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No. 1

NEGATIVE IONS

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NEGATIVE IONS

by

H. S. W. MASSEY, PH.D.

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GENERAL PREFACE

It is the aim of these tracts to provide authoritative accounts of subjects of topical physical interest written by those actively engaged in research. Each author is encouraged to adopt an individualistic outlook and to write the tract from his own point of view without necessarily making it "complete" by the inclusion of references to all other workers or to all allied subjects; it is hoped that the tracts may present such surveys of subjects as the authors might give in a short course of specialised lectures.

By this means readers will be provided with accounts of those subjects which are advancing so rapidly that a full-length book would be out of place. From time to time it is hoped to issue new editions of tracts dealing with subjects in which the advance is most rapid.

M. L. O.

J. A. R.

CONTENTS

<i>Preface</i>	<i>page xi</i>
<i>Introduction</i>	xiii
<i>Chapter I</i> NEGATIVE ATOMIC IONS	1
§ 1. The Existence of Negatively Charged Atoms	1
§ 2. General Theoretical Considerations	3
§ 3. Calculation of Negative Ion Structure by Quantum Methods	7
3.1. The Hydrogen Negative Ion	8
3.11. Remarks on Hylleraas' Method	8
3.2. Heavier Negative Ions	9
3.21. Hartree's Self-consistent Field Method	9
§ 4. Electron Affinities	10
4.1. Glockler's Empirical Method	12
4.2. Experimental Methods	12
4.21. From collisions	12
4.22. From Measurement of the Equilibrium Constant for Attachment Reactions	13
4.23. From the Energy Relations involved in Cyclic Processes	17
§ 5. Excited States of Negative Ions	19
5.1. Negative Ion Formation by Excited Atoms	19
§ 6. Doubly-charged Negative Ions	20
<i>Chapter II</i> NEGATIVE MOLECULAR IONS	22
§ 1. Introduction—Electron Affinity and Vertical Detachment Potential	22
§ 2. Enumeration and Properties of the Electronic States of Diatomic Molecules	24
§ 3. Structure of Simple Negative Molecular Ions	26
3.1. H_2^-	26
3.2. O_2^-	27
3.3. F_2^- , Cl_2^- , Br_2^- , I_2^-	29

Chapter III MODES OF FORMATION OF NEGATIVE IONS

page 31

§ 1. Capture of Free Electrons by Neutral Atoms	31
1.1. Radiative Capture of Electrons—Electron Affinity Spectrum	31
1.2. Capture of Electrons in Three-Body Collisions	38
§ 2. Formation of Negative Ions on Collisions of Electrons with Molecules	40
2.1. Processes involving Electron Capture	40
2.11. General Theoretical Considerations	40
2.12. Determination of Electron Affinities	44
2.13. Theoretical Evaluation of Cross-Sections	44
2.2. Non-capture Collisions—Dissociation into Ions	45
§ 3. Experiments on Attachment of Electrons to Molecules	48
3.1. General Remarks	48
§ 4. Experiments using Homogeneous Electron Beams	48
4.1. The Method of Tate and Lozier	48
4.2. Electron Collisions in O ₂ and CO. The Electron Affinity of O	50
4.21. Observed Cross-Sections for Collision Processes in O ₂ and CO	53
4.3. Collisions in Iodine Vapour	53
§ 5. Attachment Experiments with Electron Swarms	54
5.1. Introductory Remarks	54
5.2. General Description and Theory of Swarm Experiments	55
5.3. The Method of the Electron Filter	56
5.4. Bailey's Method	57
§ 6. Results obtained by "Swarm" Experiments and their interpretation	60
6.1. Oxygen	60
6.2. Other Gases	62
§ 7. Summary of Collision Processes leading to Negative Ion Formation in Oxygen	64

CONTENTS

ix

§8. Capture of Bound Electrons by Neutral Atoms and Molecules	<i>page</i> 65
8.1. Electron Capture from Atoms	65
8.2. Extraction of Electrons from Metals	67
§9. Summary	69

<i>Chapter IV</i> DETACHMENT OF ELECTRONS FROM NEGATIVE IONS	70
§1. Introduction	70
§2. Photoelectric Detachment	70
§3. "Ionization" of Negative Ions by Electrons and by Heavy Particles	72
§4. Detachment accompanying Molecule Formation	73
§5. Neutralization of Ions at Metal Surfaces	74
§6. Loeb's Experiments on the Energy of Detachment of Electrons from O_2^-	75
§7. Collisions of Negative and Positive Ions	78
§8. Summary	81

<i>Chapter V</i> NEGATIVE IONS IN GLOW DISCHARGES AND IN THE UPPER ATMOSPHERE	82
§1. General Effects of Negative Ions in Discharges	83
§2. The Destruction of Ions in Plasmas	86
§3. Upper Atmospheric Problems	89
3.1. Properties of the Ionized Regions	90
3.2. The Origin of the Ionized Layers	92
3.3. Recombination, Attachment and Detachment in the Upper Atmosphere	93
3.4. The Green Light of the Night Sky	99

Index

PREFACE

Although the study of negative ions dates back to the earliest days of so-called Modern Physics much still remains to be investigated in this direction. This is partly due to the experimental difficulties which beset the subject and it seems to the writer that the application of the theoretical methods of quantum theory, which have proved so reliable in dealing with extra nuclear phenomena, might do much to improve the situation. In view of the additional interest attached to negative ions because of their undoubted influence on ionospheric properties and in electric discharges it seemed worth while to survey the present extent of our knowledge making free use of quantal interpretations and suggestions. This work has been confined to phenomena concerning simpler negative ions as it did not seem profitable to attempt any account of ion clusters and high pressure phenomena. In the last chapter an attempt is made to indicate the lines along which we might expect application of a knowledge of negative ion properties to proceed as far as electric discharge and ionospheric phenomena are concerned. As this tract is one of a physical series care has been taken to avoid all elaborate mathematics and anything savouring of this has been relegated to small type. While no attempt has been made to write a comprehensive account it is hoped that nothing important has been omitted.

I am very much indebted to my colleague, Professor K. G. Emeléus, for giving me detailed information concerning the results and interpretation of his experiments on negative ions in discharges in advance of publication and also for reading the whole book in manuscript. Dr R. W. Lunt also read the whole book in manuscript and made many valuable suggestions, while Mr J. A. Ratcliffe read and criticized the section of the last chapter referring to ionospheric problems. To both of these gentlemen I am very grateful.

Finally, I must express my appreciation of the fine job the Cambridge University Press, as usual, have made of the publication.

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December, 1937

INTRODUCTION

The conception of a negatively charged ion dates back to the ionic theory of electrolysis. In this theory a molecule XY is supposed to dissociate in solution to give ions X^+ and Y^- . The application of potential difference then produces a drift of the positive ions X^+ to the cathode and of negative ions Y^- to the anode. The drift velocity of these ions in the field direction is so small, however, that the ions must be regarded as forming clusters of considerable size by solvation.

The study of the passage of electricity through gases soon showed that, in this case also, the carriers of negative charge are not by any means exclusively electrons, but often particles of molecular mass. Although the opportunities for cluster formation in these phenomena are less than in electrolysis, it is important to remember that the negative-charge carriers in a gas (at not too low pressures) may often be very complex. Simplification of experimental conditions (though not always involving simplification of experimental technique!) was necessary before the nature and properties of the negative ions could be investigated. The most fruitful source of knowledge at first was the mass spectrograph used in the classical researches of J. J. Thomson to identify a number of simple negatively charged molecules (including a number of atoms). Experiments on these lines have continued to the present time and are still capable of yielding useful results.

The study of the diffusion of ions in gases, carried out by Townsend and his collaborators, also provided further information of a semi-quantitative nature concerning electron attachment to molecules, but it is difficult to devise experiments to give quantitative results. The introduction of electron-beam methods has helped in this direction, but the fact remains that experimental information on negative ions is still very meagre and often contradictory.

Until recently there has been little attempt to supplement the rather slight knowledge of negative ions gained from experiment with theoretical considerations employing the methods of quantum theory. As these methods have been so abundantly justified in application to other atomic phenomena it is likely that valuable results may be obtained from their use.

It is the purpose of this tract to discuss the nature and properties of negative ions as determined partly by experiment and partly from quantum theory. Contrary to the usage in works on electron mobilities, we understand the term negative ion to apply to particles of molecular mass only, while, at the same time, we make no attempt to discuss the properties of ion clusters. In short, we are concerned with negative ions formed in gases at low pressures (up to a few mm. Hg). This does not affect the applicability of our conclusions to most electric discharge phenomena, nor to the study of the Earth's ionosphere.

In the first Chapter we discuss the existence and structure of negative ions formed by atoms and describe the experimental methods available for determining the electron affinity of an atom. A brief discussion of the nature of molecular negative ions follows in Chapter II, while Chapter III contains an account of the processes which lead to formation of negative ions. In this Chapter we see the greatest correlation between theory and experiment, but in Chapter IV, dealing with the destruction of negative ions, we are forced to rely almost exclusively on theory. The final Chapter deals with the possibilities of applying the study of negative ions to electric discharge phenomena and to the theory of the upper atmosphere.

Chapter I

NEGATIVE ATOMIC IONS

§ 1. The Existence of Negatively Charged Atoms.

A great number of negative ions have been observed under varying conditions by means of the mass spectrograph. Although such experiments do not place a very great lower limit on the possible lifetime (towards spontaneous dissociation) of these ions, there is no reason to believe that they are really only metastable. In fact we shall see below that the existence of certain stable negatively charged atoms is to be expected on theoretical grounds.

As an illustration of the experimental method employed in this type of investigation we will consider the recent experiments carried out by Tüxen* using modern vacuum technique and obtaining most definite results.

The method consists in producing an electric discharge in a tube with a perforated anode. A mixed stream of negative ions and electrons passes through the hole in the anode and is analysed by passage between crossed electric and magnetic fields. The experimental arrangement actually employed by Tüxen is illustrated diagrammatically in fig. 1. An electric discharge was maintained between the cathode *C* and a perforated anode *A*. Negatively charged particles passing through the anode were accelerated by a high potential difference between *A* and a tube *D* so as to pass in a beam through the slit *E* into the field space *F*. From this the various particles issued as separate beams which were recorded by the photographic plate *G*.

The potential difference between *C* and *A* was 3000 volts and that between *A* and *D*, 10,000 volts. A distinctive feature was the relatively high gas pressure (0.1 to 10 mm. Hg) used in the discharge tube. Special care was therefore necessary in

* *Zeit. für Phys.* **103**, 463 (1936).

designing the perforated anode in such a way that leakage of gas through it to the analysing chamber would be small. At the same time it was important to ensure that negative ions diffusing through the anode hole should not be destroyed by making collisions with the surrounding metal. These two conditions are to a great extent incompatible, but it was found after much experiment that a satisfactory compromise could be effected by covering a 1 mm. hole in the anode by a platinum foil 5μ thick with a concentric perforation of 10μ diameter and applying powerful diffusion pumps to the analysing chamber.

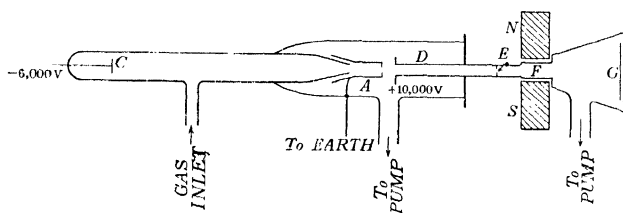


Fig. 1. Mass spectrograph used by Tüxen.

An important feature of the experiments was the provision made for avoiding the presence of impurities. Before admitting gas the cathode was induction heated and the anode foil raised to high temperature by passing a powerful discharge. It was found that, unless these precautions were taken, negative ions due to impurities appeared on the mass-spectrograms.

The gases investigated were dry air, oxygen, hydrogen, helium, neon and argon and the observed negative ions were identified as O^- , O_2^- , NO_2^- , NO_3^- , OH^- and H^- . In no case was any one of the ions N^- , N_2^- , He^- , Ne^- or Ar^- observed. It is very probable that these ions do not exist as stable entities, for the sensitivity of the apparatus was such that, even with the most extreme purification, weak traces of other negative ions were occasionally found in discharges through the rare gases. The most prominent negative ion observed in air and oxygen was the atomic ion O^- , this being much more abundant than O_2^- .

§2. General Theoretical Considerations.

It is clear from the experimental results described above that it is not only necessary to explain the existence of negative ions but also to understand why some atoms form stable ions and others do not.

Applying the general ideas of quantum theory we may regard a negative ion as a system with a number of quantum states. In general the ion will be observed in its normal state, and, if it is to be stable, the energy of this normal state must be less than that of the normal state of the corresponding neutral atom. The energy difference $E_0 - E_-$ between the normal states of the atom and ion is called the electron affinity of the atom. This energy will also be equal to that necessary to detach an electron from the ion, so may also be called the detachment energy of the ion.* A positive electron affinity indicates a stable negative ion.

To discuss the stability of an ion we must endeavour to determine the conditions under which $E_0 - E_-$ is positive. As a first approximation this quantity may be regarded as the binding energy of the added electron; hence the question arises as to the nature of the force which holds this electron bound to the atom. The fact that the ion has a negative charge does not mean that the net force acting on the electron is that of a negative charge. The electron is not influenced by its own field but only by that of the remaining atomic electrons and the nucleus. That this field is attractive may be seen as follows.

Consider for simplicity a hydrogen atom. The nucleus can be regarded as a point charge $+\epsilon$, while the charge of the atomic electron is spread out in a spherically symmetrical cloud around the nucleus as centre. Let us determine the potential energy of a charge $-\epsilon$ placed in this distribution at a distance r_1 from the centre. Suppose α is the fraction of the total charge of the atomic electron contained within a distance r_1 from the nucleus. The charge $\epsilon(1 - \alpha)$ within the sphere of radius r_1 acts as if concentrated at the nucleus and so gives rise to a potential

* See, however, Chapter II, § 1.

4 FIELD ACTING ON AN ATTACHED ELECTRON

$\epsilon(1-\alpha)/r_1$. If the remainder, $-\epsilon(1-\alpha)$, of the atomic electronic charge were concentrated at r_1 it would give rise to a potential $-\epsilon(1-\alpha)/r_1$, but it is actually distributed throughout space from r_1 to ∞ and so can only give rise to a potential $-\beta\epsilon(1-\alpha)/r_1$, where β is less than unity. The total potential energy of the charge $-\epsilon$ is therefore

$$-(1-\beta)(1-\alpha)\epsilon^2/r_1,$$

and so is negative.

This shows that the additional electron will be acted on by a net attractive force. Further, since $(1-\beta)(1-\alpha) \rightarrow 0$ as $r_1 \rightarrow \infty$, the effective field of force acting on the electron falls off much more rapidly with distance than a Coulomb field. This difference between the asymptotic behaviour of the effective field acting on an electron in a negative ion and in a neutral atom (which behaves in the same way as a Coulomb field) has important consequences for the theory of negative ions, as we shall see below.

The calculation of the potential energy of an electron in the field of a hydrogen atom may be carried out to a first approximation as follows. If we neglect polarization effects (which are actually decisive in determining the stability of H^-) the probability of finding the atomic electron at a distance between r and $r+dr$ from the nucleus is $4\pi r^2 \psi^2 dr$, where $\psi = (\pi a_0^3)^{-1/2} e^{-r/a_0}$ is the wave function of the ground state of hydrogen. The potential energy due to the atomic electron at a point distant r_1 from the nucleus is

$$\frac{4\pi e^2}{r_1} \int_0^{r_1} \psi^2 r^2 dr + 4\pi e^2 \int_{r_1}^{\infty} \frac{\psi^2 r^2 dr}{r},$$

the first arising from the charge within r_1 , the second from that without. Carrying out the elementary integrations involved gives

$$\epsilon^2 \left\{ \frac{1}{r_1} - e^{-2r_1/a_0} \left(\frac{1}{r_1} + \frac{1}{a_0} \right) \right\}.$$

Adding the potential energy $-\epsilon^2/r_1$ due to the nucleus we find for the total potential energy

$$-\epsilon^2 e^{-2r_1/a_0} \left(\frac{1}{r_1} + \frac{1}{a_0} \right). \quad (1.1)$$

This gives a field of force falling off exponentially with distance, but polarization effects probably modify this to an inverse fifth-power law. This is still qualitatively distinct from a Coulomb field.

To a first approximation we see then that a negative ion may be considered in terms of the stationary states of an electron in an attractive field of force falling off rapidly with distance. In such a field the number of stationary states is finite and not infinite as for the Coulomb field. We may illustrate this by taking a simple case. Represent the potential energy V by taking $V = -U$, a constant, for distances r less than r_0 and zero elsewhere. The wave equation for the states with zero angular momentum in this field is

$$\frac{d^2\psi}{dr^2} + \frac{2}{r} \frac{d\psi}{dr} + \frac{8\pi^2m}{h^2} (E + U) \psi = 0, \quad r < r_0, \quad (1.21)$$

$$\frac{d^2\psi}{dr^2} + \frac{2}{r} \frac{d\psi}{dr} + \frac{8\pi^2m}{h^2} E \psi = 0, \quad r > r_0. \quad (1.22)$$

The substitution $\psi = ru$ reduces the equation to the form

$$\frac{d^2u}{dr^2} + \lambda^2 u = 0, \quad (1.3)$$

$$\text{where} \quad \lambda^2 = \frac{8\pi^2m}{h^2} (E + U) = \nu^2 \quad \text{for } r < r_0 \quad (1.41)$$

$$= \frac{8\pi^2m}{h^2} E = -\kappa^2 \quad \text{for } r > r_0. \quad (1.42)$$

The boundary conditions to be satisfied are that ψ be finite, continuous and single-valued everywhere. This requires that $u = 0$ at $r = 0$.

Equation (1.3) is the familiar equation for simple harmonic motion, and the solution which satisfies the boundary conditions for $E < 0$ is

$$u = A \sin \nu r \quad r < r_0, \quad (1.51)$$

$$= B e^{-\kappa r} \quad r > r_0. \quad (1.52)$$

Continuity of the charge and current density requires that u and du/dr be continuous at $r = r_0$, so

$$A \sin \nu r_0 = B e^{-\kappa r_0}, \quad (1.61)$$

$$A \nu \cos \nu r_0 = -\kappa B e^{-\kappa r_0}. \quad (1.62)$$

$$\text{Eliminating } A/B \text{ gives} \quad \frac{\tan \nu r_0}{\nu} = -\frac{1}{\kappa}. \quad (1.7)$$

6 INSTABILITY OF CERTAIN NEGATIVE IONS

The roots of this equation give the proper energy values for $E < 0$. We see at once that, if $\nu r_0 < \pi/2$, there are no roots and no negative energy levels, while, if $\pi/2 < \nu r_0 < 3\pi/2$, there is one root and one energy level, and so on.

Similar considerations apply to the states with non-vanishing angular momenta. For example, it is easy to see that, if there is no energy level with zero angular momentum, there will be none with angular momentum $\sqrt{n(n+1)} \hbar/2\pi$ (n a positive integer). For an angular momentum of this magnitude introduces a centrifugal force corresponding to a potential energy $n(n+1) \hbar^2/8\pi^2 m r^2$. This additional energy, being positive, cannot give rise to a stronger binding than that of the deepest level with $n=0$.

We do not suggest that this crude model has any quantitative significance as applied to negative ions, but it illustrates the qualitative features of short-range fields.

When attempting to apply this to a survey of the possibilities of negative ion formation by the various elements we must take into account the key principle of atomic structure—Pauli's Principle. This makes it impossible for more than two electrons (with opposite spins) to occupy the same orbital quantum state and, in conjunction with the limited number of possible stationary states for the attached electron, severely restricts the number of elements which can form negative ions.

It is now possible to understand the behaviour of different atoms towards electron attachment. It is only necessary to consider which of the limited number of stationary states for the attached electron are excluded by Pauli's Principle. For the hydrogen atom no states are excluded, and a stable negative ion will result if the effective attractive field is strong enough. An electron can only be attached to a helium atom in a two-quantum state, for the one-quantum level is fully occupied. Although the effective field acting on the third electron will be greater than in hydrogen, it is unlikely to be strong enough to give two stationary states. The non-existence of He^- is thus understood.

These considerations can be extended to the other atoms of the periodic table. The general rule is that those atoms with

completely filled electron shells will be unlikely to form negative ions. For, in such cases, the attached electron must be bound in a state with total quantum number greater by one than that of the outer atomic electrons. The effective field is usually too weak to give such a stationary state.* Of the atoms with incomplete outer shells it is to be expected that those (F, Cl, Br, I) in which the shells are most nearly complete will form the most stable negative ions. For in these the outer atomic electrons are least effective in screening the nuclear charge from the extra electron. Of the four halogen atoms, fluorine should have the greatest electron affinity the attachment takes place to a shell with the lowest total quantum number.

All of these qualitative considerations are in agreement with observation, but they are not accurate enough to lead to any quantitative conceptions of the structure of negative ions. For this more detailed calculations must be carried out.

§3. Calculation of Negative Ion Structure by Quantum Methods.

The approximation we have been making in the preceding section of regarding a negative ion as a one-body problem is not adequate for our present purposes. When the electron is attached the binding energies of the atomic electrons are altered, and this may have a decisive influence on the sign of the electron affinity.† Consider the formation of a negative ion by an atom with Z electrons. The energy of the ion will differ from that of the atom by

$$-E_1 + \sum_{i=1}^Z (E_i^0 - E_i^-), \quad (1.8)$$

where E_1 is the energy of binding of the attached electron,‡

* See § 5.

† The effect is only important when the electron is attached in a state with the same total quantum number as that of the outer atomic electrons, e.g. H^- (see § 3.1).

‡ This is not the binding energy in the unmodified atomic field but in that modified by the presence of the additional electron. Further it is not the energy of an electron in the self-consistent field (§ 3.21) for the sum of these energies counts the contribution from electronic interaction twice over. We can regard E_1 for qualitative discussion as the energy in the self-consistent field corrected for this although for quantitative purposes it is not possible to regard the total energy as distributed among the various electrons in this way.

E_i^0 that of the i th atomic electron before addition of the extra electron, E_i^- that after. For the electron affinity to be positive we must have

$$E_1 > \sum_{i=1}^Z (E_i^0 - E_i^-). \quad (1.9)$$

We have discussed the conditions under which E_1 is positive in §2 but (1.9) shows that more stringent conditions must be satisfied to give a stable ion. It is impossible to argue in general terms about the magnitude of the expression on the right-hand side of (1.9), so we now proceed to describe the results of detailed calculations which have been carried out for special cases.

3.1. The Hydrogen Negative Ion.

The calculation of the electron affinity of the simplest negative ion, H^- , involves the solution of a two-body problem analogous to that of the helium atom. Because of this comparative simplicity we have reasonably accurate knowledge of its electron affinity and structure.

The detailed calculations, which have been carried out by Hylleraas,* show that the undisturbed atomic field of the hydrogen atom (see §2 (1.1) above) is not quite strong enough to produce a stable state of the ion. However, the strong interaction between the electrons in the same $1s$ level greatly modifies the charge distribution. When account is taken of this, it is found that each electron moves in an effective attractive field of sufficient intensity to give a total binding energy greater than that in the neutral atom.

The calculated electron affinity is 0.700 ± 0.015 e.volts. In fig. 2(a) the distribution of charge in the ion, derived also from Hylleraas' calculations, is illustrated.

3.11. Remarks on Hylleraas' Method. The method adopted by Hylleraas makes use of the minimal properties of the ground state wave function. The true wave function, which cannot be found exactly, is represented by an analytical approximation containing a number of parameters. These are adjusted so that the energy corresponding

* *Zeit. für Phys.* **60**, 624 (1930).

to the approximate wave function is a minimum. This minimum represents the best approximation to the true proper energy attainable with a wave function of the assumed form. By arranging the trial wave function to embody the physical features of the problem, it is possible to obtain a reasonably accurate value of the energy.

For H^- Hylleraas used the wave function

$$e^{-\alpha(r_1+r_2)} \{1 + \beta r_{12} + \gamma(r_1 - r_2)^2\}, \quad (1.10)$$

where r_1, r_2 are the distances of the two electrons from the nucleus and r_{12} from each other. The best values for the parameters were found to be, in atomic units,

$$\alpha = 0.76, \quad \beta = 0.31, \quad \gamma = 0.12.$$

The probable error of this method applied to H^- can be estimated by comparison with calculations carried out for other two-electron systems such as He , Li^+ , Be^{++} , etc., the accuracy of which can be tested by direct comparison with observed energy values.

3.2. Heavier Negative Ions.

The variation method has been extended by Ta You-Wu* to a study of the ions He^- and Li^- . He finds that the former is unstable but obtains a value of 0.54 e.volt for the electron affinity of lithium. Extension of the method to more complicated atoms is scarcely practicable in view of the computational difficulties. For these cases the only method available is that of the self-consistent field, applied so successfully by Hartree† to the structure of neutral atoms and positive ions.

