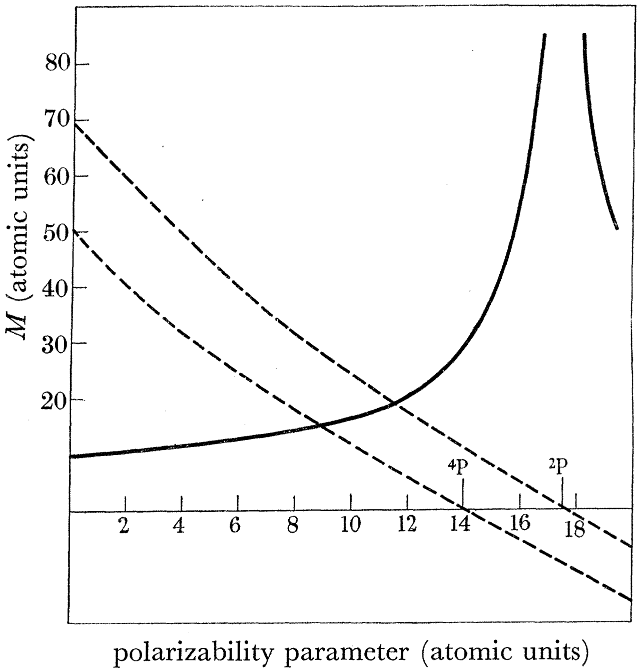

Figure 1. Illustrating the determination of the resonance values of the polarizability parameter which just introduce stable excited ^{2}P and ^{4}P terms of O$^-$. The variation with polarizability of the low-energy limit of the matrix element M which determines the rate of attachment of slow electrons of wave number k to oxygen atoms is also illustrated. ----- Asymptotic value of the slope of the $P(3s\,|\,r)$ wave function, the initial slope being fixed. The energy level first appears when the asymptotic slope vanishes. —— $\mathop{\mathrm{Lt}}_{k\to 0} M$ as function of polarizability. This curve behaves like $61{\cdot}2/|p-p_2|$ near $p=p_2$, the value which just introduces a ^{2}P level.

It will then be seen from figure 1 that a stable ^{4}P term first appears for $p = 14{\cdot}0$ a.u., while p must be as large as 17·6 a.u. to give a stable ^{2}P term. These values are 2–4 times as great as the 'observed' value 5·1 a.u., thus throwing considerable doubt on the identification of the stable excited state as belonging to the configuration $(1s)^2\,(2s)^2\,(2p)^4\,3s$. It must be remembered, however, that it is probable that the self-consistent field method we have used underestimates the binding energy (it is not quite certain, as the inclusion of a polarization potential does not follow directly from a variation method). Moreover, multipole interactions exist which give rise to long-range attractions, and their inclusion would correspond to an increase in the effective value of p, though probably not by more than 25 %. In view of these considerations and the further possibility that considerable error is introduced by representing both the average interaction and the polarization by spherically symmetrical functions when we are dealing with an incomplete shell of electrons, we cannot say definitely that the stable excited state does not belong to the $(1s)^2\,(2s)^2\,(2p)^4\,3s$ configuration. As it will be difficult to improve the theory beyond the stage described above, it will be necessary, eventually, to investigate, by the Fock method, the energy of the $(1s)^2\,(2s)\,(2p)^6$ configuration to examine whether it is likely to supply a stable excited term. Meanwhile we can examine the relation of the energy of the $(1s)^2\,(2s)^2\,(2p)^4\,3s$ configuration to other phenomena in terms of the polarizability parameter p.

4. *Elastic scattering, attachment and detachment phenomena in atomic oxygen in relation to the energy of* O⁻ $(1s)^2\,(2s)^2\,(2p)^4\,3s$

The existence or otherwise of a stable term of low binding energy belonging to the configuration $(1s)^2\,(2s)^2\,(2p)^4\,3s$ has a very pronounced influence on the probability of elastic scattering of slow electrons by oxygen atoms and of the important processes of attachment of electrons to oxygen atoms and of detachment of electrons from negative oxygen ions. As a result we cannot hope to calculate accurate values of the probabilities of these processes. Instead, we calculate the probabilities as functions of the assumed polarizability parameter p which provides the link with the energy of the $(1s)^2\,(2s)^2\,(2p)^4\,3s$ configuration of O^-. In this way we can at least review and correlate the possibilities.

4·1. *Elastic scattering.* For scattering by atomic fields which are such that neither real nor virtual s levels, with small negative or positive binding energy respectively, exist, the elastic collision cross-section is independent of electron energy in the low-energy range. At an s resonance (where the field is just such as to produce an s level of zero binding energy) the cross-section behaves like E^{-1} for small energies E. This must be taken into account in attempting to determine the collision frequency for slow electrons in atomic oxygen, and for normal temperatures the elastic collision coefficient may be as great as 10^{-6} cm.³/sec. The situation is further complicated for this case by the possibility of p resonance though this is unlikely to occur in the range of the polarizability parameter which we must consider. In view of this it has been thought best to deal in detail with the question of elastic scattering in a separate paper.

4·2. *Radiative attachment of slow electrons to form normal* O^-. The cross-section for the capture of an incident electron of energy E $(=\tfrac{1}{2}mv^2)$ into a level belonging to the ground term of O^-, by an O atom in its normal ^3P level, can be written

$$Q_A = \tfrac{64}{3}\pi^4 v^{-1} e^2 \nu^3 h^{-1} c^{-3} \Big\{\sum_i (2L_i+1)\,(2S_i+1)\Big\}^{-1} \sum_i \sum_f \sum_{M_{L_i}} \sum_{M_{L_f}} \sum_{M_{S_i}} \sum_{M_{S_f}}$$

$$\times \Big\{\Big|\int \Psi^*(\gamma_i, L_i, S_i, M_{L_i}, M_{S_i}) \sum_{q=1}^{k} \mathbf{r}_q \Psi(\gamma_f, L_f, S_f, M_{L_f}, M_{S_f})\, d\tau_1 \ldots d\tau_k\Big|^2\Big\}, \qquad (7)$$

where ν, the frequency of radiation emitted, is given by

$$\nu = (E+E_0)/h,$$

E_0 being the electron affinity of normal O (2·2 eV). In the formula γ_i, γ_f denote the aggregate of quantum numbers of the orbitals comprising the initial and final configurations respectively, L_f, S_f the quantum numbers distinguishing the particular term to which the final level belongs, M_{L_f}, M_{S_f} the quantum numbers specifying a particular level of the final term. The initial configuration, involving as it does an orbital of the continuum, will, in general, give rise to more than one term, all with the same energy, and these are distinguished by the quantum numbers L_i, S_i. Particular levels of these terms are distinguished by M_{L_i}, M_{S_i}. The co-ordinates of the k electrons concerned are denoted by $\mathbf{r}_1 \ldots \mathbf{r}_k$. The formula (7) arises as a result of averaging over all initial levels and summing over all final levels (Heitler 1935).

In the particular case in which we are concerned, the final level is one of the ground $^2\mathrm{P}^\circ$ term of O^-, so $L_f = 1$, $S_f = \frac{1}{2}$. Further, the configuration γ_f is $(1s)^2 (2s)^2 (2p)^5$, so the capture involves essentially the transition of an electron from an orbital of the continuum to a p orbital. In order that the dipole selection rules be obeyed, the electron, before capture, must be in either an s or d orbital. Let us consider first the former possibility for which the cross-section will be denoted by Q_A^s. The initial configuration is then $(1s)^2 (2s)^2 (2p)^4 (Es)$. This gives rise to $^4\mathrm{P}$, $^2\mathrm{P}$, $^2\mathrm{D}$ and $^2\mathrm{S}$ terms. Of these only $^4\mathrm{P}$ and $^2\mathrm{P}$ can occur when the atomic core is in a $^3\mathrm{P}$ level, as is the case for capture by normal O. We therefore have either $L_i = 1$, $S_i = \frac{3}{2}$ or $L_i = 1$, $S_i = \frac{1}{2}$. The first of these possibilities gives no contribution to the sum, as the integrals vanish when $S_i \neq S_f$. As they also vanish when $M_{S_i} \neq M_{S_f}$ we have

$$Q_A^s = \tfrac{64}{3}\pi^4 v^{-1} e^2 \nu^3 h^{-1} c^{-3} \frac{f_c}{18} \sum_{M_{L_i}=-1}^{1} \sum_{M_{L_f}=-1}^{1} \sum_{M_S=-\frac{1}{2}}^{\frac{1}{2}}$$
$$\times \left\{ \left| \int \psi^*(\gamma_i, 1, \tfrac{1}{2}, M_{L_i}, M_S) \sum_1^5 \mathbf{r}_q \psi(\gamma_f, 1, \tfrac{1}{2}, M_{L_f}, M_S)\, d\tau_1 \ldots d\tau_5 \right|^2 \right\}. \tag{8}$$

The number, k, of electrons concerned has been restricted to the four p electrons of atomic O and the incident electron. This is possible because the role of the inner electrons of the O atom, all in closed shells, can be regarded merely as introducing a factor f_c, very nearly unity, arising from the slight change of the closed shell orbitals when capture takes place. This separation can be effected, as it is a good approximation to write the complete wave function for either the initial or the final state in the form

$$\Psi = \phi(c)\, \psi(\gamma, 1, \tfrac{1}{2}, M_L, M_S),$$

where ϕ is a function of the co-ordinates r_c of the core electrons only, ψ of those of the remaining electrons. Then, to this approximation,

$$f_c = \left| \int \phi_i^*(c)\, \phi_f(c)\, d\tau_c \right|^2 \tag{9}$$

(see Condon & Shortley 1935).

To effect a further reduction in the form (8) for Q_A^s the functions ψ must be expressed in terms of the Hartree-Fock wave functions for the individual orbitals. This may be carried out by means of the methods described by Condon & Shortley (1935), and we find†

$$Q_A^s = \tfrac{256}{9}\pi^5 v^{-1} e^2 \nu^3 h^{-1} c^{-3} a_0^5 f f_c \left| \int P_-(2p \mid r)\, r\, P(Es \mid r)\, dr \right|^2, \tag{10}$$

where $r^{-1}P_-(2p \mid r)$ is the Hartree-Fock wave function for a $2p$ orbital of O^- normalized to unit density and $r^{-1}P(Es \mid r)$ that of an orbital in which an electron is moving with energy E in the field of an O atom in its normal ^3P state, the spin of the electron being such that the total spin is $\frac{1}{2}(h/2\pi)$. It is normalized so as to have the asymptotic form

$$(kr)^{-1} \sin (kr + \delta_0^s).$$

In the formula (10) the quantities under the integral sign are expressed in atomic units, the remainder in c.g.s. units. The factor f, arising from change of the wave functions of the four $2p$ electrons of O due to the addition of the extra electron, is given by

$$f = \left\{ \left| \int P(2p \mid r)\, P_-(2p \mid r)\, dr \right|^2 \right\}^4, \tag{11}$$

where $r^{-1}P(2p \mid r)$ is the wave function for a $2p$ orbital of O.

A similar procedure gives, for the capture of a d electron,

$$Q_A^d = \tfrac{512}{9}\pi^5 v^{-1} e^2 \nu^3 h^{-1} c^{-3} a_0^5 f f_c \left| \int P_-(2p \mid r)\, r P(Ed \mid r)\, dr \right|^2, \tag{12}$$

$r^{-1}P(Ed \mid r)$, the wave function for the d electron, being normalized in the same way as $r^{-1}P(Es \mid r)$.

The variation of the cross-sections Q_A^s, Q_A^d with energy has been discussed by Massey & Smith (1936), who show that for small E, Q_A^s behaves in general like $E^{-\frac{1}{2}}$ and Q_A^d like $E^{\frac{3}{2}}$. On the other hand, if a ^2P level exists with zero energy, Q_A^s behaves like $E^{-\frac{3}{2}}$ so, if a real or virtual level, with small negative or positive energy respectively, exists, we can expect Q_A^s to be very sensitive to the detailed form of the wave functions. In our particular problem this state of affairs prevails as is clear from the preceding section. We therefore proceed by calculating Q_A^s as a function of the energy of the incident electron for various values of the polarizability parameter p. Q_A^d is not sensitive to the value of p, as the inclusion of polarization has only a small effect on the d wave function.

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† This formula is the same as that which would be expected from first principles. Of the three $2p$ orbitals which can each accommodate two electrons with opposite spin, in normal oxygen one is fully occupied by an electron pair and the other two each include one electron with the same spin. There are therefore two possible alternative orbitals into which the additional electron can be captured, but for either it must have a spin opposite to that of the electron already occupying the orbital. The single electron capture cross-section must therefore be multiplied by $2 \times \frac{1}{4}$, the first factor arising from the two available levels, the second from the spin requirement. A further factor of 2 is introduced when there is an equivalent electron occupying the orbital, so the net result is that, apart from such factors as ff_c, the formula is the same as for the single electron problem of capture to a single untenanted $2p$ orbital.

For capture by $O^+ \, {}^4S^\circ$ into the ground configuration of O the corresponding factor is $3 \times \frac{1}{4} \times 2 = \frac{3}{2}$. In a previous paper (Bates *et al.* 1939) this was erroneously taken as $\frac{3}{4}$ owing to the omission of the factor 2 arising from the presence of equivalent electrons. The contributions from the ground state given in table II of that paper should be doubled. This has no effect on any of the conclusions or other material presented in the paper.