3.21. Hartree's Self-consistent Field Method. It would be out of place here to discuss the complete theory of Hartree's method but a brief outline will be given.

By an iterative process of successive approximation, assisted by guesses from experience, the wave functions of each atomic electron are determined so that the whole system is self-consistent. This means that the wave function of any particular electron is the solution of the Schrödinger equation for the motion of the electron in the combined field of the nucleus and of an electron charge distribution given by the wave functions of the remaining electrons. Thus, for an atom of

* *Phil. Mag.* **22**, 837 (1936).

† *Proc. Camb. Phil. Soc.* **24**, 189 (1928).

nuclear charge Ze , the wave function $\psi(k|nl)$ for the k th electron is a solution of the Schrödinger equation

$$\nabla^2\psi(k|nl) + \frac{8\pi^2m}{h^2} \left\{ E(k|nl) + \frac{Ze^2}{r} - e^2 \sum_{i \neq k} \int \frac{|\psi(i|st)|^2}{r_{ik}} d\tau_i \right\} \psi(k|nl) = 0. \quad (1.11)$$

In carrying out the calculations the further approximation must be made of averaging the charge distribution of the remaining electrons in such a way as to give a resultant spherically symmetrical field acting on the particular electron concerned.

A refinement of Hartree's method, introduced by Fock,* takes account of electron exchange effects. This involves the determination of the self-consistent solutions of a set of simultaneous differential equations and is much more tedious to work out in practice.

When dealing with weakly bound systems, the wave functions are particularly sensitive to small changes in the field parameters. For this reason the calculations are somewhat tedious for negative ions and have been carried out in very few cases. The self-consistent field has been worked out for Cl^- including Fock's modification† and for F^- without inclusion of exchange.‡ The charge distribution in the Cl^- ion calculated in this way is illustrated in fig. 2(b). It is interesting to compare this with the charge distribution of the neutral Cl atom which has also been calculated (without inclusion of exchange) by Hartree. Reference to fig. 2(b) shows that the atom is considerably more compact than the negative ion.§

§4. Electron Affinities.

The Hartree method applied to a negative ion probably gives a close approximation to the charge distribution, but it cannot

* *Zeit. für Phys.* **61**, 126 (1930).

† D. R. and W. Hartree, *Proc. Roy. Soc. A*, **156**, 45 (1936).

‡ Brown, *Phys. Rev.* **44**, 214 (1933); D. Hartree, *Proc. Roy. Soc. A*, **151**, 96 (1935).

§ The self-consistent fields for Na^- and K^- have recently been worked out by D. R. and W. Hartree without including exchange effects (in course of publication). They find that these ions are just energetically unstable but it is probable that when exchange is included they will be found to be just stable.

be relied upon to give the electron affinity with any approach to accuracy. This is to be expected, because the electron affinity represents only the small difference between the energies of the

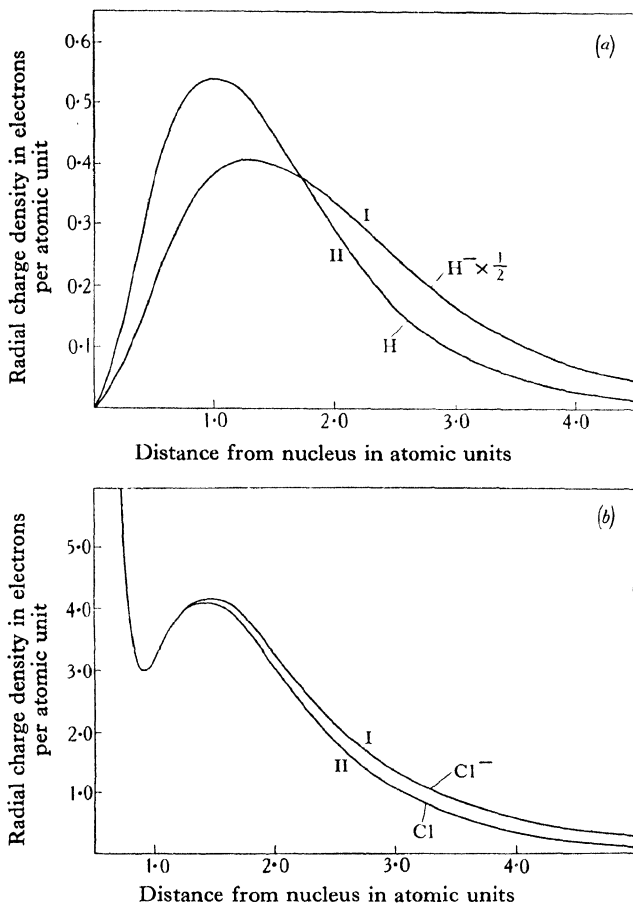


Fig. 2. Comparison of charge distributions in negative ions and the corresponding neutral atoms. (a) H^- (curve I) and H (curve II); (b) Cl^- (curve I) and Cl (curve II).

neutral atom and negative ion. The refinements introduced by the Fock method would undoubtedly improve this situation, but even in this way it is unlikely that accurate absolute calculation

of electron affinities could be carried out. On the other hand, the use of variation methods, which have been successfully applied to H^- and Li^- , is not practicable for other ions because of the prohibitive amount of numerical work involved in obtaining an accurate approximation. It is therefore most desirable to have experimental and empirical methods available for the determination of electron affinities, and such methods we now proceed to discuss.

4.1. Glockler's Empirical Method.

Glockler* has attempted to derive values of electron affinities by extrapolation of the known ionization potentials of the "stripped" atoms isoelectronic with the negative ion. He assumes a relation of the form

$$I = aZ^2 - bZ + c,$$

where I is the ionization energy of the atom of atomic number Z , and determines the constants a , b , c from the known values of I . In this way he obtains the empirical values of electron affinities listed in Table I, column E. There is very little theoretical justification for this extrapolation (particularly as Hylleraas'† calculations for two-electron systems indicate the existence of a term in $1/Z$) but it seems to give the general nature of the variation of electron affinity from element to element. The high value obtained for carbon is very suspect.

4.2. Experimental Methods.

4.21. From collisions. In Chapter III, §4, experiments are described which show that the reaction



takes place in various gases (such as O_2 , CO , H_2O , etc.). From a study of the energy relations in these reactions it is possible to determine the electron affinity of the atom Y . Refinements of experimental technique have made it possible to carry out the energy determinations with such accuracy that this method, when applicable, provides a direct and reliable means of

* *Phys. Rev.* **46**, 111 (1934).

† *Zeit. für Phys.* **60**, 624 (1930).

measuring the electron affinity. The details of its application will be deferred to Chapter III, §4.2, but we give in Table I the result obtained in this way by Lozier* for oxygen.

4.22. From Measurement of the Equilibrium Constant for Attachment Reactions. In this method the equilibrium constant of the reaction

$$X + e \rightleftharpoons X^-, \quad (1.13)$$

taking place in the neighbourhood of a hot filament, is measured. The atoms X are formed by dissociation of gas molecules X_2 by the hot filament.

If the concentrations of atoms X , electrons and ions X^- are n_0 , n_e , n_- per c.c. respectively, when equilibrium is attained, the equilibrium constant K , which is a function of the temperature T_s of the filament only, is given by

$$K = n_0 n_e / n_-.$$

Now it may be shown by the methods of statistical mechanics that†

$$K = (g_e g_0 / g_-) (2\pi m k T_s / h^2)^{\frac{3}{2}} \exp(-A / k T_s), \quad (1.14)$$

where g_0 , g_e , g_- are the statistical weights of the normal states of the atoms, free electrons and negative ions respectively, m the mass of the electron, k Boltzmann's gas constant, h Planck's constant and A the energy liberated in the reaction, i.e. the electron affinity of the atom X . Hence if K can be measured, A may be calculated. This may be done by observing the currents of electrons and of negative ions issuing from the surface. For, from kinetic theory considerations, when equilibrium is attained, the concentration n may be related to the number of particles Z of the particular species leaving the filament per sq. cm. per sec. Thus

$$Z = n(kT_s / 2\pi m)^{\frac{1}{2}},$$

giving

$$K = \frac{Z_0 Z_e}{Z_-} \left(\frac{kT_s}{2\pi m} \right)^{\frac{1}{2}}.$$

* *Phys. Rev.* **46**, 268 (1934).

† R. H. Fowler, *Statistical Mechanics*, p. 281 (1929).

Z_e/Z_- can be directly measured as the ratio of electron current i_e to negative ion current i_- proceeding from the filament. Z_0 can only be determined from the pressure of the gas X_2 which is dissociated into atoms X on striking the filament. If T_G is the gas temperature and p_{X_2} the pressure of the gas X_2 we have, on the assumption of complete dissociation at the filament,

$$Z_0 = \frac{1}{2} p_{X_2} (2\pi m_G k T_G)^{-\frac{1}{2}},$$

where m_G is the mass of a gas atom.

The determination of K then involves only the directly measured quantities i_- , i_e , p_{X_2} , T_s and T_G . It is important to remember, however, that the method assumes complete dissociation of the gas X_2 by the hot filament, and even for I_2 , the dissociation energy of which is only 1.5 e.volts, conflicting evidence* has been obtained as to the validity of this assumption. A great advantage of the method, however, is that the equilibrium constant K does not have to be measured very accurately to give a reasonably accurate value for A . Even if only half of the iodine molecules were dissociated per impact with the filament the error made in actual determinations of A would be only about 0.1 e.volt.

The two experimental methods which have been used to determine electron affinities of I and Br in this way differ simply in the method of measuring the ratio i_e/i_- . Sutton and Mayer† used the principle of the magnetron while Glockler and Calvin‡ employed space-charge effects.

In the magnetron method the apparatus consisted of a cylindrical triode with axial tungsten filament, enclosed in a coaxial solenoid, through which a current could be passed. In performing an experiment the plate and grid were maintained at positive potential with respect to the filament, iodine vapour admitted, and the plate current measured. This is effectively equal to i_e , since $i_e \gg i_-$. To measure i_- a current was then passed

* Stark and Bodenstein, *Zeit. für Elektrochemie*, **16**, 961 (1910); van Praagh and Rideal, *Proc. Roy. Soc. A*, **134**, 385 (1931).

† *J. Chem. Phys.* **3**, 20 (1935).

‡ *J. Chem. Phys.* **3**, 771 (1935).

through the solenoid to produce an axial magnetic field sufficiently large to prevent the electrons from reaching the plate. Under these conditions the plate current is equal to i_- .

TABLE I

VALUES OF THE ELECTRON AFFINITIES OF THE
ELEMENTS IN ELECTRON VOLTS

Atom	A	B		C		D	E
		1	2	1	2		
H	—	—	—	—	—	0.700	0.76
He	—	—	—	—	—	<0	-0.53
Li	—	—	—	—	—	0.54	0.34
Be	—	—	—	—	—	—	-0.57
B	—	—	—	—	—	—	0.12
C	—	—	—	—	—	—	1.37
N	—	—	—	—	—	—	0.04
O	2.2	—	—	—	—	—	3.80
O ⁻	—	—	—	-6.5	—	—	—
F	—	—	—	4.13	—	—	3.94
Ne	—	—	—	—	—	—	-1.20
Na	—	—	—	—	—	—	0.08
Mg	—	—	—	—	—	—	-0.87
Al	—	—	—	—	—	—	-0.16
Si	—	—	—	—	—	—	0.60
P	—	—	—	—	—	—	0.15
S	—	—	—	—	—	—	2.06
Cl	—	—	—	3.83	3.75	—	3.70
A	—	—	—	—	—	—	(-1.0)
Br	—	—	3.82	3.65	3.54	—	—
I	—	3.14	3.24	3.15	3.22	—	—
Hg	—	—	—	—	—	—	1.79
Ni	—	—	—	—	—	—	0.25

A, from collisions; B, from equilibrium constants of attachment reactions—1, Sutton and Mayer, 2, Glockler and Calvin; C, from energy cycles—1, from experiments only, 2, using calculated values of crystal energies; D, calculated values; E, empirical extrapolated values.

The space-charge method is based on the space-charge equation

$$\log i = \log C(e/m)^{\frac{1}{2}} + \frac{3}{2} \log V, \quad (1.15)$$

giving the space-charge limited current i between a pair of electrodes in terms of their potential difference V , a geometrical constant C and the specific charge e/m of the current carriers.

To apply this, the current i passing to the plate of a cylindrical diode *in vacuo* is measured, and, since in this case the current carriers are electrons only, e/m is known and C determined. In the presence of gas X_2 the current is transported partly by ions X^- and partly by electrons. The effective mass m of the carriers which must be used in equation (1.15) in this case may be related to the ratio i_-/i_e by the formula*

$$\frac{i_-}{i_e} = \frac{m^{\frac{1}{2}} - m_e^{\frac{1}{2}}}{m_G^{\frac{1}{2}} - m^{\frac{1}{2}}},$$

where m_e is the electronic mass, m_G that of an atom X . Knowing C , i and V , m is determined and hence i_-/i_e .

TABLE II

DETAILS OF EXPERIMENTS FOR DETERMINING
ELECTRON AFFINITY OF IODINE

Experimental method	No. of observations of A	Range of T_s , $^{\circ}\text{K}$	Range of p_{I_2} , 10^3 mm. Hg	Range of $(i_-/i_e) \times 10^4$	Range of A (e.volts)	Value of A (e.volts) (average)
Sutton & Mayer	7	1942-2072	0.13-1.84	1.07-83.6	3.06-3.23	3.14
Glockler & Calvin	13	2020-2400	0.18-30.00	1.03-163.5	2.89-3.49	3.24

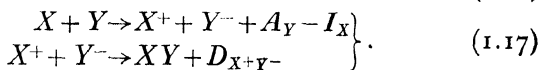
In Table II, the details of the experiments carried out in iodine by these two methods are given. The close agreement of the two sets of results obtained seems to justify the basic theoretical considerations, and there is little doubt that the values for iodine are quite accurate. Unfortunately the method has not been applied to any extent to other atoms, although Glockler and Calvin† obtained the value 3.815 ± 0.15 e.volts for the electron affinity of bromine using the space-charge method. The variation in their observed values was rather large (from 3.56 to 4.01 e.volts) and the mean value does not agree very well with that (3.55 e.volts) derived by the method described in the

* For details see Glockler and Calvin, *J. Chem. Phys.* **3**, 771 (1935).

† *J. Chem. Phys.* **4**, 492 (1936).

next section. It is not easy to see how the method could be applied to ions with small electron affinities, but its range of usefulness is probably wider than would appear from its present limited application.

4.23. From the Energy Relations involved in Cyclic Processes. The simplest illustration of this method is provided by Mayer's* determination of the electron affinity of iodine. Consider a polar molecule XY . We may regard this molecule as capable of formation in two alternative ways:

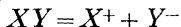


Here A_Y is the electron affinity of atom Y , I_X the ionization energy of atom X , D_{XY} the energy of dissociation of the molecule XY into atoms X , Y and D_{X+Y^-} that of dissociation into ions X^+ , Y^- .

The energies evolved in the two processes (1.16) and (1.17) must be equal, so

$$D_{XY} = D_{X+Y^-} + A_Y - I_X.$$

In certain cases all these quantities may be directly measured except A_Y , which can therefore be determined. The difficulty usually lies in measuring D_{X+Y^-} , but for the alkali halides this quantity may be found in much the same way as that described in §4.22 for determining electron affinities. The equilibrium constant of the reaction



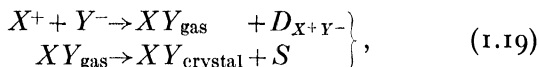
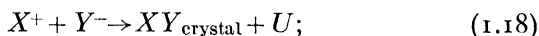
is measured in the gas phase by evaporation of the halide and electrical measurement of the percentage of ions present. From this constant D_{X+Y^-} is obtained by using the formula of statistical mechanics given in §4.22.

The values of A for the halogens found in this way are given in Table I, column C1, and are in general agreement with values found by the other methods.

* *Zeit. für Phys.* **61**, 798 (1930); see also Mayer and Helmholz, *J. Chem. Phys.* **2**, 245 (1934).

18 AFFINITIES FROM CRYSTAL ENERGIES

This method can be used only for a few atoms. An alternative method, which is potentially of greater applicability, consists in determining $D_{X^+Y^-}$ by use of a combination of theory and experiment involving consideration of the energy relations concerned in the formation of a crystalline solid from ions X^+ , Y^- . This may be carried out in two ways:



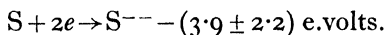
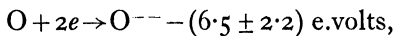
where U is the lattice energy and S the heat of sublimation per molecule XY of the crystal. The equivalence of the energy evolution in processes (1.18) and (1.19) gives

$$D_{X^+Y^-} = U - S.$$

S may be determined experimentally, but U can be determined only by calculation from the properties of the ions X^+ , Y^- . Consistency is the principal test of the validity of the results obtained in this way: the electron affinities deduced from crystals containing the same anion but different cations should be the same.

In illustration, we may consider the deduction of the electron affinity of fluorine from the properties of the alkaline fluorides.* The values obtained range from 4.07 e.volts derived from CsF to 4.19 e.volts from NaF, indicating a reasonably high accuracy for the method. Other values obtained for the halogens are given in Table I.

An interesting application of the method was made by Mayer and Maltbie† to estimate the second electron affinities of O and S from the alkaline earth oxides and sulphides. They obtained the values



We can summarize the results of the various methods, both experimental and theoretical, by saying that the electron affinities of H, O and I are the most accurate known, while those of

* Mayer and Helmholtz, *Zeit. für Phys.* **75**, 19 (1932).

† *Zeit. für Phys.* **75**, 748 (1932).

the other halogens are probably also known with fair accuracy. Of the remaining elements our knowledge is largely the result of extrapolation of empirical data, and as such is untrustworthy.

§5. Excited States of Negative Ions.

We have already noted (§1) the general result that the number of stable negative energy quantum states of a negative ion is not infinite. The small binding energy of the attached electron in its ground state makes it most unlikely that any stable discrete excited states exist with appreciable binding energy. This may be largely confirmed by a determination of the number of negative energy states existing in the unmodified atomic field, for neglect of the disturbance of the atomic electrons is not likely to be serious for an excited state of appreciable binding energy; an electron in such a state spends only a small portion of its time in the neighbourhood of the electron shells of the neutral atom and exerts only a small perturbing influence on them. When the calculations are carried out for fluorine it is found that even the ground $2p$ state of F^- exists only when account is taken of reorganization of the atomic electrons,* so, *a fortiori*, there exist no stable discrete states.

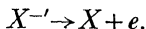
This does not apply to excited states with very small negative energy, for the existence or otherwise of such states depends in a very sensitive manner on the behaviour of the field acting on the electron at quite large distances from the atom. In practice such low energy states are indistinguishable from the low energy states of the positive energy continuum and can, for most purposes, be regarded as non-existent.

5.1. Negative Ion Formation by Excited Atoms.

As our arguments have been applied only to singly excited states of the ions we must consider the possibility of an excited atom forming a stable ion by electron attachment. Such a system would correspond to a doubly excited state of the ion.

* Brown, *Phys. Rev.* **44**, 214 (1933).

It is very probable that attachment to an excited atom can lead to a decrease of total energy. For example, Ta You-Wu* has shown by a variation method that electron attachment to a helium atom in a $2s^2$ state leads to a decrease of energy of as much as 33 e.volts. Nevertheless, ions of this type can be of little practical importance as they will usually dissociate rapidly by a process of autoionization, i.e.



For this to occur it is only necessary that the energy of the excited ion $X^{-'}$ be greater than that of the normal atom X . This requires that the electron affinity of X' be less than the energy of excitation which gives X' , a condition which is practically always fulfilled.

§6. Doubly-charged Negative Ions.

There is no experimental evidence of the existence of such ions in the gas phase and they are probably very unstable in all cases.

The small values of the electron affinities for attachment of single electrons make it improbable that a second electron could also be attached with decrease of energy. It seems possible at first sight that the lifetime of a doubly-charged ion may be quite large despite this increase of energy on attachment. For the effective field of force acting on the attached electron will be attractive at small distances and, changing sign at intermediate distances, will fall off finally according to Coulomb's Law; a state of affairs exactly analogous to that existing in atomic nuclei. This analogy with nuclei then suggests the possibility of existence of a positive energy "virtual" level for the second attached electron, with a considerable lifetime due to slow leakage of the electron through the Coulomb potential barrier. The height of this barrier for O^{-} is probably about 8 e.volts and occurs at a distance of about 1.5 A.U. from the nucleus.

* *Phil. Mag.* **22**, 837 (1936).

From these values the "half-value periods" for O^{--} may be calculated for different virtual levels. The values found are 10^{-10} , 10^{-12} and 10^{-15} sec. for virtual energy levels of 1, 2 and 4 e.volts respectively. Since it is very unlikely that a virtual level lies below 1 e.volt (cf. §4.23 and Table I, column C) the chance of observing doubly-charged negative ions in the gas phase is extremely remote.

Chapter II

NEGATIVE MOLECULAR IONS

§1. Introduction—Electron Affinity and Vertical Detachment Potential.

When discussing the structure of negative ions formed by molecules the motion of the nuclei must be taken into account. Since the electronic motion is much faster, we can, as a first approximation, regard the nuclei as at rest and calculate the energy of a particular electronic state for various relative positions of the nuclei. This energy can then be regarded as nuclear potential energy for the calculation of the levels of the nuclear motion. Corresponding to a given electronic state there will then be a series of vibrational and rotational nuclear states. In higher approximations the effect of the nuclear motion on the electron states must be taken into account (see Chapter III, §2), but for most descriptive purposes these can be neglected. The usual graphical method of representing molecular states is illustrated in fig. 3. In (a) the electron motion gives rise to a potential-energy curve with a minimum. The limit for infinitely separated nuclei is the sum of the energies of the atoms into which the molecule dissociates on adiabatic separation of the nuclei. The nuclear states form a discrete set tending to a limit at this energy, above which they form a continuum. They are indicated by the level lines such as *ab*, *cd* in fig. 3(a). In fig. 3(b) the potential energy curve has no minimum and the nuclear levels form only the continuum shown.

To the accuracy of our approximation the wave function for a given molecular state can be expressed as the product

$$\phi(r, R) \psi(R), \quad (2.1)$$

where $\phi(r, R)$ is the electronic wave function for fixed values R of the nuclear co-ordinates and $\psi(R)$ is the nuclear wave function representing motion with the effective potential energy arising

from the electron motion. The wave functions $\psi(R)$ are large only in the regions of allowed classical motion. Thus, for the vibrational level represented by ab in fig. 3(a), $\psi(R)$ is concentrated between a and b and is very small outside these limits. For a state in the energy continuum $\psi(R)$ is negligible inside the classical closest distance of approach and oscillates rapidly outside this distance. These forms for $\psi(R)$ are illustrated diagrammatically in fig. 3.

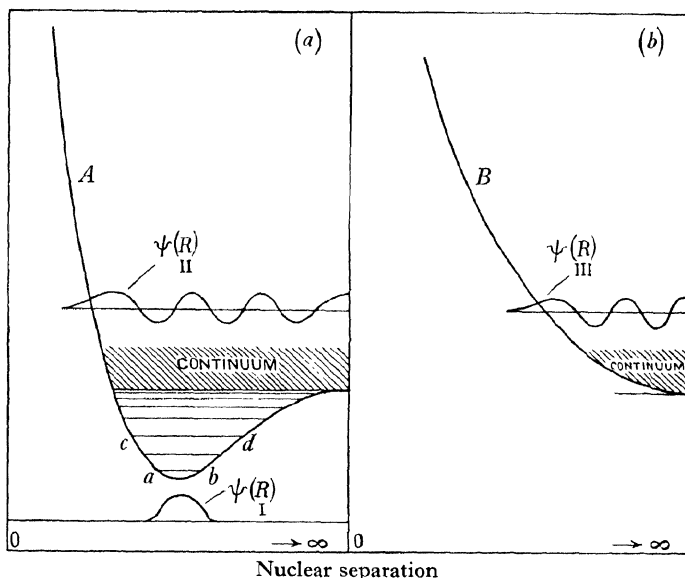


Fig. 3. Graphical representation of molecular states. A, B Effective potential energy curves. $\psi(R)$ Vibrational wave functions: I corresponding to level ab ; II, III corresponding to states of the continuum.

If a molecule is excited to a state in which the nuclear energy level lies in the continuum, the relative motion of the nuclei is no longer confined within definite limits and the molecule dissociates.

In discussing a transition between states of a molecule we must take into account the change in the nuclear motion. Thus the energy necessary to produce such a transition depends on the behaviour of the nuclei. When we talk about the electron

24 ELECTRON AFFINITIES OF MOLECULES

affinity of a molecule, we are comparing the energy of a neutral molecule with that of the molecule formed when an extra electron is added. To make this definite we must include a specification of the nuclear states of the two molecules, so we define the electron affinity as the excess energy possessed by the neutral molecule over that of the molecular ion when both are in their normal electronic and nuclear states. This does not mean that the energy necessary to detach an electron from the molecule is equal to this electron affinity, for the detachment process may not involve a transition to the normal nuclear state of the neutral molecule. In many cases, as we shall see in Chapter III, §2.11, the nuclear separation will remain unchanged in the detachment process, and the energy required will be that necessary to produce a transition from the normal state of X_2^- to the ground electronic state of X_2 without change of nuclear separation. We call this the vertical detachment energy of X_2^- in view of its analogy to the vertical ionization energy of a normal molecule, a conception introduced by Mulliken.* Except in very special cases the vertical detachment energy will not be equal to the electron affinity (see fig. 4, on which these quantities are marked for H_2^-).

§2. Enumeration and Properties of the Electronic States of Diatomic Molecules.†

Before discussing the structure of some of the simpler molecular ions we must digress to describe briefly the nomenclature of electronic states of diatomic molecules and their classification as stable or unstable.

We adopt the molecular orbital method for this purpose as it is most convenient to use. The electrons in a molecule are each assigned to separate quantum states or orbitals. These orbitals are distinguished by three quantum numbers and at most two electrons, with opposing spins, can be assigned to each.

One of the quantum numbers refers to the angular momentum of the electron round the nuclear axis. Orbitals in which this angular

* *Phys. Rev.* **46**, 549 (1934).

† For further details see van Vleck and Sherman, *Rev. Mod. Phys.* **7**, 167 (1935).

momentum is 0, ± 1 , ± 2 , ... quantum units are designated σ , π , δ , ... states. The remaining two quantum numbers cannot be simply specified in the same way as for atoms. Instead it is usual to give the quantum states of the separated atoms from which the orbitals are derived, or those of the "united" atom to which they tend when the nuclear separation tends to zero. The notation usually adopted is to write the designation of the atomic states of the separated atoms after the σ , π , δ , ..., that for the united atom before. Thus the orbital $2p\sigma$ of a molecule XY is one with zero angular momentum about the nuclear axis which, in the limit of vanishing nuclear separation, tends to the $2p$ state of the united atom. The designation $\sigma 2p^\times$, on the other hand, refers to a σ orbital which is derived from the $2p$ state of the atom X . For homonuclear molecules, each state of the separated atom gives rise to two molecular states, one symmetrical with respect to the nuclei, the other antisymmetrical. These are distinguished by the suffixes g , u .

The complete electronic state of the molecule is then specified by giving the number of electrons occupying each orbital, the total angular momentum of the system about the nuclear axis, and, for a homonuclear molecule, the nuclear symmetry of the whole. Capital Greek letters Σ , Π , Δ , ... are used to specify the total angular momentum about the nuclear axis. A Σ state of a homonuclear molecule may be either symmetrical or antisymmetrical with respect to the mid-plane through the nuclei. These are distinguished as Σ^+ , Σ^- respectively.

We note that a σ orbital can accommodate at most two electrons with opposite spin but a π orbital can take four (two for angular momentum $+1$ unit, two for angular momentum -1 unit). As an example of the nomenclature we have, for the ground state of O_2 ,

$$(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^4 (\pi_g 2p)^2 \Sigma_g^+,$$

the K electrons of each atom being supposed to play no part in the structure of the molecule as such. The indices give the number of electrons in each orbital.

The advantage of this method of describing molecular states lies chiefly in the possibility of classifying given orbitals as bonding, anti-bonding or inactive. Bonding orbitals tend to assist molecule formation and usually arise from a state of the separated atoms having the same total quantum number as that of the united atom (non-promoted orbitals). Antibonding orbitals tend to oppose combination of the atoms and usually arise from a state of the separated atoms with total quantum number less, by one or more, than that of the united atom (promoted orbitals). Inactive orbitals have little effect either way.

26 NEGATIVE MOLECULAR ION OF HYDROGEN

For homonuclear molecules formed by atoms in the first row of the periodic table the order of the states is

$$(\sigma_g 2s)^2, (\sigma_u 2s)^2, (\sigma_g 2p)^2, (\pi_u 2p)^4, (\pi_g 2p)^4, (\sigma_u 2p)^2.$$

The s shells of the separated atoms play little part in the binding of such molecules as N_2 , O_2 , etc. and we will not concern ourselves any further about orbitals arising from them. Of the remaining states $\sigma_g 2p$ and $\pi_u 2p$ are bonding, $\pi_g 2p$ and $\sigma_u 2p$ strongly antibonding, the latter particularly so. From the number of bonding and antibonding orbitals which make up a given molecular state, a good idea of the nature of the corresponding nuclear potential-energy curve may be obtained. An excess of bonding orbitals will usually give a curve with a minimum (stable state) while an excess of antibonding orbitals will have the reverse effect.

§3. Structure of Simple Negative Molecular Ions.

3.1. H_2^- .

This molecule presents a three-electron problem exactly analogous to that of He_2^+ . The ground state is the

$$(1s\sigma_g)^2 (2p\sigma_u) \Sigma_u'$$

state involving two bonding and one antibonding orbital. As a result we expect only a weakly bound molecule (compared with H_2 for which the ground state is $(1s\sigma_g)^2 \Sigma_g'$ with no antibonding orbital) and this is confirmed by detailed calculations due to Eyring, Hirschfelder and Taylor.* They applied a variation method of exactly the same type as that made use of by Pauling† for He_2^+ and obtained the potential-energy curve for the ground state illustrated in fig. 4. The corresponding curve for the ground state of H_2 is also illustrated in the figure, and we see that the electron affinity of H_2 according to our definition is about -2.4 e.volts and the vertical detachment energy about $+0.65$ e.volt. This is an extreme case, where the great difference in the equilibrium nuclear separation between the ion and neutral molecule leads to markedly different values for the two energies, and is unlikely to be a general result.

* *J. Chem. Phys.* **4**, 479 (1936). † *J. Chem. Phys.* **1**, 56 (1933).

3.2. O_2^- .

This molecule is of particular interest in connection with the collision processes discussed in Chapter III, §§ 4.2, 6.1. Its ground state will have the electron configuration

$$(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^4 (\pi_g 2p)^3 \Pi_g.$$

This differs from that of O_2 in possessing an additional electron in the antibonding $(\pi_g 2p)$ state and so a weaker binding would

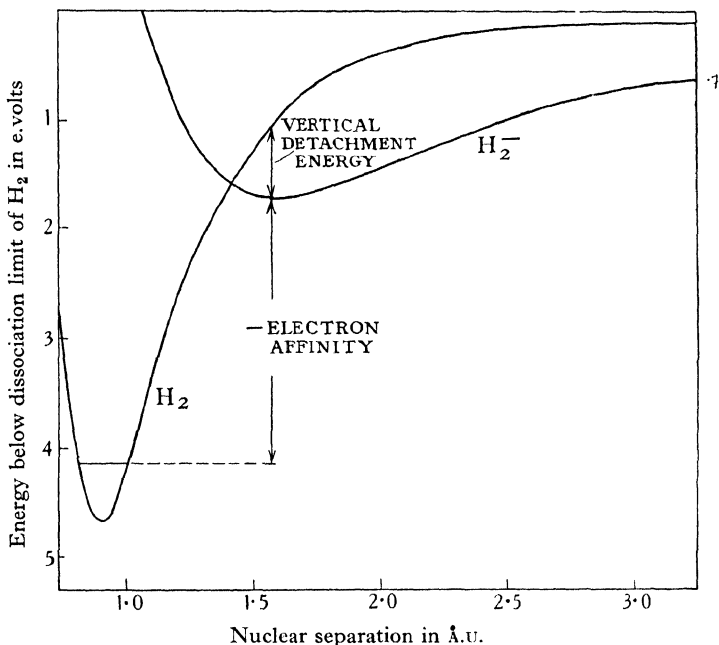
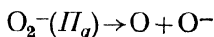


Fig. 4. Potential-energy curves for H_2^- and H_2 .

be expected. Owing to the lack of knowledge of both the iso-electronic molecules F_2^+ and FO we cannot make any reasonably accurate prediction of the value of the binding energy. Rough estimates based on the trend of the dissociation energy in proceeding from N_2 , NO to O_2 and from I_2 to Cl_2 would suggest about 4.0 e.v. dissociation energy for FO. That of the Π_g

state of O_2^- is possibly lower than this because of the "flitting" effect of the attached electron. The state $O-O$ is in exact energy resonance with OO^- , and this leads to a lowering of the energy of the Π_g state and a raising of that of the Π_u (this is the state which has the same configuration as Π_g but with $(\pi_u 2p)^3 (\pi_g 2p)^4$ instead of $(\pi_u 2p)^4 (\pi_g 2p)^3$). It is the same effect as that which leads to a stable H_2^- molecule even though the isoelectronic molecule HeH is unstable.

It is therefore possible that the energy of the dissociation



is nearly as large as that (5.09 e.volts)* of O_2 into normal O atoms, but our ignorance of the bonding effects of electrons in negative ions is so great that we cannot be at all certain of this (see Chapter III, §6.1). If it is correct, then the equilibrium nuclear separation will be about the same as for O_2 though possibly slightly less.

The next lowest level of O_2^- will be the Π_u state, which should have a dissociation energy considerably less than that of Π_g because of the "flitting" effect. As a consequence of this the equilibrium nuclear separation will be greater.

Next above the Π states will probably lie the Σ_u state with configuration

$$(\sigma_g 2s)^2 (\sigma_u 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^4 (\pi_g 2p)^2 (\sigma_u 2p),$$

which, owing to the strong antibonding character of the $(\sigma_u 2p)$ orbital, is probably repulsive.

We have attempted to represent the probable forms of the potential-energy curves of these three lowest states in fig. 5, the curve for the ground state of O_2 being also included. This assignment of potential-energy curves becomes important in the formation of negative ions by electron collision and will be discussed in that connection in Chapter III, §§4.2, 6.1.†

* Sponer, *Molekulspektren-Tabellen*, Springer (1935), p. 17.

† The results described in these sections have been taken into account in drawing the curves of fig. 5.

3.3. F_2^- , Cl_2^- , Br_2^- , I_2^- .

The electronic structure of the ground state of a typical member of the series, F_2^- , is

$$(\pi_u 2p)^4 (\pi_g 2p)^4 (\sigma_u 2p) \Sigma_u.$$

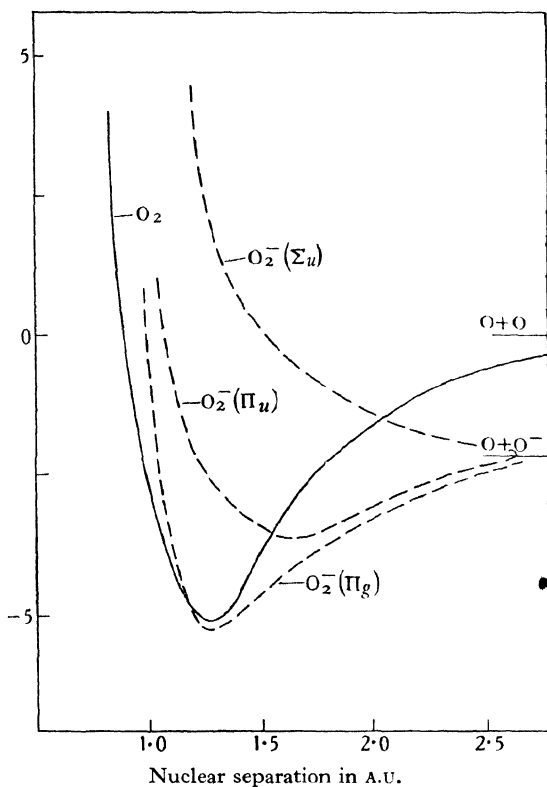


Fig. 5. Possible form of potential-energy curves for the three lowest electronic states of O_2^- .

Owing to the strong antibonding character of the $(\sigma_u 2p)$ orbital these molecules will be much less stable than O_2^- or S_2^- and probably are less so than the neutral halogen molecules. Nevertheless, from our knowledge of the dissociation energies of the neutral molecules, and of the electron affinity of the halogen

atoms, it is certain that, at least, Cl_2 , Br_2 and I_2 have positive electron affinities. This may be seen as follows. The potential-energy curves of the molecular ions will approach their limiting forms for infinite nuclear separation from below, because of polarization and van der Waals forces. Even though the major part of the potential-energy curve is repulsive it must therefore have a minimum, however small, corresponding to a stable X_2^- molecule. The electron affinity of X_2 as we have defined it (see §1) is given by

$$A_{X_2} = D_{X_2^-} - D_{X_2} + A_X,$$

where $D_{X_2^-}$ is the energy of dissociation of X_2^- into X and X^- , D_{X_2} that of X_2 into $2X$ and A_X the electron affinity of the atom X . Now for I_2 , Br_2 and Cl_2 (and probably also for F_2) $A_X > D_{X_2}$,* and so, since $D_{X_2^-}$ is positive even if very small,† A_{X_2} must be positive. For example, the electron affinity of I_2 must be greater than 1.8 e.volts ($A_{\text{I}} = 3.22$ e.volts, $D_{\text{I}_2} = 1.5$ e.volts). The vertical detachment energy may be either greater or less than this.

Other states of the molecules X_2^- which dissociate into normal X and X^- will be

$$(\pi_u 2p)^4 (\pi_g 2p)^3 (\sigma_u 2p)^2 \Pi_g; (\pi_u 2p)^3 (\pi_g 2p)^4 (\sigma_u 2p)^2 \Pi_u,$$

which are probably some e.volts higher than the ground Σ state for nuclear separations comparable with the equilibrium values for the respective neutral molecules.

* For values of D_{X_2} see Sponer, *Molekulspektren-Tabellen*, Springer (1935), p. 19.

† See Chapter III, §4.3, however.

Chapter III

MODES OF FORMATION OF NEGATIVE IONS

In this chapter we consider the processes which lead to negative-ion formation. We will not restrict ourselves to those which have been already observed experimentally, but make use of the results both of theory and experiment.

§1. Capture of Free Electrons by Neutral Atoms.

The simplest manner in which negative ions can be formed is by the direct capture of a free electron by a neutral atom. If the electron has a kinetic energy T before the encounter and the electron affinity of the atom is A , an amount of energy $T + A$ is released by the capture and must be dissipated in some way. This may occur by radiation or by transmission of the surplus energy to a third body. The different nature of these two methods makes it necessary to give them separate consideration.

1.1. Radiative Capture of Electrons—Electron Affinity Spectrum.

We have given reasons for believing that there is only one negative energy electronic state of a negative ion, so the capture of electrons by a neutral atom will give rise to a continuous emission spectrum extending indefinitely from a long wave limit at

$$\lambda = hc/A.$$

The order of magnitude of the probability of emission of a light quantum on collision may be estimated in the following way. The time taken for a 10 e.volt electron to traverse the atomic field is about 10^{-15} sec. During this period it will have about

the same chance of radiating as a bound electron in an excited (non-metastable) state of an atom, i.e. about 10^8 per sec. The total chance of radiation is therefore about 10^{-7} per collision and is very small. This result is confirmed by detailed calculations which we now describe.

The intensity of emission by a radiating electric dipole is given in quanta per second by

$$\frac{64\pi^4 e^2 \nu^3}{3hc^3} |\mathbf{M}|^2, \quad (3.1)$$

where $\mathbf{M}$ is the amplitude of the oscillating electric moment, ν the frequency of the oscillations and e , h , c have their usual significance. For an atomic system where the radiation arises from a transition of an electron from state m to state n , $\mathbf{M}$ will be the value of the electric displacement $\mathbf{r}$ measured from the nucleus of the atom and averaged over the wave functions ψ_m , ψ_n of the initial and final states, i.e.

$$\mathbf{M} = \int \psi_m^* \mathbf{r} \psi_n d\tau. \quad (3.2)$$

To apply this formula to our particular problem in which the initial state is not a discrete stationary state but one of the continuous energy spectrum, we must be careful to normalize the wave function ψ_m correctly. We wish to obtain finally a formula which will give the intensity of radiation $I_\nu d\nu$ with frequency between ν and $\nu + d\nu$ emitted per unit volume of a gas containing n_0 atoms per unit volume due to capture of electrons from a swarm with a given velocity distribution. If we normalize ψ_m to represent a stream of electrons of such intensity that one electron crosses unit area normally per second, and ψ_n to represent unit density as usual, the resulting value of $\mathbf{M}$ will give, on substitution in (3.1), the number of transitions produced per second per atom by such a stream of electrons. But, if capture were to take place when an electron hits a target of cross-section Q_a^r , the unit stream would just produce Q_a^r transitions per atom per

second. We therefore call this quantity the effective cross-section $Q_a^r(v)$ for radiative capture of electrons of velocity v . Then

$$I_\nu dv = n_0 h\nu Q_a^r(v) v N(v) dv, \quad (3.3)$$

where $N(v) dv$ is the number of electrons per unit volume with velocities between v and $v + dv$.

The calculation of $Q_a^r(v)$ for a given atom involves a knowledge of the wave functions for the motion of electrons with positive energy $\frac{1}{2}mv^2$ in the atomic field and also of the wave function for the stationary state of the electron when attached in the ion. The azimuthal quantum number of this stationary state has a marked influence on the form of the cross-section Q_a^r for low electron velocities. If the state is a p -state, apart from certain exceptional cases unlikely to arise in practice, Q_a^r behaves like v^{-1} for small v , but if it is an s -state it behaves like v . The reason for this difference may be understood in qualitative terms as follows.

Applying the usual selection rules for radiation we see that, for an electron to be captured into a p -state, it must be initially in either an s - or d -state, but for capture into an s -state it must be initially in a p -state. To avoid confusion we will henceforth distinguish the initial state by a suffix i , so an s_i electron refers to an electron initially in an s -state. Now s_i and p_i electrons differ in that the former possess zero angular momentum about the atomic nucleus while the latter possess an amount $2^{\frac{1}{2}}\hbar/2\pi$. As a consequence s_i electrons make head-on collisions at all velocities, whereas p_i electrons, when possessing a velocity v , pass the nucleus on the average at a distance $r_0 = 2^{\frac{1}{2}}\hbar/2\pi mv$. At low velocities the p_i electrons will therefore hardly penetrate the atomic field at all but s_i electrons will do so at all velocities. The overlap of the function ψ_m with ψ_n , which is only large in the neighbourhood of the atom, will therefore be small for low-energy p_i electrons but will not change much with energy for s_i electrons. We may represent this effect by introducing a factor into $\mathbf{M}$, $f(r_0/a)$, where a is a length of atomic magnitude, and f

is a function which tends to zero when r_0 tends to infinity, i.e. when v tends to zero. Finally we must introduce a factor v^{-1} for all electrons because the cross-section will be directly proportional to the time spent in the atomic field. This gives

$$Q_a^r = Av^{-1} \text{ for } s_i \text{ electrons, i.e. capture to a } p\text{-state,} \\ = v^{-1} \left\{ \begin{array}{l} |f(r_0/a)|^2 \\ |g(v)|^2 \end{array} \right\} \text{ for } p_i \text{ electrons, i.e. capture to an } s\text{-state,} \quad (3.4)$$

where A is practically independent of v , and g is an increasing function of v which vanishes when v tends to zero.

A more detailed proof may be given as follows. The wave function ψ_m may be expanded in the form

$$\psi_m = \sum_l F_l(r) P_l(\cos \theta). \quad (3.5)$$

For a completely free electron ψ_m (properly normalized) is a plane wave $v^{-\frac{1}{2}} \exp(ikr \cos \theta)$, where $k = 2\pi mv/h$, and then

$$F_l(r) = \left(\frac{\pi}{2krv} \right)^{\frac{1}{2}} i^l (2l+1) J_{l+\frac{1}{2}}(kr) \\ = \left(\frac{\pi}{v} \right)^{\frac{1}{2}} \frac{(ikr)^l}{2^{l+1} \Gamma(l+\frac{3}{2})} \left\{ 1 - \frac{k^2 r^2}{2 \cdot 2l+3} + \dots \right\} \text{ for small } kr. \quad (3.6)$$

At low velocities v , the influence of the atomic field on the wave functions $F_l(r)$ for $l > 0$ tends to zero* and so the form (3.6) may be used for all but s_i electrons. For these we must take a function

$$F_0(r) = v^{-\frac{1}{2}} G_0(r),$$

where $G_0(r)$ does not vary much in form with velocity. Then we have:

(a) For capture of p_i electrons into an s -state

$$\psi_n = \phi_s(r) \text{ is very small for } r > a, \\ |\mathbf{M}| = \int_0^\infty F_1(r) \phi_s(r) r^3 dr. \quad (3.7)$$

Since ka will be small we may use the series expansion (3.6) for $F_1(r)$ giving

$$|\mathbf{M}| = \frac{8\pi^2 m}{h} v^{\frac{1}{2}} \int_0^\infty r^4 \phi_s(r) dr, \quad (3.8)$$

tending to $Cv^{\frac{1}{2}}$ as $v \rightarrow 0$. Q_a^r therefore behaves as v .

* See Mott and Massey, *Theory of Atomic Collisions*, Oxford Univ. Press (1933), pp. 25-8.

(b) For capture of s_i electrons into a p -state

$$\psi_n = \phi_p(r) \begin{cases} \cos \theta, \\ 2^{-\frac{1}{2}} \sin \theta e^{\pm i\phi}, \end{cases}$$

$$|\mathbf{M}| = \frac{4\pi}{3} v^{-\frac{1}{2}} \int_0^\infty G_0(r) \phi_p(r) r^3 dr. \quad (3.9)$$

The integral is practically independent of velocity and so $|\mathbf{M}|^2$ and hence Q_a^r behave like v^{-1} .

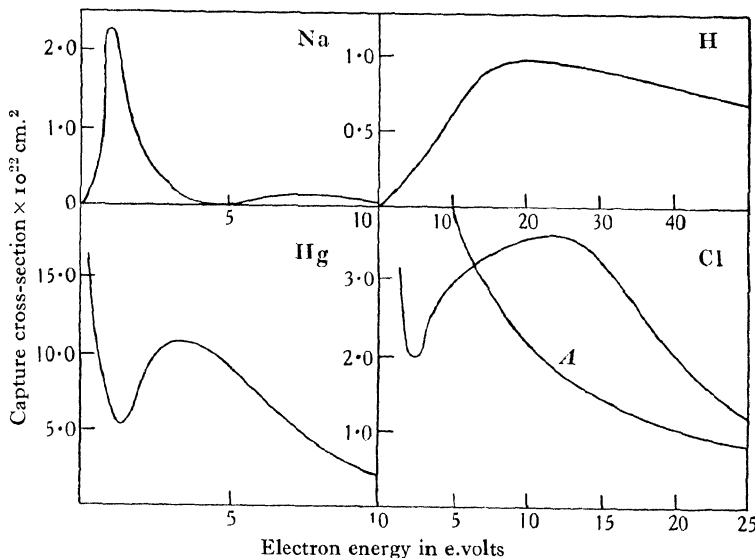


Fig. 6. Cross-sections for capture of electrons by neutral atoms. Curve A gives, for comparison, the cross-section for capture into the $1s$ -state of H (i.e. for capture by H^+).

To carry out detailed calculations the wave functions ψ_n may be obtained by numerical or mechanical solution of the wave equation for the electron moving in the atomic field and ψ_m from calculations of the self-consistent field type for the negative ion. In fig. 6 the capture cross-sections for two cases (H and Na) where the ionic state is an s -state and two (Hg , Cl) where it is a p -state are illustrated.* In all cases it will be seen that the

* Massey and Smith, *Proc. Roy. Soc. A*, **155**, 472 (1936).

order of magnitude of the cross-section (from 10^{-8} to 10^{-7} of that for elastic collisions) is that expected from our qualitative arguments, as is also the variation with velocity at low velocities. For Hg and Cl the low-velocity attachment arises from capture of s_i electrons, the secondary maximum being due to d_i electron capture.

It is of interest to compare these cross-sections with those corresponding to capture of electrons into the ground state of positive ions such as H^+ (see fig. 6). The order of magnitude is very much the same at energies above 5 e.volts, but for smaller energies the cross-section for recombination of an electron with a positive ion tends to infinity as v^{-2} in contrast to the variation as v^{-1} characteristic of capture into a p -state of a negative ion.*

Considerable importance is attached to the possibility of experimental confirmation of these results. All attempts made so far to observe the radiation emitted on capture of an electron by a neutral atom, the affinity spectrum, have been fruitless, but the experimental difficulties are very great. Two recent attempts to detect the affinity spectrum of iodine have been made by Oldenberg† and by Emeléus, Minnis and Miss Cathcart.‡ In Oldenberg's experiments the conditions which have been found most suitable for production of recombination spectra were imitated as closely as possible, and three methods were tried. These were:

(a) *Hollow Cathode Method.* The spectrum emitted from the inside of the hollow cathode of a discharge tube containing highly dissociated iodine (iodine vapour heated to $1000^\circ C.$) was examined. With pressures up to 8 mm. Hg and currents up to 70 milliamperes no affinity spectrum could be observed.