In carrying out the calculations the functions $P(2p\,|\,r)$, $P_-(2p\,|\,r)$ were taken to be those found by Hartree *et al.* (1939) by numerical solution of the Fock equations for the system. The factors f_c, f are then found, by numerical integration, to have the values 1·00, 0·90, respectively. The functions $P(Es\,|\,r)$ have been calculated by numerical solution of equation (5), using the values of the exchange terms found to be self-consistent for $E = 0$, a procedure rendered valid by the slow variation of these terms with energy. For $P(Ed\,|\,r)$ the appropriate integro-differential equations can be written down as for $P(Es\,|\,r)$. However, as the centrifugal force potential $-6/r^2$ exerts a dominating influence on the solution in the energy range concerned, it is unnecessary to include the exchange terms, and the equation was taken to be simply

$$\left(\frac{d^2}{dr^2}+2V-2v_p-6/r^2+k^2\right)P(Ed\,|\,r) = 0. \tag{13}$$

Finally, in choosing the frequency ν, the observed value of E_0, and not a calculated value, was used.

The behaviour of the integral

$$M = \int P_-(2p\,|\,r)\,rP(Es\,|\,r)\,dr$$

as a function of p at the low velocity limit may be seen in figure 1. The resonance effect is apparent at the value (17·6 a.u.) of p which first introduces a stable ^{2}P term of the $(1s)^2\,(2s)^2\,(2p)^4\,3s$ configuration—for this value of p, M tends to infinity.

The variation of the attachment coefficient† α_A with energy of the incident electron is illustrated in figure 2 for some typical cases. For values of p far from resonance α_A is constant for small E, while near resonance the variation is rapid, becoming like E^{-1} at exact resonance. At greater energies the effect of α_A^d becomes important, leading to a maximum of α_A at an energy of roughly 30 eV.

For practical applications the mean coefficient of attachment, $\bar{\alpha}_A$, for electrons with Maxwellian distribution of velocity, in a gas of atomic oxygen, is the most convenient quantity with which to deal. In terms of the attachment coefficient $\bar{\alpha}_A$ is given by

$$\int n(v)\,\alpha_A(v)\,dv, \tag{14}$$

where $$n(v) = 4\pi v^2(m/2\pi\kappa T_e)^{\frac{3}{2}}\exp\left(-mv^2/2\kappa T_e\right),$$

T_e being the electron temperature. We have calculated $\bar{\alpha}_A$ as a function of p for the four electron temperatures, 250, 500, 1000, and 2000° K. The results are given on a logarithmic scale in figure 3.

Although the variation with p is not of so complicated a nature as would be expected for the corresponding case of elastic collisions, the resonance effect, which is here associated only with the ^{2}P term, is very marked.

4·3. *Photodetachment of electrons from normal* O$^-$ *ions.* The removal of a $2p$ electron from an O$^-$ ion in its normal ^{2}P° state will leave an O atom either in a state of its normal ^{3}P term or of one of the two excited terms ^{1}D and ^{1}S. The energy of the absorption limit for the production of O ^{3}P is 2·2 eV, of O ^{1}D 4·2 eV and of O ^{1}S 6·4 eV. Using the same notation as

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† This is given by vQ_A, where v is the velocity of the incident electron.

before but noting that in each case we consider transitions from a single initial term ($^2P^\circ$), we find for the cross-section for absorption of a quantum of frequency ν which ejects an electron and leaves the O atom in the L_f, S_f term of the γ_f configuration,

$$Q_D(L_f, S_f) = \tfrac{32}{3}\pi^4 m^2 e^2 \nu v h^{-3} c^{-1} f_c \{(2L_i+1)(2S_i+1)\}^{-1} \sum_{M_L} \sum_{M_{Lf}} \sum_{M_S}$$
$$\times \left\{ \left| \int \psi^*(\gamma_i, L_i, S_i, M_{Li}, M_{S_i}) \sum_1^5 \mathbf{r}_q \psi(\gamma_f, L_f, S_i, M_{Lf}, M_{S_i})\, d\tau_1 \ldots d\tau_5 \right|^2 \right\}, \qquad (15)$$

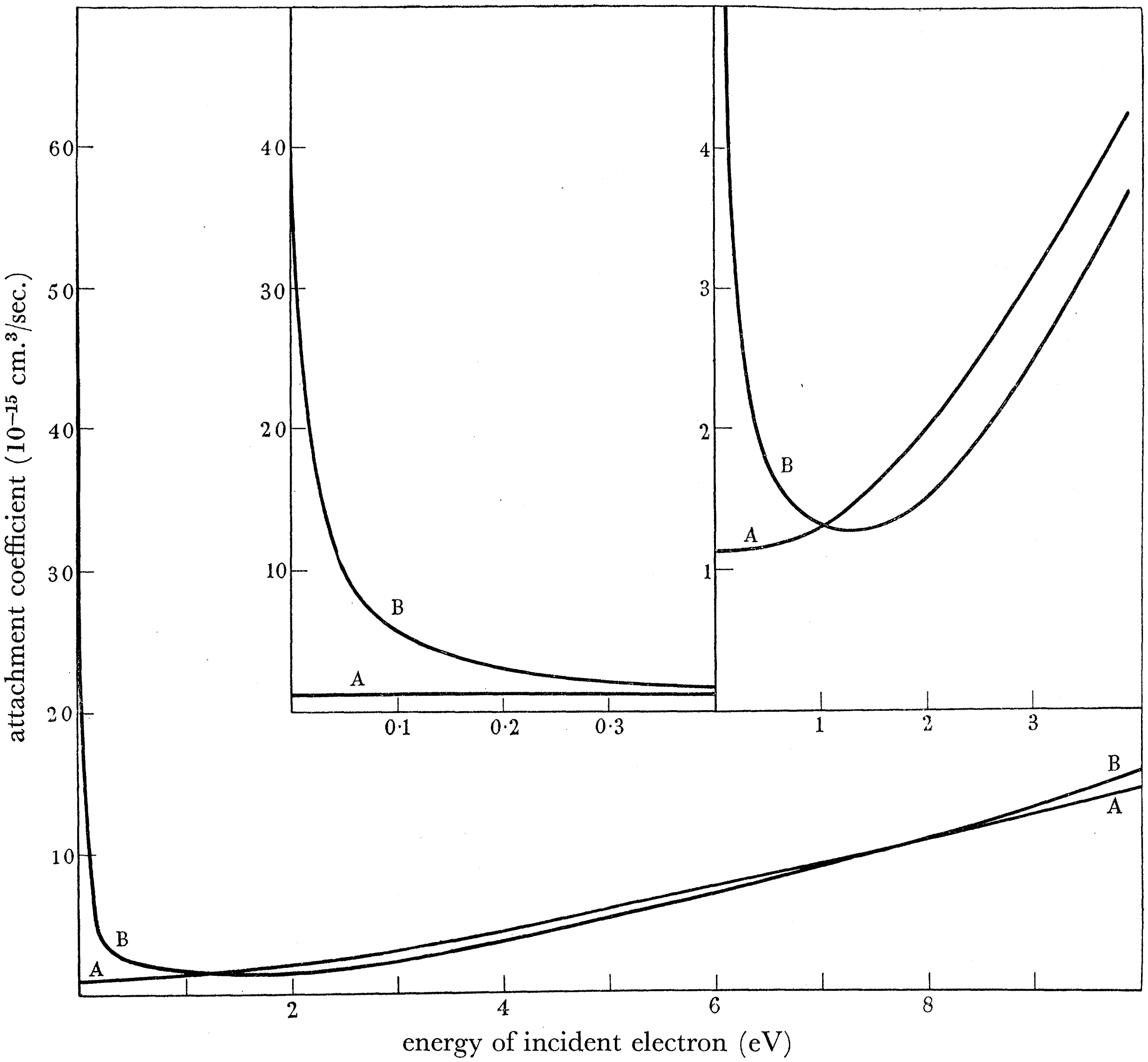

FIGURE 2. Variation, with electron energy, of the attachment coefficient for electrons in atomic oxygen on the assumption of two different values of the polarizability parameter p. A, $p = 5{\cdot}7$ a.u.; B, $p = 18{\cdot}3$ a.u.

where $L_i = 1$, $S_i = \frac{1}{2}$. In this formula allowance has been made for the fact that the integral vanishes unless $S_i = S_f$, $M_{S_i} = M_{S_f}$ and the effects of the core and outer electrons have been separated.

For absorption in which the O atom is left in a state of the normal ^3P term, the final term of the complete system O(^3P), $+e(Es)$ in an orbital of the continuum, is either ^2P or ^4P. As there is a vanishing probability of a transition to the latter term we obtain $Q_D(O^{-}\,{}^2P \rightarrow O\,{}^3P)$

by writing $L_f = 1$, $S_i = \frac{1}{2}$ in (15). Similarly, for absorption in which the O atom is left in a level of the ^{1}D or ^{1}S terms the final terms of the complete system must be ^{2}D or ^{2}S respectively. The corresponding cross-sections are therefore obtained by taking $L_f = 2$, $S_i = \frac{1}{2}$ and $L_f = 0$, $S_i = \frac{1}{2}$ respectively in (15).

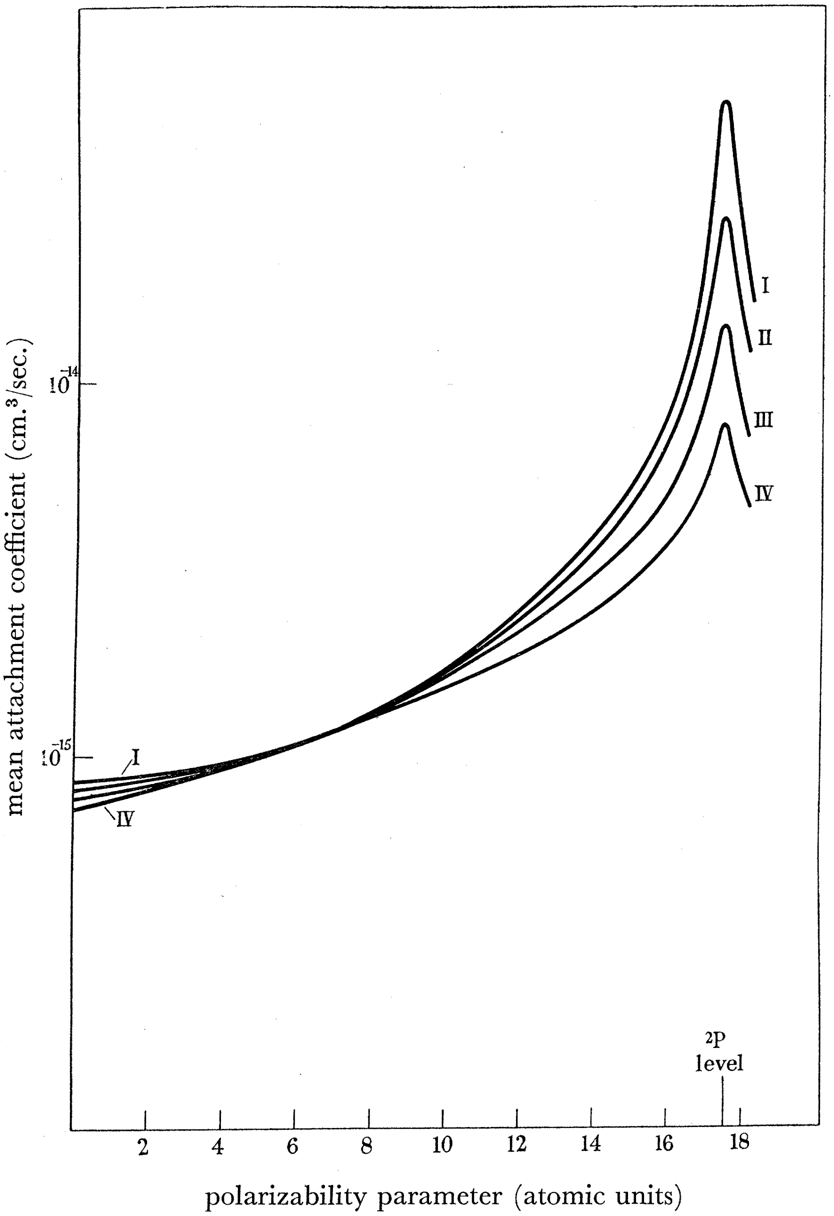

FIGURE 3. Mean attachment coefficients for electrons with Maxwellian distribution of velocities in atomic oxygen, as functions of the polarizability parameter. Curves I–IV refer respectively to electron temperatures of 250, 500, 1000 and 2000° K.

Absorption in which the ejected electron occupies a *d* orbital can be treated in the same way.