(b) *Positive Column in a Mixture with Helium.* Helium was added to a pressure of 7 mm. to the atomic iodine and the positive column projected "end-on" on the slit of the spectrograph. For iodine pressures ranging from 0.2 to 1.1 mm. no positive result was obtained.

* Morse and Stueckelberg, *Phys. Rev.* **36**, 16 (1930).

† *Phys. Rev.* **43**, 534 (1933).

‡ *Proc. Roy. Ir. Acad.* **44**, 11 (1937).

(c) *Glowing Filament Method.* The spectrum in the neighbourhood of a glowing tungsten filament in the dissociated iodine vapour was examined without result.

It is not possible to decide whether these negative results are at all in contradiction with the theoretical considerations we have just described, for the discharge conditions in Oldenberg's experiments are not known in sufficient detail. The experiments of the other three investigators were made under definite electrical conditions and it may be shown that a positive result would not have been expected from their work. The method used was to examine the light emitted from the ribbon-like positive column of a steady direct-current discharge and from other steady discharges through iodine vapour. The electrical conditions in certain of these discharges in iodine have been thoroughly investigated by Spencer-Smith* and calculation of the maximum yield of quanta due to electron capture may be carried through as follows. We use the formula (3.3) for the intensity of radiation emitted and take as first approximation for $N(v)$ the Maxwellian form,

$$N(v) = 4\pi N_e \left(\frac{m}{2\pi k T_e} \right)^{\frac{3}{2}} v^2 e^{-mv^2/2kT_e},$$

where T_e is the effective electron temperature. Assuming complete dissociation of the iodine and approximate equality of the values of Q_a^r for chlorine and iodine, the maximum number of

TABLE III

Position in discharge	Pressure in mm. Hg	Current density in amperes per cm. ²	Electron temp. in volts	Electron concentration per c.c.	Quanta per sec.
Negative glow	0.18	3.0×10^{-5}	1.5	1.2×10^8	6.0×10^7
Top of positive column	0.18	3.0×10^{-5}	4.5	1.2×10^7	4.0×10^6
Positive column	0.50	4.6×10^{-5}	13.5	3.5×10^7	2.0×10^7

* *Phil. Mag.* **19**, 806 (1935).

quanta per second emitted in a range $dE = 0.01$ e.volt (corresponding to $d\nu = 81 \text{ cm.}^{-1}$) are given for various regions of the discharge in Table III.

Using a Hilger small quartz spectrograph with a slit width of $1/50$ mm. these values would give rise at most (absorption being neglected) to a flux of 10^3 quanta per sq. cm. per sec. At a wavelength of 3000 A.U. this would require an exposure time of at least 20 hours, with even a sensitive photographic emulsion, so it is not difficult to understand the failure of this attempt to detect the spectrum. In Oldenberg's experiments the iodine was thermally dissociated and higher current densities were employed, so it is not possible to say at once that his negative results would also be anticipated. Further experimental work in this direction, using definite discharge conditions, is clearly very desirable.

1.2. Capture of Electrons in Three-Body Collisions.

We can describe the probability of this process in terms of an effective cross-section Q_a^t per unit concentration (in numbers per c.c.) of the third body. The order of magnitude of Q_a^t may be determined by arguments based on information concerning two-body collisions.

The third body (electron, atom or molecule) will be effective in absorbing the energy provided it makes an effective collision with the capturing atom when the latter is at a distance $R_0 \simeq 10^{-8} \text{ cm.}$ (the atomic radius) from the electron. If λ is the mean free path for effective collisions between the atom and third body when the concentration of the latter is unity, then this chance is very nearly*

$$\frac{R_0}{\lambda},$$

giving
$$Q_a^t \simeq \pi R_0^2 \frac{R_0}{\lambda}.$$

It remains to estimate λ . As this will vary considerably with the nature of the third body, it is necessary to consider two cases separately.

* See also Chapter IV, §7.

(a) *Electrons as "Third Bodies"*. The effective cross-section for energy transfer between an electron and an atom is of the order 10^{-16} cm.²,* so

$$\lambda \simeq 10^{16} \text{ cm.},$$

$$Q_a^t \simeq 10^{-40} \text{ cm.}^5$$

As the electron concentration n_0 per c.c. necessary to produce the same number of non-radiative attachments per second as radiative is given by Q_a^r/Q_a^t , we find that n_0 must be as great as 10^{18} per c.c. This is an impossibly large concentration for practical realization.

(b) *Atoms and Molecules as "Third Bodies"*. The efficiency in this case depends on whether or not the energy transferred is absorbed wholly as potential energy of the third body. In the first case the energy transfer is a resonance one and the cross-section for such transfer between atomic systems is known to be quite large. Values up to 10^{-14} cm.²† or even greater may occur, giving

$$\lambda = 10^{14} \text{ cm.},$$

$$Q_a^t = 10^{-38} \text{ cm.}^5$$

It is therefore possible that concentrations as low as 10^{16} per c.c. of "third bodies", capable of resonant absorption, may be as effective in producing electron attachment as radiative processes.

If resonant transfer is not possible the excess energy must be partly taken up as kinetic energy of the relative motion of the atomic systems and the corresponding effective area is known to be quite small.‡ λ may be 10^{18} cm. or more and a concentration of 10^{20} per c.c. or more may be necessary to give attachment comparable with that accompanied by radiation.

From these considerations it is clear that molecules, possessing several internal degrees of freedom, will be most effective as third bodies although it is not always easy to transfer energy to vibrational motion within the molecule.§

* Mott and Massey, *Theory of Atomic Collisions*, Oxford Univ. Press (1933), p. 178.

† *Ibid.* p. 178.

‡ *Ibid.* pp. 243-7. See also §8.1 of this chapter.

§ *Ibid.* p. 249.

Detailed confirmation of certain of the above arguments has been provided by calculations carried out by R. A. Smith* for attachment in which the third body is an electron. He finds values of the order 10^{-40} to 10^{-41} cm.⁵ for Q_a^t in reasonable agreement with our estimate of 10^{-39} to 10^{-40} cm.⁵ No detailed calculations have yet been carried out for three-body collisions involving atoms or molecules.

§2. Formation of Negative Ions on Collisions of Electrons with Molecules.

2.1. Processes involving Electron Capture.

2.11. General Theoretical Considerations. Another possibility, which we must consider, arises when the system capturing the electron is a molecule containing two or more atoms. This provides yet another means of absorbing the energy released on capture of the electron, i.e. by changing the kinetic energy of relative motion of the atomic nuclei. It may be thought of as a three-body attachment process in which the third body is bound to the capturing atom and not freely moving in the surrounding gas.

Suppose we have initially a neutral molecule in an electronic state of energy E_e^0 and a vibrational state of energy E_v^0 . Let an electron be captured into an electronic state† of energy E_e^- . Then, if E is the energy released by the capture, the molecular negative ion formed must have vibrational energy

$$E_v^- = -E_e^- + E_e^0 + E + E_v^0, \quad (3.10)$$

in order that the process should not involve radiation or a third colliding system.

To discuss the various effects which may be produced by this type of capture we make use of the Franck-Condon Principle. This states that those transitions will be most probable which leave the nuclear separation unaltered.

* *Proc. Camb. Phil. Soc.* **32**, 482 (1936).

† This will be an electronic state of the negative molecular ion formed by the capture.

The significance of this principle in terms of the wave functions for the molecular energy states may be seen as follows.

If we denote the co-ordinates of the electrons relative to the nuclei by $\mathbf{r}$, those of the nuclei by $\mathbf{R}$, the wave function for the electronic motion will be of the form $\chi(\mathbf{r}, \mathbf{R})$ and that for the nuclear motion $\psi(\mathbf{R})$. The probability of any transition between two molecular states in which the electronic state changes from n to m and the nuclear from s to t will be determined mainly by the square of the perturbation energy $V(\mathbf{r}, \mathbf{R})$ causing the transition, averaged over the wave functions of the initial and final states, viz.

$$\left| \iint \chi_m^*(\mathbf{r}, \mathbf{R}) \psi_t^*(\mathbf{R}) V(\mathbf{r}, \mathbf{R}) \chi_n(\mathbf{r}, \mathbf{R}) \psi_s(\mathbf{R}) d\mathbf{R} d\mathbf{r} \right|^2. \quad (3.11)$$

The probability will be greatest for given n, m, s when the overlap between ψ_t and ψ_s is a maximum. Now these wave functions are greatest in the regions of allowed classical motion and ψ_s is therefore only appreciable for nuclear separations confined within the amplitude of classical oscillations. The probability will be a maximum when ψ_t is also large in this region, i.e. when the nuclear separation is only slightly altered by the collision.

These considerations show that the Principle will lose its strict validity if ψ_s or ψ_t are appreciable outside the regions of classically allowed nuclear motion, but even for the lightest molecule it represents a sufficiently good approximation for qualitative argument.*

In fig. 7 (a), (b), (c) the potential-energy curves for different electronic states of both neutral and negatively charged molecules are illustrated. Curve I refers to the normal state of the neutral molecule XY , the remaining curves to states of the negative molecular ion XY^- . These latter curves all tend to a limit for infinite nuclear separation which lies below the curve I by an amount equal to the electron affinity A of the atom Y to which the electron is attached at this limit. The amplitude of oscillation of the neutral molecule in the normal state is from a to b , the range of nuclear separation being from r_1 to r_2 . The Franck-Condon Principle can now be used to show that in the transition consequent on electron capture, the nuclear separation, provided vibrational excitation of the normal molecule does not occur, will remain between r_1 and r_2 . Referring to fig. 7 we see that in

* See Coolidge, James and Present, *J. Chem. Phys.* 4, 193 (1936).

cases (a), (b) this will lead to a final state represented by some point lying between c and d on the potential curve for the state of the molecular ion. The energy involved in the transition will therefore lie between E_1 and E_2 (see fig. 7) and only electrons with energies in this range will be captured. Further, in case (a) all transitions will result in dissociation into an atom X and

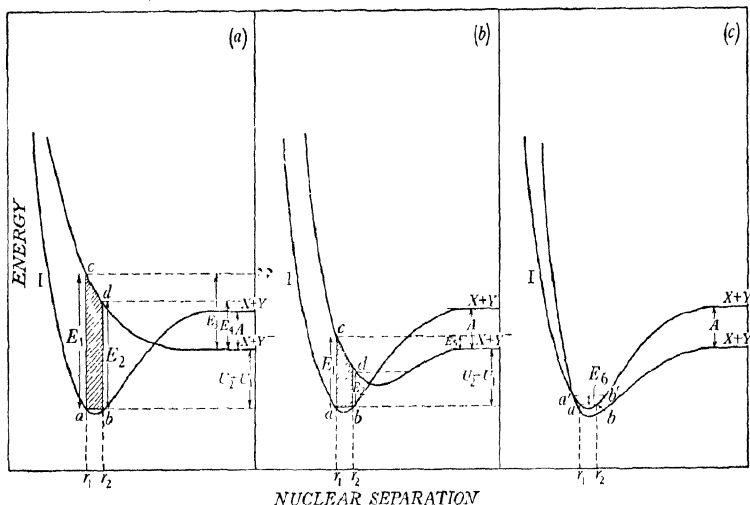


Fig. 7. Illustrating transitions which may occur on capture of an electron by a neutral molecule.

ion Y^- with relative kinetic energy between E_3 and E_4 . In case (b) some transitions will not lead to dissociation but to production of a vibrationally-excited molecule XY^- . If left to itself such a molecule will dissociate spontaneously by the reverse process to that which led to its formation, but it may be stabilized if the excess vibrational energy can be got rid of by collision.

Finally, let us consider case (c). No transition can occur without vibrational excitation of the neutral molecule to the state represented by $a'b'$ in the figure. Once excited to this state the chance of electron capture to form a vibrationally-excited molecule XY^- will be high. We may think, then, of the process occurring by the electron first exciting the neutral

molecule to the required state and then being captured. The ultimate stability of the molecule XY^- again depends on the removal of its excess energy before spontaneous dissociation by the reverse process.

The variation of attachment probability with pressure for a case such as (c) is important.* Let τ be the average time taken for the vibrationally excited molecule XY^- to transfer its excess energy to a gas molecule, and θ the time before spontaneous dissociation of XY^- . Then τ is inversely proportional to the gas pressure but θ is independent of the pressure. If now, at time $t=0$, we have an excited ion, the probability that it will still not have dissociated in time t will be $e^{-t/\theta}$. The probability of transferring its excess energy in a time between t and $t+dt$ is $e^{-t/\tau} dt/\tau$, so the total probability of the ion making a transfer collision before it dissociates will be

$$\begin{aligned}\rho &= \int_0^\infty \frac{e^{-t(\theta+t/\tau)}}{\tau} dt \\ &= \frac{\theta}{\theta + \tau} \\ &= \frac{p}{p + p'},\end{aligned}\tag{3.12}$$

where p is the gas pressure and p' a critical pressure for which $\theta = \tau$.

The attachment probability, when the reaction is of type (b) (without dissociation into X and Y^-) or (c), will therefore be independent of pressure for pressures much greater than a certain critical value, but for low pressures it will be proportional to the pressure.

Summarizing, we have the following possibilities:

Case (a). Electrons with energies between E_1 and E_2 are captured and molecular dissociation occurs giving rise to atoms X and ions Y^- with relative kinetic energies lying between E_3 and E_4 .

Case (b). Electrons with energies between E_1 and E_2 are captured, giving rise to atoms X and ions Y^- with relative

* Bloch and Bradbury, *Phys. Rev.* **48**, 689 (1935).

44 DETERMINATION OF ELECTRON AFFINITIES

kinetic energies lying between 0 and E_5 and also to vibrationally-excited molecules XY^- .

Case (c). Electrons with energies nearly equal to E_6 are captured, leading to formation of vibrationally-excited molecules XY^- .

In low-pressure experiments it will not be possible to observe the formation of XY^- molecules because they will dissociate before making sufficient collisions to get rid of their excess vibrational energy.

The range of electron energy over which the processes will occur is quite small. From the form of potential-energy curves for known molecular states it appears that a range of 2-5 e.volts is the order of magnitude to be anticipated. For processes of type (a) the range is likely to be greater than for (b) and (c) because of the greater slope of the potential-energy curve for the negative ion state in this case.

2.12. Determination of Electron Affinities.

Where dissociation occurs on capture we have the following important relation between the kinetic energy T of relative motion of the dissociated products, the kinetic energy E of the electron before capture, and the difference between the potential energy U_1 of the neutral molecule before impact and the potential energy U_2 of its dissociation products:

$$T = E - (U_2 - U_1). \quad (3.13)$$

For a diatomic molecule

$$U_2 - U_1 = D_{XY} - A, \quad (3.14)$$

where D_{XY} is the energy of dissociation of the normal state of XY and A the electron affinity of Y (see fig. 7). If D_{XY} is known and T and E can be measured, then A may be determined. The practical application of this method is described in §4.

2.13. Theoretical Evaluation of Cross-Sections.

Following the usual methods of quantum perturbation theory, the number of transitions per second between two states n, m of a system under the influence of a perturbation energy V is

$$\frac{4\pi^2}{h} |V_{nm}|^2, \quad (3.15)$$

where V_{nm} is the value of the perturbation energy averaged over the wave functions of the initial and final states. Now we have already explained in Chapter II, § 1, that in dealing with molecules we represent the molecular wave function as the product of an electronic wave function calculated at fixed nuclear separation, and a nuclear wave function corresponding to motion of the nuclei with potential energy determined by the electronic function. In this way the influence of the kinetic energy of the nuclei on the electronic wave functions is neglected and this energy may be taken as a perturbation energy which leads to coupling of nuclear and electronic motion. It is just this coupling which gives rise to reactions of the type we have been considering in § 2.1 of this chapter, so for the calculation of the probabilities of such reactions we use this kinetic energy for V .

Denoting the nuclear co-ordinates by $\mathbf{R}$ and the electronic co-ordinates relative to the nuclei by $\mathbf{r}$, the wave function of the initial state may be written

$$\phi_i(\mathbf{r}, \mathbf{R})\psi_i(\mathbf{R}),$$

where $\phi_i(\mathbf{r}, \mathbf{R})$ represents the wave function of an electron in the field of the neutral molecule and $\psi_i(\mathbf{R})$ the initial vibrational wave function. Similarly, for the final state we have

$$\phi_f(\mathbf{r}, \mathbf{R})\psi_f(\mathbf{R}),$$

where $\phi_f(\mathbf{r}, \mathbf{R})$ is the electronic wave function for the final state of the molecular ion and $\psi_f(\mathbf{R})$ that for the nuclear motion in the ion (which may or may not be unstable).

Finally, V is given by the kinetic energy operator

$$-\frac{\hbar^2}{8\pi^2M}\nabla_{\mathbf{R}}^2,$$

where M is the reduced mass of the nuclei. This gives

$$V_{nm} = -\frac{\hbar^2}{8\pi^2M} \iint \phi_f^*(\mathbf{r}, \mathbf{R})\psi_f^*(\mathbf{R}) \nabla_{\mathbf{R}}^2(\psi_i(\mathbf{R}) \phi_i(\mathbf{r}, \mathbf{R})) d\mathbf{R} d\mathbf{r}. \quad (3.16)$$

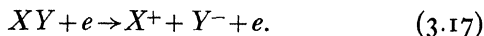
If the wave function $\phi_i(\mathbf{r}, \mathbf{R})$ is normalized to unit current and the remaining functions to unit density, (3.15) gives the effective cross-section for the process concerned.

2.2. Non-capture Collisions—Dissociation into Ions.

There is one other process of negative ion formation which may occur on collision of an electron with a molecule. The

46 DISSOCIATION OF MOLECULES INTO IONS

electron may excite the molecule to an unstable state which dissociates spontaneously into a positive and a negative ion, viz.



This differs from the type of reaction described in §2.1, as the

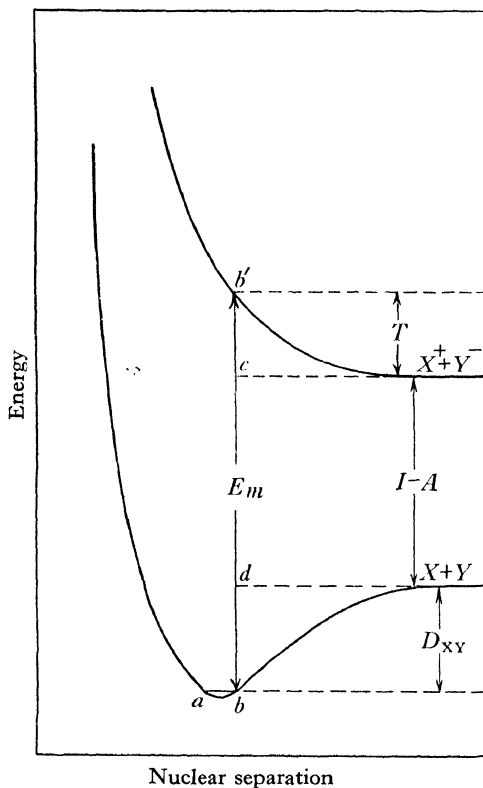


Fig. 8. Illustrating dissociation of diatomic molecules into positive and negative ions by electron impact.

electron is not captured but merely acts as a source of the energy necessary to produce the electronic transition in the molecule. The potential-energy curves for a case of this type are illustrated in fig. 8. The lower curve is, as usual, that for the ground state of the molecule, ab being the amplitude of nuclear vibration in the

ground state of nuclear motion. The other curve represents the potential curve for the upper state. Since this state dissociates spontaneously into ions the curve tends to a limit for infinite nuclear separation which is at a height $I - A$ above the limit for the normal state, I being the ionization energy of X and A the electron affinity of Y . Using the Franck-Condon Principle we see that the minimum energy which must be communicated to the molecule to bring about the transition is E_m (bb' in fig. 8). The relative kinetic energy of the ions X^+ , Y^- after the collision will be T ($b'c$ in fig. 8) and we have the relation

$$T = E_m + A - I - D_{XY}, \quad (3.18)$$

where D_{XY} is the dissociation energy of the molecule XY (bd in fig. 8). Measurement of T and E_m , combined with a knowledge of I and D_{XY} , provides a further method of determining the electron affinity A of the atom Y .

Since the electron is not captured in this type of collision, the variation of the effective cross-section with velocity is very different from that characteristic of capture reactions. As the process is essentially an electronic excitation of the molecule by electron impact the velocity variation will be similar to that for inelastic electron collisions with atoms. This is well known and consists in a sharp rise from a zero value at the appearance energy to a maximum at from two to four times this energy, after which it declines steadily as the inverse of the energy, or more slowly if the transition is to a level which combines optically with the normal state.*

The magnitude of the maximum cross-section to be expected depends on the polarity of the normal molecule. In the quantum picture of a molecule the system spends part of its time as a homopolar system and part as a polar one. A collision of the type concerned above will only take place with appreciable probability if the electron collides with the system during an interval in which the molecule is predominantly polar. For a

* Mott and Massey, *Theory of Atomic Collisions*, Oxford Univ. Press (1933), pp. 176-8, 197-8.

48 ELECTRON ATTACHMENT TO MOLECULES

symmetrical diatomic molecule such as O_2 the fraction of time spent in the polar grouping is very small and a small probability of dissociation into ions on impact is to be anticipated.

Summarizing, we see that ion formation by direct dissociation will set in at some definite electron energy and persist to quite high energies. The probability will only be large for polar molecules.

§3. Experiments on the Attachment of Electrons to Molecules.

3.1. General Remarks.

There are two main methods of experiment in this direction, one using electron beams of definite velocity, the other studying the motion of an electron swarm through the gas concerned. The first type of experiment gives more definite results because of the more precise experimental conditions employed, but for very slow electrons it is not easy to apply. Further, the use of homogeneous electron beams requires low gas pressures. Processes (such as (b) or (c) of §2) leading to vibrationally-excited molecular ions which dissociate spontaneously unless stabilized by collision will therefore not be observable, and swarm experiments must be used to provide information about them.

§4. Experiments using Homogeneous Electron Beams.

4.1. The Method of Tate and Lozier.

The most detailed experimental study has been carried out by Lozier* of the collisions of electrons with the molecules of oxygen and carbon monoxide, using an apparatus of a type first designed by Tate and Lozier.†

An electron beam of definite energy is confined by a longitudinal magnetic field to the axis of a cylindrical space containing the gas at low pressure. Ions, formed by the electrons, which pass out in radial directions are collected on the outer metal surface of the cylindrical space. By auxiliary electrodes, ions of one sign only may be collected and their velocity distribution

* *Phys. Rev.* **46**, 268 (1934).

† *Phys. Rev.* **39**, 254 (1932).

examined by retarding potential analysis. Fig. 9 is a schematic representation of the actual apparatus. An electron beam from the filament *B* issued from the hole *E* after acceleration of 12 volts from *B* to *D* and retardation by 10 volts from *D* to *E*. Between *E* and *F* this beam was accelerated to the required energy and it then passed along the axis of the cylindrical space between *H* and *K*. The beam which issued at *S* was collected on the electrode *M* by a potential of 100 volts between *L* and *M*. A magnetic field of about 150 gauss, maintained by a coaxial

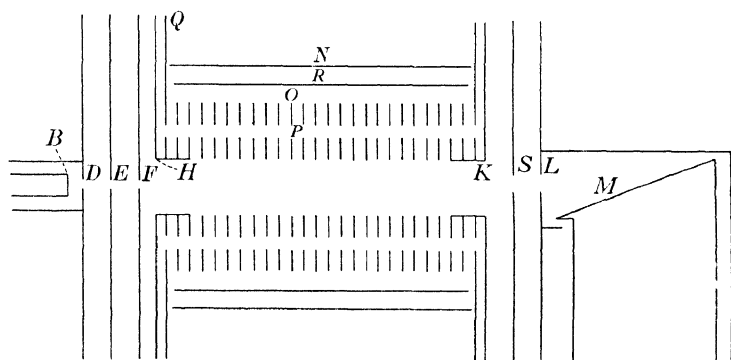


Fig. 9. Illustrating Tate and Lozier's apparatus for investigating electron impacts with molecules.

solenoid, confined the beam to the axis of the cylindrical space. *O* and *P* represent concentric sets of thin discs in electrical contact with *H* and *Q* respectively. *R* is a metal cylinder and *N* a coaxial guard cylinder insulated from *R*.

The filament assembly was maintained at high vacuum by a separate pumping system, while the gas under investigation was contained in the cylindrical space at pressures varying from 10^{-5} to 10^{-4} mm. Hg.

Those ions formed by the electron beam which travelled in radial directions passed between the sets of discs *O* and *P* and reached the collector *R*, where they gave rise to a current which could be measured. Positive and negative ions were separated and the velocity distributions of each examined by applying

appropriate potentials between the discs *O* and *P* and the collector *R*.

The entire apparatus was constructed of tantalum and could be baked out at 450° C., while the purity of the gas used was tested by examination with a mass spectrograph. It seems very unlikely that the results obtained are subject to any appreciable source of error and they are probably the most reliable we have concerning capture of electrons by molecules. The only disadvantage of the apparatus is that it cannot be used to determine the masses of the ions observed but only the ratio of the masses of two sets of ions. A supplementary investigation with a mass spectrograph is therefore necessary in certain cases to identify the ions completely.