We finally reduce the integrals to radial integrals over the Hartree-Fock wave functions for the separate orbitals as for attachment, to give

$$Q_D\left\{\begin{array}{l}\mathrm{O^-\,{}^2P^\circ \rightarrow O\,{}^3P}\\ \mathrm{O^-\,{}^2P^\circ \rightarrow O\,{}^1D}\\ \mathrm{O^-\,{}^2P^\circ \rightarrow O\,{}^1S}\end{array}\right\} = \left\{\begin{array}{c}1\\ \frac{5}{9}\\ \frac{1}{9}\end{array}\right\}\tfrac{128}{3}\pi^5 m^2 e^2 \nu v h^{-3} c^{-1} a_0^5 f_c f\{M_S^2 + 2M_d^2\}, \qquad \begin{array}{r}(16)\\(17)\\(18)\end{array}$$

where $$M_S = \int P_-(2p\,|\,r)\, rP(Es\,|\,r)\, dr, \quad M_d = \int P_-(2p\,|\,r)\, rP(Ed\,|\,r)\, dr.$$

The factors f_c, f are as defined in (9) and (11) except that, for (17) and (18), the functions $P(1s\,|\,r)$, $P(2s\,|\,r)$, $P(2p\,|\,r)$ are those for the appropriate excited term of atomic oxygen instead of for the normal ^{3}P term. The same applies to the functions which appear in the integrals in (15). Thus, while in (16) the functions $P(Es\,|\,r)$, $P(Ed\,|\,r)$ are the same as those appearing in (10), (12), those which occur in (17) and (18) are the solutions of the Fock equations for motion of an electron in the field of an O atom in a ^{1}D and ^{1}S term respectively. In the frequency range of interest, however, absorption leading to excited oxygen atoms is unimportant, and no distinction was made between the corresponding wave functions for electrons belonging to the various terms of the ground configuration of O. The normalization of the functions $P(Es\,|\,r)$, $P(Ed\,|\,r)$ is the same as in the calculation of attachment rates.

The variation with frequency of the cross-section for production of normal O atoms by photodetachment from O⁻ can be derived from the relation

$$Q_D(\mathrm{O^-\,{}^2P \rightarrow O\,{}^3P}) = (3m^2c^2v^2/2h^2\nu^2)\, Q_A(\mathrm{O\,{}^3P \rightarrow O^-\,{}^2P}), \tag{19}$$

and the discussion of Q_A given earlier. Near the absorption limit $Q_D \rightarrow 0$ as $E^{\frac{1}{2}}$ except for the resonance case which arises when a $(2p)^4\,3s\,{}^2\mathrm{P}$ level of O⁻ exists with zero binding energy relative to the ^{3}P normal state of O. Under these circumstances Q_D tends to infinity like $E^{-\frac{1}{2}}$ as the frequency tends to the value at the long-wave limit. At higher energies the effect of the integrals involving $P(Ed\,|\,r)$ becomes dominant. The cross-section frequency curve takes one of the forms illustrated in figure 4. These were calculated assuming certain definite values of the polarizability parameter p.

In practical applications a mean detachment cross-section $\overline{Q}_D$, due to a cloud of quanta having a frequency distribution characteristic of black-body radiation at different temperatures, is of most value. If N_0 is the number of quanta per c.c. capable of effecting the detachment, $\overline{Q}_D$ must be such that the number of detachments per sec. is given by $N_0 c \overline{Q}_D$. Writing

$$N(\nu) = 8\pi\nu^2/c^3\{\exp(h\nu/\kappa T_R) - 1\}, \tag{20}$$

where T_R is the black-body temperature, we have

$$N_0 = \int_{\nu_0}^{\infty} N(\nu)\, d\nu, \tag{21}$$

$$\overline{Q}_D = \int_{\nu_0}^{\infty} Q_D(\nu)\, N(\nu)\, d\nu / N_0. \tag{22}$$

ν_0 is the lowest frequency quantum capable of effecting detachment.

Values of $\overline{Q}_D$ calculated for $T_R = 1500$, 3000, 6000 and 12,000° K are illustrated, on a logarithmic scale, as functions of the polarizability parameter p in figure 5. The resonance

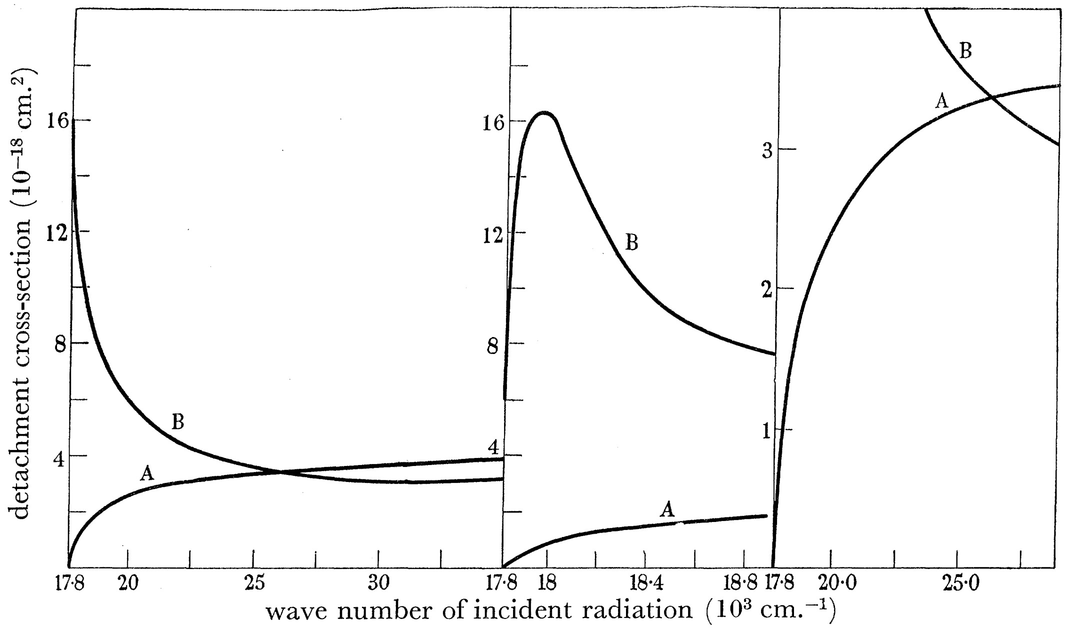

FIGURE 4. Variation, with frequency, of the detachment cross-section (absorption coefficient) for direct photodetachment of electrons from O^- by light quanta on the assumption of two different values of the polarizability parameter p. A, $p = 5{\cdot}7$ a.u.; B, $p = 18{\cdot}3$ a.u.

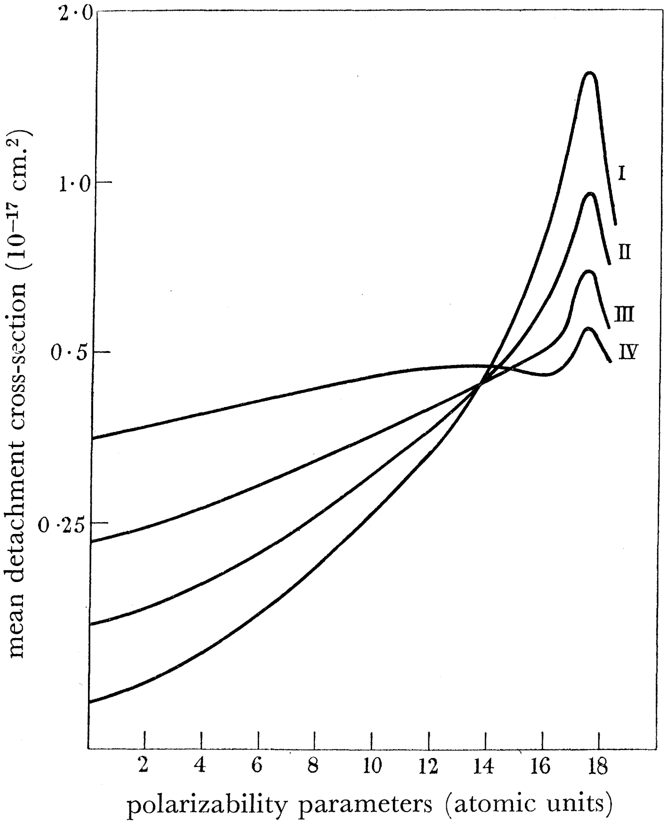

FIGURE 5. Mean detachment cross-sections for direct photodetachment of electrons from O^- by light quanta with frequency distribution characteristic of black-body radiation, as functions of the polarizability parameter. Curves I—IV refer respectively to radiation temperatures of 1500, 3000, 6000 and 12,000° K. Mean detachment rates are obtained by multiplying the cross-sections by N_0c, where $N_0c = 1{\cdot}10 \times 10^{16}$, $1{\cdot}25 \times 10^{20}$, $2{\cdot}23 \times 10^{22}$ and $5{\cdot}89 \times 10^{23}$ cm.$^{-2}$ sec.$^{-1}$ for the four temperatures respectively.

effect for $p = 17{\cdot}6$ a.u. is again apparent, particularly at the lower temperatures. It will be noticed that at the higher temperatures a broad maximum is beginning to appear at polarizabilities below the resonance value. This arises because, for higher energy quanta, resonance effects disappear and the detachment rate decreases uniformly with increasing polarizability.

5. *Production of* O⁻ *ions from* O *by other processes*

5·1. *Direct radiative processes.* Capture of a free electron to a stable excited state with emission of radiation is not likely to be important for the following reasons.

If the state belongs to the ^{4}P† or ^{2}P term of the $(1s)^2\,(2s)^2\,(2p)^4\,3s$ configuration, the phenomenon will involve capture of a p electron. For such a case the attachment coefficient behaves like E for small electron energies‡ (Massey & Smith 1936), and this, together with the fact that the frequency of the radiation emitted (which will be very small for slow electrons) enters the transition probability as ν^3, renders the process most infrequent for such electrons, even allowing for possible radiative stimulation. On the other hand, if the excited state belongs to the $(1s)^2\,(2s)\,(2p)^6$ configuration a radiative transition involving two electrons would be concerned in the attachment process. The probability of this is very small indeed.

5·2. *Dielectronic attachment.* If the $(1s)^2\,(2s)\,(2p)^6$ configuration of O⁻ does not quite give rise to a stable term the following sequence of processes could lead to the formation of normal O⁻. An electron with small positive energy is captured to a $2p$ orbital, and the surplus energy excites a $2s$ electron to the remaining $2p$ orbital. In the course of time the resulting excited ^{2}S system will either revert to the original system by "auto-ionization" or give rise to a normal O⁻ ion by a radiative transition of a $2p$ electron to the vacant $2s$ orbital. We may estimate the effective cross-section for this process, which we call dielectronic attachment, in the following way:

Let $n(E)\,dE$ be the number of free electrons, per unit volume, with energies between E and $E+dE$. The cross-section for the capture of an electron into the metastable ^{2}S term is then

$$\overline{Q}_M = w_1\,\frac{4\pi^2}{h\bar{v}}\,n(E^*)\,|M|^2, \tag{23}$$

where w_1 is the weight ($=2$) of O⁻ ^{2}S, $\bar{v}$ is the mean speed of the electrons, E^* the energy of an electron which, when captured, is just sufficient to produce the metastable ^{2}S term, and M is the transition matrix element of the interaction energy between the electron and the atom which makes the process possible. This formula has been derived by Bloch & Bradbury (1935) (see B 3) for an exactly similar process.

The lifetime of the ^{2}S complex towards 'auto-ionization' is now given by

$$\theta = (h^4/16\pi^3 w_2)\,\{(2m)^3\,E^*\}^{-\frac{1}{2}}/|\,M\,|^2, \tag{24}$$

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† Capture to the ^{4}P term will, in any case, be of little interest, as transitions from it to the ground state are forbidden.

‡ p resonance, which leads to a finite attachment coefficient at very small energies, is unlikely to occur if the atomic field is just strong enough to introduce stable excited $3s$ ^{2}P or, more especially, $3s$ ^{4}P terms.

where w_2 is the weight $(=9)$ of O ^{3}P. If τ is the lifetime of the system towards the radiative transition to the normal state of O$^-$, the cross-section for capture into this normal state becomes

$$\overline{Q}_{Ad} = \frac{\theta}{\theta+\tau}\,\overline{Q}_M. \tag{25}$$

In the special case where $\tau \gg \theta$ we then find

$$\overline{Q}_{Ad} = \frac{1}{9}\frac{h^3}{\overline{v}}\,(2m)^{-\frac{3}{2}}\,E^{*-\frac{1}{2}}\,n(E^*)\,(2\pi\tau)^{-1}. \tag{26}$$

For a Maxwellian distribution about the temperature T_e this gives, for the mean attachment coefficient due to this process,

$$\overline{\alpha}_{Ad} = \overline{v}\overline{Q}_{Ad} = \tfrac{1}{9}\tau^{-1}\{h/(2\pi m\kappa T_e)^{\frac{1}{2}}\}^3\,e^{-E^*/\kappa T_e}. \tag{27}$$

In table 1 a number of numerical values of this quantity are given for various assumed values of E^*, taking $\tau = 10^{-7}$ sec. It will be seen that the absolute value of $\overline{\alpha}_{Ad}$ is very sensitive to the value of E^*. Comparison with the results for $\overline{\alpha}_A$ illustrated in figure 3 shows that $\overline{\alpha}_{Ad}$ is only important compared with the corresponding quantity $\overline{\alpha}_A$ for direct radiative attachment, at ordinary temperatures, if E^* is much less than 0·25 eV. It must be remembered, however, that the figures of table 1 refer to a Maxwellian distribution of electronic velocities. If there are many more high-energy electrons than would be given by this distribution, $\overline{\alpha}_{Ad}$ will be relatively much larger for larger E^* than given in the table.

TABLE 1. MEAN ATTACHMENT COEFFICIENT $\overline{\alpha}_{Ad}$ DUE TO DIELECTRONIC ATTACHMENT IN UNITS 10^{-15} cm.^{3} sec.$^{-1}$. RADIATIVE LIFETIME OF COMPLEX TAKEN AS 10^{-7} sec.

E^* eV	$T_e = 250°$ K	$T_e = 500°$ K	$T_e = 1000°$ K	$T_e = 2000°$ K
0·00	$1{\cdot}14 \times 10^2$	$4{\cdot}06 \times 10$	$1{\cdot}43 \times 10$	5·06
0·25	$1{\cdot}0 \times 10^{-3}$	$1{\cdot}23 \times 10^{-1}$	$7{\cdot}89 \times 10^{-1}$	1·19
0·50	$9{\cdot}7 \times 10^{-9}$	$3{\cdot}7 \times 10^{-4}$	$4{\cdot}35 \times 10^{-2}$	$2{\cdot}79 \times 10^{-1}$
1·00	$8{\cdot}2 \times 10^{-19}$	$3{\cdot}4 \times 10^{-9}$	$1{\cdot}3 \times 10^{-4}$	$1{\cdot}5 \times 10^{-2}$
2·00	$5{\cdot}8 \times 10^{-39}$	$2{\cdot}9 \times 10^{-19}$	$1{\cdot}2 \times 10^{-9}$	$4{\cdot}6 \times 10^{-5}$

Unfortunately, it is not possible to make any reasonable estimate of E^* at this stage, but it should be possible to decide, from a self-consistent field calculation, whether it can be small enough to make this attachment process important.

5·3. *Three-body processes.* An electron can be captured by an O atom to form an O$^-$ ion with transfer of the surplus energy to a third body in the neighbourhood. The probability is proportional to the pressure, and the order of magnitude of the constant of proportionality has been discussed by Massey (1938). If the third body is able to absorb the surplus energy purely as potential energy (a 'resonance' process) the process can be quite effective. Even at pressures of the third body of the order 1 mm. Hg, the attachment rate per collision between an electron and neutral atom may be as high as 10^{-5}. If no resonance is possible, this figure must be reduced by a factor of 100 or more.

For a gas of atomic oxygen a near resonance occurs in the process

$$\mathrm{O}(^3\mathrm{P}) + \mathrm{O}(^3\mathrm{P}) + e \rightarrow \mathrm{O}^-(^2\mathrm{P}^\circ) + \mathrm{O}(^1\mathrm{D}) + 0{\cdot}24 \pm 0{\cdot}2\,\mathrm{eV}. \tag{28}$$

In this case, however, the situation is complicated by the conditions imposed by the spin.

The probability of an O(^{3}P) atom absorbing the surplus energy in making a transition to a ^{1}D term is very small unless some exchange of electrons occurs, as otherwise the transition would involve reversal of spin. We must therefore regard the reaction as one involving simultaneous capture of the free electron and exchange of a second, atomic, electron between the two atoms. This means that the reaction rate will be considerably less than it would be if only the free electron were directly involved, and it is unlikely that (28), even though nearly of 'resonance' type, is important, in comparison with radiative processes, at pressures less than 10^{-1} mm. Hg.

A similar situation exists if the gas includes molecular as well as atomic oxygen, for the only low-lying excited terms of O_2 have opposite spins to that of the ground state. The presence of molecular nitrogen is also not likely to be very effective for the same reason.

6. *Detachment of electrons from normal* O$^-$ *by other processes*

6·1. *Radiative processes.* The only one of these likely to arise in practice is the inverse of the attachment process discussed in 5·2. The incident quantum is absorbed to produce a term of the unstable $(1s)^2\,(2s)\,(2p)^6$ configuration which either reverts to the normal ion by emission of radiation or dissociates into a ^{3}P O atom and an electron.

Using the same notation as in 5·2 it follows from the principle of detailed balancing that the number of absorption processes occurring per second due to radiation in black-body equilibrium at temperature T_R is given by

$$\eta = \tfrac{1}{3}\tau^{-1}\exp\left(-h\nu_1/\kappa T_R\right), \tag{29}$$

where ν_1 is the frequency of the quantum absorbed, i.e.

$$h\nu_1 = E^* + E_0,$$

where E_0 is the electron affinity of O. Assuming, as in 5·2, that the chance of "auto-ionization" of the excited configuration is much greater than that of radiation, η gives also the rate of detachment. The mean detachment cross-section $\overline{Q}_{Dd}$, for comparison with $\overline{Q}_D$ of (15), is then given by $\eta/N_0 c$ with N_0 as in (21).

Numerical values of $\overline{Q}_{Dd}$ are given in table 2 assuming various values of E^* and $\tau = 10^{-7}$ sec. as in A 5·2. These are to be compared with the corresponding values for the direct photodetachment process, illustrated in figure 5. It will be seen that, for the dielectronic process to be important, E^* again must be less than 0·25 eV.

TABLE 2. MEAN DETACHMENT CROSS-SECTION $\overline{Q}_{Dd}$, DUE TO DIELECTRONIC DETACHMENT, IN UNITS 10^{-18} cm.^{2}. RADIATIVE LIFETIME OF COMPLEX TAKEN AS 10^{-7} sec.

E^* eV	$T_R = 1500°$ K	$T_R = 3000°$ K	$T_R = 6000°$ K	$T_R = 12{,}000°$ K
0·00	$1{\cdot}17 \times 10$	5·27	2·10	$6{\cdot}7 \times 10^{-1}$
0·25	1·69	2·00	1·29	$5{\cdot}3 \times 10^{-1}$
0·50	$2{\cdot}4 \times 10^{-1}$	$7{\cdot}6 \times 10^{-1}$	$7{\cdot}9 \times 10^{-1}$	$4{\cdot}2 \times 10^{-1}$
1·00	$5{\cdot}0 \times 10^{-3}$	$1{\cdot}1 \times 10^{-1}$	$3{\cdot}0 \times 10^{-1}$	$2{\cdot}5 \times 10^{-1}$
2·00	$2{\cdot}1 \times 10^{-6}$	$2{\cdot}2 \times 10^{-3}$	$4{\cdot}3 \times 10^{-2}$	$9{\cdot}7 \times 10^{-2}$

6·2. *Processes not involving radiation.* Ignoring boundary effects such as those which occur on the walls or electrodes of a discharge tube, three other modes of detachment of electrons from O^- can occur which do not involve radiation. These are:

(*a*) Detachment by electron impact.

(*b*) Detachment by impact with normal positive ions or neutral molecules: (1) without molecule formation; (2) accompanied by molecule formation.

(*c*) Detachment by collisions of the second kind with excited molecules.

The first of these is exactly similar to the ionization of neutral atoms by electrons, and detachment from Cl^- in this manner has been investigated by Massey & Smith (1936). For O^- the cross-section will be similar to that which they derive, the maximum occurring for electrons with energy about 5–6 times the electron affinity of O and being of the order πa_0^2.

Detachment by impact with positive ions or neutral molecules can occur in an exactly similar way to the analogous ionization of neutral atoms. In order to be effective the colliding ions or molecules must have an energy considerably in excess of that just sufficient to detach the electron (Massey 1938). On the other hand, detachment by a process such as

$$O^- + O \rightarrow O_2 + e \tag{30}$$

can occur even if the energy of the incident neutral atom is very small. It is therefore important as the only effective collision detachment process in a gas at ordinary temperature containing no excited atoms (which can produce detachment by collisions of the second kind).

There is no direct experimental evidence as to the probability of such a process as (30), and it is necessary to argue from the reverse process, some knowledge of the probability of which may be gained from the experiments of Lozier (1934) and of Hagstrum & Tate (1941). The latter authors find that electrons of 2·9 eV energy can be captured by normal oxygen molecules to produce O and O^- with small relative velocity (see (31)). The effective cross-section for this process is found to be not greater than 5×10^{-19} cm.^{2}. Application of the principle of detailed balancing (Massey 1938) gives the small value of 10^{-21}–10^{-22} cm.^{2} for the effective cross-section for associative collisions of O and O^- with thermal energies to form a molecule in its ground vibrational state. As the association of O and O^- can also lead to vibrationally excited O_2, this cross-section must be multiplied by a factor, probably at least 10, to allow for this. It seems likely then that the effective cross-section for associative detachment in O is of the order 10^{-20}–10^{-21} cm.^{2} if the ions and atoms have thermal velocities.

The third type of detachment, involving collisions of the second kind, has been discussed already (Massey 1938) and need not be considered further here.

B. Negative ions formed by and from molecular oxygen

1. *Introduction—experimental information*

The existence of O_2^- ions is almost as well established as that of the atomic ions, but their mode of production is by no means clear. In the experiments of Lozier (1934) and of Hagstrum & Tate (1941) on the production of negative ions by an electron beam fired through oxygen at very low pressure, only O^- ions were observed. The electron energy range covered by the experiments was from 2 to 40 eV. The following reactions were found to take place:

$$O_2 + e \rightarrow O(^3P) + O^-(^2P^\circ), \quad (2{\cdot}9 \pm 0{\cdot}2\,\text{eV},\ 3{\cdot}0 \pm 0{\cdot}4\,\text{eV}), \tag{31}$$

$$\rightarrow O(^5S^\circ) + O^-(^2P^\circ), \quad (12{\cdot}0 \pm 0{\cdot}2\,\text{eV},\ \text{—}), \tag{32}$$

$$\rightarrow O^+(^4S^\circ) + O^{-\prime} + e, \quad (20\,\text{eV},\ 18{\cdot}9 \pm 0{\cdot}4\,\text{eV}). \tag{33}$$

The appearance energies as given by Lozier and by Hagstrum & Tate respectively are included in brackets after each. A discussion of reactions of type (33) is given in C 2. The general theoretical description of the first two reactions has been given elsewhere (Massey 1938). We will not add to this at this stage, but remember that the interpretation of the results obtained by other types of experiment, in which the formation of O_2^- is observed and which we now proceed to discuss, must also account for the existence of the reactions (31) and (32).

For dealing with the attachment of low-velocity electrons, which might be expected to produce O_2^- ions, beam methods lose much of their usefulness, as it is very difficult to produce homogeneous beams of slow electrons. Recourse must be had instead to experiments in which a swarm of electrons is allowed to drift through the gas at some mm. Hg pressure, under the action of an electric field, and the average rate of attachment measured. Such experiments have been carried out by Bradbury (1933) in pure oxygen, and he finds that the mean attachment probability is $2{\cdot}8 \times 10^{-4}$ per Ramsauer collision† for electrons of mean energy 0·2 eV. It falls steadily to a value of roughly $0{\cdot}4 \times 10^{-4}$ for a mean energy of 1·5 eV, and then suddenly rises to a maximum of $3{\cdot}6 \times 10^{-4}$ at 2·0 eV mean energy, which is close to the energy limit, 2·2 eV, of the experiments. At the pressures employed (3 mm. Hg) the mean attachment probability is independent of pressure. There is no evidence as to the nature of the negative ions produced, but it is difficult to see how they could be atomic ions. To produce such ions by electron capture the energy of the electrons must be greater than 2·9 eV, the difference between the dissociation energy (5·09 eV) of O_2 and the electron affinity (2·2 eV) of O; the energy distribution in a swarm would have to depart very far from Maxwellian to produce a maximum yield at a mean electron energy less than this. We are therefore justified in supposing that they are O_2^- ions, for more complex ions could hardly be produced in a pressure-independent process unless the reaction rates were so fast as to produce pressure saturation.

The current interpretation of the experimental results in the low-energy range up to 1·5 eV is due to Bloch & Bradbury (1935). They suppose that the attachment of the low-energy electrons arises in the following way. The energy released by the captured electron is disposed of by producing excitation of a vibrational quantum in the resulting O_2^- ion. If left to itself this system would revert to a neutral molecule and electron by the reverse process to that which led to its formation. To stabilize the negative ion, Bloch & Bradbury suppose that it is vibrationally deactivated by collision with a neutral molecule. They find that to fit the observed attachment rate the electron affinity of O_2 must be between 0·07 and 0·17 eV. To explain the observed independence of pressure the rate of vibrational deactivation must be very great, an effective cross-section some thousand times the gas kinetic being required.

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† Over the energy range involved the Ramsauer cross-section for oxygen is about 5×10^{-16} cm.^{2} (Kollath 1930).

There are certain difficulties connected with this interpretation in its original form. It is not easy to see what justification there is for supposing that the addition of an electron to an O_2 molecule makes only a small difference to the electronic energy of the system over the region of the potential minimum. If it does, in fact, do so, it must be regarded rather as fortuitous and by no means obvious. Further, Weiss (1935) has roughly estimated the electron affinity of O_2 by applying the method of the Born cycle to certain electrolytic reactions and finds a value of 2·7 eV. Although the error involved in this estimate is probably large owing to the lack of precise information concerning a number of the energies involved, it is difficult to reconcile with Bloch & Bradbury's value of not more than 0·17 eV.[†] Thus Weiss applied his method also to obtain the electron affinity of OH, and the value he derived, 3·7 eV, is quite comparable with the 2·1 eV obtained by Goubeau & Klemm (1937) from a study of cyclic processes involving the alkali hydroxides.

Loeb (1935) has attempted to obtain direct experimental evidence as to the magnitude of the energy required to detach electrons from the negative ions formed in a high-frequency discharge in oxygen, by collisions with oxygen gas molecules. Quantitative analysis of his results is difficult owing to the complexity of the phenomena involved, but evidence was obtained indicating that collision detachment begins when the mean energy of the ions passing through the gas is between 0·14 and 0·68 eV, the latter being the more probable value. Apart from experimental uncertainties this does not necessarily mean that the vertical detachment energy[‡] of O_2^- lies between 0·07 and 0·34 eV (allowing for the fact that only half the total translational energy will be available to effect detachment in a collision between O_2 and O_2^-). The energy distribution of the ions will make the effect apparent at a mean energy less than that just sufficient for the reaction to proceed. Further, both O and O^- will be present and reactions such as

$$O^- + O_2 \rightarrow O_3 + e, \quad O + O_2^- \rightarrow O_3 + e,$$

with onset energies of about 1·1 and −0·1 eV respectively (electron affinity of O, 2·2 eV or O_2, 1 eV − dissociation energy, 1·1 eV[§], of O_3), must be taken into account. Loeb's experimental results cannot therefore be regarded as establishing Bloch & Bradbury's requirement of an electron affinity of O_2 between 0·07 and 0·17 eV. In considering alternative interpretations of the attachment phenomena we therefore do not restrict ourselves by this requirement. We rather seek an explanation consistent with a larger electron affinity of O_2.