4.2. Electron Collisions in O₂ and CO. The Electron Affinity of O.

It is found that in these gases more than one group of negative ions is formed, occurring at different electron energies. This is illustrated in fig. 10, in which the relative abundance of ions produced is represented as a function of electron energy for both gases. Referring to this figure we see that groups *A*, *B* for O₂ and *D* for CO are formed only by electrons with a narrow range of energies, so we expect them to be the result of electron capture processes (see §2.1). Groups *C* for O₂ and *E* for CO are produced by electrons with energies greater than 18 and 21.9 e.volts respectively and the velocity variation is of the type expected for dissociation into negative and positive ions (see §2.2).

These interpretations have been confirmed in detail by Lozier. The yield of ions is proportional to the intensity of the electron beam and to the gas pressure, showing that they result from primary impacts with electrons. Measurement of the kinetic energies of the ions for different electron energies established the existence of a relation of the form (3.13) for groups *A*, *B* and *D*. A typical set of experimental points is illustrated in fig. 11. From observations for group *A* the value

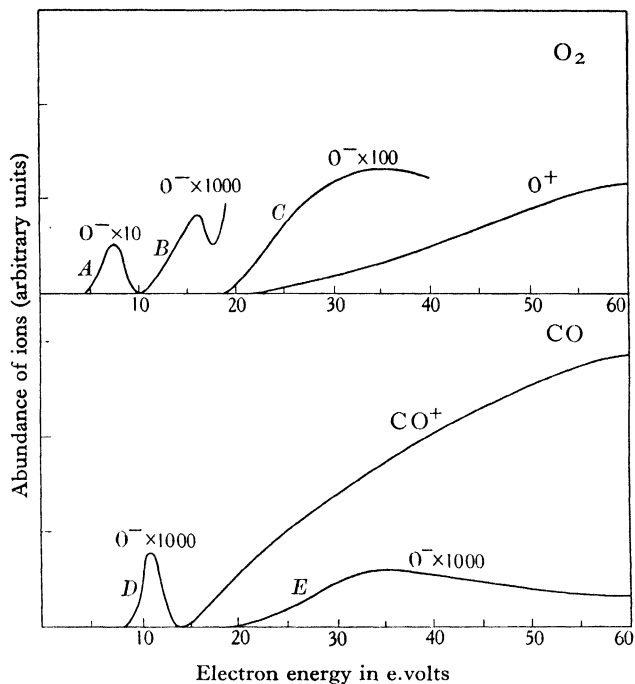


Fig. 10. Observed formation of negative ions by electron impact in O_2 and CO.

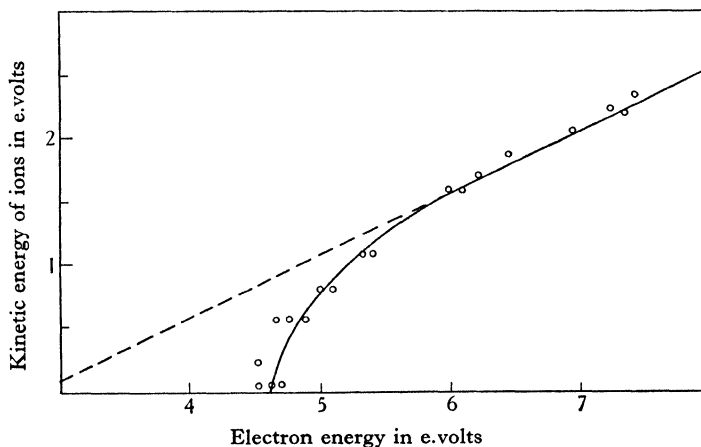
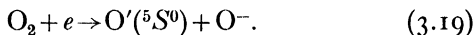


Fig. 11. Kinetic energies of O^- ions produced in O_2 by impact of electrons of various energies. $\circ$ experimental points.

2.9 e.volts was obtained for $D_{O_2} - A_O$, assuming the dissociation products to be unexcited. Since D_{O_2} is 5.09 e.volts, A_O must be 2.2 e.volts, the first direct determination of the electron affinity of O. The error is estimated at ± 0.2 e.volt.

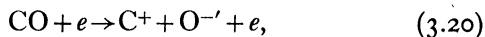
It is not possible to identify with any certainty the electronic state of O_2^- into which the electron is captured, but the fact that Lozier observed no O^- ions with energies of less than 1.3 e.volts makes it probable that the process is actually one of type (a) of §2.1. If this is correct the state is probably the unstable Σ_u state described in Chapter II, §3.2.

For group B of O_2 Lozier finds that $U_2 - U_1$ of (3.13) §2.12 is 12.0 e.volts. The excess 9.1 e.volts of this value over that for group A must be in the form of excitation energy of one of the dissociation products. Since the excitation energy of the $^5S^0$ state of O is just 9.1 e.volts, the reaction leading to group B must be interpreted as



The group C of CO corresponds to a value for $U_2 - U_1$ of 9.5 ± 0.1 e.volts. Since the dissociation energy of CO is 9.46 e.volts and there is no known excited state of carbon with an energy 2.2 e.volts (the electron affinity of O) above the normal state, we must interpret these observations as indicating the existence of a stable excited state of O^- lying very close to the positive energy continuum. It will be remembered that it was pointed out in Chapter I, §5 that such excited states might exist although it is unlikely that any occur with appreciable binding energy.

Of the remaining groups in O_2 and CO, which arise from dissociation into positive and negative ions, the CO group has been investigated in detail by Lozier. As expected, he finds that in this process positive and negative ions occur in equal numbers and the relation (3.18) of §2.2 holds if we suppose that the reaction is



the O^- ion being excited with nearly 2.2 e.volts energy. Thus, since the appearance energy E_m is 21.9 e.volts, D_{CO} is 9.46 e.volts,

the ionization potential I of carbon is 11.22 e.volts, and the minimum relative kinetic energy of the C⁺ and O⁻ ions is 1.0 e.volt, we have for the electron affinity

$$\begin{aligned} A &= T - E_m + I + D_{XY} \\ &= 1.0 - 21.9 + 11.22 + 9.46 \\ &= -0.22 \text{ e.volt.} \end{aligned}$$

As the probable error is at least ± 0.20 e.volt, this provides further evidence of the very loosely bound excited state of O⁻.

4.21. Observed Cross-Sections for Collision Processes in O₂ and CO.

From Lozier's experiments the ratio of the negative ion yield to that of the ions CO⁺, O₂⁺ can be estimated. The cross-sections for direct ionization of these molecules have been measured by Tate and Smith,* so the cross-sections for the different negative ion producing collisions may also be estimated. In this way we find the following maximum values:

TABLE IV

O ₂	Cross-section in cm. ²	CO	Cross-section in cm. ²
O ₂ + e → O + O ⁻	8 × 10 ⁻¹⁹	CO + e → C + O ⁻	5 × 10 ⁻²⁰
O ₂ + e → O' + O ⁻	1.3 × 10 ⁻²⁰	CO + e → C ⁺ + O ⁻	4 × 10 ⁻²⁰
O ₂ + e → O ⁺ + O ⁻ + e	2.2 × 10 ⁻¹⁹		

4.3. Collisions in Iodine Vapour.

A thorough investigation of electron collision processes in iodine vapour by Lozier's method has not yet been carried out, but a preliminary survey has been made by Hogness and Harkness† using a mass spectrograph.

They found that I⁻ ions were produced by electrons with energies as low as 3 e.volts, the slowest used in the experiments. As the intensity-pressure relations observed indicated that these ions are formed by a primary process, and since no positive ions

* *Phys. Rev.* **39**, 270 (1932).

† *Ibid.* **32**, 784 (1928).

were observed until much more energetic electrons were employed, it is probable that the process concerned in their formation is



It is not possible to say which electronic state of I_2^- is concerned until further experimental results are available, but it may be the unstable Π_g state mentioned in § 3.3 of Chapter II.

I_2^- and I_3^- ions were also found, and a study of the intensity-pressure relations suggests the possibility of their formation by the reactions



If these are correct the energy of dissociation of I_2^- into normal I and I^- must be greater than that of I_2 into normal atoms. This would not be anticipated (see § 3.3 of Chapter II), although the Σ_u state of I_2^- is probably stable.

Further experimental investigations in I_2 by Lozier's method are clearly required and may lead to very interesting results.

§5. Attachment Experiments with Electron Swarms.

5.1. Introductory Remarks.

The most important difference, from the point of view of interpretation, between the swarm experiments and those of the type described in the preceding section is the comparatively high gas pressures which must be employed. The possibility of three-body effects, negligible in an experiment such as Lozier's, can no longer be ignored. Processes such as (c) and (b) of §2.11 will also be observable. A feature of the results, which has vitiated much of the early work done, is the profound influence of impurities on the rate of attachment of slow electrons to molecules. This may possibly be due to three-body resonance effects in which the energy released by the electron attachment is transmitted to internal energy of a third body without any transference to or from kinetic energy of relative motion, but, in any case, it is of great importance in practice.

5.2. General Description and Theory of Swarm Experiments.

Consider a stream of electrons drifting through a gas under the influence of a uniform electric field F . Let α be the chance that an electron of the stream in passing unit distance in the direction of the field will be attached to a gas molecule. The loss of electron current in a distance dx due to this cause is

$$dI = -I\alpha dx.$$

The ratio of the electron current in the stream at two points x_1 , x_2 will therefore be

$$I_2/I_1 = e^{-\alpha(x_2-x_1)}. \quad (3.24)$$

All attachment experiments involving electron swarms have been devised to measure α , but it is necessary to obtain further information concerning the swarm before the probability of attachment per collision can be determined. In passing a distance dx in the direction of the field, an electron, because of its random motion, actually moves through a much greater distance than dx . If c and W are, respectively, the random and drift velocities of an electron, the actual distance traversed by the electron will be $c dx/W$, so that, if Q_a is the effective cross-section for attachment,

$$\alpha = NQ_a c/W.$$

This may be rewritten in terms of the chance of attachment h per collision and l , the mean free path of the electrons in the gas, to give

$$\alpha = hc/lW. \quad (3.25)$$

As the quantity h is the one required for assessment of attachment probabilities, c and W must also be determined. One only of these need be measured experimentally, for c and W may be related by Townsend's formula,

$$W = 0.75Fel/mc,$$

where e/m is the specific charge of the electron.*

* It is assumed that the free path l is known from experiments either of the Ramsauer or Townsend type. (See Mott and Massey, *Theory of Atomic Collisions*, Oxford Univ. Press (1933), p. 116.)

To determine h , α and W must both be measured and the experiments actually carried out employ different methods of doing this. The theory we have just discussed deals with mean values because we must expect Q_a and l to be functions of the electron velocity. The mean velocity of the electrons in a swarm is a function of F/p only, p being the gas pressure, and results for different mean velocities are obtained by varying this ratio.

Two main experimental methods have been employed; we describe first the most direct one developed by Loeb and Cravath* and used particularly by Bradbury.†

5.3. The Method of the Electron Filter.

In this method α is determined by direct measurement of the ratio I_1/I_2 of the electron current at two places at a distance x apart, perpendicular to the direction of the applied field. The electron content of the mixed negative ion and electron current is measured by using a high frequency filter in a manner suggested by Loeb. This filter consists of a grid between alternate wires of which a high frequency alternating electric field is applied. This field can be adjusted to sweep the highly mobile electrons to the grid wires but leave the heavy negative ions unaffected. The decrease in current when the stream passes through this filter is then a measure of the contribution of the electrons to the total current.

Fig. 12 is a schematic illustration of the apparatus actually used. Electrons generated photoelectrically from the plate A diffused under the action of an electric field between plates P and A , maintained uniform by the guard rings B, C, D, E . One half of each of the guard rings E and C consisted of a grid of fine platinum wires (G, G') which could be slid into position to intercept the electron stream. (In the figure G is shown in position, G' not.) An alternating potential could be applied across the grid wires by an oscillator O .

The apparatus was enclosed in a pyrex tube and could be baked out at 200°C . and evacuated to a pressure as low as

* *Phys. Rev.* **33**, 605 (1929).

† *Ibid.* **44**, 883 (1933).

10^{-6} mm. Hg. This is important in connection with the removal of impurities.

In carrying out measurements the current to P was measured first with one grid in place but no alternating field and then with the alternating field applied. Similar measurements were carried out at the second grid, and from these I_2/I_1 and hence α could be determined.

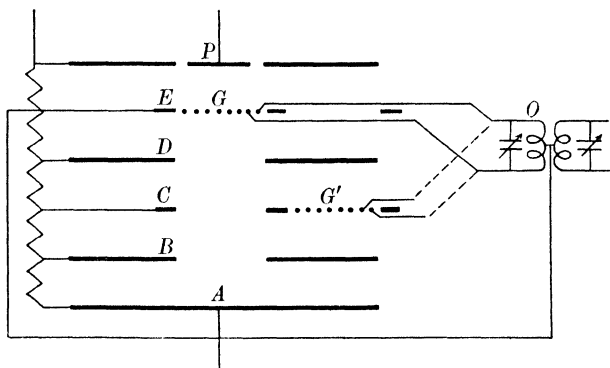


Fig. 12. Apparatus used to investigate electron attachment by electron filter method.

The drift velocity W was determined by using a formula due to J. J. Thomson* relating the photoelectric current between two parallel plate electrodes to the drift velocity and initial energy of the electrons.

5.4. Bailey's Method.

A different method devised by Bailey† has been applied to investigate attachment in a number of gases and vapours. It is by no means as direct in principle as the filter method and depends on a number of theoretical results relating to the motion of electron swarms. Most of these have been independently verified by experiment, so there is no reason to question the validity of this method on these grounds.

Fig. 13 illustrates the principle of the method. A uniform

* *Conduction of Electricity through Gases*. Cambridge Univ. Press, 1st edition (1928), p. 466.

† *Phil. Mag.* **50**, 825 (1925).

electric field F is maintained between five parallel plates A, B, C, D, E contained in the gas under investigation. B, C, D contain parallel and superposed slits. Electrons generated photoelectrically from the plate A drift downwards under the influence of the electric field. By measuring the currents reaching the electrodes C, D, E with two sets of homologous

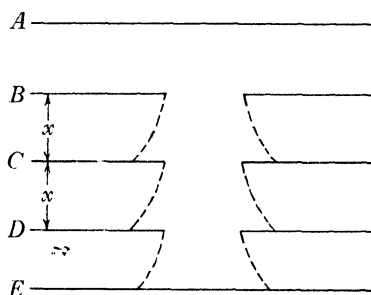


Fig. 13. Illustrating Bailey's diffusion method for investigating electron attachment.

values of plate displacement, gas pressure and electric field, the quantity α may be determined. We introduce the following symbols:

- S , the ratio of the current passing through a slit to the total current arriving on a plane containing the opening. Suffices 0, 1, 2, 3 refer to plates B, C, D, E respectively;
- R_e , the fraction of electrons falling on a plane which pass through the slit;
- R , the corresponding fraction for ions;
- r , the corresponding fraction for ions formed between plates B and C , or C and D ;
- p , the gas pressure;
- k , the factor by which the mean energy of the random motion of the swarm electrons exceeds that of gas molecules in temperature equilibrium at N.T.P.;
- n_0, N_0 , the number of electrons and ions respectively passing through the slit in plate B ;

$n_1, N_1; n_2, N_2$, corresponding quantities for plates D and E respectively;

x , the distance between the plates.

Then

$$\begin{aligned} S_1 &= \frac{n_1 + N_1}{n_0 + N_0}; & S_1 S_2 &= \frac{n_2 + N_2}{n_0 + N_0}; \\ n_1 &= n_0 R_e e^{-\alpha x}; & n_2 &= n_1 R_e e^{-\alpha x}; \\ N_1 &= N_0 R + r(1 - e^{-\alpha x}) n_0; & N_2 &= N_1 R + r(1 - e^{-\alpha x}) n_1. \end{aligned}$$

Eliminating r from these equations we obtain

$$R_e e^{-\alpha x} = \frac{S_1(R - S_2)}{R - S_1} = a_1, \text{ say.} \quad (3.26)$$

Now the quantities R_e, R are known functions of F/kx , but k , assumed equal to unity for the ions, is not known for the electrons. To avoid this difficulty use is made of the fact that k is a function of F/p , so the quantity a_n is obtained corresponding to (3.26) but with F, p, x increased in the same ratio n . k is then unaltered and so is R_e , giving

$$R_e e^{-n\alpha_n x} = a_n. \quad (3.27)$$

If it be assumed that the attachment probability h is independent of pressure (which may not always be justified in view of our introductory remarks), then $\alpha_n = n\alpha$ and

$$\alpha = \frac{1}{x(n^2 - 1)} \log \frac{a_1}{a_n}, \quad R_e = \left(\frac{a_1}{a_n} \right)^{1/(n^2 - 1)}. \quad (3.28)$$

This gives α and R_e in terms of quantities which are all, with the exception of R , directly measurable. The calculation of R depends on diffusion theory and is not likely to be seriously in error. Additional support for the general theoretical basis of the method is also provided by measurements carried out in pure hydrogen which is known to have no attachment properties.

To determine the drift velocity W the method adopted involved the application of a magnetic field H in the same direction as the electric field.* This field has no appreciable effect on the negative ions, but it may be shown that it changes

* *Phil. Mag.* 9, 560 (1930); *ibid.* 9, 625 (1930).

the distribution ratio of the electrons just as if F/kx were changed to $F\sigma/kx$, where

$$\sigma = 1 + \left(\frac{HW}{F} \right)^2. \quad (3.29)$$

By suitable choice of H , σ/k can be made unity and the stream then behaves, as far as lateral diffusion is concerned, in the same way as a beam of negative ions. When this occurs S_2 will be equal to R .

Hence, if H_0 is the value of H for which $S_2 = R$, then

$$W = \frac{F}{H_0} \sqrt{k - 1}.$$

Since k can be determined from R_e , W may be derived from this relation.

The main difficulty involved in experiments of this type is the considerable complexity of the apparatus. This makes it very awkward, if not impossible, to design the system in such a way that the whole may be thoroughly degassed by baking. Although Bailey and his collaborators have taken precautions, particularly in their later experiments, to avoid contamination of the gases used, it is difficult to be certain of this without adopting drastic measures to expel gaseous impurities. We do not imply by this that the results obtained with this ingenious diffusion apparatus are in any sense spurious but merely that some confirmatory experiments must be carried out with other apparatus in which adequate provision can be made for thorough degassing. Some comparison of results obtained by the two methods is given in §6.

§6. Results obtained by "Swarm" Experiments and their interpretation.

6.1. Oxygen.

Bradbury* has applied the filter method to investigate attachment in this gas. He obtains the probability h of attachment per collision as a function of the ratio F/p of electric field strength

* *Phys. Rev.* **44**, 883 (1933); *J. Chem. Phys.* **2**, 827 (1934).

to gas pressure. The average energy of the swarm electrons is a function of F/p and experiments carried out by Townsend* have determined the form of this function. Combining these results with Bradbury's we obtain the variation of attachment probability in O_2 with average electron energy illustrated in fig. 14. At the pressures employed (3 mm. Hg) h was found to be independent of the pressure. Some experiments carried out by Bröse† using a diffusion method have indicated qualitatively that, for pressures below 2 mm. Hg, h decreases with pressure.

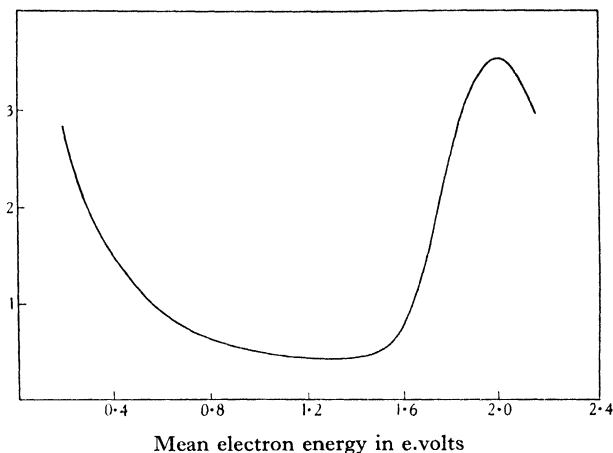


Fig. 14. Probability of electron attachment (by 10^4) to O_2 as a function of the mean electron energy (observed by Bradbury).

From the form of the curve of fig. 14 it seems probable that two separate processes are occurring—one leading to attachment of very low energy electrons, the other becoming important for electrons with energies greater than about 1.5 e.volts.

Bloch and Bradbury‡ have suggested that the low energy effect arises from a reaction



of the type discussed in § 2.11(c), leading to vibrationally-

* *J. Frank. Inst.* **200**, 563 (1925).

† *Phil. Mag.* **50**, 536 (1925).

‡ *Phys. Rev.* **48**, 689 (1935).

excited O_2^- which must be stabilized by deactivation. Assuming that the potential curves for the ground electronic states of O_2 and O_2^- are nearly the same for nuclear separations comparable with the equilibrium value for O_2 , the observed variation of h with mean electron energy can be explained if the electron affinity of O_2 is taken between 0.11 and 0.17 e.volt. The order of magnitude of h (about 10^{-4}) is also in general agreement with this interpretation and the dependence on pressure provides no contradiction. The independence of pressure observed in Bradbury's experiments only requires that the critical pressure for the reaction (see §2.11 (3.12)) is considerably less than 3 mm. Hg and is not inconsistent with Bröse's* observation of the increase of h with pressure at pressures below 2 mm. Hg. The state of O_2^- which is probably the one concerned is the II_u state described in Chapter II, §3.2.

It is not easy to give a definite interpretation of the second process, which becomes important for electrons with energies greater than 1.5 e.volts. Bradbury suggested that it may be connected with the excitation of the $^1\Sigma^+$ state of the O_2 molecule requiring 1.6 e.volts. The onset of this type of inelastic collision might provide low energy electrons capable of attachment by the first process. A difficulty about this explanation is that the energy spread of the electrons should make such an effect apparent at lower energies than the observed. It is possible that the phenomenon is connected with the II_g state of the O_2^- molecule (Chapter II, §3.2, fig. 5), but further investigation is necessary to clear up this point.

6.2. Other Gases.

The filter method has also been applied† to study attachment in NO, CO, NH_3 , HCl, Cl_2 , CO_2 , N_2O , SO_2 , H_2S and H_2O . A number of these have been investigated by the diffusion

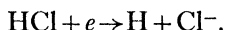
* *Loc. cit.*

† Bradbury, *J. Chem. Phys.* **2**, 827 (1934); Bradbury and Tatel, *ibid.* **2**, 835 (1934).

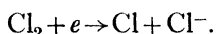
method* but usually for different ranges of F/p , i.e. for different mean electron energies. When comparison is possible there is a qualitative agreement between the results obtained by the two methods. The values of h may differ by factors of 10 or more.

In all cases except NO, h was found to be independent of pressure but, for this gas, it increased linearly with the pressure. This probably represents a case analogous to that of O_2 but with a higher critical pressure. We give now a short résumé of the results and possible interpretations for the other gases:

HCl. Both methods give h increasing from zero to a maximum of about 5×10^{-4} at a mean energy of about 0.5 e.volt. The process concerned may be



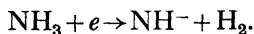
Cl_2 . The behaviour is similar to that for HCl and the process is probably



This would be in agreement with Hogness and Harkness' results for iodine (§4.3).

CO. No attachment was observed with electrons with mean energy up to 2 e.volts. This does not conflict with Lozier's measurements in this gas (§4.2).

NH_3 . Both methods give no appreciable attachment for mean electron energies below 0.17 e.volt. ($F/p=8$ volts per cm. per mm. Hg.) At higher energies, according to the diffusion method, h rises rapidly to a maximum of 3.7×10^{-4} at a mean energy of 2.05 e.volts. The filter method has not been applied up to such high energies but gives values of h as high as 72×10^{-4} . Bradbury showed that a permanent gas is formed by the diffusion of slow electrons through ammonia and so it is probable that the attachment arises from the reaction



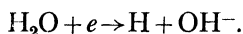
N_2O . Similar to NH_3 .

CO_2 . No attachment has been observed.

* Bailey and Duncanson, *Phil. Mag.* **10**, 145 (1930); Bailey and Rudd, *ibid.* **14**, 1033 (1932).

SO₂. The behaviour observed by Bradbury and Tatel* was much the same as for O₂.

H₂O and H₂S. In this case there is very good agreement between the results obtained by the two methods. Attachment sets in at mean energies of about 0.1 e.volt and rises steadily with increasing energy. At the highest mean energy employed (about 2 e.volts) the value of h is about 5×10^{-4} . The filter method has also been employed for very low energies and it is found that the attachment probability increases again if high pressures are used. The process responsible for the high energy attachment is probably



As the low energy effect depends on pressure it is probably due to polymerization of the water vapour approaching condensation.

Hydrogen sulphide behaves in the same way except that it has no attachment properties towards low energy electrons.

§7. Summary of Collision Processes leading to Negative Ion Formation in Oxygen.

We may summarize the combined results of swarm and low pressure experiments in oxygen (the gas most fully investigated) as follows:

TABLE V

Mean electron energy in e.volts	Reaction	Remarks
0 → 1.5	$\text{O}_2 + e \rightarrow \text{O}_2^-(H_g)$	Pressure independent in pure O ₂ above 3 mm. Hg. Of type (c), § 2.1
1.6 → ?	?	
5 → 10	$\text{O}_2 + e \rightarrow \text{O}_2^-(\Sigma_u) \rightarrow \text{O}(^3P) + \text{O}^-(^2P^0)$	Of type (a), § 2.1
12 → 18	$\text{O}_2 + e \rightarrow \text{O}_2^-(?) \rightarrow \text{O}(^5S^0) + \text{O}^-(^2P^0)$	Of type (a), § 2.1
21 → ∞	$\text{O}_2 + e \rightarrow \text{O}^+ + \text{O}^- + e$	Type described in § 2.2

* *Loc. cit.*

§8. Capture of Bound Electrons by Neutral Atoms and Molecules.

A further reaction leading to negative ion formation is the capture of a bound electron by a neutral molecule. The captured electron may have been bound either in an atom or in a metal, and we will consider these two possibilities separately.

8.1. Electron Capture from Atoms.

The reaction here is of the type



If the atoms are under ordinary temperature conditions this reaction is only possible if the electron affinity of X is greater than the ionization energy of Y . The only case when this is satisfied is that of a collision between F and Cs atoms, a most unlikely event in experimental work of any kind! However, as it is possible to prepare beams of fast atoms by neutralization of positive ion beams it is not outside the bounds of present experimental technique to investigate, say, the formation of I^- by collision of fast I atoms with Cs atoms (or vice versa). The energy which must be provided by the kinetic energy of relative motion of the colliding atoms is about 1 e.volt, but, although the process is energetically possible when the relative kinetic energy exceeds this value, the probability of transfer will not be appreciable until this energy is considerably greater (probably about 10 times). This is a feature of all inelastic collisions between heavy particles involving transfer of energy to or from electrons and is established both theoretically and experimentally.

The theoretical basis is as follows. We use the same formula as (3.15) and (3.16) of §2.13, the wave functions ϕ referring to the electron motion about the colliding nuclei in the initial and final states of excitation respectively and the functions ψ to the relative motion of the nuclei with positive total energy and potential energy determined by the respective electronic wave functions. These functions ψ can be represented with sufficient accuracy by plane waves, so we may write

$$V_{nm} = k_1 \int e^{iK_n \cdot R} W(R) dR, \quad (3.32)$$

where†
$$W(\mathbf{R}) = \frac{\hbar^2}{4\pi^2 M} \int \phi_f^*(\mathbf{r}, \mathbf{R}) \mathbf{n}_i \cdot \text{grad}_R \phi_i(\mathbf{r}, \mathbf{R}) d\mathbf{r}, \quad (3.33)$$

$k_1 \hbar / 2\pi$ is the initial momentum, and $K \hbar / 2\pi$ the change of momentum, of the relative motion of the nuclei due to the collision. The function W is only appreciable for values of $R < R_0$, a length comparable with the gas kinetic radii of the atoms.

The minimum value of K , as a function of the angle of scattering, is $k_1 - k_2$, where $k_2 \hbar / 2\pi$ is the magnitude of the final momentum of the relative nuclear motion. Since

$$k_1^2 - k_2^2 = \frac{8\pi^2 M}{\hbar^2} E_t,$$

where M is the reduced mass of the nuclei and E_t the energy transfer which takes place, we have

$$k_1 - k_2 = \frac{8\pi^2 M}{\hbar^2} \frac{E_t}{k_1 + k_2},$$

and decreases as $k_1 + k_2$, i.e. as the energy of the relative motion, increases. For small energies even $(k_1 - k_2) R_0$ will be so large that the integral (3.32) will be negligible because of the rapid oscillations of the integrand. For an appreciable value to be obtained for V_{nm} we must have

$$(k_1 - k_2) R_0 < s,$$

where s is comparable with unity. This gives

$$(k_1^2 - k_2^2) R_0 < (k_1 + k_2) s \\ \simeq 2k_1 s,$$

or

$$\frac{8\pi^2 M}{\hbar^2} E_t R_0 < 2s \left(\frac{8\pi^2 M E}{\hbar^2} \right)^{\frac{1}{2}},$$

where E is the initial relative kinetic energy. Hence

$$E > \frac{2\pi^2 M}{s^2 \hbar^2} E_t^2 R_0^2 \quad (3.34)$$

for the probability of energy transfer to be appreciable.

The exact value of s cannot be fixed except by detailed calculation for each special case but from observations of electron capture and

† In deriving this result we have used the formula

$$\nabla_R^2(\phi\psi) = \psi \nabla_R^2 \phi + 2 \text{grad}_R \psi \cdot \text{grad}_R \phi + \phi \nabla_R^2 \psi.$$

The first term is of second order of smallness and the last contributes nothing because of the orthogonality of the functions ϕ . Further since the functions ψ may be represented by plane waves

$$\text{grad}_R \psi_i = i k_1 e^{i k_1 \mathbf{n}_i \cdot \mathbf{r}} \mathbf{n}_i$$

where $\mathbf{n}_i$ is a unit vector in the direction of the initial relative motion.

ionization by positive ions it appears that, for values of E_t of the order of a few electron volts, E must be roughly 25 times greater than E_t to give a probability per collision of the order 0.1. A detailed discussion of this situation has been given by Massey and Smith.*

8.2. Extraction of Electrons from Metals.

A neutral atom colliding with a metal surface may extract an electron from the metal to form a negative ion. If this process requires provision of energy from the kinetic energy of the atom it is analogous to that discussed above for capture from a second atom and the probability will be very low unless the kinetic energy of the atom exceeds the minimum energy required by a factor of 10 or more. There will be a much greater probability for low velocity atoms if the process is a resonance one. The condition for this is that the electron affinity A of the atom be greater than the work function ϕ of the metal, for the electron levels in the metal can be regarded as filled up to a level at a depth ϕ below the energy of the free space outside the metal.

This condition is rarely satisfied for pure metal surfaces, the only ones possessing work functions less than the electron affinity of iodine being those of the alkali metals. Even though certain composite surfaces may furnish a sufficiently small work function it is unlikely that slow moving neutral atoms succeed at all frequently in capturing electrons in this way.

A second possibility, likely to be more fruitful, occurs when the atom colliding with the metal surface possesses an excitation energy E' . The condition for capture of a metal electron by a resonance process is now

$$\mu + \phi > E' + A > \phi, \quad (3.35)$$

where $-(\mu + \phi)$ is the energy of the deepest electron level in the metal. This condition can be satisfied for impact with many metals and the process may provide quite a strong source of negative ions. It would be very interesting to examine the probability of the process by direct experimental test, using, for example, metastable atoms impinging on a clean metal surface.

* *Proc. Roy. Soc. A*, **142**, 142 (1933).

68 EXTRACTION OF ELECTRONS FROM METALS

A series of experiments has recently been carried out by Arnot* which seems to indicate that capture of two electrons from a metal by a positive ion may occur with quite considerable probability. In particular he finds that Hg^+ ions of energy about 200 e.volts impinging on a nickel surface have a chance of roughly 10^{-4} of capturing two electrons to form Hg^- . For lower energy ions the probability is less.

It is not easy to see how this process occurs. It cannot be through adsorption of Hg^+ ions on the surface for a sufficiently long time to capture two electrons, because the Hg^- ions formed possess a considerable fraction of the energy of the incident Hg^+ ions. A further possibility is that the incident ion first captures an electron into an excited state of energy E' and, during the time it remains near the metal, this excited atom captures a second electron. In order that both these processes be of resonance type we must have

$$\mu + \phi > I - E' > \phi, \text{ for first capture,}$$

$$\mu + \phi > E' + A > \phi, \text{ for second capture,}$$

$$\text{or} \quad 2(\mu + \phi) > I + A > 2\phi, \quad (3.36)$$

where I is the ionization energy of the atom. The condition (3.36) is satisfied for Hg on Ni if $A > 0$. The difficulty about this explanation is that we would expect the total probability to decrease with decrease of the time spent by the atom in the neighbourhood of the metal, i.e. with increase of velocity of the incident ion. The observed result is just the reverse. One way of avoiding this difficulty is to suppose that, at the higher velocities, appreciable contributions are made by non-resonance processes. Another is to suppose that the capture of the two electrons takes place as a single process. Although this is not impossible it is rather unlikely and the whole subject requires further extensive investigation using the best possible vacuum technique. In this connection it is of interest to note that Stille,† using very good vacuum conditions, did not observe

* *Nature*, **138**, 162 (1936); Arnot and Milligan, *Proc. Roy. Soc. A*, **156**, 538 (1936); Arnot, *ibid.* **158**, 137 (1937).

† *Ann. d. Phys.* **17**, 635 (1933).

the formation of Hg^- ions until the apparatus was contaminated with hydrogen.

§9. Summary.

The following processes can give rise to negative ions:

(a) Capture of a free electron by an atom accompanied by emission of radiation.

(b) Capture of a free electron by an atom in the presence of a third body which takes up the excess energy.

(c) Capture of a free electron by a molecule accompanied by vibrational excitation of the molecule and subsequent stabilization.

(d) Capture of a free electron by a molecule with dissociation of the molecule.

(e) Dissociation of a molecule into positive and negative ions by electron impact.

(f) Capture of an electron by one molecule from another molecule.

(g) Capture of an electron by a normal atom from a metal surface.

(h) Capture of an electron by an excited atom from a metal surface.

(i) Capture of two electrons by a positive ion from a metal surface.

Under gas kinetic conditions at ordinary temperature (b), (c), (d) will be the most probable in the gas phase; (e) may also be important if the gas molecules are strongly polar. At very low pressures (b) and (c) become unimportant compared with (d), and (a) must be taken into account.

Of the reactions on metal surfaces (g) will be negligible except for fast moving atoms but (h) may be quite important even for the slowest atoms. The importance of (i) is still not quite clear though it may be considerable.

Chapter IV

DETACHMENT OF ELECTRONS FROM NEGATIVE IONS

§ 1. Introduction.

The direct experimental investigation of detachment phenomena is even more difficult than that of attachment, mainly because of the practical difficulty in obtaining large concentrations of negative ions. Such concentrations are necessary for observation of the separate action of various destructive agents, whereas a large concentration of electrons rather than ions is the desideratum in studying ion formation by electron capture.

As we cannot hope to make use of experiments for the determination of the relative importance of different detachment mechanisms, it is fortunate that information of this type may be derived from a knowledge of the efficiency of the various modes of ion formation. Corresponding to each attachment process there is one of detachment which is the thermodynamic reverse and the probabilities may be related by considerations of microscopic reversibility. We make use of such relations in §§ 2 and 4 of this chapter. In other cases it is more convenient to argue directly about the importance of the particular process concerned.

§ 2. Photoelectric Detachment.

The probability of absorption of light of frequency ν by a negative ion may be specified in terms of an effective cross-section Q_d^r , which is related to that, Q_a^r , for emission by Milne's formula*

$$Q_d^r = \frac{m^2 v^2 c^2}{2 h^2 \nu^2} Q_a^r,$$

where v is the velocity of the electron ejected by the quantum.

* *Phil. Mag.* **47**, 209 (1924).

Using the values for the emission cross-section illustrated in Chapter III, fig. 6, we obtain the cross-section for absorption of light by Cl^- ions illustrated in fig. 15. On comparing this cross-section with that obtained for absorption by a neutral atom, (H), we notice that the order of magnitude is the same for both but that, whereas the absorption of the neutral atom tends to a finite value at the long wave limit, that by the negative ion tends

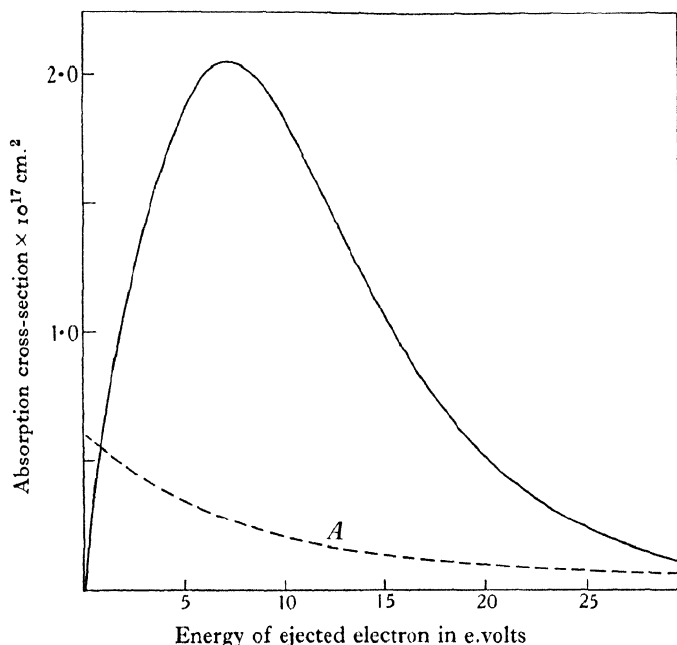


Fig. 15. Effective cross-section for absorption of radiation by Cl^- ions. Curve A gives, for comparison, the corresponding cross-section for absorption by H atoms.

to zero with the velocity of the ejected electron. This result adds to the already great difficulties in the way of experimental detection of light absorption by negative ions for it shifts the maximum absorption to wave-lengths well in the ultraviolet.

§3. "Ionization" of Negative Ions by Electrons and by Heavy Particles.

This is the reverse process to the formation of negative ions by capture of a free electron in the presence of a third body.

For electron collisions the probability of detachment may be calculated in the same way as for ionization of atoms, but is complicated by the absence of any explicit expression for the wave function of the outgoing ejected electron in the field of the neutral atom. Calculations have been carried out for Cl^- * and the cross-section for "ionization" by electron impact is illustrated

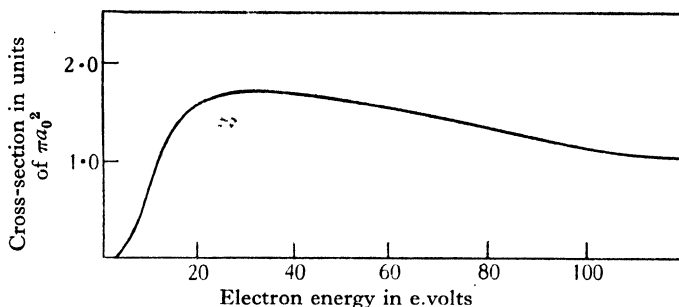


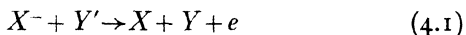
Fig. 16. Effective cross-section for ionization of Cl^- by electrons.

as a function of the energy of the incident electron in fig. 16. The difference between the form of the wave function for the detached electron in this case and that for ionization of a neutral atom has the effect of reducing the initial rate of increase of the ionization cross-section with electron energy. The cross-section for ionization of a neutral atom attains a maximum for electrons with energies about three to four times the ionization energy, but in fig. 16 it will be seen that the maximum is only reached for electrons with energies at least five to six times the detachment energy (3.7 e.v.). Similar results would be expected for other negative ions, the maximum cross-section being, to a rough approximation, inversely proportional to the detachment energy.

* Massey and Smith, *Proc. Roy. Soc. A*, **155**, 472 (1936).

We may apply similar considerations to those of Chapter III, §8.1 to determine the conditions under which collisions with atoms or molecules will be likely to detach an electron from the negative ion. For detachment without capture the energy of relative motion of the ion and atom must exceed the detachment energy by a factor of at least 10 before the probability of detachment per collision will be at all comparable with unity. If the detached electron is captured the same considerations apply except that the change of potential energy involved is to be substituted for detachment energy.

Collisions with excited atoms or molecules are much more likely to result in detachment than other types of collision, for in this case no change in the kinetic energy of the relative motion of the nuclei need take place. Thus we have the possibility of the reaction



occurring on impact of a negative ion X^{-} and an excited atom Y' . Provided the electron affinity of X is less than the excitation energy of Y this process can occur and the excess energy is taken up by the electron and not by the relative motion of X and Y . For these processes the cross-section might be quite large (even of the order 10^{-14} cm.²), so collisions with excited atoms might often be effective in removing negative ions in the gas phase.

§4. Detachment accompanying Molecule Formation.

The reverse process to that described in Chapter III, §2 is exemplified by a reaction such as



We may derive information as to the probability of such reactions from the experimental observations of the inverse reactions described in Chapter III, §4.2. If we denote the momentum of the relative motion of the atoms X and Y^{-} by P and that of the motion of the electron relative to the molecule XY after the collision by p , the thermodynamical relation between the cross-

sections Q_a^d and Q_a^a for the attachment and detachment processes respectively is

$$Q_a^a = \frac{g_{XY} g_e p^2}{g_Y - g_X P^2} Q_a^d, \quad (4.3)$$

where g is the statistical weight of the particular body concerned. For the reactions



in which the kinetic energy of relative motion of the negative ion and neutral atom is of the order of a few e.volts, Lozier's experiments give Q_a^d about $10^{-3} - 10^{-4}$ times the gas-kinetic cross-section.* Since p^2/P^2 is about 10^{-3} for these reactions and the statistical weights are of order unity, we find Q_a^a under these conditions is only about 10^{-7} times the gas-kinetic cross-section.

In practice it will be very unusual for the colliding ion and atom to possess a relative kinetic energy much greater than the gas kinetic. For such cases p^2/P^2 is roughly 10^{-2} and the cross-section Q_a^a will be between 10^{-5} and 10^{-6} times the gas kinetic. The upper limit of 10^{-5} will probably be approached when account is taken of the fact that the atoms X, Y may combine to form a molecule in an excited vibrational state. In Lozier's experiments attachment to molecules in such states cannot be investigated, so Q_a^a derived from his results may be too small by a factor of order 10.

A reasonable average value to take for the probability of an atom X and ion Y^- combining on collision to form XY is therefore 10^{-5} . More exact information can only be obtained by detailed calculation on the lines sketched out in Chapter III, §2.13.

§5. Neutralization of Ions at Metal Surfaces.

In an encounter with a metal, a negative ion can lose its electron easily to the metal, provided the work function of the metal is greater than the detachment energy of the ion. For in

* See Chapter III, §4.

this case there is an unoccupied level for the electron in the metal, with energy equal to that of the level which it occupies in the ion, and the transfer will be a resonance phenomenon.

Since most metal surfaces have work functions greater than the electron affinity of even fluorine it is clear that such surfaces will play a very important role in the destruction of negative ions.

§6. Loeb's Experiments on the Energy of Detachment of Electrons from O_2^- .

The only experimental work on detachment of electrons from negative ions which can claim any approach to a definite result is the very interesting application made by Loeb* of the high frequency electron filter to the problem. Although he did not succeed in obtaining any very accurate estimate of the energy necessary to detach an electron from O_2^- the method may be capable of further development and is of such intrinsic interest that we will describe its general features and the results.

In the attachment experiments carried out by Cravath and Bradbury (see Chapter III, §5) using the high frequency filter to determine the percentage of electrons in a swarm, it was found that negative ions were also captured in appreciable quantities by the grid if the alternating potential applied exceeded a certain value. As the frequency of the alternations was too high for the ions to be swept to the grid wires during a half-cycle the obvious interpretation to be made is that for these high field strengths the ions pick up sufficient energy in the field to suffer detachment on collision with other molecules. This suggested the possibility of determining the detachment energy by observation of the field strength necessary, at a given pressure, to effect detachment to an appreciable extent.

In Loeb's experiments, the apparatus used, illustrated diagrammatically in fig. 17, consisted of a tube inside which a high frequency arc was operated across the platinum ring electrodes *E*. Electrons and negative ions were drawn from the arc by a

* *Phys. Rev.* **48**, 684 (1935).

potential of 137 volts through a gauze A . This mixed stream was filtered through the mesh S_1 at a potential 67 volts above A . Frequency and field strength conditions at S_1 were adjusted to remove the electrons without affecting the ions. These were driven by a further 45 volts to the second filter S_2 consisting of copper wires 0.317 cm. in diameter with axes 0.617 cm. apart. Alternating potentials of from 10 to 1000 volts could be applied between alternate wires at frequencies of 1, 3 and 10×10^6 cycles. Any ions passing through this filter were collected on the plate P maintained at 22.5 volts above S_2 . The pressures employed were from 2 to 20 mm. Hg for which swarm conditions apply.

The current i_1 , captured by S_2 , and that i_2 , falling on P , could both be measured. Observations of these currents were made for varying alternating potentials applied across the alternate wires of S_2 , for a number of gas pressures and for each frequency of the alternations. Extremely complicated results were obtained which could only be interpreted with difficulty. A few typical curves are illustrated in fig. 18. Provided the pressure and frequency were not too high it was found that a more or less sudden decrease of ion current passing through the filter S_2 was observed at an alternating potential (B in fig. 18) approximately proportional to the pressure. This effect is probably due to the detachment process concerned and from the geometry of the mesh it was found to occur at a ratio of electric field to pressure of about 90 volts per cm. per mm. Hg. It is very difficult to estimate from this the average energy acquired by the negative ions. From estimates of the free paths of the ions, Loeb places this average energy between 0.68 and 0.14 e.volt, the former

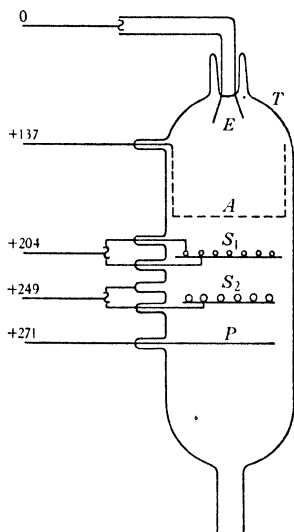


Fig. 17. Apparatus used by Loeb to investigate detachment of electrons from O_2^- .

being more probable. It would appear therefore that the energy required for the detachment process is comparable with 0.34 e.volt (only half the kinetic energy of an ion will be available for conversion to detachment energy on collision with a molecule of the same mass).

This result cannot be taken as indicating more than the right

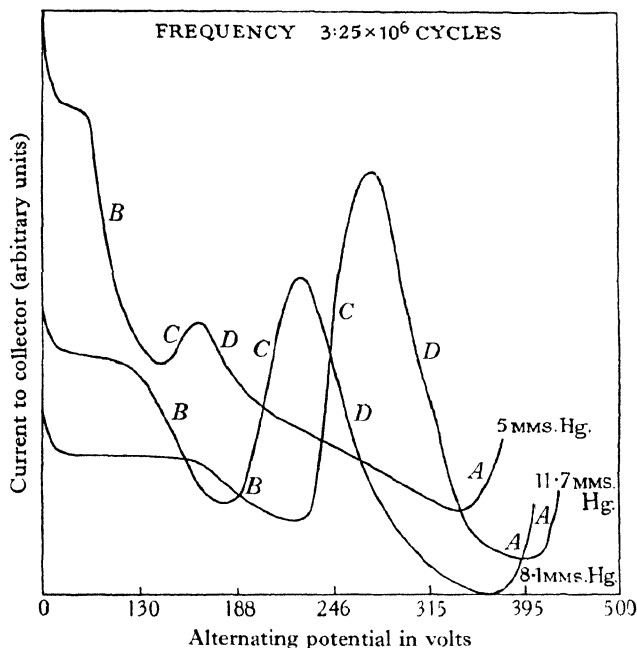
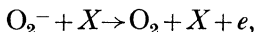


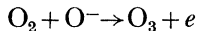
Fig. 18. Illustrating results obtained in Loeb's investigation of detachment from O_2^- .

order of magnitude for the detachment energy. The complications inherent in the method are obvious from the curves of fig. 18. The sharp rises marked *C* appear to be due to impact ionization by electrons arising from various secondary sources, the subsequent sharp decline *D* can be explained in terms of electron attachment while *A* indicates the breaking of an arc between the wires of S_2 . Apart from these experimental com-

plexities it is difficult to interpret the results in terms of an energy of detachment and it is not possible to tell what detachment process is concerned. There is no reason to expect that it is necessarily a direct ionization by a molecule X :



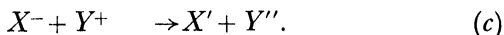
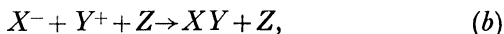
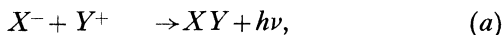
for O^- ions are probably also present and a number of possibilities such as



occur. Further, we have shown in §3 of this chapter that ionization of a negative ion by an atom or molecule will not set in sharply at the detachment energy but will only occur with appreciable probability at rather higher energies. This would render the determination of the energy required rather indefinite, just as in the study of the ionization of atoms by positive ions. Nevertheless, the work seems to establish the existence of detachment processes in the gas phase apart from recombination with positive ions, and the value of 0.34 e.volt is surprisingly close to the electron affinity of O_2 which Bloch and Bradbury found necessary for their explanation of the observed attachment processes in that gas (Chapter III, §6.1).