It is also necessary to understand how the vibrational deactivation by collision takes place with such apparent ease, particularly as it is well known that transfer of large quanta of vibrational energy between molecules takes place very slowly (Zener 1931; Oldenburg & Frost 1937).

[†] The electron affinity of O_2 might be expected to lie between that of the separated O atoms and that of the "united" S atom, as is the case for the ionization energy. Unfortunately, there is no reliable value available for the electron affinity of S. Glockler (1934) derived empirically a value of 2·06 eV, but, as his method, which gives good results for the halogens, overestimates the electron affinity of O by 1·6 eV, it is difficult to decide how far his estimate is in error.

[‡] For the distinction between vertical detachment energy and electron affinity see Massey (1938).

[§] Schumacher (1935).

It is further necessary to determine what process leads to the sudden increase in the attachment rate for electrons of energy 1·6 eV. Bradbury has suggested that this may be due to the excitation of the $^1\Sigma_g^+$ state of O_2 (requiring 1·6 eV) providing a source of low-energy electrons which attach by the Bloch-Bradbury process. There are a number of objections to this suggestion which may be enumerated as follows:

(i) The energy spread of the swarm is such that any effects due to energy loss by excitation of O_2 by 1·6 eV would become apparent at a considerably lower mean energy. However, as the mean energy scale is probably not very accurate in this region, this difficulty may only be apparent.

(ii) The observed rate of increase, with mean electron energy, of the attachment probability is very great—an increase by a factor of four to five occurs in the energy range 1·6–2·0 eV. If Bradbury's suggestion were correct a slower rate of rise would be expected, since not only is the rate of increase limited by the energy distribution of the electrons, but also certain effects which tend to reduce the attachment rate become more and more important as the mean energy increases. Those electrons, whose energies are reduced to thermal, take less time to regain their original energy owing to the increased value of the strength of the controlling electric field relative to the gas pressure (as the mean energy increases from 1·6 to 2·0 eV this ratio increases by a factor of roughly 2). In addition, at the higher mean energies more and more electrons are present with energies so high that they are not efficiently reduced to thermal values by single excitation collisions. Such electrons would remain inactive from the point of view of attachment.

(iii) The attachment probability per collision observed in the neighbourhood of the second maximum appears too great. Thus the number of electrons with thermal energy produced by inelastic collisions is at most one-third of the whole in a swarm of 2 eV mean energy and, owing to their reduction in speed, each makes about one-quarter the number of collisions per second with oxygen molecules the higher energy electrons do. This implies that the true attachment rate per collision for the thermal electrons in the swarm would have to be about 12 times the mean attachment rate per collision for all the swarm electrons. The mean rate observed reaches the value of $3{\cdot}6\times10^{-4}$ per collision for a 2 eV swarm, so that the thermal electrons in the swarm would have to attach as frequently as $4{\cdot}2\times10^{-3}$ per collision, over 15 times the rate found for the swarm with the lowest mean energy (0·2 eV) investigated.

(iv) There is no evidence from experiments on the diffusion and mobility of electron swarms in oxygen which indicates the existence of an effective slowing down process due to inelastic collisions.

To attempt to resolve the difficulties it is necessary to analyse the possible electronic states of O_2^- in detail using the semi-empirical methods which have received severe tests and wide applications in the interpretation of the energy levels of diatomic molecules.

2. *Electronic states of* O_2^-

The discussion in this section is best followed in connexion with figure 6, which illustrates two alternative distributions of potential curves for the deep states of O_2^-. These represent the most plausible possibilities which result from the discussion.

We first consider the states which arise from electron configurations (in molecular orbitals) derived from two-quantum orbitals of the separated atom and ion. The molecular orbitals concerned are, in order of looseness of binding,

$$(z\sigma_g),\quad (y\sigma_u),\quad (x\sigma_g),\quad (w\pi_u),\quad (v\pi_g),\quad (u\sigma_u).$$

using Mulliken's notation (1932).

2·1. *Ground state.* As there are thirteen electrons to dispose of, apart from the four K electrons, the ground state of O_2^- will have the configuration

$$(z\sigma_g)^2\ (y\sigma_u)^2\ (x\sigma_g)^2\ (w\pi_u)^4\ (v\pi_g)^3, \tag{34}$$

giving rise to a $^2\Pi_g$ term only. This will dissociate into a normal atom and ion, and it is possible to estimate the binding energy in the usual way. The number of homopolar valence bonds in a molecule is defined as the difference between the number of pairs of bonding and of antibonding electrons. In the configuration (34) the orbitals $z\sigma_g$, $x\sigma_g$ and $w\pi_u$ are bonding, the others antibonding, so the number of valence bonds is $1\frac{1}{2}$. The dissociation energy is now given approximately as a little more than 2·5 eV per valence bond (Mulliken 1932), i.e. as 3·8 eV. As the energy of the $^2\Pi_g$ state at infinite separation of ion and atom is 2·2 eV below that of the $^3\Sigma_g^-$ ground state of O_2 in its dissociation limit, the total energy of the O_2^- $^2\Pi_g$ state at its minimum would then be 0·9 eV below that for O_2 $^3\Sigma_g^-$ at its minimum (5·09 eV). This is considerably greater than the value 0·17 eV required by the Bloch-Bradbury theory, and it is unlikely that our estimate is as far wrong as this.

If information were available concerning isoelectronic molecules such as F_2^+, Cl_2^+, Cl O, etc., the matter could be more definitely decided, but such information is unfortunately very meagre. However, Elliott & Cameron (1938) have made a preliminary examination of the band spectra of Cl_2^+ and find a system of doublet bands which are either of Π-Π or Δ-Δ type. As it is difficult on theoretical grounds to see how they can be Δ-Δ bands, it is almost certain that they arise from transitions to the ground $^2\Pi_g$ level from an upper $^2\Pi_u$ level (see B 2·2). The binding energy of this ground level is found to be 4·4 eV. As the configuration of this level, if a $^2\Pi_g$ term, is exactly the same as that of the ground level of O_2^- we are considering, except that the orbitals are three-quantum ones, it seems unlikely that our estimate of 3·8 eV as the binding energy of O_2^- $^2\Pi_g$ is in error in excess. Some further evidence to this end is afforded by the fact that the binding energy of F_2, which is admittedly not very well known, indicates that, for molecules containing nearly complete two-quantum shells, the binding energy per bond is greater, not less, than 2·5 eV. We therefore take 1 eV as a reasonable estimate of the electron affinity of O_2^-.

The internuclear distance in the ground state is probably somewhat greater than in that (1·20 A) of the neutral molecule. A rough estimate may be made in the following rather indirect way. In the $^2\Pi_g$ state of Cl_2^+ the equilibrium nuclear separation is 1·88 A, slightly less than in the ground state of the corresponding neutral molecule Cl_2. We can therefore assume that the nuclear separation in the ground $^2\Pi_g$ state of F_2^+ is about 1·4 A (slightly less than that, 1·5 A, regarded as probable for F_2). A value between 1·3 and 1·4 A is therefore a reasonable one to take for O_2^-, as it should be very similar to F_2^+.

2·2. *Excited states.* The lowest excited configurations of O_2^- which will dissociate into oxygen atoms and ions in normal configurations (though not necessarily in their ground states) will be (omitting the deep $y\sigma_u$ and $z\sigma_g$ orbitals)

$$(x\sigma_g)^2\,(w\pi_u)^3\,(v\pi_g)^4, \quad (x\sigma_g)^2\,(w\pi_u)^4\,(v\pi_g)^2\,(u\sigma_u) \quad \text{and} \quad (x\sigma_g)\,(w\pi_u)^4\,(v\pi_g)^4.$$

We consider these separately.

$(x\sigma_g)^2\,(w\pi_u)^3\,(v\pi_g)^4$. This configuration gives rise to a $^2\Pi_u$ term which is either repulsive in nature or has only a low binding energy with respect to dissociation into normal ion and atom. This conclusion can be arrived at from two distinct lines of approach.

First, the configuration arises by addition of an anti-bonding $v\pi_g$ electron to the excited $(x\sigma_g)^2\,(w\pi_u)^3\,(v\pi_g)^3$ configuration of O_2. The lowest terms of this configuration which dissociates into normal O atoms are $^3\Sigma_u^+$, $^3\Delta_u$. The first of these is known to have a dissociation energy of only 0·4 eV (Herzberg 1932), and, although it has not yet been identified spectroscopically, it is probable that the $^3\Delta_u$ term lies no more than 1 eV lower. As $^2\Pi_u$ is derived from these by addition of an anti-bonding $v\pi_g$ electron, its binding energy relative to normal O and O^- is probably considerably less than that, 1·4 eV, which we have estimated for the O_2 $^3\Delta_u$ term.

Secondly, the $^2\Pi_u$ term we are considering is presumably the analogue of the $^2\Pi_u$ term which forms the upper state of the Cl_2^+ bands observed by Elliott & Cameron. They find that the binding energy of this term is between 1·62 and 1·67 eV which is 2·6 eV less than that of the ground $^2\Pi_g$ term. For the lighter isoelectronic system of O_2^- the difference, which is due to the splitting arising from the indistinguishability of OO^- and O^-O, is probably at least as great as this. This would make the binding energy of the $^2\Pi_g$ term of O_2^- less than 1·2 eV, in agreement with the first line of argument.

The nuclear separation in the $^2\Pi_u$ state, if stable, can be expected to be large, in the neighbourhood of 2 A (Elliott & Cameron find 2·26–2·29 A for Cl_2^+ $^2\Pi_u$.)

$(x\sigma_g)^2\,(w\pi_u)^4\,(v\pi_g)^2\,(u\sigma_u)$. This gives $^2\Sigma_u^+$, $^2\Sigma_u^-$, $^2\Delta_u$, $^4\Sigma_u^-$ terms probably with energy in this order, $^4\Sigma_u^-$ being deepest. All terms probably dissociate into normal O and O^-.

The configuration arises by addition of a strongly anti-bonding $u\sigma_u$ electron to the normal configuration of O_2. It is not easy to decide how much decrease in binding energy the addition of this electron introduces. The excitation of an electron from a $v\pi_g$ to a $u\sigma_u$ molecular orbital in Cl_2 involves a decrease in binding energy of about 2 eV. This is probably larger in O_2^-, so the 'mean' binding energy of the terms arising from the configuration we are considering may be as much as 2·5 eV less than that of the ground term. On the other hand, the $^4\Sigma_u^-$ term may be as much as 1·5 eV below this mean. This would give an excited term lying only 1 eV above the ground state. The $^2\Delta_u$ term would then be between 1 and 1·5 eV higher, with the other terms very much higher still and possibly repulsive in character.

The nuclear separation in any of the stable levels is likely to be large.

$(x\sigma_g)\,(w\pi_u)^4\,(v\pi_g)^4$. This gives a $^2\Sigma_g^+$ term and arises by addition of an anti-bonding $v\pi_g$ electron to the excited $(x\sigma_g)\,(w\pi_u)^4\,(v\pi_g)^3$ configuration of O_2. The $^3\Pi_g$ term, which is the lowest arising from this configuration which dissociates into normal O atoms, is almost certainly repulsive, so the $^2\Sigma_g^+$ term of O_2^- is also not likely to be a stable one.

2·3. *States dissociating into normal* O *and excited* O^-. One remaining possibility which may lead to a deep excited state of O_2^- arises if the $(1s)^2\,(2s)^2\,(2p)^4\,3s\,^4P$ term of O^- is stable. If this is so the molecular configuration $(x\sigma_g)^2\,(w\pi_u)^4\,(v\pi_g)^2\,(3s\sigma_g)$ will include terms with considerable binding energy relative to dissociation into $O(^3P)+O^-(^4P)$, for the $3s\sigma$ orbital is strongly bonding in character in normal molecules.

The deepest term arising from this configuration is probably $^4\Sigma_g^-$, and its minimum may lie some eV below the dissociation limit of $O(^2P)+O^-(^4P)$. As this limit is practically coincident with that of the ground state of O_2, the minimum of this excited O_2^- term may not be much above that of the O_2 ground term.

If the stable excited state of O^- belongs to the configuration $(1s)^2\,2s\,(2p)^6$ this no longer applies, and it is difficult to see how any deep excited state of O_2^-, tending in the dissociation limit to $O(^3P)$ and this excited state of O^-, could result.

We now proceed to the application of the energy level scheme we have discussed for O_2^-, to the experimental results obtained by Bradbury.

3. *Interpretation of experimental results*

3·1. It is clearly impossible to arrive at a completely definite and certain interpretation of Bradbury's results, as there is too much uncertainty in the scale, position and order of the O_2^- potential-energy curves. Instead, we must enumerate the possible interpretations with remarks as to the likelihood of each being the correct one. It will be found that, even with the considerable degree of arbitrariness which exists, some valuable conclusions can be derived.