§7. Collisions of Negative and Positive Ions.

So far we have been concerned only with detachment reactions involving a negative ion and one or more neutral molecules or electrons. Further possibilities arise from reactions between positive and negative ions. A negative ion X^- and a positive ion Y^+ may interact in any of the following ways:

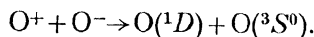


(a) and (c) are two-body reactions and their probabilities will not vary with pressure. (b) is a three-body process which can be neglected at low pressures.

The radiative process (a) is comparable with radiative recombination of electrons and positive ions and is never likely

to occur with a probability much greater than 10^{-6} per collision except for very slow ions. In fact, the probability is roughly $m(M_1 + M_2)/M_1 M_2$ times as great as that for a positive ion and an electron moving with the same energy as that of the relative motion of the two ions, M_1, M_2 being the masses of the ions and m of the electron.

The importance of the charge exchange reaction (c) depends, as usual, on the change of potential energy involved. For energies of relative motion of the ions X^-, Y^+ which are much larger than (about 25 times) this energy change, the probability will be comparable with unity, but otherwise will be small. To take a special case, the electron affinity of oxygen is 2.2 e.volts (Chapter I, Table I) and its ionization energy is 13.55 e.volts. The smallest possible change of potential energy will occur when the reaction is



The excitation energies are 1.96 and 9.48 e.volts respectively, so about 0.10 e.volt is the change of potential energy. A probability comparable with unity will therefore be attained only for ions with energies of a few e.volts.

For three-body reactions of type (b) the same general considerations as those of Chapter III, § 1.2 apply at low pressures.* As the pressure is increased a more detailed account of the probability is provided by J. J. Thomson's theory of ion recombination.† This theory is based on the assumption that recombination occurs when either of two neighbouring ions of opposite sign loses sufficient kinetic energy by collision with a third body to describe a closed orbit relative to the other. For such an orbit to be described the relative velocity v of two ions of charges $\pm e$ and masses M_1, M_2 at distances r apart must satisfy

$$\frac{1}{2} \frac{M_1 M_2}{M_1 + M_2} v^2 \leq \frac{e^2}{r}. \quad (4.6)$$

* The only important difference is that the effective radius for collision of the two ions must be taken much greater than the gas-kinetic value (more nearly equal to Thomson's critical distance r_0 (see equation 4.8)).

† *Phil. Mag.* **47**, 337 (1924).

Assuming that each ion possesses the mean kinetic energy $\frac{3}{2}kT$, where T is the absolute temperature, this may be written

$$\frac{3}{2}kT \leq \frac{e^2}{r}. \quad (4.7)$$

The ions will not recombine unless they approach each other within a distance

$$r_0 = 2e^2/3kT. \quad (4.8)$$

If, then, there is some mechanism whereby two ions, approaching each other within a distance r_0 , have their relative kinetic energy reduced to the mean value $\frac{3}{2}kT$, recombination will occur. Thomson assumes that collision with a third atom will provide such a mechanism. To calculate the recombination rate it is then only necessary to find the number of these collisions effected by either ion when within a distance r_0 of the other.

Let λ_1, λ_2 be the mean free paths of the +ve and -ve ions respectively. Then it may be shown that the chance of the +ve ion colliding with a third body when within a distance r_0 of the -ve ion is

$$s_1 = 1 - \frac{\lambda_1}{2r_0} (1 - e^{-2r_0/\lambda_1}). \quad (4.9)$$

Similarly we obtain s_2 for the -ve ion. The number of times the ions come within a distance r_0 of each other is roughly

$$\pi r_0^2 (u_+^2 + u_-^2)^{\frac{1}{2}} n^+ n^-, \quad (4.10)$$

where u_+, u_- are the mean velocities of the ions and n^+, n^- their concentrations. This gives for the rate of recombination

$$\pi r_0^2 (u_+^2 + u_-^2)^{\frac{1}{2}} n^+ n^- (s_1 + s_2),$$

i.e. an effective cross-section

$$Q_r = \pi r_0^2 (s_1 + s_2). \quad (4.11)$$

For low pressures $\lambda_1, \lambda_2 \gg r_0$ and we have

$$Q_r = 2\pi r_0^2 \left(\frac{r_0}{\lambda_1} + \frac{r_0}{\lambda_2} \right), \quad (4.12)$$

while for high pressures

$$Q_r = 2\pi r_0^2. \quad (4.13)$$

This formula agrees quite well with observed results for

pressures ranging from a few mm. Hg to a few atmospheres. It has not been tested at lower pressures but it probably gives too large values for very low pressures. Thus for recombination at ordinary temperature, $r_0 = 4.2 \times 10^{-6}$ cm., and at a pressure of 10^{-3} mm. Hg Q_r is still as large as 10^{-2} of the gas-kinetic value. For cases of this type, where three-body collisions are very infrequent, it is no longer possible to deal with average values and individual collisions must be separately considered. Experimental results for low pressures though very difficult to obtain, would be very valuable.

§8. Summary.

We find that the individual reactions leading to detachment are, in the order of effectiveness:

Process	Remarks
(a) Collisions with metal surfaces	Very effective if the work function of the metal is greater than the electron affinity
(b) Collisions with excited atoms	Effective cross-section may be greater than the gas-kinetic, particularly if the excitation energy is only slightly greater than the electron affinity
(c) Absorption of light	Cross-section roughly gas-kinetic for frequencies greater than twice the limiting value
(d) Ionization by electrons or fast moving ions or molecules	Maximum cross-section roughly gas-kinetic
(e) Ionization by low energy ions or molecules	Probability 10^{-1} or less per collision
(f) Collisions with neutral atoms leading to molecule formation	Probability 10^{-5} or less per collision

Of course this order refers to the individual processes. In any mixture involving negative ions it would be necessary to take account of the frequency of the different types of collision in assessing their relative importance in bringing about detachment (see Chapter v, §2).

Chapter V

NEGATIVE IONS IN GLOW DISCHARGES AND IN THE UPPER ATMOSPHERE

In glow discharges through gases and vapours containing electronegative substances, negative ions are often present in considerable quantities and exert a marked influence on the nature of the discharge.* There are a number of problems in this direction which await solution and it is hoped that the account of the properties of negative ions given in the preceding chapters may be of use in dealing with them.

It is possible to provide a general explanation of the modifications produced in the form of a glow discharge by the presence of negative ions, and to discuss the equilibrium concentration of the ions, in terms of the probabilities of the ion-forming and ion-destroying processes which we have described in Chapters III and IV. These applications have not yet been developed very far and it is not our intention to attempt any exhaustive survey here. Instead, we will give a short account of the general influence of negative ions in discharges, and of the relative importance of different processes in destroying negative ions in discharge plasmas.

Our present knowledge of conditions in the upper atmosphere is in much the same situation. Problems such as the nature of the recombination processes which reduce the ionization density in the ionosphere during the night, or that of the reactions leading to formation of those excited atoms which give rise to the "forbidden" green line in the night sky spectrum, still remain unsolved to a large extent. In many of these phenomena negative ions must play some role and in §3.3 of this chapter we draw attention to their possibilities without attempting to arrive at definite conclusions. These must await a more detailed analysis and possibly also further experimental information.

* See, for example, Sommermeyer and Seeliger, *Zeit. für Phys.* **98**, 733 (1936).

§ 1. General Effects of Negative Ions in Discharges.*

By way of illustration we first describe the effect of adding a trace of chlorine to a discharge in pure neon.

At a pressure of 2 mm. Hg with an anode-cathode potential difference of 500 volts the pure neon discharge takes the form illustrated in fig. 19(a). (1) is the primary dark space, (2) the cathode dark space, (3) the negative glow and (4) the Faraday dark space.

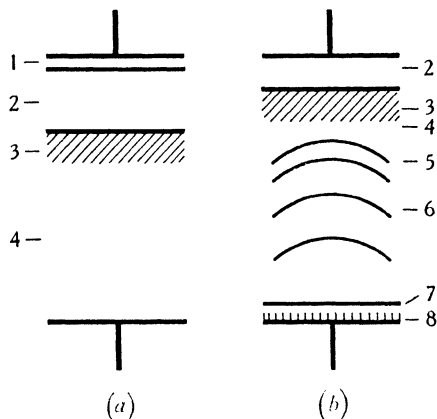


Fig. 19. Illustrating the effect of adding a trace of chlorine to a discharge in pure neon. (a) Before addition of chlorine; (b) after addition of chlorine.

Addition of a little chlorine changes the appearance to that shown in fig. 19(b). The modifications are:

- (a) Disappearance of the primary dark space.
- (b) Shortening of the Faraday dark space.
- (c) Appearance of a striated positive column (6) with strongly curved units.
- (d) Separation of the positive column from the Faraday dark space by a dark sheath (5).
- (e) Separation of the positive column from the anode by a dark sheath (7) bounded on the anode surface by a layer of neon light (8).

* K. Emeléus and J. Sayers, *Proc. Roy. Irish Acad.* **44**, 87 (1938). The neon used contained some helium.

Similar, though more pronounced, effects accompanying glow discharges in pure iodine vapour and in helium containing a trace of iodine, have been observed by Spencer-Smith.* In these cases it was found also that the positive column tends to turn into either a stationary or mobile ribbon. Certain organic vapours produce similar effects when added to inert gases.

In discharges through gases containing less electronegative substances such as oxygen, it is found that there are greater longitudinal fields in the positive column and a greater tendency for this to break into striations than for discharges through pure inert gases, but there is no important change in the behaviour of the discharge nearer the cathode.

These general effects may be explained in terms of the presence of negative ions in considerable quantity in the discharge tube. Since the properties of negative ions are very different from those of electrons, their presence leads to three main consequences:

(a) *Increased Collisional Resistance to Electrons.* Even in the most electronegative vapours the discharge current is carried mainly by free electrons. The formation of negative ions by attachment of electrons gives rise to additional possibilities of collisional resistance to the motion of the electrons; this affects the discharge in much the same way as an increase in pressure would do. We have thus a possible explanation of the shortening of the Faraday dark space and the space between striations, the increase of longitudinal field in the positive column, and the tendency of this column to leave the walls.†

(b) *Large Axial Concentration of Negative Ions.* Because of their small mass and hence large random motion, the space distribution of the electrons in a plasma can usually be described by a Boltzmann relation involving an electron temperature.‡ The massive positive ions tend, however, to move unidirectionally along the lines of force,‡ and we should expect the behaviour of negative ions to be very similar.

* *Phil. Mag.* **19**, 806 (1935).

† Seeliger, *Phys. Zeit.* **33**, 313 (1932).

‡ Tonks and Langmuir, *Phys. Rev.* **34**, 876 (1929).

In a positive column the axis is positive relative to the walls, so the negative ions will tend to concentrate along the axis. This will be particularly marked at the higher pressures, for then there will be sufficient collisions with atoms and molecules to prevent the ions acquiring enough momentum to move far from the axis. As a result the negative ions will rarely come under the destructive influence of the walls of the discharge tube and will be exposed only to the much less potent detachment reactions which can occur in the gas phase (see Chapter IV, Summary). Quite high concentrations of the ions may therefore be established even when the rate of generation is small, so explaining the considerable effects produced by small quantities of electronegative substances. For example, in a glow discharge in helium at 0.84 mm. Hg pressure containing a partial pressure of 0.06 mm. Hg of iodine, the negative ion random current was found by Spencer-Smith* to be approximately equal to that of the positive ions.

When a large concentration of negative ions is built up a uniform field can only be maintained by the establishment of an equal concentration of positive ions at each point. This could give rise to an axial concentration of the positive column which, again, might be unstable under certain conditions. The stationary and mobile ribbon forms observed probably arise in this way.

(c) *Regions of Negative Space Charge—Striations.* If the positive column does not take up the ribbon form the negative ions will set up regions of resultant negative space charge or tend to decrease the thickness of any already present. The conditions are then suitable for the formation of a striated positive column (there being a double space charge layer in each striation), the sharpness of the striations increasing with increasing influence of the negative ions.†

* *Phil. Mag.* **19**, 806 (1935).

† It must still be regarded as an open question whether striations can be formed in the absence of negative ions (except in extremely low current density layer discharges, cf. Holst and Oosterhuis, *Phil. Mag.* **46**, 1117 (1923)). Although K. T. Compton (Compton, Turner and McCurdy, *Phys. Rev.* **24**, 597 (1924)) has proposed a mechanism for the production of a

The sheath (7) on the anode is almost certainly a negative ion sheath with an anode potential fall across it greater than the excitation potential of neon. Again, it is very probable that the sheath (5) between the Faraday dark space and positive column is either a negative ion or double negative and positive ion sheath.

As there is usually a longitudinal potential minimum in the Faraday dark space, ions formed there will tend to move either into the head of the positive column or into the negative glow. It is consequently difficult at first sight to explain the observed result that the negative glow and Faraday dark space are unaffected laterally by the negative ions. Since in the negative glow there exists the greatest concentration of excited atoms which are very efficient in bringing about the destruction of negative ions (Chapter IV, §3) the relative number of negative ions in this region may well be so much less than that in the positive column as to render any lateral effects inappreciable.

§2. The Destruction of Ions in Plasmas.

The explanation we have suggested above depends largely on the slow destruction of negative ions in the gas phase; it is therefore pertinent to consider the rate at which negative ions are actually destroyed in a discharge plasma. It is not possible to do this with any approach to precision, but some important results may be derived by taking account of the conclusions of Chapter IV.

Neglecting the possibility of direct recombination of negative and positive ions, which will certainly be small except at pressures sufficiently great to make three-body collisions frequent, the processes to be considered are

- (a) photoelectric detachment,
- (b) detachment on collision with excited atoms,

striated column requiring only the occurrence of inelastic collisions between electrons and molecules, the experimental evidence in support of this theory was derived from observation of discharges in mercury and hydrogen in which the formation of negative ions may occur (Stille, *Ann. d. Phys.* **17**, 635 (1933)).

- (c) ionization in collisions between fast ions and atoms,
- (d) ionization by electron impact.

Of these (a) cannot be dealt with because of our ignorance of the intensity of the ultraviolet radiation prevailing in plasmas. The other three may be treated as follows:

Let ρ_1, ρ_2, ρ_3 be the rates of destruction of ions per c.c. per sec. due to processes (b), (c), (d) respectively. The effective cross-sections for processes (b) and (c) will be functions $Q_1(E^-)$, $Q_2(E^-)$, of the energy E^- (corresponding to an ion velocity v^-) of the negative ions, that for (d) a function $Q_3(E_e)$ of the electron energy E_e (corresponding to a velocity v). If n_e, n^-, n', n_0 are the numbers of electrons, negative ions, excited atoms and normal atoms per c.c. respectively, then

$$\rho_1 = n' n^- \int Q_1(E^-) N^-(E^-) v^- dE^-,$$

$$\rho_2 = n_0 n^- \int Q_2(E^-) N^-(E^-) v^- dE^-,$$

$$\rho_3 = n_e n^- \int Q_3(E_e) N_e(E_e) v dE_e.$$

Here $N^-(E^-) dE^-$ is the fraction of negative ions with energies between E^- and $E^- + dE^-$, $N_e(E_e) dE_e$ the fraction of electrons with energies between E_e and $E_e + dE_e$. n_e and N_e may be obtained from probe experiments for a given region in a discharge and it is reasonable to assume that n' is approximately equal to the number n^+ of positive ions per c.c. which may also be determined in this way. To obtain N^- use may be made of the theory of diffusion of heavy ions through a gas to show that the mean energy of the ions is roughly λeF , where F is the strength of the electric field acting, $-e$ the charge on an ion and λ the mean free path of the ions. Taking a gas-kinetic value for λ and a Maxwellian distribution of ion energies about the mean λeF gives N^- in terms of the observable quantity F . It remains to consider the cross-sections. From the considerations of Chapter IV we take:

(b) Q_1 practically independent of E^- and of order $5 \times 10^{-15} \text{ cm.}^2$ (a rather large value is taken because the reaction is a resonance one),

(c) $Q_2(E^-) = \beta_2(E^- - 2E_i)$, where β_2 is a constant and E_i the detachment energy,

(d) $Q_3(E_e) = \beta_3(E_e - E_i)$.

The linear forms for Q_2 and Q_3 will be sufficiently accurate for the low energies concerned (see §3 of Chapter IV) and reasonable values to take for β_2, β_3 are 10^{-18} and $10^{-17} \text{ cm.}^2/\text{e.volt}$.

In this way we find the following values for the detachment rates in the apparently uniform positive column of two discharges in iodine vapour investigated by Spencer-Smith:*

TABLE VI

Pressure, in mm. Hg	n_e per c.c.	$n^+ \simeq n'$ per c.c.	F , volts per cm.	Mean energies		ρ_1/n^-	ρ_2/n^-	ρ_3/n^-
				Elec- trons, e.volts	Nega- tive ions, e.volts			
0.18	1.7×10^7	2×10^9	30	4.5	0.50	2×10^{-1}	5×10^{-6}	7×10^{-4}
0.5	3.5×10^7	2×10^{10}	100	13.5	0.60	1.60	3×10^{-3}	1.1

The values for destruction by "ionization" on collision with neutral molecules are the least reliable, for they are very sensitive to the form assumed for the energy distribution of the negative ions. They are also the most dependent on the value of the electron affinity; thus for O_2 , with an electron affinity of $\frac{1}{3}$ e.volt, ρ_2/n^- is much more important than the other terms (assuming similar discharge conditions to those taken for iodine and a pressure of 0.18 mm. Hg, the value of ρ_2/n^- for O_2^- comes out to be about 50). The smaller the value of the electron affinity the greater is the effect of "ionization" by neutral molecules, and this process is probably responsible for the failure to detect weakly bound negative ions, such as O_2^- , in many types of discharge.

* *Phil. Mag.* **19**, 806 (1935).

We cannot calculate the rate of formation of negative ions in iodine with any accuracy as there is no detailed experimental study of the fundamental processes involved. Assuming, however, that they are similar to those described in Chapter III, §4.2 for oxygen, the rate of formation can be estimated from the discharge data given above. It is then found that such a rate of formation, although slow, is quite sufficient, when related to the rates of destruction given in Table VI, to give equilibrium concentrations of negative ions in the positive column of 10^{10} per c.c. or more. The difficulty is rather to understand why the observed concentrations are not larger. For atoms and molecules with smaller electron affinities the concentrations will be lower because of the increased rate of destruction by process (c).

Although these considerations are far from precise, it does appear that the development of a satisfactory theory of the behaviour of negative ions in discharges is not out of the question, particularly as wall effects, which are so important in dealing with electrons and positive ions, need not be taken into account to a first approximation.

§3. Upper Atmospheric Problems.

The investigation of the properties of the upper atmosphere has developed rapidly since the discovery of the ionized layers. Nevertheless we are still far from possessing anything like a complete understanding of the phenomena observed. To understand the problems which arise it is necessary to summarize our present knowledge of the subject.

It is known that there exist a number of atmospheric layers, some kilometres in thickness, which possess peculiar properties. Thus at a mean height of roughly 20 km. there is an ozone layer. At greater heights there are a number of layers in which there is a considerable concentration of ions. The most important of these are the *E* and *F* regions which, in the night-time, lie near 100 km., and 200 or 300 km., respectively. During the day these regions each split into two, the E_1 and E_2 , and the F_1 and F_2 . The ionization density in each layer exhibits

characteristic annual and diurnal variations besides irregular variations of considerable magnitude. A satisfactory theory must not only account for the existence of the layers but explain the variations, both regular and irregular, which they exhibit.

A further and related subject concerns the intensity and spectral distribution of the light emitted by the night sky and by aurorae.

As negative ions must certainly exist in the ionized layers their properties must be taken into account in developing a satisfactory theory. Before showing how the knowledge of negative ions which we have described in preceding chapters may be utilized, it is necessary to summarize the present knowledge of the properties of the ionized regions in more detail.

3.1. Properties of the Ionized Regions.

At the present time information on the following properties of the ionized regions is available:

- (a) Maximum electron density (also, in some cases, total ion density).
- (b) Collision frequency for electrons.
- (c) Gas pressures.
- (d) Chemical composition.
- (e) Diurnal and annual variations of electron density.

The average electron density, determined by observation of the critical frequency for penetration of the layer by wireless waves, exhibits a considerable diurnal and seasonal variation. At midday in midsummer the average values are 3×10^5 electrons per c.c. for the *F* region and 1.4×10^5 per c.c. for the *E* region. During the night the ionization falls to a value which remains roughly constant until sunrise. The average electron densities when constancy is attained are 0.80×10^4 electrons per c.c. for the *E* region and 2×10^5 for the *F* region.* Heavy ions are comparatively ineffective in producing reflection of wireless waves, but the phenomenon of daily magnetic variations indicates† that

* Appleton and Naismith, *Proc. Roy. Soc. A*, **150**, 685 (1935).

† Chapman, *Proc. Roy. Soc. A*, **132**, 353 (1931).

in the *E* region there may be as many as 10^8 ions per c.c., so there must be a marked preponderance of heavy ions.

The average collision frequency of an electron may be determined from measurement of the reflection coefficient of radio waves from the layer (particularly for the *F* region)* and from the phenomenon of interaction of radio waves (for the *E* region only).† Mean values found are roughly 6×10^3 and 2×10^5 collisions per sec. for the *F* and *E* regions respectively.

The only information we have concerning the gas pressure is derived from the observed collision frequencies and from Lindemann and Dobson's theory of meteors‡ (for *E* region only). At the height of the *E* region it appears to be about 10^{-3} mm. Hg. For the *F* region the average pressure as judged from the collision frequency, must be about 3×10^{-5} mm. Hg.§

Direct information about the composition of the layers can be obtained only from observation of auroral and night sky spectra. In some cases the height of the aurora from which the light is emitted may be determined by triangulation, but this height has rarely been ascertained. It appears that atomic oxygen is the main substance present in the *F* region but some molecular oxygen and nitrogen and some water vapour are also present. At the lower level of the *E* region the percentage of molecular oxygen is greater, and other molecular species may be present. It is always possible that there are atoms or molecules present which could not be detected spectroscopically because of their high excitation potentials. For example, it is difficult to conceive of any process whereby helium could be excited in the upper atmosphere. The failure to observe its spectrum is then no evidence that helium is not present in quantity.

The diurnal variation|| of the electron density is usually of a complicated nature. For the *E* region the main features are

* Eckersley, *Nature*, **135**, 435 (1935).

† Bailey and Martyn, *Phil. Mag.* **18**, 369 (1934).

‡ *Proc. Roy. Soc. A*, **102**, 411 (1923).

§ This value is only a vague indication as we have no certain information concerning the temperature in the *E* and *F* regions.

|| Appleton and Naismith, *loc. cit.*

that the ionization rises rapidly during sunrise, and then more slowly till noon when a maximum is attained. It then falls off steadily till sunset after which it decreases rapidly to a low value which is constant during the night. This approximately constant value is reached a few hours after sunset.

For the F region the variation is much more complicated but one important feature is that, on the average, a constant density of ionization is maintained throughout the night at a value not very different from the daytime maximum.

Two main types of seasonal variation* are observed. For the E region and the lower F region (F_1) the ionization density is greater in summer than in winter. The F_2 region exhibits the opposite effect, the maximum midwinter ionization being greater than the midsummer.

3.2. The Origin of the Ionized Layers.

It has been shown by Chapman† that, if a radiation entering from without is absorbed by an atmospheric constituent whose density falls off exponentially with height, the rate of absorption has a sharp maximum at a certain level. The actual height of this level depends on the density distribution of the absorbing material and the absorption coefficient. If the radiation is ultra-violet light from the sun and the absorption process is one of photoelectric ionization there will be levels of maximum ion production corresponding to each atom or molecule which can be ionized, i.e. corresponding to the ionization of O, O₂, N₂, etc.

Although this would account for the existence of regions of maximum ion production it is not sufficient to explain the occurrence of levels of maximum electron density. This requires consideration of the rate of electron removal. If we assume that this depends only on the actual ionization density and not on the density of neutral particles, the levels of maximum electron density will coincide with those of maximum ion production. To examine the validity of this assumption we must analyse the possibilities of ion neutralization.

* Appleton and Naismith, *loc. cit.* † *Proc. Roy. Soc. A*, **132**, 353 (1931).

3.3. Recombination, Attachment and Detachment in the Upper Atmosphere.

During the day-time ions are produced continually by the solar radiation and at some time before sunset an equilibrium is reached at which the rate of ion production is exactly balanced by that of ion neutralization. After sunset no further ion production occurs and the ionization decays by recombination to a minimum just before sunrise.* The interesting quantity, from the point of view of radio effects, is not the total ionization but only that part of it due to free electrons. The variation of the electron density is more complicated than that of the total ion density because an electron can be removed effectively, not only by recombination with a positive ion, but also by attachment to a neutral molecule. This type of removal is not permanent in the same sense as recombination because of the finite probability of detachment occurring.†

One further factor which may be important concerns the variation of atomic oxygen content. Dissociation of molecular oxygen by solar radiation is probably the main source of oxygen atoms and, if this is so, the density of these atoms should exhibit diurnal variation.

Let us now consider the average behaviour in an ionized layer of which O, O₂, N₂ and N are the principal constituents. The reactions given in Table VII must be considered.

If the Sun is regarded as a black body with temperature 6000° K. the photo-dissociation and photo-ionization reactions which require the lowest frequency quanta will be the most important. Hence we need only consider, as a first approximation, the reactions (1), (3), (4), (5) in the first column.

The recombination of oxygen atoms may take place as a radiative process or in the presence of a third body. The former is very infrequent (probably about 10⁻⁸ per collision), but at the low atmospheric pressures it may be as important as the three-

* The ionization density may actually increase before sunrise owing to thermal contraction.

† This possibility was first pointed out by Martyn and Pulley (*Proc. Roy. Soc. A*, **154**, 455 (1936)).

TABLE VII

I Dissociation and ionization	II Recombination	III Attachment	IV Detachment
$O_2 + h\nu \rightarrow O + O$ (1) $N_2 + h\nu \rightarrow N + N$ (2) $O_2 + h\nu \rightarrow O_2^+ + e$ (3) $N_2 + h\nu \rightarrow N_2^+ + e$ (4) $O + h\nu \rightarrow O^+ + e$ (5) $N + h\nu \rightarrow N^+ + e$ (6)	$O + O \rightarrow O_2 + h\nu$ (a) $O + O + X \rightarrow O_2 + X$ (b) and similar reactions for N $O^+ + e \rightarrow O + h\nu$, and similar reactions for O_2^+ , N^+ , N_2^+ $O_2^+ + e \rightarrow O_2' + O''$ (3) $O_2^+ + e + X \rightarrow O_2 + X$ (4) $O^+ + O^- \rightarrow O_2 + h\nu$ (5) $O^+ + O^- + X \rightarrow O_2 + X$ (6)	$O + O' \rightarrow O^- + h\nu$ (1) $O_2 + e \rightarrow O_2^- + h\nu$ (2)	$O + O^- \rightarrow O_2 + e$ $O^- + N \rightarrow NO + e$ $O^- + N_2 \rightarrow N_2O + e$ $O^- + h\nu \rightarrow O + e$

body process. Ion recombination will, for the same reason, almost always be associated with the emission of radiation. A process such as (3) of column II, exactly analogous to the dissociation of a neutral molecule on electron attachment, may, however, be important. The probability of radiative recombination of electrons varies inversely as the square of the electron velocity for low electron energies and for electron energies of about 1 e.volt is about 10^{-5} per collision. The non-radiative two-body process (3), leading to formation of two excited oxygen atoms, will only be important for electrons with energies lying in a range of about 2 e.volts on either side of a certain critical energy value which we cannot fix without more detailed knowledge. The maximum probability will be about 10^{-5} per collision.

The attachment processes (1) and (2) are also of a radiative type. Reference to Chapter III, § 1.1, shows that the probability will vary inversely as the electron velocity for low energy electrons and will be of the order of 10^{-6} per collision for energies near 1 e.volt. Attachment to O_2 is likely to be much less probable than that to O for slow electrons as the frequency radiated on formation of O^- is much greater than for O_2^- .^{*} The chance of attachment is proportional to the cube of this frequency and this is probably the determining factor. Non-radiative attachment is likely to be unimportant. Three-body processes will be negligible at the low pressures concerned, attachment by Lozier's process (Chapter III, § 4.2) cannot occur at low electron energies, and that by Bradbury and Bloch's process (Chapter III, § 6.1) will be small because of the low pressure.

The detachment processes given have been discussed in Chapter IV, § 4, where it was shown that the maximum probability is about 10^{-5} per collision.[†]

It is clear that we can, to a first approximation, neglect the influence of the nitrogen. Let n_0 , n_1 , n_2 , n^+ , n^- , n_2^- , n_e be the

^{*} See Chapter III, § 1.1.

[†] The low electron and ion energies make it unnecessary to consider other processes which were important in discharge phenomena.

total number of molecules, oxygen atoms, oxygen molecules, positive ions, negative oxygen atoms, negative oxygen molecules and electrons respectively per c.c. Then the variation of these quantities with time will satisfy the following equations:

$$\frac{dn_1}{dt} = \alpha n_2 - \beta n_0 n_1^2 - \gamma n_1^2,$$

$$\frac{dn^+}{dt} = \lambda n_1 + \mu n_2 - \nu n^+ n^- - \xi n^+ n_e,$$

$$\frac{dn_e}{dt} = \lambda n_1 + \mu n_2 - \xi n^+ n_e - \eta n_e n_1 - \zeta n_e n_2 + \kappa n^- n_0 + \rho n^-,$$

$$n_1 + 2n_2 = \text{constant} = n, \text{ say,}$$

$$n^+ = n^- + n_e.$$

The various terms in these equations refer to the rates of the following processes listed in Table VII:

$$\begin{aligned} \alpha n_2, & \text{ I (1); } \quad \lambda n_1, & \text{ I (5); } \quad \mu n_2, & \text{ I (3); } \quad \beta n_0 n_1^2, & \text{ II (1) (a); } \\ \gamma n_1^2, & \text{ II (1) (b); } \quad \nu n^+ n^-, & \text{ II (4); } \quad \xi n^+ n_e, & \text{ II (3); } \quad \eta n_e n_1, & \text{ III (1); } \\ \zeta n_e n_2, & \text{ III (2); } \quad \kappa n^- n_0, & \text{ IV (1); } \quad \rho n^-, & \text{ IV (2).} \end{aligned}$$

As the equations stand they cannot be solved in simple form, and, until we have detailed knowledge of the constants involved, a complete solution would be of little value. Instead we will content ourselves by considering very much simplified versions of the equations. If any differences of behaviour between O and O₂ are neglected, the first equation can be ignored. Further, at night-time $\lambda = \mu = \rho = 0$. This leaves

$$\frac{dn^+}{dt} = -\nu n^+ n^- - \xi n^+ n_e,$$

$$\frac{dn_e}{dt} = -\eta n_e n_0 + \kappa n^- n_0 - \xi n^+ n_e,$$

with $n^+ = n_e + n^-, \bar{\eta} n_0 = \eta n_1 + \zeta n_2.$

When we examine the magnitudes of the various terms involved for the *E* region the general nature of the solution of the equations becomes apparent. Before doing this something must be said about the electron velocity distribution. In the absence of

electric fields it is probable that the electrons come into thermal equilibrium with the gas molecules, so we assume that they have an average energy of the order 0.1 e.volt. If electric fields are permanently present this would have to be taken much greater.

The term $\bar{\eta}n_0n_e$ is the rate of attachment to neutral molecules. Each electron makes about 2×10^5 collisions per sec., giving the rate of attachment per electron as roughly

$$2 \times 10^5 \times \sqrt{10 \times 10^{-6}} = 0.6 \text{ per sec.}$$

For the detachment rate $\kappa n^- n_0$ we must calculate the frequency of collision between negative ions and neutral molecules. Since that of electrons and neutral particles is 2×10^5 per sec. we find

$$2 \times 10^5 \times \left(\frac{1}{16 \times 1840} \right)^{\frac{1}{2}} \simeq 10^3 \text{ collisions per sec.}$$

This gives, for the rate of detachment per negative ion,

$$10^3 \times 10^{-5} = 10^{-2} \text{ per sec.}$$

Since, in deriving this result, we have assumed complete thermal equilibrium between electrons and molecules and the maximum value 10^{-5} of the detachment probability per collision, this is an upper limit.

To calculate the rate of loss by recombination the number of collisions per second between electrons and positive ions must be determined. Assuming 10^8 positive ions per c.c. and 5×10^{13} gas molecules per c.c., a fraction 2×10^{-6} of the 2×10^5 collisions per sec. made by an electron will be with a positive ion. This gives for the rate of recombination per electron

$$2 \times 10^{-6} \times 2 \times 10^5 \times 10^{-5} \times 10 = 4 \times 10^{-5} \text{ per sec.}$$

The significant feature of these numerical values is that the rate of recombination is very much smaller than that of attachment or detachment. An equilibrium ratio of 100 to 1 or greater will be set up between the negative ions and electrons in a time of the order of seconds and will be maintained while both electrons and negative ions are lost much more slowly by recombination. The recombination rate is such that a time of the order of several hours will be necessary to reduce the electron

ionization density to a low value. This is in agreement with observation for the *E* region. It is likely that similar considerations will be valid in the day-time. A definite ratio will be maintained between negative ions and electrons at all times and the maximum ion concentration produced will be limited by recombination alone. This assures that the level of maximum ionization coincides with that of maximum rate of ion production.

The seasonal variation of midday ionization in the *E* layer can also be easily understood on these lines. The maximum ionization density N will be proportional to the square root of the rate q of ion production by the sunlight, and so

$$\frac{N_{\text{summer}}}{N_{\text{winter}}} = \left(\frac{q_{\text{summer}}}{q_{\text{winter}}} \right)^{\frac{1}{2}}$$

$$= \left(\frac{\sin(\theta + \delta)}{\sin(\theta - \delta)} \right)^{\frac{1}{2}},$$

where θ is the colatitude of the place of observation and δ is the Sun's maximum declination. This is in quite good agreement with experiment.*

It is interesting to enquire into the possible effect of the variation of the extent of oxygen dissociation. This may considerably affect the attachment rate. During the night, recombination of oxygen will reduce this and so tend to increase the electron concentration. This may lead to a night-time maximum. The reverse might occur in the day-time. Similar effects might also arise from a difference in the probability of ionization of oxygen atoms and molecules.

The term ρn^- may also be of importance in the lower layers during the day-time. Although n^- is only a small fraction of n_0 the detachment energy of O is also small, being 2.2 e.volts. Quanta with this or greater energy are much more abundant in solar radiation than those which produce ionization of O.

We encounter a difficulty when the *F* region is considered. To explain the slow fall of electron density during the night the rate of recombination must be considerably less than in the *E* region.

* Appleton and Naismith, *loc. cit.*

But, if the density of positive ions bears the same relation to that of the electrons in each layer, the reverse will be the case. For, if q is the fraction of electrons lost per second by recombination, ν the electron collision frequency, f^+ the fraction of the total number of collisions made by an electron which occur with positive ions, and n^+ the concentration of positive ions,

$$\begin{aligned}\frac{q_F}{q_E} &= \frac{\nu_F f_F^+}{\nu_E f_E^+} \\ &= \frac{n_F^+}{n_E^+},\end{aligned}$$

ν_F/ν_E being the ratio of the total number of particles in each region. If n^+ is proportional to the electron concentration, then q_F will be greater than q_E by a factor of 10 or more. To avoid this difficulty, it is necessary to assume that the number of heavy ions is much more nearly equal to the number of electrons in the *F* region than in the *E*. This would be the case if attachment were very improbable in the upper layer, a state of affairs which would be realized if the main atmospheric constituent of these levels were an inert gas such as helium (see § 3.1). There may be some connection between this possibility and the abnormally high pressure in the *F* region.

Although the conclusions at which we have arrived in this section must be regarded as tentative it does seem at least possible to provide a reasonably plausible picture of the behaviour in the *E* region. Detailed evaluation of the various collision rates should greatly clarify the whole situation.

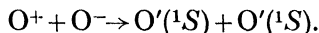
3.4. The Green Light of the Night Sky.

The green light which is the most prominent feature of the spectrum of night sky and auroral light arises from transitions between the metastable ^1S and ^1D states of the neutral oxygen atom. Rayleigh* has estimated the intensity as corresponding on the average to 10^8 transitions per second in a column of the atmosphere of 1 sq. cm. base. As the calculated transition

* *Proc. Roy. Soc. A*, **129**, 458 (1930).

probability is about 1.8 sec.^{-1} * this means that a concentration of ^1S atoms of oxygen of order 10 – 100 per c.c. must be maintained during the night. The problem is to determine the nature of the processes which lead to this continuous night-time production of metastable oxygen.

It is not easy to think of any reactions involving negative ions which could give an adequate yield.† One possible process is



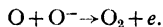
This is energetically possible but involves an energy evolution of 3.0 e.volts which must appear as kinetic energy. It is therefore unlikely to occur more frequently than 10^{-5} to 10^{-6} per collision between ions moving with gas-kinetic velocities. Using the properties of the E region, this would give rise to only about

$$2 \times 10^3 \times 2 \times 10^{-6} \times 10^8 \times 10^{-5} \simeq 4 \text{ metastable atoms per sec.}$$

It is much more probable that some process involving only neutral atoms and molecules in their normal states is responsible; even a rare collision process of this type is important because of the comparatively large concentration of neutral species.

* Condon and Shortley, *The Theory of Atomic Spectra*, Camb. Univ. Press, 1935, p. 283.

† Martyn and Pulley (*Proc. Roy. Soc. A*, **154**, 455 (1936)) suggested that the ^1S atoms arise by excitation of normal oxygen atoms by electron impact. The electrons, which must have at least 4.1 e.volts energy, they suppose provided by reactions such as



This is not possible, for the energy of such electrons could not exceed

$$5.09 - 2.2 = 2.89 \text{ e.volts.}$$

INDEX

- Affinity, electron, effect of, in discharge equilibria, 88
- — — of atoms, calculation of, 7
- — — definition of, 3
- — — determination of, by experiment, from collision, 12, 44, 51
- — — — from cyclic processes, 17
- — — — from equilibrium constants, 13
- — — empirical, 12
- — — values of, 15
- — — of molecular oxygen, 62, 75
- — — of molecules, 22
- Appleton and Naismith, diurnal ionospheric variations, 91
- electron density in ionosphere, 90
- seasonal ionospheric variations, 92, 98
- Arnot and Milligan, double capture of electrons by positive ions, 68
- Atmosphere, upper, problems relating to, 89
- — recombination, attachment and detachment in, 93
- Attachment, in upper atmosphere, 93
- of electrons to atoms, in three-body collisions, 38
- — with emission of radiation, 31
- of electrons to molecules, experiments on, using homogeneous beams, 48
- — — using electron swarms, 54
- — — results of, 50, 53, 60, 62
- — — theory of, 40
- reactions, electron affinities from, 13
- Bailey, method of observing attachment, 57
- Bailey and Duncanson, attachment in gases and vapours, 63
- Bailey and Martyn, interaction of radio waves, 91
- Bailey and Rudd, attachment in vapours, 63
- Bloch, F., and Bradbury, electron attachment to O_2 and NO , 43, 61, 63, 78, 95
- Bodenstein and Stark, 14
- Bradbury, electron filter method, 56
- swarm experiments in oxygen, 60, 75
- *see* Bloch, F.
- Bradbury and Tatel, swarm experiments in gases and vapours, 62
- Bröse, swarm experiments in oxygen, 61
- Brown, self-consistent field of F^- , 10, 19
- Calvin and Glockler, electron affinities from attachment reactions, 14
- Capture, of bound electrons, from atoms, 65
- — from metals, 67
- of free electrons, by atoms, in three-body collisions, 38
- — — with radiation, 31, 95
- — by positive ions, 36, 95
- — in collision with molecules, 40, 50, 60
- Cathcart, Miss, and Emeléus and Minnis, detection of iodine affinity spectrum, 36
- Chapman, daily magnetic variations, 90
- origin of ionized layers, 92
- Collisions, electron affinities from, 12, 44, 47, 52
- of electrons, in iodine, 53
- — in ionosphere, frequency of, 91
- — in O_2 and CO , 50
- — with molecules, involving electron capture, 40
- — — non-capture, 45
- of negative and positive ions, 78
- Compton, K. T., and Turner and McCurdy, theory of striations, 85
- Condon, Franck-Condon Principle, 40

- Condon and Shortley, 100
 Coolidge, James and Present, Franck-Condon Principle, 41
 Cravath and Loeb, electron filter method, 56
 Cross-sections, for capture of electrons, by atoms, in three-body collisions, 38
 — — — with radiation, 32
 — — — by molecules, theoretical evaluation of, 44
 — — — by positive ions, 36
 — for detachment of electrons, in molecule formation, 73
 — — photoelectrically, 70
 — for ionization of Cl^- by electrons, 72, 87
 — for recombination of positive and negative ions, 73
 Detachment, accompanying molecule formation, 73
 — in discharges, 86
 — in upper atmosphere, 93
 — of electrons from O_2^- , Loeb's experiments on, 75
 — photoelectric, 70
 — summary of reactions leading to, 81
 Discharges, destruction of ions in, 86
 — in iodine, 36, 88
 — negative ions from, 1
 — negative ions in, general effects of, 83
 Dissociation of molecules, accompanying attachment, 40
 — in upper atmosphere, 93
 — into ions, 45
 Dobson and Lindemann, theory of meteors, 91
 Duncanson, *see* Bailey
 Eckersley, measurement of collision frequencies in ionosphere, 91
 Electrons, attachment of, in upper atmosphere, 93
 — — to molecules, experiments on, 48
 — bound, capture of, by neutral atoms, 65
 — capture of, by atoms, in three-body collisions, 38
 Electrons, capture of, *cont.*
 — — by molecules, experimental, 48
 — — — theoretical, 40
 — — with radiation, 32
 — collision, frequency of, in ionosphere, 91
 — collisions of, in I_2 , 53
 — — in O_2 and CO , 50
 — — with negative ions, ionization by, 72, 87
 — density of, in ionosphere, 90
 — detachment of, from negative ions, 70
 — — from O_2^- , energy of, 75
 — extraction of, from metals, 67
 — states of, enumeration of, in diatomic molecules, 24
 — — in molecules, 22
 — — in negative atomic ions, 3
 — — in simple negative molecular ions, 26
 — wave functions of, in self-consistent field, 9
 Emeléus, K., negative ions in discharges, 83
 — *see* Cathcart, Miss
 Energy, distribution of, among electrons in discharges, 37, 87
 — — among ions in discharges, 87
 — of binding of electrons to neutral atoms, 3
 — vertical detachment, of molecular ions, 24
 — — of H_2^- , 26
 — — of O_2^- , 75
 Experiments, electron affinities from, 12
 — establishing existence of negative ions, 1
 — on attachment, with electron beams, 48
 — — with electron swarms, 54
 — on detachment from O_2^- , 75
 — on double capture of electrons by positive ions, 68
 — to detect affinity spectra, 36
 Eyring, Hirschfelder and Taylor, energy of H_2^- , 26
 Fock, self-consistent fields with exchange, 10
 Fowler, statistical mechanics, 13
 Franck, *see* Condon

- Glockler, empirical electron affinities, 12
 — *see* Calvin
- Harkness and Hogness, electron collisions in iodine, 53
- Hartree, D. R., self-consistent field method, 9
 — and Hartree, W., self-consistent fields of Cl^- , Na^- , K^- , 10
- Hartree, W., *see* Hartree, D. R.
- Helmholz and Mayer, electron affinities from cyclic processes, 17
- Hirschfelder, *see* Eyring and Taylor
- Hogness, *see* Harkness
- Holst and Oosterhuis, striations in layer discharges, 85
- Hylleraas, electron affinity of H, 9
- Iodine, atomic, electron affinity of, 14, 17
 — — affinity spectrum of, attempts to detect, 36
 — molecular negative ions of, electron affinity, 30
 — — electronic structure, 30
 — vapour, collisions in, 53
 — — discharges in, 36, 88
- Ions, negative, atomic, calculation of structure of, 7
 — — — doubly-charged, 18, 20
 — — — electron affinities of, 10, 15
 — — — excited states of, 19, 52
 — — — existence of, 1
 — — collisions of, with positive ions, 78
 — — detachment of electrons from, accompanying molecule formation, 73
 — — — by impact, 72, 87
 — — — from O_2^- , 75
 — — — photoelectrically, 70, 87
 — — — summary of processes leading to, 81
 — — formation of, by capture of bound electrons, 65
 — — — by electron collisions with molecules, 40
 — — — by excited atoms, 19
 — — — by extraction of electrons from metals, 67
 — — — by impact dissociation of molecules, 45
- Ions, negative, formation of, *cont.*
 — — — by radiative attachment, 32
 — — — by three-body collisions, 39
 — — — in oxygen, experiments on, 48, 60
 — — — — summary of processes leading to, 64
 — — — in various gases, experiments on, 53, 62
 — — — summary of processes giving rise to, 69
 — — in discharges, general effect of, 83
 — — in plasmas, destruction of, 86
 — — in upper atmosphere, 93
 — — neutralization of, at metal surfaces, 74
 — positive, collisions of, with negative ions, 78
 — — double capture of electrons from metals by, 67
 — — in ionosphere, density of, 90
 — — — recombination of, with electrons, 97
 — — of hydrogen, capture of electrons by, 36
- James, *see* Coolidge
- Langmuir and Tonks, heavy ions in discharges, 84
- Light, absorption of, by Cl^- , 71
 — emission of, on attachment of electrons, 31
 — green, of the night sky, 99
- Lindemann, *see* Dobson
- Loeb, energy of detachment of electrons from O_2^- , 75
 — *see* Cravath
- Lozier, collisions of electrons with molecules, experiments on, 13, 48, 74, 95
- Lozier and Tate, 48
- McCurdy, *see* Compton, K. T.
- Maltbie and Mayer, electron affinities of O^- and S^- , 18
- Martyn, *see* Bailey
- Martyn and Pulley, detachment in upper atmosphere, 93
- Massey and Mott, theory of atomic collisions, 47, 55

- Massey and Smith, R. A., electron capture cross-sections, 35, 67
 — — ionization of negative ions by electrons, 72
 Mayer, electron affinities, from cyclic processes, 17
 — see Helmholtz
 — see Maltbie
 Mayer and Sutton, electron affinities from attachment reactions, 14
 Metals, extraction of electrons from, 67
 — neutralization of ions at surfaces of, 74
 Milligan, *see* Arnot
 Milne, relation between emission and absorption coefficients, 70
 Minnis, *see* Cathcart, Miss
 Molecules, diatomic, enumeration of electronic states of, 24
 — dissociation of, into ions by impact, 45, 52
 — electron affinities of, 22
 — experiments on attachment of electrons to, 48, 54
 Mott, *see* Massey
 Mulliken, vertical ionization potential of molecules, 24

 Naismith, *see* Appleton

 Oldenberg, attempt to detect iodine affinity spectrum, 36
 Oosterhuis, *see* Holst
 Oxygen, atomic, electron affinity of, 12, 15, 50
 — — in upper atmosphere, 93
 — — negative ions of, excited state of, 52
 — molecular, collisions of electrons in, 50
 — — detachment of electrons from negative ions of, 75
 — — electron affinity of, 62, 75
 — — negative ion formation in, summary of processes leading to, 64
 — — swarm experiments in, 60

 Pauling, energy of He_2^+ , 26
 van Pragh and Rideal, dissociation of I_2 in filaments, 14
 Present, *see* Coolidge

 Pulley, *see* Martyn

 Radiation, absorption of, by Cl^- , 71
 — emission of, on electron attachment, 31
 Rayleigh, intensity of nocturnal green light, 99
 Recombination, in upper atmosphere, 93
 — of positive ions, and electrons, 36, 95
 — — and negative ions, 79
 Regions, ionized, in upper atmosphere, origin of, 92
 — — — properties of, 90
 — — — recombination, attachment and detachment in, 93
 Rideal, *see* van Pragh
 Rudd, *see* Bailey

 Seeliger, constricted positive column, 84
 Sherman and van Vleck, 24
 Shortley, *see* Condon
 Smith, R. A., electron capture in three-body collisions, 40
 — *see* Massey
 Spectrum, electron affinity, attempts to observe, 36
 — — theory of, 33
 Spencer-Smith, discharges in iodine, 37, 84, 85, 88
 Sponer, *Molekulspektren-Tabellen*, 28, 30
 Stark, *see* Bodenstein
 States, excited, of negative ions, 9, 52
 — of diatomic molecules, 22
 — — electronic, enumeration of, 24
 — — — of F_2^- , Cl_2^- , Br_2^- , I_2^- , 29
 — — — of H_2^- , 27
 — — — of O_2^- , 26
 — of negative atomic ions, 3
 Stille, formation of Hg^- , 68, 86
 Structure, of negative ions, calculation of by quantum methods, 7
 — of simple negative molecular ions, 26
 Sutton, *see* Mayer

 Tate, *see* Lozier
 Tatel, *see* Bradbury

- Taylor, *see* Eyring
Thomson, J. J., drift velocities by
photoelectric current, 57
— theory of ion recombination,
79
Tonks, *see* Langmuir
Townsend, average energy of elec-
trons in oxygen, 61
Turner, *see* Compton, K. T.
Tüxen, negative ions by mass
spectrograph, 1
van Vleck, *see* Sherman
You-Wu, Ta, energies of He^- and Li^- ,
9
— negative ion formation by ex-
cited helium, 20