There are two phenomena we wish to explain: attachment of very slow electrons with a probability decreasing with electron energy and the sudden increase in the probability again as the energy rises beyond 1·6 eV. We call the first attachment process A, the second process B. The following possible interpretations must be considered:

(I) Process A involves attachment to produce O_2^- in the ground $^2\Pi_g$ state with highly excited vibrational energy.

This may arise because the minimum of the $^2\Pi_g$ state probably lies at larger nuclear separations than that of the $^3\Sigma_g^-$ ground state of O_2. To stabilize the molecule the vibrational excitation must be removed in some way. Bloch & Bradbury, whose interpretation differs from this only in that they suppose the $^2\Pi_g\,O_2^-$ and $^3\Sigma_g^-\,O_2$ potential energy curves to be nearly coincident so only one quantum of vibrational energy is excited, suggest that the energy is removed by transfer in a 'near-resonance' collision to a normal O_2 molecule. Such a transfer is well known to be difficult when large vibrational quanta are involved (but see (35) below). With the comparatively high degree of excitation which would occur in our case, a larger collision area for transfer should result, but it is doubtful whether it would be large enough to make the attachment probability independent of pressure at the experimental pressures (see B (3·2)).

The process B could then result from capture into the $^4\Sigma_u^-$ state accompanied again by considerable vibrational excitation. Stabilization would then occur as in process A. The existence of the reaction (31) can be allowed for by including a potential-energy curve (as in figure 6*a*, curve III) which may belong to the $^2\Delta_u$ or other state.

In this scheme the potential energy curves would be as sketched in figure 6*a*.

It is to be noted that, if this interpretation is correct, the probabilities of both attachment processes should fall off as the pressure at low pressures, there being no radiative process likely to be at all effective in removing the surplus energy in either case (see 3·2). Radiative transitions between vibrational levels belonging to the same electronic term occur with very low probability and the ${}^4\Sigma_u^- \rightarrow {}^2\Pi_g$ electronic transition is optically forbidden.

(II) A second possible scheme is illustrated in figure 6*b*. Here the ${}^2\Pi_g$ potential curve never intersects that of the ${}^3\Sigma_g$ ground state of O_2 and is not concerned directly in either process. Process A is then regarded as due to capture into the ${}^4\Sigma_u^-$ state of O_2^- (with configuration $(w\pi_u)^4\,(v\pi_g)^2\,(u\sigma_u)$), the potential curve of which is supposed to intersect that of $O_2\,{}^3\Sigma_g^-$ near its minimum. Stabilization requires the transfer with high probability of a large quantum of vibrational energy as in the original Bloch-Bradbury process. This may be effected indirectly by electron transfer, viz.

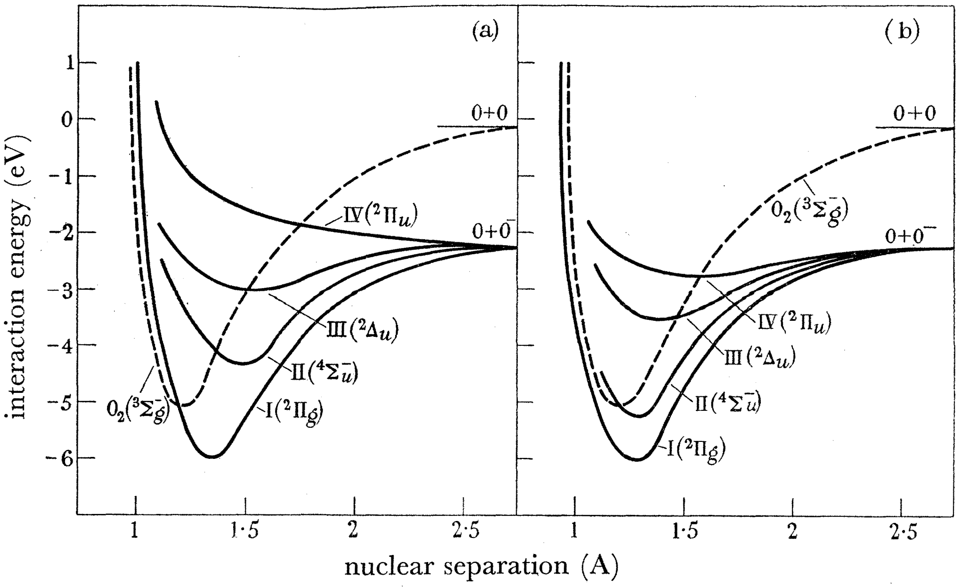

FIGURE 6. Illustrating two possible sets of potential-energy curves for O_2^-. The dotted curve is that for the ground state of O_2.

$$O_2'^-({}^4\Sigma_u^-) + O_2({}^3\Sigma_g) \rightarrow O_2'({}^3\Sigma_g) + O_2^-({}^4\Sigma_u^-), \tag{35}$$

the ′ indicating the presence of vibrational excitation, but again it is doubtful if the rate of deactivation would be large enough to give a pressure-independent attachment probability in the experimental pressure range (see B 3·2).

Process B can then be ascribed either to capture into the

$$(w\pi_u)^4\,(v\pi_g)^2\,(u\sigma_u)\,{}^2\Delta_u \quad \text{or} \quad (w\pi_u)^3\,(v\pi_g)^4\,{}^2\Pi_u$$

states of O_2^-. The former is the more probable, as the process can occur without simultaneous excitation of an O_2 electron to the $(w\pi_u)^3\,(v\pi_g)^3$ configuration. In either case, stabilization can be affected both by collision and by radiation as both ${}^2\Delta_u$ and ${}^2\Pi_u$ combine optically with the ground ${}^2\Pi_g$ state.

With this interpretation the probability of process A would again fall off as the pressure for low pressures, but that of process B would tend to a considerable finite value. The existence of the reaction (31) can be allowed for in this scheme by including a potential-energy curve such as curve IV of figure 6*b* which may belong to the ${}^2\Pi_u$ or other state.

(III) A variant of (II) is that the process A might involve a transition to the ${}^4\Sigma_g^-$ state belonging to the configuration $(w\pi_u)^4\,(v\pi_g)^2\,(3s\sigma_g)$—this could be the case if the stable excited state of O^- involves a 3*s* electron. Process B could then arise either from ${}^2\Delta_g$ of this configuration, ${}^4\Sigma_u^-$ of the $(w\pi_u)^4\,(v\pi_g)^2\,(u\sigma_u)$ configuration, or ${}^2\Pi_u$—in either of these last two cases radiative as well as collision stabilization could occur.

(IV) Process B may also arise in the following way. The incident electron first excites the O_2 molecule to a low excited electronic state such as ${}^1\Delta_g$ requiring 0·9 eV excitation energy or ${}^1\Sigma_g^+$ which requires 1·6 eV.† The excited molecule then captures the electron to produce an O_2^- ion in an excited state which is stabilized as above. The O_2^- ion produced may be in the ground ${}^2\Pi_g$ state with highly excited vibration if the potential-energy curves are distributed as in figure 6*a*. Otherwise it may be formed in an excited electronic state such as the ${}^4\Sigma_u^-$ state of (II). Strong evidence for this type of capture in I_2 has been obtained by Buchdahl (1941), but in this case the I_2^- ion produced has energy in excess of that necessary to produce dissociation and only I^- ions result.

Summarizing we see that in all possibilities process A would involve collision stabilization only, and so, at low pressures, attachment by this process (involving slow electrons) must decrease as the pressure. On the other hand, process B would be pressure-independent at low pressures if either (II) or (III) is correct, but behave like process A if (I) is correct. Observation of the pressure variation of the attachment probability for both 2 eV and slow electrons would therefore provide valuable additional evidence to distinguish the different possibilities.

The energy excess, 0·17–0·07 eV, of the ground state of O_2 above the state of O_2^- first formed on attachment, which Bloch & Bradbury found necessary to give the correct magnitude for the probability of process A, does not, in our interpretations, represent the electron affinity. We consider that the initially formed level of O_2^- is not the ground level but that vibrational level of the particular electronic state concerned with energy nearest to that of the ground level of O_2.

We have thus been able to introduce interpretations which are consistent with an electron affinity as large as 1 eV and, since in all, process B is considered to involve only single electron collisions, the difficulties inherent in Bradbury's suggested origin of this process are avoided. Nevertheless, there is one unsatisfactory feature common to all interpretations, including the original one of Bloch & Bradbury—the very large rate of collision deactivation of the vibrationally excited molecule which must occur to yield a rate of attachment independent of the pressure at pressures as low as 3 mm. Hg. To examine why this arises and to compare the effectiveness of collision and radiative stabilization we proceed, in the next section, to estimate the various magnitudes involved.

3·2. *Effectiveness of collision and radiative stabilization in the formation of* O_2^-. If θ is the mean lifetime of the excited molecular ion against spontaneous dissociation, τ_C is the mean time before the excess energy is removed by collision, and τ_R the mean time before it is removed by radiation, then the mean attachment coefficient for the process is given by

$$\bar{\alpha} = (w_2/2w_1)\,\{h^3 f(\epsilon^*)/4\pi(2m^3\epsilon^*)^{\frac{1}{2}}\}\,\{\theta+\tau_R\tau_C/(\tau_R+\tau_C)\}^{-1}. \tag{36}$$

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† This possibility is unlikely if the mean energy scale in Bradbury's experiments is accurate.

w_1 is the statistical weight of the ground state of the original molecule, w_2 that of the ion. ϵ^* is the energy of excitation required to produce the initial unstable ion complex and $f(\epsilon)\,d\epsilon$ is the number of electrons with energies between ϵ and $\epsilon+d\epsilon$. This formula is the same as that (26) given for the essentially similar process of attachment to O by inverse autoionization except for the inclusion of the possibility of collision stabilization.

Assuming a Maxwellian distribution about a temperature T_e, we have

$$\bar{\alpha} = (w_2/2w_1)\,\{h^3/(2\pi m\kappa T_e)^{\frac{3}{2}}\}\,e^{-\epsilon^*/\kappa T_e}\,\{\theta+\tau_R\tau_C/(\tau_R+\tau_C)\}^{-1}. \tag{37}$$

Substituting numerical values appropriate to Bradbury's experiments, we have, approximately, for process A,

$$\bar{\alpha} = 5\times 10^{-21}\{\theta+\tau_R\tau_C/(\tau_R+\tau_C)\}^{-1}\,\text{cm.}^3/\text{sec.} \tag{38}$$

To give the attachment coefficient observed by Bradbury $\theta+\tau_R\tau_C/(\tau_R+\tau_C)$ must be about 10^{-9} sec. Two limiting cases then arise:

(i) If collision stabilization is predominant $\tau_C \ll \tau_R$. In addition, if the process is to be independent of pressure $\tau_C \ll \theta$. Hence θ alone must be of the order 10^{-9} sec.—a very reasonable value. τ_C must, however, be much less than this—say 3×10^{-10} sec. at 3 mm. Hg pressure. This requires a very large collision cross-section for the deactivation process—10^3 times the gas-kinetic value.

(ii) Radiative stabilization is predominant if $\tau_R \ll \tau_C$. In this case

$$\bar{\alpha} = 5\times 10^{-21}(\theta+\tau_R)^{-1}\,\text{cm.}^3/\text{sec.}$$

$$\simeq 5\times 10^{-21}/\tau_R\,\text{cm.}^3/\text{sec.},$$

since θ is much smaller than τ_R, which is unlikely to be less than 10^{-8} sec. In fact radiative stabilization, for process A, can only occur through vibrational transitions or electronic quadrupole and magnetic dipole transitions, for which τ_R will be greater than 10^{-6} sec., will be negligibly small in all cases. This gives an attachment coefficient of less than 5×10^{-13} cm.^{3}/sec., which is 10 times smaller than the rates observed by Bradbury.

For process B greater deactivation cross-sections are required even if allowance is made for the possibility that several vibration levels of the O_2^- complex may contribute. The collision cross-section for deactivation of the complex must be some 10^4 times the gas kinetic or the radiative lifetime less than 10^{-10} sec.

The reason for the large collision deactivation rate is far from clear. For the Bloch-Bradbury process or for our suggestion (II) a large quantum of vibrational energy must be transferred. This cannot easily take place directly, as noted earlier, and it seems unlikely that the effective cross-section for the indirect process (35), involving electron transfer, can greatly exceed the gas-kinetic value. Although near-resonance conditions prevail, the fact that the transfer can only proceed through coupling between electronic and vibrational motion must certainly tend to reduce the probability. Again, for our suggestion (I) for process A, the stabilization involves transfer of small quanta of vibrational energy from a molecule in a highly excited vibrational state. Although such energy is readily transformed into translational energy on collision, the effective collision radius is not likely to be much greater than the extreme nuclear separation in the excited molecule. That this is as large as 3×10^{-7} cm. seems most improbable.

It seems, therefore, that the attachment phenomena observed with electron swarms in oxygen at a few mm. Hg pressure must still be regarded as only imperfectly understood. Any numerical extrapolation to lower pressures must be regarded as hypothetical until the difficulties still remaining are resolved. Further experiments, particularly directed towards the investigation of the pressure variation of the attachment rate, are required. It would also be most valuable to develop experimental technique designed to measure detachment energies, etc., as in the pioneering investigations of Loeb (1935).

Notwithstanding the above difficulties the conclusion that, apart from direct radiative attachment (see B 4), no process of attachment of thermal electrons to oxygen molecules is likely to occur with a probability independent of the pressure at low pressures seems to be a definite one, no matter which interpretation is the correct one and how the difficulty regarding the collision stabilization rate is resolved. This is very important in applications to the low pressure regions of the upper atmosphere.

4. *Direct radiative attachment and photodetachment in* O_2

Little can be said in detail about the probabilities of these processes in molecular oxygen. They are probably of the same order as for the corresponding processes in atomic oxygen. It is important to note, however, that the quantum energy released on radiative attachment of a very slow electron to normal O_2 to form $O_2^- \,{}^2\Pi_g$ and also that necessary to produce photodetachment from $O_2^- \,{}^2\Pi_g$ need bear no simple relation to the electron affinity of O_2. Thus, following the Franck-Condon principle, the energy radiated on capture of a very slow electron by normal O_2 to form $O_2^- \,{}^2\Pi_g$ will be very small (of order 0·1 eV), but that required to produce photodetachment from normal O_2^- as much as 2 eV if the potential curves are distributed as in figure 6*a*. On the other hand, if they are as in figure 6*b* the corresponding energies will be about 0·75 and 1·2 eV respectively. These are to be compared with our estimated electron affinity of 1 eV.

C. THE PRODUCTION AND MUTUAL NEUTRALIZATION OF PAIRS OF POSITIVE AND NEGATIVE IONS AT LOW PRESSURES

In the discussion of reactions involving the production and the mutual neutralization of ion pairs in oxygen and other gases at low pressures, the probability of a transition occurring at the crossing-point of two molecular potential-energy curves is important. We will first summarize the theory of this subject before further discussing the individual processes.

1. *The crossing of molecular potential-energy curves*

Suppose, as illustrated in figure 7*a*, the potential-energy curves for two electronic states of a molecule AB, which dissociate into separated atomic states A_1+B_1, A_2+B_2 respectively, calculated to zero order approximation, intersect at a point S. Then if the properties of the states are such that they can interact (Jevons 1932), this interaction will modify the potential energy diagram to that shown in figure 7*b*. Thus curve I*b* has the character of an A_1+B_1 combination at small nuclear separations but of A_2+B_2 at larger and vice versa for curve II*b*. This means that if atoms A, B in states A_1, B_1 respectively are allowed to come together with infinite slowness (i.e. adiabatically) the interaction between them will follow curve II*b*.

On the other hand, if the atoms in these states are brought together with finite velocity v, there is a finite chance of a transition occurring near S in which the system jumps from IIb to Ib. Let $P(v)$ be the probability of such a transition so $1-P$ is the probability that the system continues along IIb. Then, if the atoms are allowed to come together with a finite velocity v from infinity and then allowed to separate again, the chance that, when again at infinite separation, they will be found in the initial states A_1, B_1 is $1-2P(1-P)$ while that of finding them in the A_2, B_2 states is $2P(1-P)$.

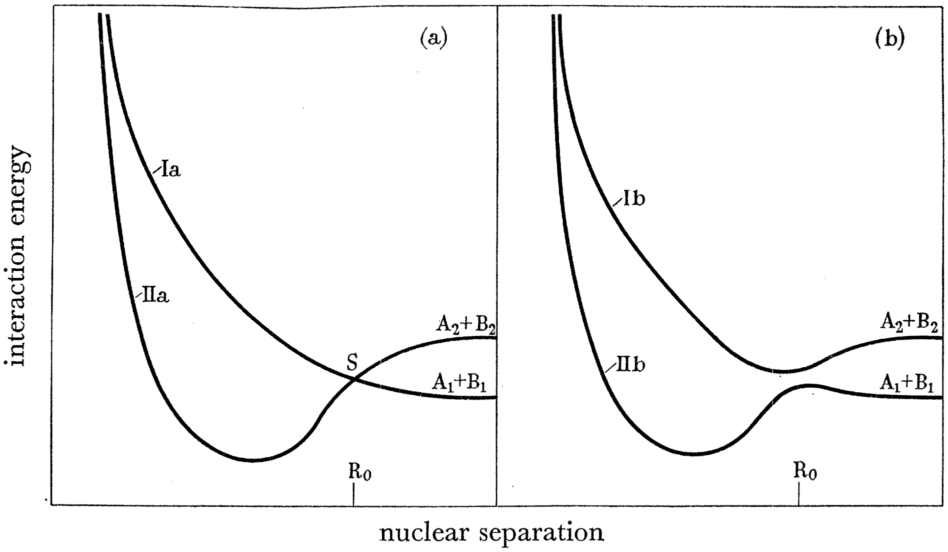

FIGURE 7. Illustrating the interaction of molecular potential energy curves. (a) Two curves in the absence of interaction. (b) Modified curves due to interaction.

The formulae for P, obtained using slightly different methods and approximations, have been given by Landau (1932), Zener (1932), Rice (1931) and Stueckelberg (1932). Let $U_i(R)$, $U_f(R)$ be the two potential-energy functions in zero order approximation, $U_{if}(R)$ the transition potential energy. In terms of the zero order electronic wave functions ψ_i, ψ_f for two potential-energy curves these functions are given by

$$U_i = \int \psi_i^* V \psi_i \, d\tau, \quad U_f = \int \psi_f^* V \psi_f \, d\tau, \quad U_{if} = \int \psi_i^* V \psi_f \, d\tau, \tag{39}$$

where $V(r, R)$ is the appropriate interaction energy between the colliding systems and the integration is taken over the electronic co-ordinates $\mathbf{r}$. Then it is found that

$$P = \exp\left\{-\frac{4\pi^2}{hv} \mid U_{if} \mid^2 \Big/ \left| \frac{d}{dR}(U_i - U_f) \right| \right\}, \tag{40}$$

where the quantities, including the relative velocity v of the atoms, are all calculated at the crossing-point where $R = R_0$ (figure 7b). If ΔE is the energy difference between the two curves at infinite nuclear separation, then R_0 is the solution of the equation

$$U_i - U_f = \Delta E.$$

This result is obtained on the assumption that the relative motion of the atoms takes place along the line of centres. If they possess relative angular momentum, this will be quantized and introduces a centrifugal force term $l(l+1)\,h^2/8\pi^2MR^2$ into the functions U_i, U_f, M being the reduced mass of the atoms. This reduces the value of the velocity v, which is now given by

$$\tfrac{1}{2}Mv^2 = E_i - U_i - \frac{h^2}{8\pi^2MR^2}\,l(l+1), \tag{41}$$

where E_i is the kinetic energy of relative motion at infinite separation in the initial state. We see then that no appreciable transition probability is associated with relative motion in which, at $R = R_0$, the value of v given by this equation is small and it may be shown that the same holds if the right-hand side of (41) is negative. Use will be made of this in C 3.

2. *The production of ion pairs*

2·1. *By electron impact.* Lozier, in his experiments (1934) on the products of the collisions of a beam of electrons of homogeneous velocity in O_2 and CO at low pressures (10^{-4}–10^{-5} mm. Hg), found that, when the electron energy exceeds a certain amount (19 and 21 eV respectively), there is a finite probability of splitting a struck molecule into a positive and negative ion, viz.

$$O_2 + e \rightarrow O^+ + O^- + e. \tag{42}$$

Hagstrum & Tate (1941) have made a further investigation of these processes and also of the similar reaction in NO which first sets in when the electron energy exceeds 20 eV. In all cases the variation of the probability cross-section with electron energy is of the same form as for excitation of a single optically allowed transition in an atom by electron impact (Massey & Smith 1936) but the magnitude (10^{-19} cm.^{2}) is of a smaller order. Another feature appears to be that the negative oxygen ions formed are in that excited state we have discussed earlier but, for reasons indicated below, the evidence for this cannot yet be regarded as completely convincing.

We must regard the process as one in which the struck molecule is first excited to a state which combines optically with the ground state. This state may be either of a polar or homopolar character at small nuclear separations, but, owing to the complicated interaction which must occur with other potential-energy curves when the nuclear separation increases, the final products which result at very large separations may not bear any simple relation to those which might be expected from the initial excitation. Owing to the absence of all but a very few excited states of O^- there are many more potential curves which yield excited O atoms than pairs of O ions, so it is to be anticipated that the chance of an ion pair resulting from the initial excitation is quite small. If, then, $Q_{\text{ex}}(e)$ is the cross-section for the initial excitation by electron impact, that for production of an ion pair will be $PQ_{\text{ex}}(e)$, where P is small.

On this interpretation it is difficult to see why P should have a greater value for a particular excitation than for any other satisfying the energy conditions. We must suppose, then, that the observed existence of only one definite excitation potential for the dissociation process is due to $Q_{\text{ex}}(e)$ having a considerably larger value for excitation of a certain molecular level than for any other in the neighbourhood which satisfies the energy conditions for ion production.

It is not clear why the chance of producing an ion pair involving an excited O^- ion should be so much larger than that of a pair in their normal states. However, the current interpretation of the experimental results, though plausible, is not completely definite. Some uncertainty is introduced by lack of detailed knowledge of the relative velocities of the ions produced. Further, in the case of CO the knowledge of the dissociation energy of the molecule is unreliable,† and for NO and O_2 the interpretation involving the excited atomic ion is not the only one available, although it is the one which fits the energy relations closest. It is therefore very desirable that further experimental investigations be carried out.

2·2. *By light absorption.* The probability of production of ion pairs from molecules by light absorption can be estimated from the observed probability of the production by electron impact.

The effective cross-section $Q_{ex}(e)$ for the initial excitation by electron impact is given to a close approximation by Bethe's formula (1930)

$$Q_{ex}(e) = 64\pi^5 m^2 e^4 k^{-2} h^{-4} \, | Z_{if} |^2 \log (4E/E_{ex}), \tag{43}$$

where $kh/2\pi$ is the momentum of the incident electron, E its energy, E_{ex} the excitation energy and Z_{if} the matrix element, with respect to the initial and final electronic states of the molecule, of the component, in the initial direction of motion of the electron, of its displacement from the centre of the molecule. For 40 eV electrons we have, using Lozier's observed value, 19 eV, for E_{ex},

$$Q_{ex}(e) = 9 \, | Z_{if} |^2 \, \text{cm.}^2. \tag{44}$$

For excitation by optical absorption we have the corresponding mean cross-section

$$Q_{ex}(q) = \frac{32\pi^4 e^2}{3hc} \frac{E_{ex}}{\Delta E} \, | Z_{if} |^2, \tag{45}$$

where ΔE is the uncertainty in the excitation energy due to the molecular vibration. Taking this to be of the order 5 eV gives

$$Q_{ex}(q) \simeq 5 \, | Z_{if} |^2 \, \text{cm.}^2. \tag{46}$$

As $PQ_{ex}(e)$ as found by Lozier is of the order 10^{-19} cm.^{2}, it follows that $PQ_{ex}(q)$ is also of this order. However, unlike the electron impact process the optical absorption is limited to radiation of quantum energy between E_{ex} and $E_{ex}+\Delta E$; for O_2 between 18·9 and 24 eV, the latter figure being only approximate. Owing to the high frequency involved it is unlikely that direct production of ion pairs by radiation occurs to any extent in the earth's atmosphere even though the effective cross-section $PQ_{ex}(q)$ is by no means negligible.

3. *Mutual neutralization of positive and negative ions*

At ordinary pressures the recombination of ions proceeds mainly in the presence of third bodies which remove the excess energy. The theory of this process has been given by J. J. Thomson (1924), and is known to be in satisfactory agreement with experiment (Sayers 1938). The rate of three-body recombination is proportional to the gas pressure at low

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† The interpretation of the experiments which suggests the existence of the excited ion assumes the dissociation energy of CO to be 9·46 eV. There is very considerable doubt as to the validity of this value (see Gaydon and Penney (1942)).

pressures. The recombination coefficient α has the value 2×10^{-6} cm.^{3}/sec. in air at N.T.P. and it falls to 8×10^{-11} cm.^{3}/sec. at a pressure of 10^{-2} mm. Hg. At pressures of this order contributions from pressure-independent processes are likely to become the more important. The only reactions of this type in a gas of atomic oxygen are represented by

$$\mathrm{O}^- + \mathrm{O}^+ \rightarrow \mathrm{O}' + \mathrm{O}'', \tag{47}$$

in which the energy liberated by the mutual neutralization of the ions is used partly in producing excited O atoms and partly in providing kinetic energy of relative motion of the atomic products. It is possible to obtain some estimate of the order of magnitude which can be attained by the effective cross-section for these mutual neutralization processes, under suitable conditions, by using the theory of non-adiabatic transitions between potential curves. For mutual neutralization to be more effective than three-body recombination at pressures of 10^{-2} mm. Hg this cross-section must be greater than 10^{-15} cm.^{2}.

We restrict ourselves to ions moving with thermal velocities, so the potential energy of the excited atoms must not be appreciably greater than that of the ions. Two cases then arise. In the first the zero order potential energy curve for the interaction of the normal ions intersects the corresponding curve for the interaction of the excited atoms at some separation R_0, while in the second the curves do not cross. We first consider in detail the former case.

Following the notation of C 1, but introducing a suffix to distinguish the quantized angular momentum of the relative motion of the ions, the probability of the ions emerging as excited atoms after the collision is given by

$$2P_l(1-P_l), \tag{48}$$

with P_l as in (40) and (41). To obtain the effective cross-section we must average over all relative angular momenta and normalize the relative current of colliding ions appropriately. This normalization is such that the average cross-section per collision is π/k_i^2, where $k_i^2 = 8\pi^2 ME_i/h^2$ and a weight $2l+1$ attaches to an angular momentum of l quantum units. We therefore have for the mutual neutralization cross-section

$$Q_n = \frac{2\pi}{k_i^2}\,\Sigma(2l+1)\,P_l(1-P_l). \tag{49}$$

Now, from (41) we have, writing $E_{i,f} = \dfrac{h^2}{8\pi^2 M}k_{i,f}^2$,

$$\begin{aligned}\tfrac{1}{2}Mv_l^2 &= \frac{h^2}{8\pi^2 M}k_i^2 - U_i(R_0) - \frac{h^2}{8\pi^2 MR_0^2}l(l+1)\\ &= \frac{h^2}{8\pi^2 M}k_f^2 - U_f(R_0) - \frac{h^2}{8\pi^2 MR_0^2}l(l+1).\end{aligned} \tag{50}$$

$U_f(R)$, being the interaction between neutral atoms, will fall off rapidly for large R, so if R_0 is large, v_l will vanish when

$$k_f R_0 \simeq l = l_0. \tag{51}$$

Even for atoms moving with thermal velocities l_0 will be large (of order 100 for $R_0 = 10^{-7}$ cm.). The sum in (49) can therefore be replaced by an integral to give

$$Q_n = (4\pi R_0^2 k_f^2/k_i^2)\int_0^{\frac{1}{2}\pi} e^{-\pi\gamma}(1-e^{-\pi\gamma})\sin\theta\cos\theta\,d\theta, \tag{52}$$

where $\sin\theta = l/R_0 k_f$,

$$\gamma = 4\pi \mid U_{if}(R_0) \mid^2 \Big/ \left(h\nu_l \left| \frac{dU_i}{dR} \right|_{R=R_0} \right), \tag{53}$$

and $U_f(R_0)$ has been neglected. Since the integral is always less than one-eighth, the maximum value of Q_n is of order $\frac{1}{2}\pi R_0^2 k_f^2/k_i^2$. If R_0 is large $U_{if}(R_0)$ will be small and this will tend to reduce the cross-section very much below the maximum value. It is not possible to calculate U_{if} with any accuracy for particular transitions but we may obtain a good idea of the possibilities in the following way.

We write
$$U_i = e^2/R, \quad U_{ij} = e^2/a_0 \exp(-R/A),$$

and, treating A as a variable parameter, calculate Q_n for various values of ΔE, the potential energy difference between the ions and excited atoms. The only important cases arising in practice are those in which the colliding ions have thermal energies, so we calculate Q_n for the cases where $E_i = 1{\cdot}7 \times 10^{-2}$ eV and $0{\cdot}68\ (10)^{-1}$ eV, corresponding to temperatures of 250° K and 1000° K respectively, Q_n being nearly inversely proportional to the temperature. Results are given in table 3 which includes also the maximum possible value of Q_n for a given value of A together with the energy difference which yields this maximum.

TABLE 3. CROSS-SECTIONS FOR MUTUAL NEUTRALIZATION OF OXYGEN IONS IN UNITS 10^{-14} cm.^{2} ASSUMING VARIOUS VALUES OF THE INTERACTION PARAMETER A†

		relative kinetic energy of ions in eV							
		$1{\cdot}7\times10^{-2}$ (250° K) values of A				$6{\cdot}8\times10^{-2}$ (1000° K) values of A			
energy excess of ions above atoms ΔE (eV)	crossing-point radius R_0 (in a.u.)	1	2	4	8	1	2	4	8
0	∞	0	0	0	0	0	0	0	0
0·125	216	—	—	—	$<10^{-5}$	—	—	—	$<10^{-5}$
0·25	108	—	—	$<10^{-5}$	8×10^{-1}	—	—	$<10^{-5}$	0·2
0·50	54	—	—	6×10^{-2}	1×10^{-5}	—	—	2×10^{-2}	$<10^{-5}$
0·75	36	—	$<10^{-5}$	97	$<10^{-5}$	—	$<10^{-5}$	24	—
1·00	27	—	6×10^{-3}	18	—	—	1×10^{-3}	5·0	—
1·50	18	$<10^{-5}$	10	$<10^{-5}$	—	$<10^{-5}$	2·6	$<10^{-5}$	—
2·0	13	5×10^{-4}	85	—	—	1×10^{-4}	21	—	—
3·0	9·0	1·0	$<10^{-5}$	—	—	0·2	$<10^{-5}$	—	—
4·0	6·7	23	—	—	—	5·6	—	—	—
6·0	4·5	2·7	—	—	—	0·7	—	—	—
10·0	2·7	$<10^{-5}$	—	—	—	$<10^{-5}$	—	—	—
energy excess for maximum cross-section (eV)		4·6	2·0	0·9	0·4	4·6	2·0	0·9	0·4
maximum possible cross-section		37	88	210	520	9·2	22	53	130

† A is such that the intersection U_{if} at the crossing point is given by
$$U_{if} = e^2/a_0 \exp(-R_0/A).$$

Before considering the significance of the numerical values given in the table it is convenient to examine the actual transitions which are energetically possible with oxygen ions at ordinary temperatures. If W_i is the potential energy of the ions, W_f of the atoms, we must have
$$E_f + W_f = E_i + W_i,$$

so, since E_i is small, W_f must be less than W_i. As the ionization energy of O is 13·55 eV and the electron affinity 2·2 ± 0·2 eV, $W_i = 11{\cdot}35 \pm 0{\cdot}2$ eV, and the only possible atomic products of the neutralization (with corresponding values of ΔE) are as given in table 4.

Table 4. Possible states of oxygen atoms which can result from mutual neutralization of oxygen ions moving with thermal energy

	terms	electron configurations	energy released on neutralization (ΔE in eV)†
(i)	$^3\mathrm{P}+{}^3\mathrm{P}$	Both $(1s)^2\,(2s)^2\,(2p)^4$	$11{\cdot}35 \pm 0{\cdot}2$
(ii)	$^3\mathrm{P}+{}^1\mathrm{D}$	Both $(1s)^2\,(2s)^2\,(2p)^4$	$9{\cdot}39 \pm 0{\cdot}2$
(iii)	$^1\mathrm{D}+{}^1\mathrm{D}$	Both $(1s)^2\,(2s)^2\,(2p)^4$	$7{\cdot}43 \pm 0{\cdot}2$
(iv)	$^3\mathrm{P}+{}^1\mathrm{S}$	Both $(1s)^2\,(2s)^2\,(2p)^4$	$7{\cdot}18 \pm 0{\cdot}2$
(v)	$^1\mathrm{D}+{}^1\mathrm{S}$	Both $(1s)^2\,(2s)^2\,(2p)^4$	$5{\cdot}22 \pm 0{\cdot}2$
(vi)	$^1\mathrm{S}+{}^1\mathrm{S}$	Both $(1s)^2\,(2s)^2\,(2p)^4$	$3{\cdot}01 \pm 0{\cdot}2$
(vii)	$^3\mathrm{P}+{}^5\mathrm{S}^\circ$	$(1s)^2\,(2s)^2\,(2p)^4+(1s)^2\,(2s)^2\,(2p)^3\,(3s)$	$2{\cdot}25 \pm 0{\cdot}2$
(viii)	$^3\mathrm{P}+{}^3\mathrm{S}^\circ$	$(1s)^2\,(2s)^2\,(2p)^4+(1s)^2\,(2s)^2\,(2p)^3\,(3s)$	$1{\cdot}87 \pm 0{\cdot}2$
(ix)	$^3\mathrm{P}+{}^5\mathrm{P}$	$(1s)^2\,(2s)^2\,(2p)^4+(1s)^2\,(2s)^2\,(2p)^3\,(3p)$	$0{\cdot}65 \pm 0{\cdot}2$
(x)	$^3\mathrm{P}+{}^3\mathrm{P}$	$(1s)^2\,(2s)^2\,(2p)^4+(1s)^2\,(2s)^2\,(2p)^3\,(3p)$	$0{\cdot}40 \pm 0{\cdot}2$
(xi)	$^1\mathrm{D}+{}^5\mathrm{S}^\circ$	$(1s)^2\,(2s)^2\,(2p)^4+(1s)^2\,(2s)^2\,(2p)^3\,(3s)$	$0{\cdot}29 \pm 0{\cdot}2$

For the first five transitions the crossing-point occurs at such small values of R_0 that the potential functions are no longer of the simple form taken in the calculation but the cross-section for at least one of these may be of order $\frac{1}{2}\pi R_0^2 k_f^2/k_i^2$ which is quite large owing to the factor k_f^2/k_i^2 characteristic of collisions of the second kind. Thus for $\Delta E = 7$ eV k_f^2/k_i^2 is as large as $400 \times (250/T)$. However, much larger values for Q_n may arise from the remaining transitions involving terms of excited configurations. For these the probable value of A is between 2 and 4. A variety of possible values in this range can occur from the numerous potential energy curves which arise from the interaction of O atoms in the configurations listed in (vi)–(xi) of table 4. Reference to table 3 shows then that it is quite possible and almost probable that for one of these a cross-section between 10^{-12} and 10^{-13} cm.^{2} will result, though one as large as 10^{-11} cm.^{2} would seem very unlikely.

It remains to consider whether larger cross-sections can arise from cases where the potential energy curves do not cross. Since U_i behaves as e^2/R at distances greater than atomic dimensions, it follows for exothermic reactions, which are the only ones likely to arise in collisions of thermal ions, that the curves always cross except possibly when ΔE is so large that $e^2/\Delta E$ falls inside atomic dimensions. For such cases the separation between the two potential curves is not likely to reduce to values comparable with U_{if} except when R is comparable with atomic dimensions. As transitions between non-intersecting curves only take place when they approach to a separation of order U_{if} (Stueckelberg 1932) it is not likely then that these cases will give rise to large cross-sections. Even for the few endothermic reactions which can proceed with thermal ions the separation of the curves at large nuclear separations will be $|\Delta E| + e^2/R$, much greater than U_{if}. Large cross-sections can therefore not be expected in these cases either.

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† The uncertainty 0·2 eV in these values arises from the uncertainty in the electron affinity of O as given by Lozier (1934).

D. Summary of results and conclusions

The more important of these are as follows:

1. Experimental evidence of the existence of a stable excited state of O^- of very small binding energy has been obtained by Lozier and by Hagstrum and Tate.

2. The lowest excited state must belong either to a $(2s)^2(2p)^4 3s$ or $(2s)(2p)^6$ configuration.

3. It is probable, on empirical grounds, that the $(2s)(2p)^6$ lies above the $(2s)^2(2p)^4 3s$ configuration.

4. According to the Hartree-Fock self-consistent field method (including exchange) a value of the polarizability of atomic oxygen two to four times greater than that derived from the observed molar refractivity of O_2 is necessary to provide even a stable $(2s)^2(2p)^4 3s\ {}^4P$ term of O^-.

5. In view of the conflict between the theoretical results (3) and (4) and the experimental evidence (1), it is not yet possible to decide what is the sign and magnitude of the binding energy of the $3s$ electron in O^-.

6. The rates of radiative attachment of electrons to atomic oxygen and of photodetachment of electrons from O^- are both very sensitive to the value of the binding energy of the $3s$ electron, if it is small in absolute magnitude.

7. In view of (5) and (6) these rates have been calculated for a range of assumed binding energies of the $3s$ electron, these being specified by the introduction of an effective polarizability of atomic oxygen just sufficient to give a $3s$ level of the particular energy (according to the Hartree-Fock method).

8. To facilitate application, mean rates have been derived for a Maxwellian distribution of electrons and for black-body radiation.

9. The rate of attachment of electrons, with Maxwellian velocity distribution, to O by a dielectronic process analogous to inverse auto-ionization, involving a virtual level of the $(2s)(2p)^6$ configuration, is only likely to be of comparable importance to that by radiative attachment if the energy of the virtual level is much less than 0·25 eV above that of the ground state of O^-. The same conclusion applies to the inverse (detachment) process associated with black-body radiation.

10. Attachment of electrons to O by three-body processes is unlikely to be important, compared with radiative attachment, at pressures less than 0·1 mm. Hg.

11. The effective cross-section for associative detachment in atomic oxygen, viz. $O+O^- \rightarrow O_2+e$, is likely to be of the order 10^{-20}–10^{-21} cm.^{2}.

12. The experimental evidence on attachment from electron swarms in O_2 indicates the existence of two processes, one operative at very low energies, the other setting in at a mean energy of 1·5 eV.

13. Reasons are given why it is unlikely that slow electrons, produced by inelastic collisions, are responsible for the observed attachment at the higher mean energies.

14. Difficulties of detail associated with the current Bloch-Bradbury interpretation of the low-energy attachment are discussed.

15. Possible alternative interpretations of the observations in terms of molecular potential energy curves for O_2^- are derived and a difficulty common to all is revealed.

16. The electron affinity of O_2^- is probably about 1 eV.

17. The distribution of potential-energy curves for O_2^- is such that any process of attachment of thermal electrons to oxygen molecules, with probability independent of pressure at low pressure, apart from direct radiative attachment, is unlikely to occur.

18. The relative magnitude of the rate of radiative attachment of electrons of O_2 and of photodetachment from O_2^- can depend very markedly on the relative position of the potential-energy curves for the ground electronic states of O_2 and O_2^-.

19. The rate of production of pairs of O^+ and O^- ions by impact of electrons or of quanta on O_2 molecules is discussed, the excitation energy required being between 19 and 21 eV.

20. Mutual neutralization of O^+ and O^- ions can occur by transfer of an electron on impact. For mutual neutralization of thermal ions the effective cross-section is probably between 10^{-13} and 10^{-12} cm.^{2} but is unlikely to be as high as 10^{-11} cm.^{2}.

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